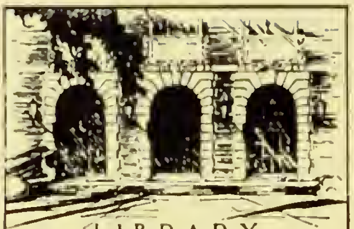

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Inorganic Seminar

1947-48

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1947 - 1948

PARAMAGNETISM

John Huizenga October 14, 1947

I. Introduction
   A) Quantum numbers
   B) Various types of magnetism
      1) Diamagnetism - magnetic moment associated with the orbital motion of the electron.
      2) Paramagnetism - the permanent magnetic moment resulting in part from the spin magnetic moment of unpaired electrons and in part from the orbital magnetic moment.
      3) Ferromagnetism - a ferromagnetic substance is one whose magnetic properties are like those of iron.
   C) General methods for measuring magnetic susceptibility
      1) Gouy method

Solvent is placed in upper half of a tube, while the solution to be measured is in the lower half of the tube. The tube is placed between magnets with the ends extending beyond the magnets. A diamagnetic substance will be heavier and a paramagnetic substance lighter than their actual weights.

      2) Faraday method

The substance is placed in a region where the strength of the field H changes rapidly with displacement along the axis of symmetry (x), then the substance will be subjected to a force along the axis

$f = mXHdH/dx$ where m is the mass of the sample, X the mass susceptibility, H the field strength, and dH/dx the rate of change of field strength along the x axis. The displacement can be measured directly or by mirror.

      3) Rankine balance (20)

If a bar magnet stands parallel to a plane surface, the induced polarity on the surface exerts force on the magnet. This force is an attraction if the surface consists of a paramagnetic substance, a repulsion if the substance is diamagnetic.

      4) Magnetically neutral method

Salceanu (23) developed this method. If a paramagnetic substance is dissolved in a diamagnetic solvent, there must be a certain concentration at which the susceptibility is zero.

II. Theory

The classical theory of paramagnetism was developed by Langevin on the assumption that each atom is a little magnet, and that these atomic magnets tend to line up parallel to an applied magnetic field. Langevin's formula was as follows,

$$X_m = N\mu^2/3kT$$

where,

X_m = molar polarization
μ = permanent moment
N = Avogadro's number
k = Boltzman's constant
T = absolute temperature

Langevin's expression was substantiated by Curie's Law and was valid for the temperature dependent magnetism. Van Vleck then by quantum mechanics developed the similiar expression,

$$\chi_m = N\mu^2/3kT - N\alpha$$

where α is a measure of the temperature independent moment. In general the magnetic moment of an atom consists of two parts, the orbital contribution and the electron spin contribution. In the calculations one must remember the three different cases.

1) Multiplet intervals very narrow compared to kT.
2) Multiplet intervals very wide compared to kT.
3) Multiplet intervals of comparable size to kT.

III. Rare earths

A) Configuration

$4f^{0-14}$ $5s^2$ $5p^6$ $5d^2$ $6s^1$

The electrons responsible for the paramagnetism are to a great degree shielded from external influence. Hund[10] assumed the multiplets all very wide as compared to the thermal energy.

B) Spectroscopic notation

$$^{2S+1}L_J$$

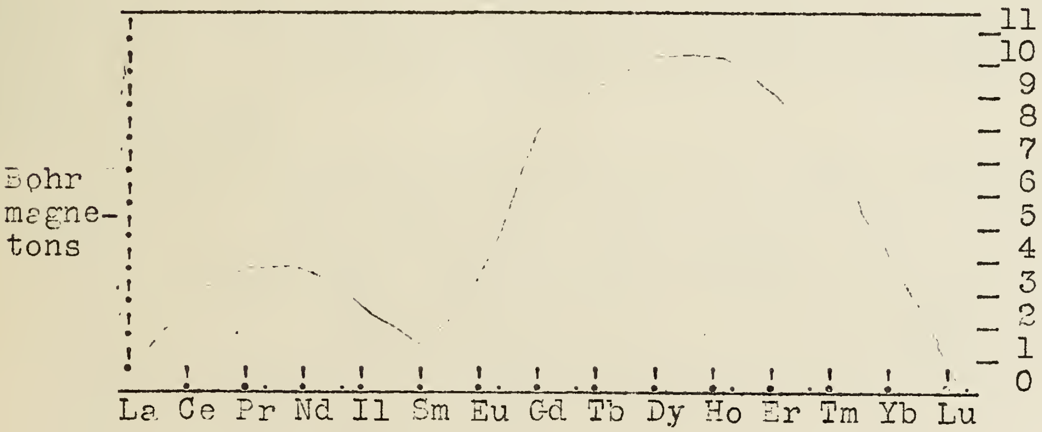
where,
S = 1/2 for each unpaired electron
L = S, P, D, F, G, H, I, ----
J = the resultant of L and s

<u>Hund's</u> <u>rule</u>: of the terms given by equivalent electrons, those with greatest multiplicity lie deepest, and of these the lowest is that with the greatest L.

C) Generalizations from rare earth measurements

1) Regular and inverted multiplets - the general rule is multiplets formed from equivalent electrons are regular when less that half the shell is occupied, but inverted when more than half the shell is occupied.
2) Double maximum in magnetic susceptibility curve

FIGURE I



3) Disagreement between Hund's theoretical values of samarium and europium and the values observed.

Van Vleck recognized Hund's error and recalculated the moment assuming the multiplet intervals of Sm and Eu comparable to kT instead of being very wide compared to kT. These two elements obey the Weiss Law,

$X = C/T + \triangle$ $\triangle$ is sometimes called the "molecular field" (9), it has several meanings.

D) States in which the magnetic moment of the rare earths have been measured.
1) Solution[6]
2) Octahydrated sulfates[27]
3) Oxides

E) Some applications
1) Manner in which 4f orbitals fill
2) Structure of divalent and tetravalent rare earths u,18,19,24

IV. Transition group ions

A) Configuration

$3s^2$ $3p^6$ $3d^{1-10}$ $4s^2$

B) Magnetic moments of first transition series

Many have speculated to the degree that the orbital moment has been quenched. Best agreement with experiment is obtained however by completely neglecting the orbital motion. The effective moment in Bohr magnetons is given by

$\sqrt{n(n+2)}$ where n is the number of unpaired electrons.

C) Other transition series
1) Yttrium to cadmium

$4s^2$ $4p^6$ $4d^{1-10}$ $5s^2$

2) Rare earths to mercury

$5s^2$ $5p^6$ $5d^{1-10}$ $6s^2$

V. Odd molecules

G. N. Lewis[13] first pointed out that molecules with an odd number of electrons should be paramagnetic. There are however a few molecules with an even number of electrons that are also paramagnetic such as oxygen and sulfur. The most common paramagnetic substances having an odd number of electrons are nitric oxide, nitrogen dioxide, chlorine dioxide, superoxides of alkali metals and free radicals in organic chemistry.

VI. Complex compounds

A) Introduction

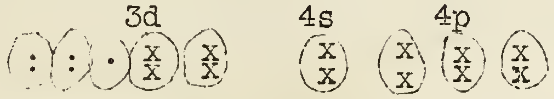
Pauling's interpretation[15,16,17] of these compounds in terms of wave functions and directed bonds is the most suitable. One of the most common hybrid bond orbitals is the tetrahedral carbon atom, the four bonds, one 2s and three 2p, are equivalent and directed toward the corners of a regular tetrahedron. A wave function for this system can be constructed by adding together the various functions, the wave function for the normal state being the one which miminizes the energy of the system. The best s-p orbitals for carbon can have a strength of 2 compared to 1.732 for 2p orbitals and 1 for 2s orbitals respectively.

We can of course have other hybrids involving d orbitals.

B) Octahedral complexes (d^2sp^3)

It should be pointed out that ionic and covalent compounds will behave differently. For example, FeF_6^{---} is ionic and has a moment of 5.9 Bohr magnetons corresponding to five unpaired d electrons. On the other hand $Fe(CN)_6^{---}$ is covalent of the d^2sp^3 type and has a moment of 2.3 corresponding to one unpaired electron.

$Fe(CN)_6^{---}$



C) Square and tetrahedral complexes (dsp^2 and sp^3)

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CO-ORDINATION COMPOUNDS OF THE GROUP VIII METALS WITH OLEFINS

Peter Arvan October 21, 1947

The ability to combine with olefins is quite widely distributed among the metals, but is perhaps most strongly exhibited by platinum. This coordinating tendency is not limited to olefins alone, but has been shown by substances such as unsaturated alcohols, acids, aldehydes, and esters. In each of these cases it appears that the unsaturated molecules occupy only one coordination position in the complex.

Platinum-olefin compounds.

Zeise (1), in 1827, prepared the first coordination compound between platinum and an olefin, by the reaction of platinic chloride and ethyl alcohol. Upon concentration in the presence of potassium chloride Zeise obtained a compound which analyzed for the formula $KCl.PtCl_2.C_2H_4$. Later Berzelius (2) prepared a substance which he considered to be identical with that of Zeise, by heating a mixture of ethyl alcohol and sodium chloroplatinate, and then concentrating the solution in the presence of potassium chloride.

Zeise believed that he had prepared the parent compound of the series $PtCl_2.C_2H_4$ by treating the ammonium salt $NH_4Cl.PtCl_2.C_2H_4$, with chloroplatinic acid. The product obtained from this reaction was probably the substance now referred to as "Zeise's acid", $H[PtCl_3.C_2H_4].H_2O$.

This original work was confirmed by Griess and Martius (3), who also demonstrated that ethylene is liberated when Zeise's compounds are pyrolyzed. These investigators prepared compounds similar to Zeise's salts, but containing aniline hydrochloride, and ethylenediamine hydrochloride, instead of ammonium chloride or potassium chloride.

In an attempt to prove that these substances actually contain ethylene, Birnbaum (4) undertook the following synthesis:

$$PtCl_2 + C_2H_4 \xrightarrow{KCl} KCl.PtCl_2.C_2H_4.H_4O$$

Since the reaction of ethyl alcohol with platinic chloride yielded a variety of products and the ethylene obtained from the pyrolytic treatment of Zeise's salts need not necessarily be in the original product, Birnbaum reasoned that if the complexes could be synthesized directly from ethylene, then all doubts as to the constituents of the complexes could be eliminated. He succeeded in making not only ethylene, but also several of its homologs combine with platinous chloride dissolved in hydrochloric acid.

Jorgensen (5) improved the yields of these olefin compounds by a modification of Berzelius method. In this procedure he isolated Zeise's acid as its tetrammine platinous salt, $[Pt(NH_3)_4][PtCl_3C_2H_4]_2$.

It was further shown by Biilman (6) and by Pfeiffer and Hoyer (7) that the same general type of compounds could be made using unsaturated alcohols, acids, aldehydes, and esters.

$$CH_2 = CHCH_2OH + K_2PtCl_4 \dashrightarrow K[PtCl_3.CH_2 = CHCH_2OH] + KCl$$

Anderson (8) isolated the primary member of the ethylene series, $PtCl_2.C_2H_4$, by reducing sodium chloroplatinate with alcohol. He isolated the compound by evaporation of the alcoholic solution below 50°C in a high vacuum.

Styrene was found to displace ethylene quantitatively from $PtCl_2.C_2H_4$, and thus the analogous compound, $PtCl_2.C_6H_5{=}CH_2$ was also obtained.

As a result of a systematic investigation, Anderson drew the conclusion that the coordinating abilities of the olefins decreased in the order ethylene > styrene > indene > cyclohexene > 1,1-diphenyl ethylene > methyl ethyl ethylene.

Birnbaum obtained the amylene compound by using the method of Zeise, that is, refluxing amyl alcohol with platinic chloride, and proposed the following equation as the probably course of the reaction:

$$PtCl_4 + 2RCH_2OH \dashrightarrow PtCl_2.C_2H_4 + RCHO + H_2O + 2HCl$$

Kharasch and Ashford (9) prepared compounds of the type $PtCl_2.Un$ (Un = unsaturated molecule) by treating anhydrous platinic chloride or bromide in an anhydrous solvent with the olefinic substance. The reactions involved in this preparation are not very well understood. Hydrogen halide is usually evolved during the reaction, and in some instances a small quantity of platinum separates. Halogenation of the unsaturated compound may also occur. These investigators found that *trans*-dichloroethylene and *trans*-diphenylothylene formed crystalline coordination compounds with platinum, whereas the corresponding *cis*-isomers failed to react.

Hellman (10) used butadiene in order to determine whether it would be possible for a diene to occupy two coordination positions and thus form a five-membered ring. The evidence indicates that no ring is formed and that each double bond functions separately, and only one coordination position is used in such compounds as $[PtCl_2.C_5H_5N.C_4H_6]$ and $[PtCl_2.NH_3.C_4H_6]$.

Palladium-olefin compounds.

Palladous chloride was converted into the dibenzonitrile-palladous chloride (11), and from this derivative compounds of the type $(PdCl_2.Un)_2$ were obtained as follows:

$$PdCl_2 + 2C_6H_5CN \dashrightarrow (C_6H_5CN)_2PdCl_2$$

$$2(C_6H_5CN)_2PdCl_2 + 2Un \dashrightarrow (PdCl_2.Un)_2 + 4C_6H_5CN$$

(Un = ethylene, isobutylene, cyclohexene, styrene.)

Iridium-olefin compounds.

The preparation of the iridium chloride-ethylene complex has been reported (12) by treatment of iridic chloride with absolute ethyl alcohol. When the resulting solution was treated with ammonium chloride however, a mixture of substances was obtained:

$IrCl_2.C_2H_4.NH_4Cl.H_2O$ or $NH_4[IrCl_3.C_2H_4].H_2O$

$IrCl_2(C_2H_4)_2.2NH_4Cl$ or $(NH_4)_2[IrCl_4.(C_2H_4)_2]$

$IrCl_2.C_2H_4.2NH_4Cl\cdot x\ H_2O$

Iron-olefin compounds.

Kachler (13) reported the preparation of $FeCl_2.C_2H_4.2H_2O$ as follows:

$$2C_2H_5OC_2H_5 + 2FeCl_3 \longrightarrow 2C_2H_4.FeCl_2 + 2C_2H_5OH + Cl_2$$

Other investigators (14), however, were unable to repeat the work of Kachler and claimed that the reported complex was a partially decomposed ether addition compound.

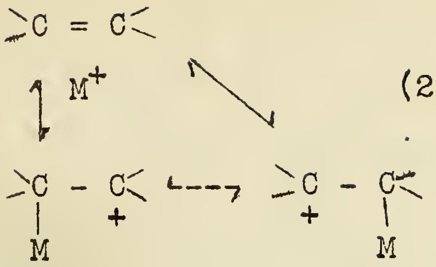
The long heating of iron pentacarbonyl with butadiene was reported (15) to give the complex $Fe(CO)_3C_4H_6$, in which two of the five carbon monoxide molecule had been replaced by one molecule of butadiene.

Structure of the Metal-Olefin Compounds.

The electron-pair theory is generally accepted as offering the best picture of the formation of a coordinate bond and the most satisfactory explanation of the properties of coordination compounds.

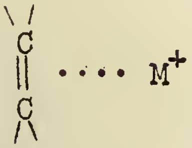
The acceptance of the electron-pair theory calls for the presence of a "lone pair" of electrons in order that an atom may exhibit "donor" properties, and thus act as a coordinating group. This is not apparent in the usual formulation of olefinic substances.

There has been much speculation (6,7,8,9,16,17,18,19,22) as to how an olefinic bond may be rearranged to free a pair of electrons for coordination to a metallic ion. After a consideration of the properties of this group of complexes and of the structures which have been suggested, it appears that the structure of the olefin-metal complexes cannot be formulated in the terms of the classical electron-bond theory. Below are shown the most probably structures for the metal-olefin complexes:



(20)

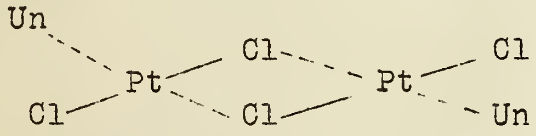
Structure is a reasonance hybrid of the three forms pictured. The bond is stabilized by resonance with the rest of the molecule. Polymerization and rearrangement are not found because-C ------ C- is not an intermediate.



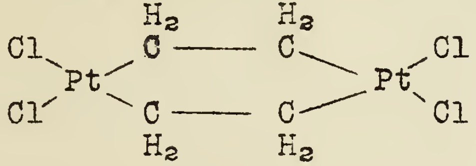
(21)

This structure is analogous to the "protonated" double bond which Pitzer postulates for diborane. In this structure the metal ion must have an S orbital available. The following properties are ascribed to the bonds; (1) The -C=C- distance is increased to roughly a single bond value; (2) The bond resists twisting as a double bond; (3) The usual conjugation or resonance phenomena of the bonds can occur; (4) It is much easier to convert this double bond to a single bond than an ordinary one.

Pfeiffer (16) has proposed a formula for ethylene-platinous chloride in which platinum is tetracovalent, the ethylene molecule occupies one coordination position on the platinum atom, and two of the chlorine atoms serve as bridging atoms in the dinuclear complex.



Kharasch and Ashford (9) have objected to such a formula on the basis that it postulates the formation of two coordinate bonds by one chlorine, They have proposed a ring structure for compounds of the type $MCl_2.Un_2$, in which the olefin molecule acts as a briding unit between the metal atoms:



The objection of Kharasch and Ashford to Pfeiffer's formula need not be given much weight, since stable compounds are known in which halogen atoms act as bridge groups.

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METAL CARBONYLS

Leo F. Heneghan

October 28, 1947

The physical properties of the metal carbonyls known today* are summarized in Table 1.

Table I

VIa	VIIa	VIII		
$Cr(CO)_6$ colorless cryst. sublimes at room temperature.		$Fe(CO)_5$ clear colorless liq. m.p.-19.5 b.p.-10.6° $Fe_2(CO)_9$ yellow cyst. decomp.100° $Fe_3(CO)_{12}$ gr. black decomp. 140°	$CO_2(CO)_8$ orange cayst. m.p. 51° decomp. 52° $Co_4(CO)_{12}$ black cryst. decomp. 60°	$Ni(CO)_4$ colorless li m.p. - 25° b.p. - 43.2°
$Mo(CO)_{16}$ colorless cryst. sublimes 30-40°		$Ru(CO)$ orange yell. cryst. $Ru(CO)_2$ choc. brown powder $Ru_2(CO)_9$ yell. cryst. $[Ru(CO)_4]x$ green cayst.	$Rh_2(CO)_8$ orange yell. needles sublimes at room temp. $[Rh(CO)_3]x$ brick red cayst. $Ru_4(CO)_{11}$ black scales	
$W(CO)_6$ colorless cryst. sublimes 50°	$[Re(CO)_5]_2$ colorless cryst. sublimes 140° m.p.-177° decomp. complete 400°	$Os(CO)_5$ also colorless cryst. m.p. - 15° $Os_2(CO)_9$ yell. cryst. sublimes 130°. M.p.-224°	$Ir_2(CO)_8$ yell. gr. cryst. sublimes in CO at 160° $[Ir(CO)_3]x$ yell. cryst. sublimes in CO at 210°	

* also $[Cu(CO)_3]_2$ is claimed - see top p12 ff

Preparation

The metal carbonyls may be prepared by a number of general methods. Perhaps the most widely used method involves the passage of carbon monoxide over the finely divided metal at suitable temperatures and pressures. Successful application of this method has been reported in the preparation of $Ni(CO)_4$, $Fe(CO)_5$, $Co_2(CO)_8$, $Mo(CO)_6$, $Ru(CO)$, $Ru(CO)_2$, and $Ru(CO)_5$. The temperatures and pressures required increase, and the yields decrease in the order in which the compounds are listed. Recently $Rh_2(CO)_8$ has been prepared by this method(6).

Nickel carbonyl is probably the most typical of the carbonyls. If finely divided metallic nickel is prepared by heating nickel formate at the lowest possible temperature (below 200°C.), the active nickel will take up carbon monoxide to give nickel carbonyl at room temperature and pressure (18). Very active nickel may also be prepared by forming a nickel amalgam by electrolysis of a solution of nickel sulfate using mercury as a cathode. The mercury is subsequently distilled from the nickel at a low temperature in vacuum (16). Carbon monoxide may then be passed directly into the reaction vessel to form the nickel carbonyl.

With iron pentacarbonyl, the direct synthesis is usually effected at 173° C., although temperatures as high as 400° C. have been reported. The pressures used vary from 20 to 200 atmospheres, although pressures as high as 1200 atmospheres have been reported. Mond and Wallis (12) found that temperature accelerates the reaction and increased pressure prevents excessive decomposition of the carbonyl. Above ca. 200°C. the metal catalyzes the disproportionation of carbon monoxide to form carbon dioxide and to deposit carbon on the iron and thereby lower the rate of formation.

The preparation of carbonyls by direct combination of the activated metal and carbon monoxide gives appreciable yields only in the cases of nickel and iron.

Manchot and Gall (9) observed that nickel carbonyl is formed when carbon monoxide is passed into a suspension of a nickel salt in caustic alkali and alkali sulfide. Windsor and Blanchard (16) worked out the mechanism of this process. Blanchard, Rafter and Adams (2) found that cyanide is fully as effective as sulfide in promoting carbonyl formation in an alkaline suspension of a nickel salt.

Job and Reich (8) found that the reaction between nickelous chloride and Grignard reagents produced some nickel carbonyl. This is the only practical method for the preparation of chromium, molybdenum, and tungsten carbonyls. Owens and his co-workers (12) obtained chromium carbonyl in yields of 67% by this method.

Osmium pentacarbonyl was prepared by treating OsO_4 with carbon monoxide (7). Likewise rhenium pentacarbonyl was prepared from Re_2O_7 (4).

Hieber and Lagally (5) prepared $Ir_2(CO)_8$ and $Ir(CO)_3$ by treating $Ir\ Cl_3$ with carbon monoxide. All of these reactions require elevated temperatures and pressures.

Additional isolated preparations which make use of certain reactions of the carbonyls themselves should be mentioned. For example, iron enneacarbonyl, $Fe_2(CO)_9$, is prepared by the action of light on the pentacarbonyl with the liberation of carbon monoxide (11). By heating the enneacarbonyl in solution in ether or benzene, a green solution of $Fe_3(CO)_{12}$ is formed without the liberation of more carbon monoxide (10). $Ru_2(CO)_9$ and $[Ru(CO)_4]_x$ can be prepared in s similar manner. $Co_4(CO)_{12}$ is prepared by heating $Co_2(CO)_8$ to 60°C. (1)

Pospekhov (14) claims to have detected a carbonyl of copper in the methanol condensates synthesized from carbon monoxide and hydrogen over a copper catalyst. According to Pospekhov this carbonyl is probably a polymer $[Cu(CO)_3]_2$.

Structure

The modern concept of the structure of nickel carbonyl and its isosteres, $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ is based on a resonance between:

$$(OC)_3\ Ni:C:::O: \rightleftharpoons (OC)_3\ Ni::C::O:$$

This structure, advanced by Brockway and Cross (3) on the bases of electron diffraction experiments, explains the shortening of the Ni-C bond from the predicted 2.00 Å to 1.82±0.03 Å. It also agrees with the 1.15 A C-O distance. The double bond between nickel and carbon is formed by bringing a pair of unshared 3d electrons from the nickel into the Ni-C bond, and shifting an unshared pair of electrons to the oxygen.

Powell and Ewens (15), on the bases of the optical and refractive nature of $Fe_2(CO)_9$, concluded that the iron atoms are in the ferric state and are linked by three carbon atoms, which in turn hold double bonded oxygens. In addition each iron has three -C=O groups.

The structures of the metal carbonyls are still a source of controversy, and more work is necessary before definite conclusions can be reached.

Properties

The metal carbonyls are not salt like; they are poor conductors of electricity, and they are, in general, insoluble in polar solvents and soluble in organic solvents.

In some cases, the carbon monoxide groups may be replaced by such groups as ammonia, pyridine, ethylenediamine, o-phenanthroline, etc.

Iron and cobalt carbonyls show many properties which are not possessed by metal carbonyls in general. Nitrosyl carbonyls such as $Fe(CO)_2(NO)_2$ and $Co(CO)_3(NO)$ can be prepared by treating the carbonyl with nitric oxide. Reaction with the halogens yield compounds such as $Fe(CO)_4X_2$. The carbonyl hydrides react as weak acids. The hydrogens can be replaced by metals to give compounds such as $Fe(CO)_4Hg$, $Co(CO)_4Ag$, $KCo(CO)_4$, and $K_2Fe(CO)_4$.

In their sensitivity to oxygen and oxidizing agents the metal carbonyls vary from pyrophoric nickel carbonyl to the relatively inert hexacarbonyls.

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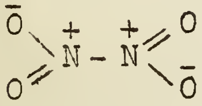
Roll Call

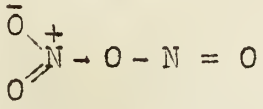
THE CONSTITUTIONS OF NITROGEN TETROXIDE AND TRIOXIDE

T. H. Dexter Nov. 4, 1947

The following structures for nitrogen tetroxide have been suggested:



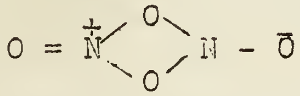
I



II

$O = N - O - O - N = O$

III

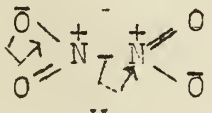


IV

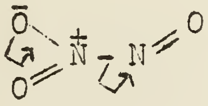
Physical evidence in the form of spectroscopic studies (1), entropy measurements (2), and X-ray data (3,4) have supported formula I.

Before 1946 chemical evidence in the form of the addition of nitrogen tetroxide to olefins was best explained in terms of formula II. Such a formula was necessary to account for addition products containing -NO and $-ONO_2$ as well as $-NO_2$ and -ONO. In 1946 Levy and Scaife (5) reported that in carefully controlled experiments only $-NO_2$ and -ONO addition products were formed and that $-NO_2$ always became attached to the carbon atom carrying the greater number of hydrogen atoms.

Ingold and Ingold (6) correlated these recent data to establish formula I (with electronic shift as indicated in V to account for the addition reactions to olefins). From analogous data (5) on nitrogen trioxide, they concluded that the structure indicated in formula VI should be correct for nitrogen trioxide.



V



VI

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Roll Call

PASSIVATION OF 18 - 8S STAINLESS STEEL

Carlyle E. Shoemaker November 4, 1947

Stainless Steel (18-8S) may be rendered inactive to acids by immersing it for three minutes into 10% boiling sulfuric acid followed by an exposure to air. If the specimen is placed in a vacuum of 0.001 mm of mercury, passivation is destroyed after 1 1/2 - 4 hours. The process is reversible and can be repeated, that is alternately exposed to air and a vacuum resulting in inactive and active metal respectively. This sulfuric acid treatment prevents pitting which other methods do not eliminate. Apparently, nitric acid does not passivate stainless steel.

Some evidence was found for the ability of argon to passivate this steel, replacing air. The evidence was not conclusive, however.

Electron diffraction studies gave no evidence for the formation of an oxide on the surface of stainless steel though a diffuse and unidentified pattern was found which might be a hydrous oxide of nickel or chromium.

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Roll Call

PROTON-DEUTERON EXCHANGE BETWEEN AMMONIA AND AMMONIATED DIBORANE

J. R. Mills November 4, 1947

Decisive evidence for the borinc theory of the base-reaction of diborane has been obtained by investigation of the proton-deuteron exchange between ammonia and ammoniated diborane. The H-D exchange reaction between ND_3 and $B_2H_6.2NH_3$ was found to reach equilibrium quite rapidly in liquid ND_3 solution at -78°C., and the extent of exchange shown to correspond to only 6 protons, or the number of N-H links in $B_2H_6.2NH_3$, even at temperatures as high as 18°C. The compound $B_2H_6.2ND_3$ shows no exchange of protons with excess ND_3, either when prepared at low temperatures and allowed to soak in excess ammonia-d_3 for several hours or at relatively high temperatures (40°C.) with extensive ammonolysis. Only indescribably slow exchange involving protons from the diborane is possible therefore which cannot be reconciled with theories of the base-reactions of diborane involving the transfer of proton from the diborane to the base.

ROLL CALL

AMPHOTERISM AND COMPLEX COMPOUND FORMATION IN LIQUID SULFUR DIOXIDE

Paul Mohr . November 4, 1947

Characteristic of water-like solvents (1) such as ammonia (2), hydrogen cyanide (3), sulfur dioxide (4), and others is the homology of a system of properties in regard to the solvents themselves and their solutions and also the homology of many reaction types of the dissolved materials. Both neutralization reactions and amphoteric behavior can be observed in these systems.

The liquid sulfur dioxide system has been investigated recently along with its base analogue, tetramethylammonium sulfite, and an amphoterism was observed in the compound, phosphorous trichloride (5), which was readily soluble in liquid SO_2 to form a colorless solution. Portionwise addition of tetramethylammonium sulfite to this solution caused a precipitation of phosphorous trioxide, which dissolved in excess reagent to give a colorless solution. Solution was complete after four moles of base had been added to two moles of phosphorous trichloride. Further excess of base simply developed the characteristic yellow color of sulfites in liquid SO_2. Conductance curves showed three slopes, corresponding to precipitation, dissolution, and the presence of excess precipitant. This last region was checked by back titration with the acid analogue, thionyl chloride. The reactions for these steps are as follows;

1) $2PCl_3 + 3[(CH_3)_4N]_2SO_3 \dashrightarrow P_2O_3 + 3SO_2 + 6[(CH_3)_4N]Cl$

2) $P_2O_3 + [(CH_3)_4N]_2SO_3 + SO_2 \dashrightarrow 2[(CH_3)_4N](PO_2SO_2)$

3) $2[(CH_3)_4N](PO_2.SO_2) + SOCl_2 \dashrightarrow 2[(CH_3)_4N]Cl + P_2O_3 + 2SO_2$

The phosphorous trioxide was found to be insoluble below -60°, but readily soluble at higher temperatures. The conductrometric titrations of phosphorous trioxide in liquid SO_2 with tetramethylammonium sulfite showed the formation of a compound which was readily isolated as pale yellow, hygroscopic crystals. Analysis of this compound indicated the formula to be either $(Me_4N)(PO_2).SO_2$ or $(Me_4N)PO(SO_3)$. It still remains to be determined whether it is a metaphosphite-SO_2 solvate or a complex sulfitometaphosphite.

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THE AMPHOTERISM OF CERTAIN METALLIC HYDROXIDES

Dale E. Jackson November 11, 1947

I. Introduction

Definitions of amphoterism are conflicting. Kraus (1) considers all elements of the 4th, 5th, 6th and 7th groups having a deficiency of from four to one electrons with respect to the rare gas configuration as being amphoteric. Lithium (2) and Barium (3) have been spoken of as amphoteric. It has been observed that if one divides the charge of an ion by its radius and takes the square root of the dividend, the root will be between 2.2 and 3.2 for elements usually known as amphoteric.

II. Theories as to the Mechanism of Amphoterism

A. The Oxy-acid Theory

This is best illustrated by the dissolution of aluminum hydroxide in a strong alkali according to the following equation:

$$Al(OH)_3 \quad + \quad OH^- \quad \dashrightarrow \quad AlO_2^- \quad + \quad 2H_2O$$

Blum's studies with the hydrogen electrode (4) give indications of the formation of a meta-aluminate ion, AlO_2^-. The same type of work by Britton (G_3) confirms this statement.

Prescott (5) states that since a mole of sodium hydroxide is needed for dissolution of a mole of aluminum hydroxide, the solution must contain the meta-aluminate ion. Herz (6) found an ortho-aluminate, AlO_3^{---}, to form if the precipitate is dried first.

Copper hydroxide dissolves appreciably in concentrated alkali solutions, giving a deep blue color, and the bulk of the evidence supports the view that the coloration is due to the cuprate ion, CuO_2^{--}, and not to colloidal cupric oxide (8).

Mellor (9) mentions the formation of sodium meta- and ortho- chromite. Hildebrand (10) used the hydrogen electrode to prove the existence of hydrogen-zincate ion, $HZnO_2^-$, during the reaction of the zinc ion with alkalies.

The acid character of beryllium hydroxide has been investigated by Hantzsch (11) and Krüss and Moraht (12).

Grube and Feucht (13) claim to have formed potassium cobaltite, K_2CoO_2, and to have proved that the dissolution of cobalt(II) hydroxide in potassium hydroxide is due to the formation of this compound.

B. The Complex Theory

This theory was first suggested by Pfeiffer (14) in 1907. It is interpreted by Seward (G_1) to mean that the dissolution of aluminum hydroxide in alkali proceeds as follows:

$$Al(OH)_3 \quad + \quad nOH^- \quad \dashrightarrow \quad Al(OH)_{3+n}^{n-}$$

The number of hydroxyl ions combining would be determined by the coordination number of the metallic ion but might vary with the concentration of hydroxyl ions.

In support of this theory it is to be noticed that the amphoteric elements usually form complexes with anions other than hydroxyl. The studies of Johnston (15) and Laue (16) remove an exception to this statement as they have shown the solubility of silver hydroxide to increase with increasing concentrations of sodium hydroxide.

Scholder and Schletz (17) isolated many compounds with pyrocatechol-magnesium anions, such as $Na[Mg(O_2C_6H_4)_2(OH)_2]$. Scholder (18) also found nickel(II) hydroxide to dissolve in concentrated sodium hydroxide in the presence of pyrocatechol to give a complex pyrocatechol-hydroxy-nickel anion.

Dialysis experiments of Brintzinger and Wallach (19) indicate anionic weights in alkaline solutions of amphoteric hydroxides which are consistent with the weights expected on the basis of the complex theory. Newly formed zinc hydroxide dissolves readily in alkali, one zinc ion being taken up by approximately six hydroxyl ions according to Rubenauer (20).

Jander and Scholz (21) write the equation

$$Fe(CN)_3 + 3HCN + Et_3NHCN \dashrightarrow (Et_3NH)_3[Fe(CN)_6]$$

to show the amphoterism of ferric cyanide in hydrogen cyanide.

Scholder and Pätsch state that alkaline plumbite solutions contain the hydroxy anions, $Pb(OH)_3^-$, $Pb(OH)_4^{--}$ and $Pb(OH)_6^{----}$, depending on the concentration and temperature of the alkali used. These could not be crystallized. (22)

C. The Addition Theory

Pfeiffer also points out that amphoterism may be a matter of addition. Scholder (23) and co-workers prepared the following salts in support of this theory:

Zincates:	$Na[Zn(OH)_3] \cdot 3H_2O$	$Na_2[Zn(OH_4)]$	$Sr\ Zn(OH)_4 \cdot H_2O$
	$Na[Zn(OH)_3]$	$Ba[Zn(OH)_4] \cdot H_2O$	$Sr_2\ Zn(OH)_6$
	$Na_2[Zn(OH)_4] \cdot 2H_2O$	$Ba_2[Zn(OH)_6]$	
Cuprates:	$Na_2[Cu(OH)_4]$	$Ba_2[Cu(OH)_6] \cdot H_2O$	
	$Sr[Cu(OH)_4] \cdot H_2O$	$Sr_2[Cu(OH)_6] \cdot H_2O$	
Cobaltites:			
	$Na_2[Co(OH)_4]$	$Ba_2[Co(OH)_6]$	$Sr_2[Co(OH)_6]$
Stannites:			
	$Na[Sn(OH)_3]$	$Ba[Sn(OH)_3]_2$	$Sr[Sn(OH)_3]_2$
Plumbites:			
	$Na_2[Pb(OH)_4]$ (?)	$Na[Pb(OH)_3]$	$Na_2[Pb(OH)_3X]$; $x = CNS^-$, Br^-, I^-

The behavior of these salts when heated is cited as proof of their structures. The compound $Na_2[Zn(OH)_4]$ should lose two molecules of water at a reasonably low temperature if it is only the dihydrate of sodium zincate, $Na_2ZnO_2 \cdot 2H_2O$. It was found to lose one molecule of water below 200°, but the second was not removed even on heating to 465° for many hours.

Fitzgerald (24) has prepared crystalline $KZn(NH_2)_3$.

D. Hammett's Development (G_4)

Hammett observed that any solution saturated with zinc hydroxide must satisfy the equation:

$$[Zn^{++}][OH^-]^2 = K_b \qquad (1)$$

He assumed the existence of the $Zn(OH)_4^{--}$ ion and stated that any solution containing zincate must satisfy the equation:

$$\frac{[Zn^{++}][OH^-]^4}{[Zn(OH)_4^{--}]} = K_e \qquad (2)$$

Dividing (1) by (2) he obtained an equation:

$$\frac{[Zn(OH)_4^{--}]}{[OH^-]^2} = \frac{K_b}{K_e}$$

According to this expression the concentration of zincate ion and thus the solubility of zinc hydroxide in a sodium hydroxide solution is proportional to the square of the hydroxyl ion concentration. This is borne out by experiment. In a like manner aluminate, chromite, plumbite and stannite ions involve the addition of only <u>one</u> hydroxyl ion to the hydroxide. Metastannic acid adds two.

Davidson and co-workers (25), (26) prepared compounds in anhydrous acetic acid which were analogous to the tetra-hydroxy zinc complex; they were $(NH_4)_2[ZnAc_4] \cdot 6HAc$ and $Na_2ZnAc_4 \cdot 4HAc$.

E. The Theory of Peptization

Working with the hydrogen electrode Britton found only aluminum hydroxide to be truly amphoteric. Mahin (27) considers even aluminum to form mainly colloidal suspensions, but his conclusions are rendered nearly invalid by Blum (4).

Weiser thinks it likely that the first step in the dissolution of some or all hydroxides is peptization, followed in most cases by compound formation. Seward sums up this argument.

III. Fundamental Considerations

The essence of the question is what will occur when the hydroxyl ion of the alkali encounters the M-O or M-OH bond. A small, highly charged cation means an acidic nature, and the reverse is true with a large cation of low charge. (G_5) The effect of the small cation as seen by Lewis (28) is to make the bond between it and the oxygen atom more covalent by distorting the electron cloud around oxygen.

Although it is necessarily an approximation, Bernal and Megaw (29) have tried to relate the strength of the M-O bond to the dipole moment with a small addition for what they call core interaction for ions with incomplete or eighteen electron shells. Their formula for the electrostatic potential energy is

$$z\left(-\frac{1.5}{r_1} + \frac{0.5}{r_2}\right)$$

where r_1 is the M-O distance; r_2 is the M-H distance: "z" is the valence divided by the coordination number; 1.5 is the charge at the oxygen atom and 0.5 is the charge at the hydrogen atom.

The energies calculated in this way are given below:

Hydroxide	CN	Bond Energy (arbitrary scale)	Correcting Factor	Corrected Energy
LiOH	4	0.093	1.00	0.093
$Mg(OH)_2$	6	0.153	1.00	0.153
$Mn(OH)_2$	6	0.164	1.06	0.174
$Zn(OH)_2$	6	0.165	1.10	0.181
$Co(OH)_2$	6	0.170	1.06	0.180
$Ni(OH)_2$	6	0.174	1.06	0.184
$Fe(OH)_2$	6	0.169	1.06	0.179
$Cd(OH)_2$	6	0.155	1.10	0.170
$Zn(OH)_2$	4	0.187	1.20	0.225
$Al(OH)_3$	6	0.292	1.00	0.292

Assuming the initiation of dissolution by peptization, the surface development of the colloidal particles under attack by alkali could determine the extent of true amphoteric behavior.

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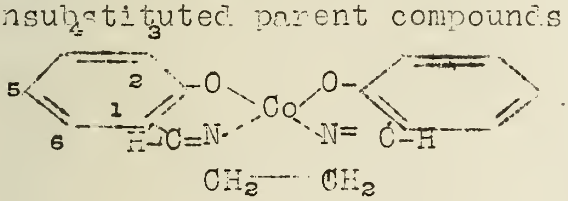
OXYGEN-CARRYING SYNTHETIC CHELATE COMPOUNDS

P. J. Pizzolato November 18, 1947

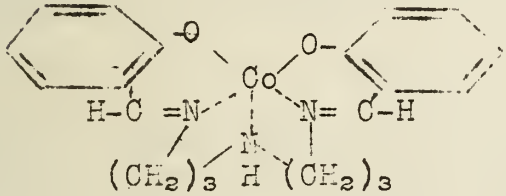
Introduction. The occurrence of chelate compounds in biological oxidation-reduction systems led Calvin and co-workers to the study of synthetic chelate compounds in an effort to gain an understanding of their nature and the properties related to oxygen-carrying activity. In addition to studies on cobaltous bis-salicylaldehyde ethylenediimine which had been shown earlier to have oxygen-carrying activity, the investigations included a search for other compounds showing the oxygen-carrier property and a study of the mechanism of the oxygenation reaction involving an examination of rates, equilibria, x-ray crystallography, magnetism, solutions, cycling properties, etc. Since one of the primary purposes of this work was the development of compounds which could be used to prepare pure oxygen from air, the efforts of Calvin and co-workers were directed toward three main objectives: (1) to increase the weight per cent of oxygen carried, (2) to increase the stability of the compound, so as to allow cycling a greater number of times, and (3) to increase the rate at which oxygen would be absorbed and released.

Of the compounds studied, two types showed oxygen - carrying activity in the solid state as well as in solution in certain organic solvents. They may be represented by the following unsubstituted parent compounds:



2-1 compounds
(in proper form, take up
one molecule of oxygen
for each two atoms of Co)

Type I
(CoSaEn)



1 - 1 compounds

Type II
(CoSaPrtr)

Compounds of both types showed a variety of crystal forms, some active oxygen-carriers, others inactive toward oxygen.

Equilibrium Studies. In studies in which the equilibrium oxygen pressure over the solid chelates was measured as a function of the degree of oxygenation, four Type I compounds showed a characteristic behavior (5). An initial sharp rise in pressure, which was understood to indicate slow uptake of oxygen was followed by considerable interval of approximately constant pressure, during which oxygen uptake was rapid, and this in turn was followed by a final rapid rise in pressure occurring before the oxygenation was complete, the compounds appearing to under-

go oxygenation to a product containing less than the stoichiometrical amount of oxygen. The intermediate interval of approximately constant pressure has been shown by x-ray studies, in the case of CoSaEn, to coincide with a crystalline phase change, and the interval of higher oxygen pressure which follows has been shown to be a region of solid solution. Thus it was demonstrated that the system is not a simple three phase one (gaseous oxygen, original chelate, oxygenated chelate) but rather that at the higher degrees of oxygenation (about 75% of complete oxygenation) the unoxygenated phase disappears entirely and a solid solution is formed.

Equilibrium Oxygen Pressures at 50% Oxygenation

Compound	O_2 Pressure (mm.) 0°	O_2 Pressure (mm.) 25°
Type I CoSaEn (parent compd.)	~5	~50
Type I 3-F-CoSaEn	~0.4	~2

Equilibrium oxygen pressures over the solid compounds of Type II are much higher than for Type I compounds.

Kinetics of Oxygenation and Mechanism. All three compounds studied (CoSaEn, its 3-ethoxy and 3-fluoro derivatives) showed a temperature at which the rate of oxygen absorption is a maximum. At temperatures well below the optimum, the reaction is of the first order with respect to the active chelate in the cases of the parent CoSaEn and its 3-ethoxy derivative, while in the case of the 3-fluoro derivative the reaction is of the second order (1). The mechanism proposed consists of two steps, the first of which is an equilibrium involving formation of activated oxygen molecules in proportion to the number of unoccupied chelate molecules in the crystal mass. The activated oxygen behaves as though it were in solid solution in the crystal mass, possibly bonded to one chelate molecule and free to migrate from cobalt atom to cobalt atom with no change in the position of the chelate molecules, that is, no phase change.

1) $A + O_2 \rightleftharpoons AO_2$ A = chelate

In the second step the completely oxygenated chelate pair is formed in some crystallite by suitable collision of an activated oxygen with another chelate molecule.

2) $AO_2 + A \longrightarrow A_2O_2$

With the formation of a complete oxygenated chelate pair rearrangement of the chelate molecules begins, and once rearrangement has begun in any given crystallite, complete oxygenation of that crystallite is effected very rapidly, directly by oxygen in the gas phase as well as by the activated oxygens. For the case of the first order reactions, the first step is rate-determining, the second a relatively fast reaction. In the second order reaction, the first step is a rapid reversible equilibrium and the second is rate-determining.

Magnetic Properties. No correlation was observed between magnetic properties and oxygen-carrying activity of chelates in the solid state. All active cobalt compounds of Type I gave

paramagnetic susceptibility values corresponding to one unpaired electron per cobalt atom, evidence for covalent square planar structure, while those of Type II gave values corresponding to three unpaired electrons per cobalt atom, evidence for ionic cobalt (3). The Type I CoSaEn showed a linear decrease in susceptibility with increased oxygenation, the value approaching zero when the full complement of oxygen had been absorbed, indicating that the single unpaired electron in the active material is in the peroxide paired with one of the oxygen electrons. The Type II parent compound showed a similar linear decrease in susceptibility on oxygenation, giving values corresponding to one unpaired electron when saturation was reached.

Stability to Cycling. The stable peroxides formed by the reaction of gaseous oxygen and these chelates are, upon heating or exposure to reduced pressures, decomposed reversibly to form the original reactants, but on continued cycling, that is, alternate oxygenation and deoxygenation, the chelate slowly loses its oxygen-carrying capacity. The Type I parent compound, CoSaEn, deteriorated to 70% of its original productivity after 300 cycles, corresponding to the production of about 15 lb. of oxygen per pound of chelate deteriorated to one-half its original productivity. The 3-fluoro compound of Type I showed much greater stability, deteriorating to 60% of its original productivity only after 1500 cycles, and producing about 65 lb. of oxygen per pound of chelate deteriorated to one half its initial productivity (6).

The decrease in activity was shown to be due not to a recrystallization into the more stable inactive crystal form, but rather to an irreversible oxidation of part of the compound by molecular oxygen, the oxidation products poisoning the remaining material. It is believed that either the peroxide or the transition state molecules undergo most of the destructive oxidation. The point of attack by the oxygen and the products formed are now known.

Crystal Structure. Type I compounds appear to be coplanar molecules arranged in layers and in the active crystal form they are so arranged as to leave "holes" in the lattice large enough to accomodate oxygen molecules (2). The passage between holes being only slightly smaller than these holes, the oxygen molecules may pass completely through the lattice by passing over relatively low potential barriers between the holes. Since in the inactive form no such holes exist, this picture seems to account for the difference in behavior of active and inactive forms of a given chelate. There is evidence, however, indicating that the steric factor is not the only one determining oxygen-carrying activity.

Oxygenation of Chelate Solutions. Nearly all of the cobalt compounds of both Types I and II as well as certain other types were found capable of absorbing oxygen reversible when dissolved in the proper organic solvent (4). Equilibrium oxygen pressures over solutions of Type II compounds were much higher than for the Type I. Chelate solutions, however, could not stand very many cycles, a very appreciable amount of irreversible oxidation taking place at each cycle. Most of the studies involved the use of quinoline as solvent, a few runs having

been made with ethyl benzoate, α-methylnaphthalene and pyridine. Although oxygen capacity of the solutions varied from compound to compound, and also depended on the solvent used, values reached as high as 0.9 mole of oxygen per mole of chelate at the higher pressures and lower temperatures.

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CORROSION AND CORROSION CONTROL

Philip Faust November 25, 1947

Introduction

One of the important reasons for corrosion control is economy. It is estimated that the annual loss to the world through the corrosion of metals is approximately two to two and a half billion dollars.

The Electrochemical Nature of Corrosion

When a metal corrodes it is oxidized and some substance in the environment is reduced. The combination of anode and cathode areas which result from this oxidation and reduction and the aqueous solution constitute a small galvanic cell. Magnesium, aluminum, manganese, chromium, zinc and iron 1,^{G}1, can corrode in water in the absence of oxygen. Cadmium, cobalt, nickel, lead, copper, mercury and silver do not corrode in oxygen free water, but can corrode spontaneously in water saturated with air.

The principal factors that determine which areas will be anodic and which cathodic are:

Anodic Areas

1. Strained metal
2. Areas at which there is a low concentration of oxygen
3. Areas at which a protective film has been broken
4. Impurities in metal or electrical contact with a metal which is anodic to the metal in question.

Cathode Areas

1. Unstrained metal
2. Areas at which oxygen concentration is high
3. Impurities in metal upon which there is a low oxygen or low hydrogen overvoltage.
4. Impurities in metal which are cathodic to the metal[2]

Anodic and Cathodic Control

The corrosion rate of low carbon steel in pure water in the presence of air is determined by the rate at which oxygen can reach the cathode areas by diffusion. As the depth of immersion is increased, the anodic area is increased, but the weight loss remains the same because the cathode area is still the area just below the air-liquid interface. The process is therefore under cathodic control.

The corrosion of aluminum, stainless steel and other metals that form adherent, non-porous films on their surfaces in common environments provides examples of processes under anodic control, i.e., the corrosion rate decreases as the anodic area decreases[3].

Inhibitors

Any substance that, when added to the environment of a metal or alloy, decresses the corrosion rate is called an inhibitor. Anodic inhibition can be accomplished by the use of chromates, phosphates, silicates, etc. These appear to adsorb strongly and satisfy secondary valence forces of the surface so that the metal atoms no longer have the same tendency to leave the lattice.[4]

Oxygen can act as an inhibitor or a stimulator of corrosion depending on conditions. Oxygen tends to make a surface cathodic because it is a reactant in the cathodic reaction in "oxygen type" corrosion. (This is the case of corrosion in water in the presence of oxygen as opposed to corrosion in oxygen free water, called "hydrogen type"--an example of the oxygen type is: at cathode areas O_2(in air) + $2H_2O + 4e = 4OH^-$ at anode areas $2Zn + 4OH^- = 2Zn(OH)_2 + 4e$). Also in many cases it helps keep in repair a passivivating oxide film. However, once weak points on a metal surface are attacked, the rate of attack will be stimulated by increasing the oxygen concentration.[5]

If insufficient anodic inhibitor is added to a system in which the process is under cathodic control, intense attack will result, especially if anodic areas are small. This will cause failures in a metal because moderate corrosion spread over large areas is usually not serious.[6] Inhibitors are also used to decrease acid attack on iron and steel in the pickling baths to prepare the surface for galvanizing, enameling, electroplating, etc. It is believed that inhibitors function by being adsorbed on the metal surface to form a well organized film which serves to increase the polarization for hydrogen evolution or by introducing a high transfer resistance between the solution and the metal surface.[7] In general, organic compounds that possess inhibitor properties will be found to contain nitrogen, oxygen, sulfur or other elements in the 5th and 6th periodic groups. It seems also that an inhibitor must consist of a hydrocarbon part attached to a polar or ionizable group.

Water Line Attack

If the liquid at the air interface is in motion and contains chlorides and anodic inhibitors such as hydroxide, carbonate, chromate, etc. in an amount insufficient to stifle the corrosion reaction completely, the situation is favorable for intense attack at the water line.[8] Also a variable position of the water line favors attack because the porous layer of corrosion product is made more compact and adherent when above the liquid medium and, when submerged again, will screen the metal surface from oxygen and make that portion of the surface anodic.

Influence of Bacteria or Corrosion

Sulfate reducing bacterial live best in the absence of oxygen and they act on iron in an oxygen excluding soil, such as heavy clay, if some sulfate is present. They use up the polarizing hydrogen to reduce sulfate to hydrogen sulfide and water. This reacts to form iron sulfide.[9]

Stress Corrosion, Grain Boundary Corrosion

Internal stresses due to such operations as cold working and quenching and stresses due to applied loads will make a metal more anodic and tend to increase the rate of corrosion. In alloys whose failure by cracking has been initiated by corrosion, the failure is usually along grain boundaries. Alloys susceptible to this type of failure contain material in or adjacent to the grain boundaries which is anodic to other grain boundary material or to the main portion of the grain.

Stray Current Corrosion

Metallic structures such as water and gas pipes and lead cable sheath, adjacent to direct current circuits, may suffer severe attack due to leakage from the main circuit, a portion of the current flowing throught the adjacent structure. The most serious trouble is in the vicinity of street-car lines. To reduce corrosion due to these stray currents to a miminum, it is neccssary

to make the resistance of the rail system as low as possible. Good electrical contact between rails and drainage of soil between rails and adjacent pipe lines and structures will produce beneficial results.

Electrolytic Protection

The principle of application of external electromotive force involves neutralization of the electric currents that account for the observed corrosion and that operate between the many anodes and cathodes of the metal surface. The protection is accomplished using an external anode and connecting it to the positive terminal of a source of C. C. current, and the structure to be protected to the negative terminal.[4]

Influence of Contact Between Dissimilar Metals

If dissimilar metals in contact are exposed to a corrosive environment in which the more active metal does not become passive, the more active metal will be anodic and give cathodic protection to the less active metal. In most, but not all[10], environments zinc affords such protection to iron.

Contact between metallic and non-metallic materials is likely to bring about an intensification of the attack on the metal because the non-metal screens the metallic surface from ready access to oxygen.

Alloying

The stainless steels are among the most popular corrosion resistant alloys. They are iron-base alloys containing 12 to 18% chromium and other metals, such as nickel, manganese, molybdenum, etc. These alloys are called passive. Uhlig[4] ascribes their corrosion resistance to the satisfaction of the secondary valence forces of the metal by means of an adsorbed film of oxygen rather than a protective film of chromium oxide.

Inorganic Coatings

The most common metal coating is zinc. Tin is another important coating material, but it is cathodic to iron and therefore does not afford galvanic protection. Consequently tin (as well as nickel) coatings must be free from pores to be of good use. Alloys such as brass are used as coatings, as are porcelain enamels.

Organic Coatings and Paints

Organic coatings serve mainly to isolate the metal from its environment. Such things as Bakelite[11] and thermo setting plastics[12] have been used on the inside of pipes to prevent corrosion.

Protective paints contain such things as red lead, zinc dust, zinc oxide, zinc chromate, etc. in some organic vehicle.

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INFRA-RED STIMULATED PHOSPHORS

J. C. Brantley   November 25, 1947

I. Introduction. Phosphors are substances which are capable of emitting light after exposure to some kind of radiation. Classically, the term fluorescence has been applied to the light emitted while the phosphor is being irradiated, with the term phosphorescence applied to the light emitted after the radiation has ceased. In some cases the rate of emission of light can be accelerated by radiation with light of another wave length than that used to excite the phosphor. This phenomenon is called stimulation. The infra-red stimulated phosphors, after excitation by light radiation, emit visible light when placed in infra-red light.

II. Infra-Red Stimulated Phosphors. The effect of infra-red radiation on certain materials was first observed by Seebeck and Becquerel. In 1889 Klatt and Lenard (4) observed a momentary intensification of the afterglow upon irradiation with infra-red. The effect was more objectively observed by Dahms in 1904 (1).

The phenomenon of luminescence may be explained by energy changes of the electrons in the atom. After excitation to higher energy levels, the electrons return to lower levels with the emission of quanta of light.

In the infra-red stimulated phosphors, these energized electrons are trapped in some way in the lattice. The absorption of infra-red light accelerates the electrons, allowing them to escape and return to their lower levels, emitting light.

Urbach (11) lists six requirements for good infra-red phosphors.

1. Efficiency of conversion of infra-red to visible light.
2. Spontaneous emission should be low at time of use.
3. Spectrum of emitted light must be favorable for use.
4. Sufficient energy must be stored to avoid need for frequent re-excitation.
5. High infra-red sensitivity to long wave lengths.
6. Adequate excitation possible with available sources.

III. Preparation of Infra-red Stimulated Phosphors. Lenard, an early worker in the field, has described the general methods (5). They consist of the reaction of the alkaline earth carbonates with sulfur at 1000°. To this mixture is added calcium fluoride, some sulfate, and the activators.

The general formula for a phosphor of this type includes a base material, usually an alkaline earth sulfide or selenide, activators, and flux.

Early in 1942 Urbach and his co-workers (11) tried to reproduce Lenard's results, but without success. An investigation into the flux and activators used led to success in producing sensitive phosphors.

All infra-red phosphors contain activators. Although Lenard used only one, Urbach early recognized that a large class of phosphors require a dominant activator to produce the emission and an auxiliary activator to sensitize it to infra-red.

The effects of different activator pairs may be seen in the following table.

EMISSION COLORS OF INDIVIDUAL SULFIDE AND SELENIDE PHOSPHORS

Base	Activators	Exciting light	Emission
SrS	Eu-Sm	Blue-green	Orange-red
SrS	Ce-Sm	Ultraviolet or radium radiation	Green
SrSe	Eu-Sm	Blue-green or ultra-violet or radium	Yellow
CaS	Eu-Sm	"	Red
CaSe	Eu-Sm	"	Orange-red

Investigation showed that samarium was the most efficient of the auxiliary activators, with cerium and europium becoming the most important dominant activators.

Primak, Osterheld, and Ward (8) showed that the flux functioned as a recrystallization medium to distribute the activators in the lattice. A second function lies in the production of a cationic rearrangement between calcium ion and strontium ions, which results in a very sensitive phosphor. A third function was found to be due to the sulfate ion in the flux. A phosphor when heated in nitrogen was found to lose weight and evolve selenium. The only explanation advanced for this is shown by the equations:

$$SrSO_4 + 4SrSe \dashrightarrow 4SrO + SrS + 4Se$$
$$SrSO_4 + SrSe \dashrightarrow 2SrO + SO_2 + Se$$

Similar reactions have been reported by other investigators (12).

IV. Examples of Efficient Phosphors. Three successful phosphors have been been prepared. The first of these was Standard VI:

$$100SrS(0.020Sm,0.020Eu)(6SrSO_4,6CaF_2)\ (6)\ (10)$$

This phosphor had an emission macimum at 0.63μ in the red.

The second was Standard VII with a Ce-Sm activator and lithium fluoride flux. This was more efficient than Standard VI with an emission maximum at 0.485μ in the green. Ultraviolet light or radium radiation was required for excitation.

The third, called B-1, was more efficient than Standard VI and was excited by visible light, an advantage over Standard VII.

Formula: $100SrSe(0.20Sm,0.020Eu)(6SrSO_3,6CaF_2)(10)(11)$

A fourth phosphor is interesting although not efficient. Pitha, Smith and Ward (7) prepared an active lanthanum salt which proved to be La_2O_2S. The salt was prepared by heating the sulfate in nitrogen producing the oxysulfate. This was reduced with hydrogen to the oxysulfide. Analysis of the product coincided closely with the theoretical values.

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CHARACTERIZATION OF CIS-TRANS ISOMERS OF INORGANIC COORDINATION COMPOUNDS BY USE OF THE POLAROGRAPH

Jack Nyman Roll Call December 2, 1947

In coordination compounds of the type $[MA_4B_2]^{n+}$ or $[MA_4B_2]^{n-}$, the trans form is symmetrical and has no dipole moment, while the cis form is a dipolar ion. This property is used in the characterization of these isomers by polarographic measurement of the limiting current of these ions in solution.

In normal polarographic measurements an excess of indifferent electrolyte is used to suppress the migration current of the reducible ion, and a curve, such as Curve I, is obtained due to diffusion only. However, there is not enough diffĕrence in the diffusion currents of the cis and trans forms to distinguish between them on the basis of diffusion alone. In the absence of an indifferent electrolyte the migration current is important, and since a positive ion moves toward the negative electrode, the limiting current is the sum of the migration and the diffusion currents. The limiting current of both cis and trans positive ions is therefore greater than the diffusion current. Being a dipole and also being in a non-homogeneous electric field, the cis ion will orient with respect to the electrode and move toward it under the influence of this force as well as by migration. This orientation effect is not present in the case of the trans form, and consequently the cis form moves faster and carries more current. (Curves II and III). This has been proven to be true in the case of $[Co(NH_3)_4(NO_2)_2]^+$ and $[Co(pn)_2Cl_2]^+$. For a negative ion, whose diffusion current curve is also illustrated by Curve I, the migration of the ion is away from the negative electrode and consequently the limiting current is the difference between the diffusion and migration currents. Again the cis form is attracted by the electrode because of its dipole and should show a greater limiting current than the trans (Curves IV and V). However, the limiting current for both the cis and trans forms should be less than the difussion current because of the migration away from the electrode. This theory has not been proven for the negative ions because of the lack of suitable stable ions.

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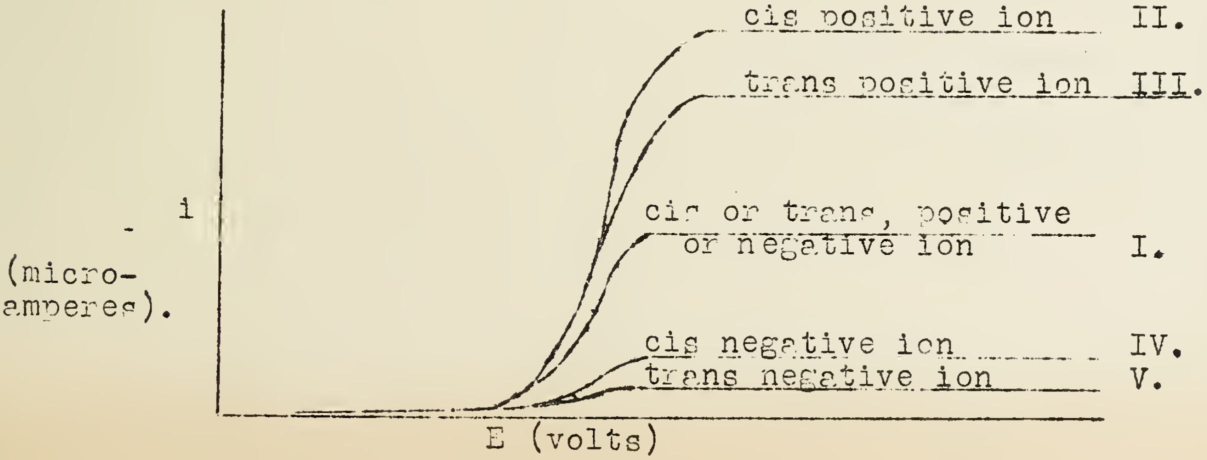

THE STRUCTURE OF URANIUM HYDRIDE

O. F. Hill Roll Call December 2, 1947

Uranium forms a metallic hydride, UH_3(1). This hydride is unique in that it does not fall in any of the three classes: volatile hydrides, salt-like hydrides or interstitial hydrides. It has metallic properties (inconsistent with ionic structures); it is non-volatile and has a high melting point (>>600°), and it is a compound of definite chemical composition with a structure completely unrelated to any of the three forms of uranium metal. Metal-metal bonds of any strength are almost completely lacking; therefore, bonding between uranium and hydrogen must play a predominant role.

Debye-Scherrer powder patterns have shown that the unit cell contains eight uranium atoms, two type (a) atoms in equivalent positions and six type (c) atoms in equivalent positions. Each (c) atom is surrounded by two other (c) atoms as nearest neighbors at 3.316A (by far the shortest metal-metal bond of any strength) and by four (c) atoms at 3.707A. Each (a) atom is surrounded by twelve nearest (c) atoms at 3.707A in the arrangement of a deformed icosahedron.

The high melting point and the brittleness are in keeping with a valence type compound, i.e, a continuous structure held together by covalent bonds. Since metal-metal bonds of any strength are absent, the continious structure can only be provided by hydrogen forming bridges between uranium atoms. Rundle proposes that these bridges are between metal atoms of type (a) and (c) and that they consist of electron deficient "half-bonds" of the type which he has proposed for boron hydrides and the aluminum alkyl dimers. The bridges contain only one electron pair for the two bonds. This structure accounts for the formula of the hydride and is consistent with the theory of electron deficient structures recently proposed by Rundle (2).

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TERNARY FISSION OF URANIUM

B. P. Block Roll Call December 2, 1947

It has become usual to formulate the fission of uranium 235 by slow neutrons in the following fashion.

$$ {}^{235}_{92}U + {}^{1}_{0}n \longrightarrow \left[{}^{236}_{92}U\right] \longrightarrow {}^{m_1}_{z_1}A + {}^{m_2}_{z_2}B + \nu\,{}^{1}_{0}n + K.E. $$

$$ m_1 + m_2 + \nu = 236 \qquad z_1 + z_2 = 92 $$

This formulation implies that there are two large particles formed upon fission of the complex nucleus. When the log of the fission yields of all the isotopes so far detected is plotted versus the mass number for each isotope, a curve is obtained which has an area of 197% under it as compared with a theoretical area of 200% for the formation of two large particles per fission. Although the possibility of ternary fission was recognized in work carried out in this country, no evidence could be obtained for fissions of higher order than the second.

Recently Tsien and coworkers at the College of France in Paris have reported the existence of ternary and quaternary fission of uranium. The evidence they put forth is the occurrence of tracks on special photographic plates which have been bombarded with slow neutrons after being treated with aqueous 10% uranyl nitrate solution. In several instances two heavy, short tracks and one light, long track were observed to originate at one point on the plate. This is interpreted by them as due to the fission of uranium into two large particles and one smaller particle.

They list the following three points as evidence that the light fragment is emitted simultaneously with the other two so that a true ternary fission is occurring. 1. The time between fission and observation of the particle is so short (within $2x10^{-4}$ sec.) that the two are probably simultaneous. 2. The direction of emission of the particle is invariably perpendicular to the paths of the two heavier particles. If the particle were emitted before the fission, it would be emitted preferentially in the axis of the elongated nucleus because of energy barriers; whereas the direction of emission would be random after the fission. 3. The mass of the light particle is found to vary from 2 to 32.

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A GENERAL MECHANISM FOR THE FORMATION OF VOLATILE HYDRIDES BY HYDROLYSIS REACTIONS

J. C. Richards Roll Call December 2, 1947

A very general reaction of inorganic chemistry is the hydrolysis of a binary compound of a metal and a non-metal to yield a volatile hydride. The non-metals having electronegativities on Pauling's scale greater than 1.6 all will undergo this type of reaction; this includes Boron and the elements of the fourth, fifth, sixth and seventh B-sub-groups of the periodic table.

Hurd (1) has postulated a simple ionic mechanism for this general reaction based on the assumption that a certain degree of ionic character is necessary in the binary compound to be hydrolyzed

$$M^+ X^- \quad H^+ Y^- \longrightarrow XH \quad M^+ Y^-$$

M - Metal
X - Non-metal
Y - Convenient anion, such as halide

He postulates attack by Y^- which removes metal ions from the lattice, thus making X^- vulnerable to attack by the protons present. This means that the presence of water should not be necessary, and in fact it has been found that Mg_2Si can be reacted with hydrogen halides in liquid ammonia or in fused ethylene diamine to yield silanes.

The need for ionic character in the binary compound has been demonstrated by Hurd, since he has pointed out that only if the ratio of electronegativity of the non-metal to that of the metal exceeds 1.5 will volatile hydrides be formed.

The formation of hydrides other than the simplest members of their families is explained by Hurd in the basis of association of the non-metal atoms in the original binary compound. In a few cases, there seems to be hydrogenation taking place during the hydrolysis, and in others subsequent reactions such as polymerization of the hydride complicate the picture.

Several rather interesting generalizations may be made pertaining to the type of binary compound which will undergo the hydrolysis reaction:

1. Metallic component - Compounds most readily forming volatile hydrides are usually those in which the metallic component is strongly electropositive.
2. Although increased electronegativity of the non-metallic component does not necessarily indicate increased reactivity, it does increase the number of metals with which it can form binary compounds that will be hydrolyzable to the volatile hydride.
3. Compounds which form volatile hydrides are of definite composition and have formulas which correspond to the normal chemical valencies of their elements. In some cases, it must be assumed that the negative component is present as a complex ion in the crystal lattice to account for apparent valence anomalies.

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ORGANOSILICON CHEMISTRY

David Wallace December 9, 1947

Nomenclature:

The committee on nomenclature of the American Chemical Society has established the root name of silane for SiH_4, and the names of the simpler type compounds become;

$R_3Si-O-SiR_3$ siloxane
$R_3Si-NH-SiR_3$ silazane (R = organic group or H)
R_3SiOH silanol

Cyclic derivatives are named in a similar manner. Groups are named as derivatives of the hydride group such as silyl (H_3Si-), silylene ($H_2Si=$), siloxy (H_3SiO-), etc.

Methods of Synthesis:

The organosilanes and organochlorosilanes may be prepared by a great variety of methods, with these methods falling into two general classes, substitution and direct.

Substitution:

1. Friedel and Crafts
   $2ZnR_2 + SiX_4 = SiR_4 + ZnX_2$
2. Ladenburg
   $2Na + Zn(C_2H_5)_2 + Si(OC_2H_5)_4 = (C_2H_5)_2 \quad Si(OC_2H_5)_2 + Zn$
3. Gregnard
   $RMgX + SiCl_4 = RSiCl_3 + MgXCl$
   $RSiCl_3 + RMgX = R_2SiCl_2 + MgXCl$
   etc. (X = Cl, Br, I)
4. Lithium alkyls--more active than the Grignard reagent.

Direct

$2RCl + Si = R_2SiCl_2$
$4RCl + 2Si = R_3SiCl, \quad RSiCl_3$, etc.

A metallic or metal oxide catalyst reduces the temperature necessary for reaction, thereby decreasing pyrolysis of the organic groups.

The organofluorosilanes may also be prepared by the Grignard reaction, but the product is principally R_3SiF. Silicon tetrafluoride is used in place of silicon tetrachloride, Organofluorosilanes are also preparable from silicones and from organochlorosilanes.

Chemical Behavior of Classes of Organosilicon Compounds

A. Normal alkyls (SiR_4, $R_3Si-SiR_3$, etc.)

These compounds are the most stable of the organosilicon compounds. In cases where the organic substituents are not all the same, the alkyls show reactions characteristic of all the substituent groups.

B. Alkylsilanes (R_nSiH_{4-n})

Prepared by:

$$SiH_4 \xrightarrow[AlCl_3]{HCl} ClSiH_3$$

$$ClSiH_3 + RMgX \longrightarrow RSiH_3 + MgXCl$$

C. Organosilanes with substituted alkyl and aryl groups:

In general the organic groups may be halogenated, sulfonated, and nitrated under special conditions.

D. Alkyl-and aryl- halogenosilanes, R_nSiX_{4-n}.

These compounds readily undergo hydrolysis and ammonolysis to form siloxanes and silazanes. From compounds of the formula R_3SiCl are obtained the hexa-alkyldisiloxanes and

disilazanes. Hydrolysis of the dilkyldihalosilanes yields corresponding diols of the type $R_2Si(OH)_2$, which can be isolated if the condensation to a siloxane does not proceed rapidly at room temperature. With silanetriols, $RSi(OH)_3$, the condensation is more rapid.

The organochlorofluorosilanes have properties intermediate between the fluorosilanes and chlorosilanes. They hydrolyze, but more slowly with increasing fluorine content.

In the liquid state, the organofluorosilanes are colorless, mobile liquids, soluble in organic solvents. Their thermal stability is their most remarkable property. Trifluoromethylsilane decomposes only slowly at 600°. These compounds are generally much more stable than the corresponding chlorine compounds.

E. Compounds of the formula $RnSi(OR)_{4-n}$
These compounds may be prepared by reaction of the corresponding chlorosilanes with alcohols or phenols, or reaction of the Grignard reagent with an orthosilicate. The ether groups are removed by hydrolysis in the presence of strong mineral acids.

F. Organosilanols, $RnSi(OH)_{4-n}$
The preparation of the organosilanols is discussed in the two preceeding paragraphs. The silanols are subject to condensation with the elimination of water, the rate of condensation being dependent on the size and number of the organic groups as well as on the external factors of temperature and catalysts. Many are sufficiently stable to permit isolation.

G. Esters
The esters of the organosilanols are formed by the interaction of the silanol with either inorganic or organic acids or their anhydrides. The silanol behaves as an alohol rather than as a silicic acid.

H. Silazanes
Due to the ease with which silazanes hydrolyze to give ammonia and the corresponding siloxane, the use of these compounds is limited.

The Silicone Polymers

It is obvious that silanols containing two OH groups may condense to form molecules containing more than two silicon atoms, and actually polymeric siloxanes may be formed by such condensations. Where three OH groups are available, a high degree of cross linking is possible. Thus it is seen that many polymers are possible with different, and controllable, properties.

Silicone oils find wide application at lubricants at low temperatures. They exhibit a very small change of viscosity with temperature. Organosiloxane polymers also find use as water repellent films.

Special Investigation of Physical Properties

A. Crystal structure of some silanols
Some silanols were studied and shown to be orthorhombic and anorthic in crystalline structure.

B. Brockway and co-workers made a study of hexamethyl disilane and found the following bond distances:

Si-C (bonded) = 1.90 ± .02Å

Si-C (non-bonded) = 3.47± .04Å

∠ C-Si-Si = 109± 4°

Si-Si = 2.34± .10Å

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HARDENING AND PASSIFYING ALUMINUM FILMS

Robert L. Bohon

December 16, 1947

I. Purpose

The purpose of this paper is to review the processes of chromate sealing used for the passification of aluminum and to correlate the structure and formation-mechanism of these films with those formed by a commercial process of hardening aluminum mirrors.

II. Definition and Generalities Concerning Passivity

Many metals and alloys are not considered members of the true "passive" series because of surface layers formed under expected corrosive conditions (Pb in sulfuric acid, for example), but in many of these cases a good deal of dispute has arisen as to what *causes* passivity and what merely enhances it. The three early theories on the subject are discussed in an earlier seminar by Mr. Aryan (4), viz., the oxide-film theory of Faraday, the valency theory of Finkelstein, and the reaction velocity theory of LeBlanc The passivity of the transition elements with incomplete 3rd energy orbits has been explained by Russell (2,3) by electron transitions from the 4th orbit of the active metal to the 3rd orbit of the passive state. We shall concern ourselves with passivity of Al produced by either anodic oxidation or chemical surface treatments involving chromates.

III. Characteristics of Fresh, Untreated Aluminum Surfaces.

Haas (5) has shown that the structure of evaporated Al films resembles that of isolated grains which grow with increasing film thickness to form crystallites. Several of these crystallites are combined to form the grains of over 1000Å in the thicker films.

Most investigators (6,9) believe that the natural oxide film on aluminum is vitreous and anhydrous; however, Steinheil (7) gives the film a face-centered cubic structure. The investigators show that the amorphous nature disappears upon heating to yield ordinary gamma-oxide. Infrared absorption studies (10) indicate that water is present as such but not as a hydroxide. The rate of formation and thickness of this film has been debated heatedly for a long time, but Steinheil (7), Vernon (8), and Cabrera (11), have all shown independently that the film grows rapidly for about four days, and very slowly thereafter. All of these experimenters place the thickness between 0.15-0.001μ except Cabrera whose values are much higher (6,7,8,11,12,30).

IV. Anodic Oxidation Processes

This type of process protects the Al by formation of a continuous film of Al_2O_3 on the anode in a cell using oxalic, sulfuric, chromic, or boric acid as an electrolyte. Hundreds of recipes are available for these electrolytic processes and baths. A few of the more common are discussed here.

The Germans pooled their knowledge on the subject and use the "Eloxal Processes" (electrolytisch oxydiertes aluminium) employing primarily sulfuric or oxalic acid with variable temperature, bath composition, voltage, and time of oxidation. Their WGX process employs both a.c. and d.c. current to overcome some difficulties inherent in one or the other type of emf. D.C. often gives a pitted or burned surface while a.c. films are rather soft. (8)

Bengough and Stewart developed the chromic acid treatment which involves a stepwise increase in voltage (8,9,14) and gives an excellent corrosion-resistant film. This has been much employed for treatment of aircraft parts, but it is an expensive procedure. Sulfuric acid baths have been widely used in the U.S. because of the ease of varying the type of film formed merely by

changes in voltage, temperature, etc. Most investigators agree that very little water is present in the majority of these films (perhaps some mono-hydrate present) (8).

Such electrolytes as boric acid do not dissolve the film formed; oxalic, chromic, and sulfuric acids partially dissolve it; and some baths completely dissolve the oxide (electrolytic polishing with hydrofluoric acid (16), perchloric acid (8), or sodium phosphate and carbonate (13).). The anodic reactions in the intermediate group are postulated by Jenny and Lewis as follows (8):

$2Al + 3O = Al_2O_3$ or $2Al + 3O + H_2O = Al_2O_3.H_2O$ (0-15% water)

This film then dissolves in the dibasic acid H_2R thus:

$3H_2R + Al_2O_3 = Al_2R_3 + 3H_2O$ and $3H_2R + 2Al = Al_2R_3 + 3H_2(g)$

Phosphate, ammonia (9), and even sulfamic acid (15) baths have been recorded in the literature for anodic oxidation electrolytes.

V. Formation and Properties of Film from Anodic Oxidation

Müller's "Bedeckungspassivität" theory of film formation during oxidation of iron is summarized by Evans (9) and is based upon the formation of a non-conducting film over a portion of the surface which effectively decreases the area and hence raises the anode current density at the uncovered part to 100 to 1000 times the original value. These high anode potentials supposedly cause some change in the electronic state of the metal so that it either ceases to dissolve, or dissolves at a higher valence state. Evans states that Müller finally accepts the oxide contribution to passivity but insists that the valency change occurs first.

Experimenters have shown that these anodic films are quite porous (about 0.1 μ diam. pore), possess little or no crystalline structure, and vary in thickness depending upon the time of oxidation and conditions. (17,18,19,20,22). Rummel states that the pores are filled with air and have a film of hydroxide on their walls. The growth of the film progresses from the bottom of the pores (20,21), and Anderson (23) has proposed the following theory for this mechanism. The growth occurs within a thin compact barrier of oxide adjacent to the metal. The mode of electrical conduction within the oxide film is such that Al^{+3} ions dissolve from the sheet into the oxide, thus leaving spaces into which $O^{=}$ ions may be forced by the electrical field (10^7 volts per cm.)

VI. Sealing after Anodizing (closing the pores)

The anodized specimen is usually given a hot-dip treatment in some solution to close the pores and enhance the corrosion resistance of the film. Chromates are by far the most powerful of these passifiers. Tomashov and Tyukina (24) sealed anodically oxidized aluminum specimens in chromate solutions and very beautifully show by weight measurements, pH determinations, and leaching that an aluminum oxychromate is formed simultaneously with hydration. Hydration increases with increasing alkalinity of the solution and chromate adsorption decreases, although the chromate from an alkaline-sealed specimen was much harder to leach out than from an acid-sealed specimen. Hydration accounts for the changes in volume and density.

Arlt (25) shows that the hardness of anodic films decreases with the amount of hydration; thus, water-sealed films are very soft, chromate-sealed are fair, and untreated are hardest.

VII. Chemical Surface Treatments to Produce Passivity

The most common surface treatments are similar to the German's MBV process which consists of dipping the unoxidized aluminum article into a boiling, dilute solution of aqueous sodium chromate. (8,27). The resulting film is grey and corrosion-resistant and has been called "complex oxides of Al and Cr". (27). The Jirotka Process (9,33) is similar but also employs heavy metal salts for

coloring effects. The films are soft compared to aluminum oxide. Tosterud obtained a patent (29) in which he claims that a process like the MBV treatment stabilizes the reflecting power of the surface. He emphasizes that temperature is critical in this respect. Tronstad and Hőverstad (30) found only small optical changes in the natural oxide film when a surface treatment was applied. Uhlig (31,37,38,39) visualizes a chromate layer covering the surface of iron treated in this manner; the chromate ions are assumed to adsorb electrons from the 4s shell of the surface iron atōms, thereby rendering them passive. He states that "no stoichiometric compound forms".

Since aluminum cannot undergo the electronic transitions proposed by Uhlig for the transition elements like iron, some mechanism such as Tomashow and Tyukina's must occur. Callendar in 1925 (26) proposed that $Al(OH)_3$ is formed initially with subsequent adsorption of chromate and reprecipitation to form the protective layer. He shows that nitrate solutions containing equal quantities of available oxygen are only one-tenth as effective as chromates; hence, oxide alone does not cause passivity on aluminum.

VIII. Surface Treatments to Produce Hardness

Arlt (25) and also Keller and Edwards (12) have shown that sealing with chromates decreases the hardness of the surface. Pure water sealers decrease it even more. A large American company currently "hardens" evaporated aluminum mirrors by the following process: the mirror is covered with an aq. soln. of 1% $K_2Cr_2O_7$ and 2% Na_2CO_3 at room temperature. The excess soln. is drained off and the remaining film of solution is allowed to dry. The remaining crystalline powder is rinsed off and the mirror dried. Such a mirror is hard compared with a non-treated mirror fresh from the evaporator. This process does not alter the reflectivity and increases the chemical passivity of the surface. If a soft mirror is allowed to stand for several weeks, it finally becomes as hard as a treated mirror. A "hardened" mirror scatters less light than a soft one, is harder to electrolytically oxidize, and appears to consist of denser agglomerates. The film is so thin ($<30Å$) that optical methods are limited (see Tronstad and Hőverstad's work). (33)

Assuming that the chromate ion is someway introduced into the "hardened" aluminum surface the reviewer would like to propose that this hardening is analogous to passification but without the softening effect of a great deal of hydration. If it could be proved that some sort of oxide film is necessary before hardening will occur, the mechanism of Tomashov and Tyukina could feasibly be applied. This, however, assumes a stoichiometric reaction in contradiction to Uhlig.

In addition to these chemical treatments for passifying and hardening Al, there are, of course, alloying methods. One of special interest was developed by Edwards: the Pancro films. This alloy contains from 10-50% Mg and is formed by simultaneous evaporation of Mg and Al in a vacuum to form films especially useful in the ultra-violet and visible regions. The mirrors are claimed to have good durability, untarnishability, panchromatic reflectivity, thin and even films, and of controlled transmission values. The Pancro mirrors are supposedly 2 1/2 times as hard as Aluminum (34,35,36).

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ALUMINUM ALLOYS

A. G. Buyers December 16, 1947

DISCUSSION OF ALUMINUM AS AN ALLOYING MATERIAL

1. Arguments in favor of aluminum as an alloying material are:
    a. Resistance to chemical attack
    b. Light weight
    c. Ease of fabrication
    d. High thermal conductivity
    e. Alloys can be joined by standard methods
2. Cathodic protection provided by aluminum alloys

BINARY ALLOYS

1. Al-Bi, Al-Cd, and Al-Pb Alloy Series
    a. Tendency to form nonhomogeneous alloys
    b. Emulsion type material formed
    c. These three binary alloy series are of little value
2. Al-Cr Series
    a. Large increases in strength and hardness
    b. Good for high temperature work
3. Al-Cu Series
    a. Duralumin
        1. One of strongest aluminum alloys
        2. Age hardenable alloy; properties change with elapsed time
            a. Other age hardenable alloys
4. Al-Mg Series
    a. Important properties
        1. Light weight
        2. Sonorous qualities of specially cast alloys
        3. Ability to take mirror-like polish
        4. Extreme hardness and strengths
    b. Disadvantages-expensive, imflammable, formation of nitrides
5. Al-Mn Series
    a. Formation of emulsions or suspensions of uniform nature
6. Al-Ni Series
    a. 3% Al alloy called lumel is used in thermocouples
    b. Decrease in the electrical conductivity
    c. Added Strength
7. Al-Si Series
    a. Existance of solid solutions near pure sil[illegible]nd pure aluminum extremes of phase diagram
    b. Crystaline nature of alloys
        1. Modification of alloy using sodium fluoride or hydroxide
    c. Properties of the 14% silicon eutectic material
        1. Known as alpax or silumin
8. Al-Zn Series
    a. Formation of Zn_3Al_2
    b. Existance of different solid solutions at various temperatures
    c. Heat treatment of Al-Zn alloys and non premanent increase in hardness and tensile strength which occurs on aging.
    d. Reasons for unsuitability of Al-Zn alloys when used in casting--high shrinkage factor, weakness in vicinity of melting points, failure of alloys containing over 20% zinc to reach equilibrium, resulting in contraction.

TERNARY ALLOYS

1. General discussion of ternary aluminum alloys
    a. Existing possibilities
        1. Both added elements combine with aluminum, but not mutually
        2. One added element combines with aluminum, but other combines with first added material.-Special case for the Al-Mg-Si alloy
        3. Two added elements form compounds, mutually, but only one combines with aluminum
        4. Two added elements and aluminum form compounds mutually
2. Al-Mg-Si Series
    a. Hanson and Gayler showed the formation of various binary and ternary compounds. Heat treatment of these alloys results in a great improvement of mechanical properties
    b. Existance of pseudo binary series-Al-Mg_2Si
    c. Decrease in solubility of Mg_2Si at both high and low temperatures in the presence of excess magnesium
3. Al-Ni-Cu Series
    a. Haughton and Bingham showed that alloy structure is binary when copper is 0.8 and the percentage of nickel 0-10. High copper content and low nickel cause ternary structure to exist

IMPORTANT INDUSTRIAL ALUMINUM ALLOY SERIES

1. Eight percent copper alloys
    a. Alloy No. 12 - 8% copper added to commercial aluminum ingot
    b. Alloy No. 112 - 1.0-1.5% iron, 1.0-2.5% zinc, remainder aluminum
    c. Alloy No. 212 - 7.0-8.5% copper, .8-1.2% iron, 1.0-1.5% Silicon, remainder aluminum
2. Four percent copper - heat treated
    a. Alloys Nos. 195-4, 195-16, and 195-10, differing only in method of heat treatment. (Solution and precipitation heat treatments)
    b. Alloy No. 196 - No. 195 plus 0.2 % magnesium
3. Twelve percent copper alloy
    a. Composition-11.0-13.5% copper, not over 0.2% zinc, not over 1.7% silicon, iron, maganese and tin
4. The Y alloy or No. 142
    a. Composition-4.0% copper, 2.0% nickel and 1.5% magnesium
    b. Complex structure- $NiAl_3$, Cu-Ni, Mg_2Si and one or more iron compounds
    c. Useful at high temperatures
5. Ten percent silicon alloy
    a. Eutectic composition alloy most important
    b. Brittleness caused by iron contamination

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THE STRUCTURE OF FERRIC AND ALUMINUM HYDROUS OXIDES

R. S. Sprague January 6, 1948

The structure and classification of the gelatinous, slimy precipitates obtained when alkali is added to a ferric or aluminum salt solution is a problem that has, and still is, baffling chemists. Our purpose will be to very briefly examine the principal theories proposed for their structure.

It was early recognized that these hydrous oxide precipitates do not have a formula that corresponds to any definite, simple hydroxide or hydrate, although they can be dehydrated to the oxide at high temperatures. Hence the name, hydrous oxide. These precipitates are definitely of a colloidal nature, forming sols quite readily. They have no external crystalline character. Foreign salts are extensively dragged down with these hydrous oxide precipitates. On aging, the precipitates lose some of their gelatinous character and assume a more crystalline nature. These are some of the simpler, observed properties of the hydrous oxides and any theory of their structure should, therefore, take these observations into account.

The Structure of the Hydrous Oxide Gels-

Early attempts to show whether or not these hydrous oxide precipitates conform to any definite hydroxide or hydrate formula were made by the usual hydrate study method of dehydration isobars. In the case of the iron and aluminum hydrous oxides, these attempts showed no definite, integral amount of water to be present.

In light of these findings, Von Bemmelen (1) in 1888 proposed that both the hydrous oxide sols and gels consist of colloida size particles of oxides or simple hydrate with adsorbed and contained water of indefinite amount. Hence, no simple formula can represent the solid phase. Zsigmondy (2) proposed a "capillary" structure whereby the hydrous oxide is shown as having a sponge-like structure with many tiny pores or capillaries capable of holding water molecules. The colloidal metal oxide framework was believed to consist of anhydride when first formed, but on aging, some of the entrained or adsorbed water was fixed as a hydrate. Willstätter and coworkers attempted to wash out this capillary water with acetone and so arrive at the amount of chemically combined water or water of hydration, but were unsuccessful in that reproducible results could not be obtained. Foote and Saxton (3) attacked the problem by a freezing method, in which the precipitates were frozen, and the amount of water freezing at any given temperature would be proportional to the volume expansion produced by the freezing. They found that for hydrous iron oxide loosely attached water froze out at -5° while more intimate or capillary water froze out at -30°. Assuming the remainder to be water of hydration, they found a ratio of 4.25 moles of water to 1 of ferric oxide. This confirmed Ruff's (4) earlier work in which he found 4.2 moles of water to one of ferric oxide. Hence, the results are not conclusive.

Hüttig and coworkers (G-1) have made extensive investigations in this field using x-rays. They found that freshly precipitated hydrous aluminum oxide is amorphous to x-rays, but on aging, gives a pattern corresponding to hydrargillite, a naturally occurring trihydrate of aluminum oxide. On removing the water by heating, a pattern due to bohnite is obtained. Bohnite has the same composition as bauxite and an unoriented sturcture. On further heating,

They found no definite hydrate pattern produced. If the hydrous oxide is allowed to age at room temperature, the loss of water follows a different course. In the case of hydrous ferric oxide, Hutting and coworkers found that aging produces the slow elimination of water from the gel to form hematite. Some water appears to be held in the hematite lattice in variable amounts, and is therefore zeolitic in character. Slow elimination of this zeolitic water produces gothite, α ferric oxide monohydrate. Limonite is an intermediate in this process. Limonite has the same structure as gothite, but contains zeolitic water.

Weiser and Milligan (G-2), as a result of their work with x-ray diffraction patterns and dehydration isobars, proposed that the hydrous oxide sols and gels consist of agglomerates of minute crystals of oxide, simple hydrate or hydroxide. Freshly formed and aged gels of hydrous aluminum oxide were found to be agglomerates of minute crystals of γ aluminum oxide monohydrate (bohmite), α aliminum oxide trihydrate (bayerite), and γ aluminum oxide trihydrate (gibbsite or hydrargillite), or mixtures of these phases. No other hydrates or polymerized bodies were found. Since mixtures of these hydrates are often present, and since the small size of the crystals gives a large surface area with consequent hig degree of adsorption of water, and since some of the dehydration products are highly hygroscopic, good dehydration isobars of these gels cannot be obtained. These workers have shown the various paths followed on aging under various conditions. The exact crystal sturctures of the above hydrates are not known with certainty, although Megaw (5) has shown that γ aluminum oxide trihydrate (gibbsite or hydrargillite) has a layer lattice (characteristic of true hydroxides) in which the aluminum ions lie between six hydroxyl ions in two-thirds of the possible positions. Hence, $Al(OH)_3$ would be a justifiable formula.

In the case of hydrous ferric oxide gel, Weiser and Milligan found that the ordinary brown gel gave no indication of hydrate or hydroxide from the dehydration isobar. The fresh gel is amorphous to x-rays. On standing with water for several weeks, bands corresponding to α ferric oxide appear, and on further standing for several months, the bands go over to sharp hematite lines. The gel thrown down at 100° gives immediate hematite bands, and on standing several hours, sharp hematite lines appear. The brown gel then appears to be hydrous α ferric oxide. The yellow gel, obtained by the slow hydrolysis of ferric acetate, was found to be hydrous α ferric oxide monohydrate (gothite), while the yellow gel produced by the slow hydrolysis of ferric chloride proved to be β ferric oxide monohydrate.

In contrast with the theory of structure just described, a complex polymerization structure has been proposed by several workers (G-3, G-4). This theory, in connection with the Werner coordination complex concept, will be dixcussed in greater detail when the structure of the hydrous oxide sols is taken up. Krause and coworkers (G-3, 6) developed a polymerization concept for the structure of the hydrous ferric oxide gels. Approaching the problem from an organic proof of sturcture viewpoint, they synthesized silver ferrites from the brown hydrous oxide (called ortho-hydroxide) and from the yellow hydrous oxide (called meta-hydroxide). From the ratio of silver oxide to ferric oxide in these silver ferrites, they concluded that the yellow or meta-hydroxide has a ring sturcture and that the brown or ortho-hydroxide has a chain structure for the changes which take place. On aging, they propose a polymerization mechanism whereby the ring structure goes to gothite and the chain structure goes to hematite.

This theory is plausible in light of the fact that freshly precipitated hydrous ferric oxide (precipitated in the cold) is amorphous to x-rays, as has been previously shown.

The Structure of the Sols-

The ease with which the hydrous ferric and aluminum oxides form stable colloids has received much investigation. It is believed by some that these sols are probably not dispersions of the oxide alone, since ions other than those of the metal hydrogen, and hydroxyl are required for stability. Thomas and Frieden (7) have shown that ferric and aluminum oxide hydrosols always contain the anion of the original metallic salt. Graham (8) did much of the early work on these hydrosols and showed that their properties and compositions depend on the experimental conditions of preparation- concentration, temperature, anion of metallic salt, and age of hydrosol. These colloids show very high molecular weights- 300 or greater.

The earlier theories explaining the stability of these colloid were electrical in nature. They all picture that, in some way, the colloidal particles acquire a charge of like sign and the resulting mutual repulsion keeps the particles dispersed in a colloidal condition. Various theories have been proposed for the origin of this charge, the most acceptable being that of Helmholtz (9) and the extension by Debye and Huckel (10) and Gouy (11). Ions from the solution are adsorbed by the surface ions of the lattice of the colloidal particle and these give the particle an electric charge. This charge attracts ions of opposite charge around the particle forming a diffuse cloud and giving rise to an electrical double layer around the particle, which partially, but not completely, neutralizes the charge on the colloidal particle. Since each particle has a charge of the same sign, the particles repel one another and the colloid is stable. The colloid may be coagulated by the addition of electrolytes whose ions will neutralize the particle charges and allow them to coalesce.

Weiser and Milligan (G-2) found that ferric and aluminum oxide hydrosols were composed of dispersed particles of ferric oxide or of aluminum oxide monohydrate, by using x-ray diffraction methods. The x-ray technique with hydrosols is difficult inas much as water bands appear which may mask crystal lines, the concentration of the solid phase is usually quite low, and there is the possibility that the x-rays may cause some coagulation. By using concentrated sols and flowing them continuously thru the x-ray camera, these difficulties were obviated.

Other workers attribute the stability of these hydrosols to the formation of complex polymerized bodies. The arguments for this theory are summarized by Whitehead (G-4) and much of the work supporting these arguments was done by Thomas, Whitehead, and their coworkers. While recognizing that the adsorption of ions and the electrical double layer concept may account for the stability of some colloids, this is not the whole story in the case of the iron and aluminum oxide hydrosols, according to Whitehead. According to the Werner concept, the aluminum ion from aluminum chloride exists in water as $Al(H_2O)_6^{+++}$, and hydrolyzes according to the equation--

$$Al(H_2O)_6^{+++} + 3Cl^- \rightleftharpoons Al(H_2O)_5(OH)^{++} + 2Cl^- + H^+ + Cl^-$$

If less than the required amount of alkali for neutralization and precipitation is added, and the solution is warmed, a colloid is formed by polymerization. Stiasny and Balanyi (12) explained this on the basis of the formation of diol complexes, then polynuclear complexes, by hydrolysis and olation. This process continues until a polynuclear complex of colloidal dimensions is reached.

There are several pieces of evidence supporting this viewpoint. Thomas and Whitehead (13) found that when an aluminum oxychloride hydrosol was heated, the pH of the sol decreases. On cooling back to room temperature, the pH did not return to its original value, but only did so after standing for six weeks. This is explained by the fact that ol groups lose hydrogen ions on heating, forming oxo groups. Since the oxo group is less reactive than the ol group, equilibrium is not restored immediately on cooling. Further evidence supporting this concept is found in the fact that the oxolated particle moves more slowly in an electric field than does the olated particle, since its charge is smaller. Hydrosols prepared at room temperatures and aged at room temperature show a decrease in pH. This is because hydrolysis is the principal reaction. On the other hand, if the hydrosols are prepared at elevated temperatures or if those prepared at room temperature are heated, and then allowed to age at room temperature, the pH increases. This is explained by the fact that heating causes olation to occur first after hydrolysis, then oxolation follows, making the sol acid. On aging, a reversal of these processes occurs, and the sol becomes less acid. The hydrous oxide gels are always found to contain more or less of the anion of the original iron or aluminum salt and this has been attributed to adsorption and occlusion. On the complex theory basis, assuming the hydrous oxide gel to be a polymerized body similar to those just described, this adsorption of anions is explained as a replacement of the OH groups inside the coordination sphere by the anion, the displacement power being oxalate > acetate > sulfate > chloride > nitrate. The washing out of these ions is quite difficult and indicates that they are fimrly held. Thomas and Vartanian (14) found that equivalent amounts of different acids were not equally effective in peptizing hydrous aluminum oxide. The effectiveness of the acid as a peptizing agent was inversely proportional to the coordination power of the acid anion, i.e., nitric acid is a good peptizing agent and oxalic acid is a poor one. This is explained by the fact that the hydrous oxide gel containes many hydroxo and aquo groups coordinately bound to central metallic ion. A weakly complexing acid converts the hydroxo and ol groups to aquo groups and renders the gel more soluble or dispersable. A strongly complexing acid causes replacement of the aquo and hydroxo groups with the acid anion and so decreases the solubility.

Thus we have two general theories to account for the structure and properties of hydrous ferric and aluminum oxides- the colloidal crystal theory and the complex polymerized body theory. The first has much indisputable x-ray evidence to back it up, while the second explains very well many of the observed properties of the hydrous oxide sols and gels. Possibly the correct explanation involves some or all of both concepts.

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INVESTIGATION OF COMPLEX METAL IONS BY MEANS OF THE POLAROGRAPH

L. M. Burdett January 6, 1948

I. Introduction

The use of the polarograph as a practical instrument in analytical chemistry is quite generally known but application of this instrument to more abstract problems in other fields of chemistry, especially in inorganic and electrochemistry, is not as extensively recognized. One of the most interesting of these applications is in the study of complex metal ions in aqueous solution.

II. Basis and extent of study of complex ions

The study of complex ions by the polarographic method rests on the fact that the reduction potentials of metal ions at the dropping mercury electrode are shifted (usually to a more negative value) by complex formation. The principal pieces of information obtained in the study of complex metal ions are the value of the dissociation constant and the number of coordinating groups in the complex ion. A limiting factor in obtaining this information is the fact that only when the reduction or oxidation of the metal ion complex is reversible at the dropping mercury electrode is the data obtained valid for the calculation of these values.

In addition to the values for the dissociation constant and coordination number, other information concerning the nature of the complexes may be gleaned from the nature of the polarographic wave (or waves) obtained.

III. Possible electrode reactions involving complex ions.

A. Reduction to the metallic state with the formation of an amalgam on the surface of the electrode.
B. Reduction or oxidation from one ionic state to another.
C. Stepwise reduction resulting in the appearance of two or more separate waves.
D. Reduction of incompletely dissociated metal salts.

IV. Reduction to the metal state

A. Reduction of the complex metal ion may be represented by the following equation:

$$Mx_p\,(n-pb)^{+} + ne + Hg \rightleftharpoons M(Hg) + pX^{-b} \qquad (1)$$

B. Equation of the wave as derived from fundamental principles of poloraography is:

$$E_c = (E\,1/2)_c + \frac{0.0591}{n} \log \frac{id - i}{i} \qquad (2)\ \text{where:}$$

$$(E\,1/2)_c = E^\circ_{am} + \frac{0.0591}{n} \log \frac{\gamma Mx}{\gamma am} \frac{ka}{kc} Kc - p\,\frac{0.0591}{n} \log C_x \qquad (3)$$

C. Determination of reversibility of the reaction

Plot $\log \frac{id-i}{i}$ vs. E at constant C_x

If reversible, the slope should be equal to $2.3\,\frac{RT}{nF} = \frac{0.0591}{n}$

D. Evaluation of p, the coordination number

Plot $E\,1/2$ as a function of $\log C_x$. p may be calculated from the fact that the slope is equal to $p\,\frac{2.3RT}{nF}$.

E. Evaluation of Kc, the dissociation constant..

The equation of the wave of a simple (or aquo complex) metal ion is given as follows:

$$E_s = E°_{am} + \frac{RT}{nf} \ln \frac{id-i}{i} + \frac{RT}{nF} \ln \frac{\gamma_{M^{n+}}\, k_{am}}{\gamma_{am}\, k_{M^{n+}}} \quad (4)$$ and

$$(E\ 1/2)_s = E°_{am} + \frac{RT}{nF} \ln \frac{\gamma_{M^{n+}}\, k_{am}}{\gamma_{am}\, k_{Mn^+}} \quad (5)$$

from equations (3) and (5)

$$(E\ 1/2)_c - (E\ 1/2)_s = \frac{RT}{nF} \ln \frac{\gamma_{Mx}}{\gamma_{Mn^+}} \cdot \frac{k_{M^{n+}}}{k_{M_x}}\ K_c - p\,\frac{RT}{nF} \ln C_x \gamma_x \quad (6)$$

which for approximate purposes may be simplified to

$$(E\ 1/2)_c - (E\ 1/2)_s \cong \frac{RT}{nF} \ln K_c - p\,\frac{RT}{nF} \ln C_x \quad (7)$$

from which Kc may be calculated.

F. Examples of investigations of this type of electrode reaction.

(1) Reduction of the biplumbite ion (1)(2). Lingane ran a polarogram of 5×10^{-4} M lead nitrate in 1.09 N sodium hydroxide solution.

Reversibility of this reaction was proved as mentioned previously; since n=2, a slope of 0.0296 should be obtained Lingane found it to be 0.029.

To determine p, the coordination number, E 1/2 was plotted against varying concentrations of OH^-. The slope of the curve was found to be - 0.083 while the theoretical value with p=3 and n=2 would be -0.089. The equation for the reduction would therefore be

$$HPbO_2^- + 2e + H_2O + Hg \rightleftharpoons Pb(Hg) + 3OH^-$$

(2) Reduction of cadmium-ammonia complex ion
   (a) The coordination number, p, was found to be four.
   (b) The dissociation constant, Ke, was calculated to be 3.3×10^{-7}

(3) Reduction of cupric-glycinate and cupric alaninate complex ions. (3)
   (a) In the presence of 0.01 to 0.08 M excess glycinate or alaninate ion the complex ion is mainly CuG_2 or CuA_2. From 0.2 to 1.0 M excess glycinate ion the complex is CuG_3^-
   (b) The value of the dissociation constant of the cupri glycinate complex was calculated to be 5.3×10^{-16} in 0.01 M glycinate ion and 5.4×10^{-17} in 1 M glycinate. Ke for the alaninate complex was calculated to be 9.8×10^{-16} in 3.2 M glycinate solution.

V. <u>Reduction or oxidation from one ionic oxidation state to another</u>

A. This type of reaction may be expressed by the following general reaction:

$$M_{xp}^{(n-pb)+} + ae \rightleftharpoons M_{xg}^{(n-a-qb)+} + (p - q)x^{-b}$$

B. Equation of the wave

$$E_c = (E\ 1/2)_c + \frac{0.0591}{a} \log \frac{(id)_c - i}{i-(id)_a}$$

$$E\ 1/2 = E°am - \frac{0.0591}{a} \log \frac{kox}{k\ red} - \frac{(p-q)}{a}\ 0.0591 \log C_x$$

C. Test for reversibility of the reaction

Plot $\frac{(id)_c - i}{i-(id)_a}$ against E: slope should be equal to $\frac{0.0591}{a}$ if the reaction is reversible

D. Evaluation of p and q, the coordination numbers of the two metal complexes

The relationship between p and q may be determined and if either is known the other may be calculated.

E. Evaluation of Kc, the dissociation constant

From the equation

$$(E\ 1/2)_c - (E\ 1/2)_s = \frac{0.0591}{a} \log \frac{koc.}{krc.} - \frac{(p-q)}{a}\ 0.0591 \log C_x$$

we can get the ratio of the two dissociation constants and if the value of either is known the other may be calculated.

F. Example of this type of electrode reaction

(1) Study of ferric and ferrous oxalate complexes

Lingane (1) (4) found that the formula of the ferrous complex is $Fe(C_2O_4)_2^{=}$ when $C_{C_2O_4^{=}}$ is less than 0.15 M and $Fe\ (C_2O_4)_3^{\equiv}$ in a larger excess of oxalate ion. Using a previously determined value for the dissociation constant of $Fe(C_2O_4)_3^{\equiv}$, he calculated the dissociation constant of both the ferrous complexes.

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RECENT DEVELOPMENTS IN THE FIELD OF METAL HYDRIDES

Neal O. Brace January 13, 1948

I. Introduction

Several articles have appeared in recent journals describing the preparation and properties of some new metal hydrides. The discovery of lithium aluminum hydride (Li AlH_4) has led to important advances in the fields of inorganic and organic chemistry. Through its use, hydrides (both simple and complex) of many other elements have been made easily acessible. Studies of the hydrides of tantalum and columbium (6) and of barium and zirconium (7) have also been published recently.

II. Li AlH_4

A. Preparation

This new compound has been prepared by the reaction: $4LiH + AlCl_3 \xrightarrow{ether} LiAlH_4 + 3LiCl$. The ether soluble hydride may be freed from the solvent completely, and exists as a white solid which may be safely handled even in humid air, though in general it should be used in nitrogen-filled apparatus. In addition sodium and calcium aluminum hydrides have been analogously prepared (1). AlH_3 may be prepared from lithium aluminum hydride by the addition of $AlCl_3$.

B. Properties

$LiAlH_4 + 4H_2O \dashrightarrow LiOH + Al(OH)_3 + 4H_2$. The compound reacts immediately and completely when dropped into water. It reacts with ammonia and with amines. This is in contrast to the otherwise similar Li BH_4 (1). $LiAlH_4$ is 7 to 8 times more soluble in ether than Li BH_4, and has a decomposition temperature of 125-150° as compared to 250-275° for the borohydride. This points to a somewhat less polar character for the aluminum compound. Examination of the electronegativity data given by Pauling (2) shows indeed a somewhat greater ionic character (about 25%) for the borohydride as compared to the aluminum hydride compound (about 20%).

C. Uses

Lithium aluminum hydride is a versatile hydrogenating agent. The compound has four replaceable hydrogens and exhibits a specific reducing action towards many types of organic compounds. It has a favorable ratio of reducing capacity to mass, which partially offsets the high cost of the LiH; it reacts readily and smoothly at ordinary temperatures; it gives practically quantitative yields in most cases. Aldehydes, ketones, acid chlorides, esters, acid anhydrides (3) and carboxylic acids (4) are reduced to alcohols, nitriles to amines and aromatic nitro compounds to azo compounds (3). Olefinic bonds are not attacked unless conjugated with an activitating group such as phenyl or carbonyl. Only primary amines have been obtained from nitriles.

Li Al H_4 has valuable uses in preparing inorganic compounds. It reacts with diborane to give $Al(BH_4)_3$, with BCl_3 to give diborane, and with the halides or mixed alkyl or aryl halides of elements of the fourth group of the periodic system to give the corresponding hydrides or alkyl or aryl hydrides, respectively (5). The reaction may be represented as:

$$4\ E\ Ry\ X_4{-}y + (4-y)\ LiAlH_4 \xrightarrow{ether} 4\ E\ Ry\ H_4{-}y + (4-y)\ LiX + (4-y)\ Al\ X_3-$$

in which E represents silicon, germanium, or tin, X represents a halogen and R an alkyl or an aryl radical; y may vary from zero to three. When applied to lead the reaction appeared to give partial reduction to metallic lead and to the formation of volatile, unstable, unidentified compounds.

The reactions with $LiAlH_4$ proceed smoothly, usually at room temperature to produce products of high purity. For example, 50 cc. of the pure gas stannane was prepared in small scale apparatus in 2 to 3 hours.

Several new compounds have been prepared by this procedure (5). $C_2H_5SiH_3$ $(C_2H_5)_2SiH_2$ and the corresponding C_3H_7- and C_4H_9-derivatives, $C_6H_5SiH_3$; also CH_3SnH_3, $(CH_3)_2SnH_2$, and $(CH_3)_3SiH$.

The organo-silanes are liquids or gases at room temperature, not spontaneously infammable in air. They react very slowly with water and somewhat more rapidly with aqueous alkali. They are soluble in solvents such as diethyl ether or benzene. No measurable decomposition has occurred in a years' time.

The methyl stannanes are less stable than the alkyl-silanes, although considerably more than stannane (SnH_4). They are not spontaneously inflammable in air, and also react slowly with water, producing white gels.

VII. Other studies of metal hydrides

A. Tantalum and zirconium hydrides (6). These interstitial hydrides exhibit the phenomena of superconductivity at very low temperatures as do the carbides, nitrides and borides. In an attempt to correlate the transition temperature at which superconductivity occurs with the crystal dimensions of these compounds Horn and Zeigler prepared them and measured the physical data necessary to establish the general empirical rule, "In a series of interstitial alloys containing the same parent metal, the superconducting transition temperature varies inversely with the dimension of the lattice parameters, provided the same crystal structure is maintained". Increasing amounts of hydrogen up to 54.37 % served merely to "expand" the crystal lattice of tantalum and caused a corresponding decrease in the transition temperature. Columbium, though very similar in atomic radius, gave a homogeneous crystal structure with amounts of interstitial hydrogen only up to 9.98%; at 24 and 33% hydrogen, heterogeneity was observed with one crystal form identified as the body centered cubic and the other form unidentified.

The hydrides were prepared from the pure metals by reaction with hydrogen gas in a quartz tube at 800°.

B. Barium and zirconium hydrides (7). In a search for suitable cathode materials for a hydrogen-filled thyratron tube these two compounds were prepared and tested. BaH_2 is a salt-like hydride (30% ionic, Pauling (1)) and $ZrH_{1.98}$ is supposed to be an interstitial hydride. The equilibrium gas pressures in the zirconium-hydrogen and barium-hydrogen systems were measured at 650° and 600°, respectively. Combination of hydrogen with metallic barium occurs readily when the metal is finely divided or in a thin film. At 600° the dissociation pressure is only 0.24 mm; and the metal begins to evaporate rapidly, recombining with hydrogen in a cooler part of the tube, rendering its use as a hydrogen resevoir impractical.

The zirconium-hydrogen system appeared to be reversible at temperatures ranging from 150° to 650°. A pressure of 0.16 mm was obtained at 150° and 2.1 mm. at 650°.

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OXYACIDS AND SALTS OF CHROMIUM; MAGNESIUM DICHROMATE

J. P. Huselton January 13, 1948

OXYACIDS OF CHROMIUM

Some of these are quite well-known; others exist only in the form of their salts, the acids being hypothetical.

$HCrO_2$ -- metachromous acid

H_3CrO_3 -- orthochromous acid
Below 10N NaOH, $NaCrO_2$ forms; above, Na_3CrO_3.
Below 8N KOH, $KCrO_2$ forms; above, K_3CrO_3[10].

H_2CrO_4 -- chromic acid (probably non-existent, except in solution). The normal salts form; the acid salts are unknown though $HCrO_4^-$ does exist in solution.

$H_2Cr_2O_7$ -- dichromic acid. Conductivity measurements[8] show its existence in acidified chromate solution.

$H_2Cr_3O_{10}$ -- trichromic acid; $H_2Cr_4O_{13}$ - tetrachromic acid. When the solid ammonium salt of either is dissolved in water, dichromate and chromium trioxdie result.

H_4CrO_5 -- parachromic acid (hypothetical). Possibly represented by a basic salt such as $PbO.PbCrO_4$.

H_6CrO_6 -- orthochromic acid (hypothetical). Possibly represented by other basic salts such as $2PbO.PbCrO_4$.

$HCrO_5$ - peroxychromic acid. Molecular weight determinations are against the doubled formula, so this allies the acid with $HMnO_5$.

H_3CrO_7 -- peroxychromic acid. Bluish-violet $NH_4H_2CrO_7$ forms. Unstable dark blue ether-soluble compounds RH_2CrO_7 provide the basis for qualitative tests for chromate solutions after acidification and treatment with hydrogen peroxide.

H_3CrO_8 -- peroxychromic acid. Dark blue crystals are formed at -30°C. by reacting chromic acid with 97% hydrogen peroxide in a solution of methyl ether, then drying over P_2O_5 and separating at - 30°C. by evacuation.

NORMAL CHROMATES AND DICHROMATES

Normal chromates and dichromates are well-known[4] for the following group I elements: Li, Na, K, Cu, Rb, and Ag. Cesium chromate[4] and dichromate[9,11] are known. Auric chromate has been reported.[3]

For the following group II elements normal chromates[4] are well-known: Mg, Ca, Zn, Sr, Ba, Hg (ous and ic). Cadmium chromate has been prepared; beryllium chromate, though described, is questioned. Only zinc and barium dichromates are well-known.[4] These have also been reported: magnesium[12], calcium[6], strontium[6,19], cadmium[17], and mercury[3].

Other well-known[4] chromates are: Sn (ous and ic), Pb, Tl, Co; dichromates: Pb, Tl. A chromate of cerium has been prepared. Rare earths are separable by fractional precipitation with potassium chromate. The order for the cerium earths: La, Pr, Nd, Sm; for the yttrium earths: Tb, Yb, Er, Y, Gd. Thorium, uranyl, ferric (questioned), cobalt, and nickel dichromates have been reported.

Ammonium chromate and dichromate are known. Garnet-red crystals of the latter result when half of a chromic acid solution is saturated with ammonia and then mixed with the other half.

RELATION BETWEEN CHROMATES AND DICHROMATES

Dichromates are readily formed by addition of acid to normal chromates; trichromates form upon further addition of acid. The color goes from yellow through orange-red to the red of the trichromates. Numerous studies[8,13] show that solutions of chromic acid always contain some dichromate:

$$2H_2CrO_4 \rightleftharpoons 2H^+ + 2HCrO_4^-$$
$$\rightleftharpoons H_2O + Cr_2O_7^=$$

Hydrolysis explains the alkaline reaction of chromates and the acidic nature of dichromates:

$$CrO_4^= + H_2O \rightleftharpoons HCrO_4^- + OH^-$$
$$Cr_2O_7^= + H_2O \rightleftharpoons 2HCrO_4^- \rightleftharpoons 2H^+ + 2CrO_4^=$$

Dichromate solution is converted into chromate by finely divided aluminum oxide which shows a strong preferential adsorption for hydrogen ions[18]. The colloidal oxide, stabilized by previous adsorption of hydrogen ion, has little effect on this equilibrium.

PERIODIC PRECIPITATION

Liesegang[15] noticed the phenomenon that bears his name after placing a drop of silver nitrate on a slab of gelatine impregnated with potassium chromate. Periodic precipitation of silver chromate resulted.

USES OF CHROMATES AND DICHROMATES

Leather tanning (reduced to trivalent form); color printing, block printing, photography (inasmuch as light causes a mixture of gelatine and potassium dichromate to become insoluble); pigments and corrosion resistant finishes; dyes, intermediates, mordants; water resistant glues and cements; external caustics for ulcers.

PHYSIOLOGICAL ACTION

Inflammation of nasal passages, ulceration, then complete destruction of the septum. Painful skin ulcerations which workmen call "chrome holes" start from skin abrasions. Hexavalent chromium, more toxic than trivalent, destroys red blood corpuscles.

MAGNESIUM DICHROMATE

This compound is interesting, for it represents an apparently simple material which, evidently because of its properties, had not been studied until very recently. In contrast to the insoluble barium salt which has been prepared[7] by addition of hydrochloric acid to barium chromate, magnesium dichromate is very soluble and its preparation long remained in doubt. Reinitzer[16] states that it is only slightly soluble in alcohol, but he gives no details. Friend[5] and Abegg[1] state that the dichromate has not been prepared. The Handbook[4] does not list it.

Kränzlein and Voss[14] in U.S. Patent 1,774,018 describe the preparation of magnesium dichromate from sodium dichromate and magnesium chloride. The preparation of the penta and monohydrates has been reported for the first time by Hartford[12].

HYDRATES OF MAGNESIUM DICHROMATE

The pentahydrate was formed by addition of magnesium oxide slowly and with agitation to an aqueous solution of chromium trioxide to a pH of 2.8-3.0 as measured with a glass electrode. The dark color-2 caused by traces of trivalent chromium was removed by oxidation with lead electrodes. Then the solution was filtered, concentrated, and allowed to form the deliquescent orange-red crystals upon agitation and slow cooling. Since the solution is

very viscous, it is desirable to seed it with magnesium dichromate to hinder supersaturation. pH control is important as too high a pH causes separation of the normal chromate; too low a pH allows the excess chromic acid to adhere to the dichromate crystals.

The solubility at 25°C. was determined by agitating an excess of the salt with water in a closed thermo-statically-controlled container, then withdrawing a sample through a sintered-glass funnel and analyzing for magnesium oxide and chromium trioxide. The solution averages 81% as the pentahydrate. The salt is soluble in ethanol to the extent of 200 g./l. at 25°C.; less so in acetone and other polar solvents. Light promotes oxidation of the organic solvent by the dichromate.

Drying of the pentahydrate under 75 mm. at 160°C. results in the formation of brick-red deliquescent crystals of the monohydrate which is stable up to 300°C. at which partial decomposition of the dichromate results. The transition point (89.4°C.) for the phase relationship was determined by cooling curve measurements in the range 0-100°C. Though these hydrates are still in the laboratory stage of investigation, the extreme deliquescence would suggest a possible use in the refrigeration and air conditioning field.

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THE STRUCTURE AND PROPERTIES OF CARBIDES AND ACETYLIDES

Bodie E. Douglas January 20, 1948

Carbides are normally classified according to their reaction with water or dilute acids. This divides them into two large classes:

A. The carbides which react with water or dilute acids are formed by the elements whose oxides are basic. They are classified according to the products formed (1).

1. Methanides.

These are essentially non-polar carbides with the carbon atoms separated in the crystal lattice by the metal atoms. The products obtained are the result of the action of the hydrogen set free on the individual carbon atoms separately. Some of these carbides yield almost pure methane, but some other hydrocarbons may be formed by hydrogenation and polymerization. The products of hydrolysis depend a great deal upon the conditions. Some examples are: Be_2C, Al_4C_3, $Mn_3C_{\cancel{2}}$, $Fe_3C_{\cancel{2}}$ and $Ni_3C_{\cancel{2}}$. Little free C with Fe_3C.

2. Acetylides.

Most of the acetylides are ionic and crystallize in ionic space lattices. The acetylenic linkage, -C≡C-, occurs in the crystal lattice and is retained on hydrolysis. This type of carbide is formed by the metals with large ionic radii, such as the metals of groups IA, IIA, IIIA including the rare earths and thorium. Acetylene is the main product of hydrolysis of these compounds, but hydrolysis of the acetylides of group IIIA and thorium also yields other saturated and unsaturated hydrocarbons due to the oxidation of the metal to the trivalent or quadrivalent state.

Covalent acetylides are formed by the metals of group IB and IIB. These are stable toward water, but decomposed by dilute acids to give acetylene (2).

Since acetylene has distinctly acid properties and one hydrogen is much more easily lost than the other, monobasic acetylides of calcium and the alkali metals are formed by passing acetylene into a solution of the metals in an 'inert' solvent. On heating, the normal acetylides are formed. (3).

$Na_2O_2 \xrightarrow[\Delta]{CaC_2} Na$

3. Derivatives of allylene.

The only carbide which is known to yield allylene on hydrolysis is magnesium carbide, Mg_2C_3. Almost pure allylene is obtained from this carbide and this is the only basis for assuming that the -C-C≡C- linkage occurs in the crystal lattice, since no data on the crystal structure are available. Magnesium carbide is prepared by passing hydrocarbons over the molten metal (4). This carbide has potentialities as a source of organic derivatives of allylene, similar to calcium carbide as a cheap source of acetylene and its derivatives (5).

4. Miscellaneous carbides.

Uranium carbide, UC_2, gives large amounts of solid and liquid hydrocarbons on hydrolysis. The carbides of K, Rb and Cs formed by direct combination with carbon are of the type MC_8. @ 70-80° They yield pure hydrogen upon hydrolysis.

B. The carbides which are inert toward water and dilute acids are formed by the elements whose oxides are acidic. These carbides are classified according to their structures (6).

1. Non-polar carbides.

These are the volatile carbides formed by the elements in the upper right corner of the periodic table. Examples are compounds such as CH_4, CCl_4 and CS_2.

2. Diamond-like or tetrahedral carbides.

Silicon carbide is one of the carbides of this class. They are non-polar molecules of unlimited size. They are high melting and very hard, formed by the elements very near to carbon in the periodic table.

3. Alloy-like carbides.

The alloy-like carbides are formed by the elements in the lower middle portion of the periodic table. These carbides are non-polar and metallic in character. They have true atomic space lattices and conduct and reflect like metals. In these compounds the valences are abnormal, the force causing combination being a "packing effect" due to van der Waal's forces. The small atomic radii and electron defects of the transition elements seem to be factors in the metallic nature of these compounds (7) e.g. TiC, WC, Cr_2C.

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COORDINATION COMPOUNDS OF ALUMINUM CHLORIDE

David H. Campbell January 20, 1948

Complex compounds of aluminum halides have been known to exist for many years. The halides themselves have been shown to exist as dimers; thus, aluminum chloride has the formula Al_2Cl_6, the structure of which is represented as two tetrahedra of chloride ions with an edge in common, and aluminum at the centers of the tetrahedra. The aluminum halides form hydrated compounds, as $AlCl_3.6H_2O$, and the similar ammonia complexes, as $AlCl_3.6NH_3$. Aluminum halides form other complexes, including many with metallic halides. Latimer and Hildebrand (1) state, concerning the stability of these compounds, "Aluminum fluoride exhibits strong tendencies to form complex salts, giving the radical, AlF_6^{---}, as in cryolite, Na_3AlF_6. These compounds are analogous to the aluminate, and owe their stability to the large value of $ee^1/(r + r^1)$ for aluminum and fluoride ions. The tendency of the other halides of aluminum to form complexes decreases with increasing weight." Actually there are many more compounds of $AlBr_3$ than of $AlCl_3$ reported in the literature.

As early as 1827 Wohler (2) prepared a yellow compound by passing aluminum chloride vapor over heated sodium chloride. The compound did not give off aluminum chloride when strongly ignited; it dissolved in water, forming a solution which yielded sodium al-crystals on evaporation. The compound $NaCl.AlCl_3$ was once used in the manufacture of aluminum. In 1864 Bassett (2) reported that the compound could be reduced to free aluminum by Bi, As, Sb, Sn, Zn, Hg, and amalgams of Sn, Zn and Sb. Bunsen (2) also obtained aluminum by electrolysis of the fused compound.

Baud (3) prepared complex compounds of aluminum chloride with ammonium chloride and several metallic chlorides by fusing together the calculated amounts of the component salts. He reported, as a result of these experiments, the following complex compounds: $NH_4Cl.AlCl_3$, $NaCl.AlCl_3$, $3NaCl.2AlCl_3$, $3NaCl.AlCl_3$, $KCl.AlCl_3$, $3KCl.2AlCl_3$, $3KCl.AlCl_3$, $AgCl.AlCl_3$, $3CaCl_2.4AlCl_3$, $3SrCl_2.4AlCl_3$. Baud determined heats of formation of these compounds and calculated the contribution of each molecule of the donor salt to the heat of formation of the compound in the cases of the alkali chloride compounds.

	Heat of formation	
	NaCl	KCl
1st two molecules per molecule Al_2Cl_6	5.92kcal.	13.19kcal.
3rd molecule	3.45	4.15
4th, 5th and 6th molecules	1.41	2.035

For example, the heat of formation of $3NaCl.AlCl_3$ is 9.6 k. cal., and that of $3NaCl.2AlCl_3$ is 15.28 k. cal.

Kendall and coworkers (4) criticized Baud's methods and conclusions. They performed freezing point determinations upon a great many fused salt mixtures throughout the entire range of concentrations, including several systems containing aluminum chloride. They confirmed some of the compounds Baud had reported, but did not find evidence for the 3:1 and 3:2 compounds of sodium and potassium chlorides with aluminum chloride. As a result of their studies they reported $LiCl.AlCl_3$, $NaCl.AlCl_3$, $KCl.AlCl_3$,

$NH_4Cl.AlCl_3$, $CuCl.AlCl_3$, $AgCl.AlCl_3$, $BaCl_2.2AlCl_3$, $MgCl_2.2AlCl_3$, $TlCl.2AlCl_3$, $TlCl.AlCl_3$, $SnCl_2.2AlCl_3$, $SnCl_2.AlCl_3$ and $MnCl_2.2AlCl_3$. Their studies also indicated the existence of x:y compounds in several of the above systems in which x and y could not be determined by their experimental methods. In the case of the $NaCl-AlCl_3$ system, such a compound was indicated in the region between 0.2 and 18 mol % NaCl.

Schwartzmann (5) and Chrétien and Lōus (6) also performed thermal analyses upon the systems $AlCl_3-NaCl$ and $AlCl_3-KCl$. Their results did not indicate the existence of the 3:1 and 3:2 complexes reported by Baud.

Plotnikov and Jacobson conducted thermal analyses of mixtures of $AlBr_3$ and $AlCl_3$ with metal salts and determined heats of formation of the complex compounds formed. They found that heats of formation for the $AlCl_3$ complexes are less than for the corresponding $AlBr_3$ complexes, and in each case the heats of formation rise with increasing atomic weight of the alkali metal. They, as well as Kendall and coworkers, found many more complex compounds of metal salts with $AlBr_3$ than with $AlCl_3$. In several cases $AlBr_3$ forms both a 1:1 and a 2:1 compound with a metal salt while $AlCl_3$ forms only the corresponding 1:1 compounds.

Kryagova (7) investigated the system $NaCl-AlCl_3$, determining the specific gravity, viscosity and conductivity throughout a range of concentrations. Specific gravity determinations were carried out from 190° to 280°. The data indicate the presence of a highly dissociated compound in the fusion. Viscosities were determined at 200° to 300°; the data fit equations for viscosity of non-associated liquids. The viscosity curve has a minimum at equimolar amounts of the components. Kryagova found the molecular conductivity of the system to be directly proportional to the temperature. The maximum conductivity occured at equimolar amounts of $AlCl_3$ and NaCl, that is, at $NaAlCl_4$. He states that the compounds are not associated in the melt.

Mellor (2) lists another group of compounds under the name enneachlorodialuminates, of which Baud (3) reported $3CaCl_2.4AlCl_3$ and $3SrCl_2.AlCl_3$, having heats of formation of 18.56 kcal and 17.42 kcal respectively, and melting points less than 300°. A similar compound, $3BaCl_2.4AlCl_3$ has been prepared by heating $BaCl_2.2AlCl_3$ to 500°, at which temperature it loses $AlCl_3$. Its heat of formation is 14.6 kcal. Kendall and coworkers(4) did not report this compound, but did report $BaCl_2.2AlCl_3$. The compound $3ZnCl_2.4AlCl_3$ has also been reported, and is described as a pasty, translucent mass, less stable than the three similar compounds mentioned before, and having a negative heat of formation.

Kendall and coworkers attempted to determine the factors which influence compound formation in fused salt mixtures. From their investigation of systems of $AlCl_3$ and $AlBr_3$ and of other salts, they concluded that the most important factor is what they termed the diversity factor. Salts of metals which are much more electropositive than aluminum provide the largest number of complex compounds and the most stable compounds with aluminum chloride or bromide. This was more evident in the case of aluminum bromide systems since many more compounds were formed than

with aluminum chloride. The alkali metals provide the most compounds and the most stable ones; the alkaline earth metals form fewer and less stable compounds. Magnesium and zinc bromides each give single compounds with aluminum bromide, each compound being very highly dissociated into its components on fusion. Going further from aluminum down the electromotive series compound formation again increases in extent.

The complex compounds mentioned thus far are all composed of aluminum chloride with a metallic chloride which is principally ionic in character, the metals being either uni- or divalent. Compounds with aluminum chloride are not limited to these, however. The only salt complexes with aluminum chloride which were found were those of uni- and divalent metals and ammonium. These are not limited to the chlorides; 1:1 compounds of sodium, potassium and silver bromides with aluminum chloride have also been found. The chlorides of these three metals have also been found to complex with aluminum bromide, those of sodium and potassium forming both the 1:1 and 1:2 compounds. Turning to chlorides more covalent in character, Kendall and coworkers (4) studied the system $HgCl_2$-$AlCl_3$ and found no evidence of compound formation. Shibata and Inoue (8) found the compound $HgCl_2.AlCl_3$ to be stable in 0.002M solutions. Its exist ence under other conditions was not reported.

Fischer and Jübermann (9) investigated the system PCl_5 - $AlCl_3$ by thermal analysis, and found that the 1:1 compound is unexpectedly stable. It melts above 330° (above the critical temperature of both components). Pfeiffer had studied the system previously and formulated the compound as $Cl_4PCl.AlCl_3$ or $PCl_4^+ AlCl_4^-$. Fischer and Jübermann doubt the existence of the ion PCl_4^+, but they suggest that the compound has a structure similar to an ionic aggregate MCl_4, in the chloride lattice of which the aluminum and phosphorus particles represented by M are distributed stoichiometrically in regular order, and in the melt, statistically. As partial evidence for this they report that the compound is not completely miscible in the melt with PCl_5 which is composed of molecular aggregates, but is completely miscible with $AlCl_3$ which is more nearly the ionic aggregate type. The compound, then, may or may not be a true coordination compound.

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OXIDATION STATES AND COMPOUNDS OF GALLIUM, INDIUM AND THALLIUM

Glendall King January 27, 1948

I. Introduction

The rare metals gallium, indium, and thallium constitute the lower portion of group IIIB of the periodic table. Thallium is the only one of this group which appears as a major constituent of naturally occuring minerals. Consequently it is available in greater amount than the other two. All three of these metals were discovered between 1850 and 1875 and it was the discovery of gallium that did so much to strengthen faith in Mendeleeff's periodic classification of the elements. The experimentally determined properties of gallium are almost identical with those predicted by Mendeleeff, who had called it eka-aluminum.

II. Electronic Configuration and Predicted Valences.

By considering the position that these three elements occupy in the periodic table one can see that the outer configuration of each element is characterized by a ns^2np^1 arrangement. It is therefore quite probable that this outer p electron could be lost, forming the univalent metal ion. This actually does take place. The stability of the univalent state increases from gallium to thallium. The change of the metal from univalency to a higher valency involves the unpairing of the $\underline{s}^2$ electron pair of the highest quantum level and promotion of one electron to a p level (5). In general, trivalency will result from the two extra unpaired electrons thus rendered available. Although it would not be an impossibility for the +2 oxidation state to exist, the probability that it does exist is very small. The trivalent state actually is the most common oxidation state for gallium and indium. In the case of thallium, however, a certain discrepancy is observed and the thallous (+1) is the most common oxidation state. This tendency of the thallous ion to keep the two available valence electrons has been discussed by Sidgwick (7) who refers to them as the "inert pair" of electrons. In connection with removing this inert pair of electrons, it can be said that the ionization energy for complete ionization would be so high that, in the compounds of maximum valency, the bonding is covalent instead of electrovalent. This fact is brought by the following table (6).

	Mean ionization energy per electron removed (~~electron volts~~) kcal	B.P. of chloride (degrees C)	Conductivity of chloride at B.P. ($ohm^{-1} cm^2 equiv^{-1}$)
Tl^1	140	806	46.5
Tl^3	430	100	0

III. Discussion of Compounds

Compounds of the halogen family of the type InX, TlX, GaX_2, InX_2, GaX_3, InX_3, and $TlCl_3$, were X = Cl, Br, or I, have all been reported. (1,2,3,4). If the above formulations are all correct, it would appear that gallium can exist in the di or trivalent state, indium in the mono, di or trivalent state, and thallium in the mono and trivalent state. It has also been shown for another compound, namely Ga_2O (3) that gallium can exist in the monovalent state. Before any definite conclusions can be reached that there is a +2 state for these metals, the evidence for and against such a state must be considered. If the +2 state does exist in these materials, there would naturally be an unpaired electron in the material. This unpaired electron would lead to paramagnetic qualities for such a compound. Klemm and Tilk (8) have carried out magnetic measurements on these supposed dihalides and all exhibited diamagnetic properties. Certain authors (9) have tried

Tabulation of oxidation states

		I	II	III
Ga	Cl	–	+	+
	Br	–	+	+
	I	–	+	+
In	Cl	+	+	+
	Br	+	+	+
	I	+	+	+
Tl	Cl	+	–	+
	Br	+	–	?
	I	+	–	?
Ga	O	(+)	–	+
	S	(+)	+	+
	Se	(+)	+	+
	Te	(+)	+	+
In	O	+	+	+
	S	+	+	+
	Se	+	+	+
	Te	+	+	+
Tl	O	+	–	+
	S	+	–	–
	Se	+	–	–
	Te	+	–	–

+ = prepd.

– = not prepd.

to nullify this evidence by assuming that the M^{+2} ion is doubled up to a M_2^{+4} ion, which would be similiar to the Hg_2^{+2} ion, and this ion would be diamagnetic. These same authors believe that the vapor density determination of Nilson and Petterson (10) supported the probability of the associated molecules of In_2Cl_4. The fact that the material was In_2Cl_4 would by no means prove the existence of the In_2^{+4} ion. This material could just as easily be formulated as $In^{+1}(In^{+3}Cl_4$. in which indium exists in two valencies.

It may be said that all of the "divalent" salts may be formulated as salts containing the mono and trivalent metal. One material that might show the presence of a divalent metal ion is a very doubtful oxide of the composition In_3O_4 (13). If this compound exists, the supporters of the +2 oxidation state will have gained some proof of their convictions. However, at the present time, the experimental evidence does not seem to support the existence of divalent ions of either gallium, indium, or thallium.

A brief mention of the hydroxides of these metals is needed here to bring out some of the interesting facts concerning the family. Since compounds of gallium and indium in valence states other than three decompose in contact with water only the trivalent hydroxides need be considered. Gallium hydroxide is a white gelatinous precipitate which, in keeping with the acidic properties of gallium, is soluble in excess alkali. Indium hydroxide, although said by many to be soluble in excess alkali (1), is also reported to be insoluble in sodium, potassium, and ammonium hydroxide (11). About the only case in which the acidic qualities of indium are shown is that of magnesium indate (12). This material is produced by heating MgO and In_2O_3 together at 1300 C for twenty hours.

Thallic hydroxide is a very insoluble brown precipitate which is not affected by excess alkali. However, thallous hydroxide is readily soluble in both water and alcohol, its solution are strongly alkaline, absorbing CO_2 quickly and attacking glass and porcelain readily.

In concluding it may be said that the compounds of these metals provide interesting examples of various valence states. The mono and trivalent states are definitely established. The existence of the divalent metal ion is a subject still open to consideration.

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"SUB-COMPOUNDS"
and
INORGANIC FREE RADICALS

Sister Martinette January 27, 1948

Definitions:

"Sub-compounds" are molecules of extremely simple types with apparently anamolous valences associated with their constituent atoms. (1)

Free radicals are complexes of abnormal valency, which possess additive properties, but do not carry an electrical charge and are not free ions. (2)

Discussion:

Spectroscopic analysis has indicated the existence of some extremely simple molecules with which the chemists are unfamiliar. Most of these molecules are diatomic and exhibit apparently anamolous valences. The band spectra which identify certain of these compounds appear in electric discharges, flames, etc., that is, under conditions which are not ordinary. Under ordinary conditions these same molecules are not chemically stable. Not only the existence and physical stabilities of these radicals have been proven but also their internuclear distances, vibrational frequencies, heats of dissociation and electronic structures have been determined. (3) Preliminary calculations have been made on the equilibria governing the coexistence of many free radicals which are thought to be important constituents of stellar atmospheres and to coexist at the high temperatures existing in stars. (4)

Many possible sub-compounds have eluded detection and characterization by chemical means. In some cases the inability of a sub-compound to exist as such in the solid state is one of its characteristics. Frequently the equilibrium involved in a sub-compound formation undergoes rapid reversal and this, again, inhibits isolation. Silicon has long been known to form "lower oxides" and at one time a product, "Monox", was marketed as SiO. X-ray examinations have shown "Monox" to be an intimate admixture of silica and silicon. (5) Only in 1940 were the important characteristics of SiO known. (6) Zintl and his co-workers made a careful study of its formation in the "Monox" preparation. Other methods are also well know. (4) Although SiO is not stable there is some evidence that it exists in dilute solutions from studies on silicon-oxygen equilibria in molten steel. (7)

e.g. Cb_2O_5 or Ta_2O_5 $+ Si \rightarrow Cb$ or Ta $+ SiO$

dolomite
Zn ore
$Ca_3(PO_4)_2$ $\xrightarrow{\text{"SiO"}}$ Mg
Zn
P([illegible])

BO, boron monoxide, appears to exist under conditions similar to those under which we find SiO. (8) The unusual volatility of the lower oxides of titanium-oxygen (9) and vanadium-oxygen (1) systems would indicate the possible existence of sub-oxides in the vapor phase. Sulfur monoxide chemistry, also, fits well into sub-compound chemistry. (10) An interesting sub-compound study was made by Klemm and Voss (11) on AlF, aluminum subfluoride.

$$CaCl_2 \xrightarrow[800^\circ]{Ca} CaCl$$ red violet

$$CaF_2 \xrightarrow[1400^\circ]{Ca} CaF$$ red orange

$$BaCl_2 \xrightarrow[\Delta]{Ba} BaCl$$ white

$$MgI_2 \xrightarrow[\Delta]{Mg} MgI$$

$$Cd \xrightarrow[\text{bomb}]{I_2} CdI$$ greenish yellow

1000°
10 hrs.
→ cool sud.

$$Zn \xrightarrow[\text{"}]{I_2} ZnI$$ black

A very few of the interesting sub-compound investigations have been indicated here. However, it is obvious that various branches of inorganic chemistry are involved in the lower-valency compound field. There are indications that many earlier conclusions need to be reviewed. Many "sub-compounds" may in reality be intimate mixtures of elements with compounds which exhibit more normal valency. These mixtures may even be disproportionation products of true sub-compounds which are stable only at high temperatures. The fine line of distinction between free radicals and subcompounds seems to be a relative one. Many "sub-compounds" may be correctly regarded as free radicals and vice versa.

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Diatomic Molecules for Which There is Spectroscopic Evidence: (3)

0	I	II	III	IV	V	VI	VIII
	HS H						
He	Li_2 LiK LiCs LiRb Li	BeCl BeF BeH Be	BBr BH BCl BO BF B	CCl CP CH CS CN CSe CO C	NBr NH (16) NO NS N	OH O	F
Ne	Na_2 NaK NaCs NaRb Na	MgI MgF MgH MgBr MgCl Mg	AlCl AlO AlF (11) AlH AlI Al	SiBr SiH SiCl SiN SiF SiO SiSe SiS(12)Si	PH PN PO P	SO S	Cl

0	1A	2A	3A	4A	5A	6A	7A	8			1B	2B	3B	4B	5B	6B	7B
	K_2	CaBr CaCl (14) CaF CaH CaI	ScO	TiCl TiO TiS (13)	VO	CrH	MnH	FeCl FeH	CoBr CoCl CoH	NiH NiBr NiCl		ZnCl ZnH ZnI (15)	GaO	GeBr GeCl	**AsO**	Se_2 SeO	
A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
	Rb_2 RbCs	SrBr SrCl SrF SrH SrI	YO	ZrO								CdBr CdCl CdH CdI (15)	InH InO	SnBr SnCl SnF SnH	Sb_2 SbO SbN SbF SbCl SbBi	Te_2 TeO	
Kr	Rb	Sr	Y	Zr	Cb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
		BaBr BaCl BaF BaH	R. LaO E.										TlH	Pb_2 PbBr PbCl PbF PbH	BiBr BiCl BiF BiH BiI BiO		
Xe	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
Rn	Fa	Ra	Ac	Th	Pa	U											

Rare Earths	Ce	PrO Pr	Nd	Il	Sm	Eu	GdO Gd	Tb	Dy	Ho	Er	Tm	Yb	LuO Lu

SOME OXYACIDS OF BORON

J. N. Coker February 24, 1948

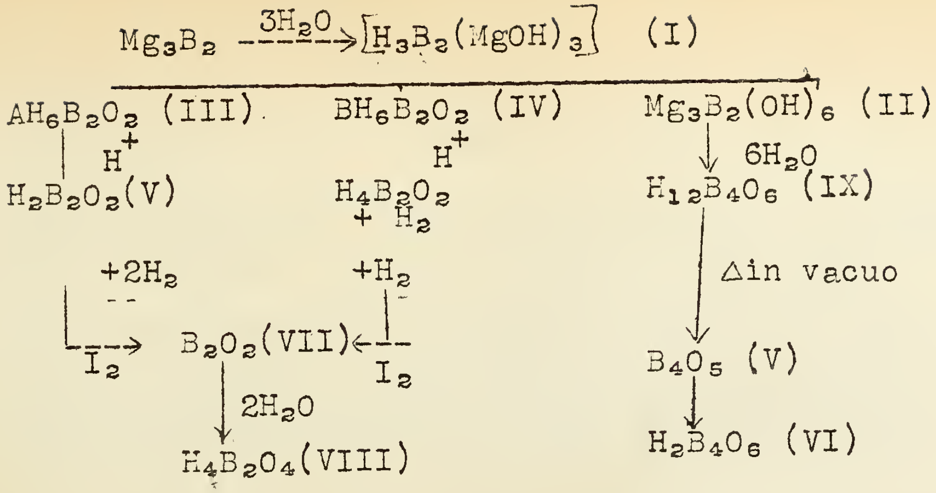
I. Introduction. Three types of these acids will be considered here; borohydrates, hypoborates, and sub-borates. Ortho-boric acid, H_3BO_3, and some of its derivatives, such as meta-boric acid, HBO_2, and tetraboric acid, $H_2B_4O_7$, have not been included in the discussion.

II. Preparation and Properties of Acids of the type, $H_6B_2O_2$. The name, borohydrates, was first applied by Travers and Ray to compounds of this type because of a similarity they believed existed between these compounds and carbon compounds having similar formulae. Though it is now known that this reasoning is not strictly accurate, the name has been retained for the lack of a more suitable one. While the borohydrates have sometimes been assumed to be in a class by themselves, it can be shown that they differ only relatively from carbon compounds of similar composition.

Rather extensive investigations into the nature of compounds of this type have been carried out by Travers, Ray, and Gupta. Their studies were confined largely to aqueous extracts of magnesium boride samples, prepared by heating magnesium and boron trioxide to red heat (1). All such solutions were found to contain a compound with the empirical formula, $H_6B_2O_2$, in addition to small amounts of magnesia. On the basis of the reactions which the various extracts gave with mineral acid, the existence of two isomeric forms of the compound was postulated. Neither of these two isomers could be isolated from the aqueous solutions in the form of a magnesium salt. However, a prediction that the potassium salts of the material would possess more stability was, in part, borne out by the isolation of one of the isomers in this form (2). Attempts to isolate the second isomer as the potassium salt were unsuccessful until the conditions used for the preparation were made much less severe (3). The stable isomer has been designated as alpha, and the more unstable one as beta.

The potassium salts which were isolated were found to be white, deliquescent materials, possessing well defined, crystallinw structures, and are readily soluble in water. The alpha form proved to be stable enough to be preserved rather well in a moistur free, carbon dioxide-free atmosphere. The materials were found to give the same reactions with acid, iodine, and heavy metals as does the original extracts from which they were obtained, and they possess excellent reducing properties. Analytical evidence, coupled with equivalent conductance measurements, indicates the molecular formula, $H_6B_2O_2$.

On the basis of a careful investigation of the stages involved in the hydrolysis, the extracts which Travers and Ray obtained were divided into two classes. Solutions of the first class were prepared by the hydrolysis of magnesium boride samples which had been allowed to deflagrate gently during their preparation. Solutions of the second class were obtained from samples of the boride which has not been allowed to deflagrate during their formation. The most marked difference in the two classes of extracts involved their behavior towards acid, this difference being indicated in the foll wing scheme of hydrolysis (4):



The above hydrolysis is the one which was observed to occur at room temperature, and is essentially the same whether it is effected by water or dilute acid. The main product of the hydrolysis is $Mg_3B_2(OH)_6$. If the hydrolysis is carried out at slightly below -10°, it was found to proceed almost entirely by reaction (c), yielding product (II), and insoluble white material, which possesses considerable stability. Treatment of this salt with concentrated aqueous ammonia, followed by a fractional crystallization yielding the salts, $(NH_4)_2B_2(OH)_2$ and $(NH_4)_2B_4O_6$, which were found to be stable in a dry state below 0° (5).

The tetraboron borohydrate, $H_{12}B_4O_6$, the existence of which has been indicated in aqueous solutions of magnesium boride, has not been successfully isolated (6).

III. Preparation and Properties of Acids of the Type, $HOBH_3$ (14). Compounds of this type are generally known as hypoborates, and have been investigated by Stock and his coworkers. Stock and Kuss first prepared hypoborates by treating tetraborane, present in large excess in the reaction micture, with a very concentrated aqueous solution of potassium hydroxide, the hypoborate separating out of the solution as a crystalline material. An alternate method of preparing the compound involves diborane in a similar reaction. The crystalline salt which was produced was found to possess the usual properties associated with the borohydrates already considered. Potassium hypoborate proved to be fairly stable in the cold, and aqueous solutions of it were found to give the usual alkaline reactions. The role of this salt as a reducing agent was thoroughly investigated by Stock and Kuss. With the salts of heavy metals, such as silver, bismuth, arsenic, mercury, and anitmony, dark precipitates, apparently of the free metals themselves, readily formed. If solutions of barium, calcium, magnesium, aluminum, or zinc salts were treated with the material, especially if heat were applied, white precipitates of the corresponding hydroxides and borates separated from the solution. The reaction of potassium hypoborate with nikelous salts is a rather unusual one, since an insoluble black boride, Ni_2B, precipitates immediately from the solution. The formation of a boride of this type in the cold is distinctive, since most of the known borides are obtainable only at high temperatures.

Thermal decomposition of the potassium hypoborate was found to occur at temperatures above 500°, with a portion of the potassium in the compound separating out in the metallic form. Analytical considerations of the products obtained in the decomposition allowed Stock and Kuss to represent the reaction by the following equation:

$$5\ KOBH_3 \dashrightarrow K_3B_5O_3 + 2K + 2H_2O + 11\ H$$

Since this equation does not take into consideration certain side reactions which are possible, it is only a partial representation of the chemical processes involved in the decomposition.

IV. Preparation and Properties of Acids of the Type, $H_4B_2O_4$(13). The preparation of a material having the formula, $H_4B_2O_4$, as well as several of its esters, has been reported by Wilberg and Ruschmann, and they have applied the name, sub-boric acid, to the compound. Its preparation is indicated in the following equation:

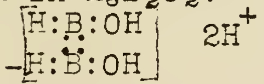
$$2B(OCH_3)_2Cl \xrightarrow{NaHg} B_2(OCH_3)_4 \xrightarrow[HCl]{in\ vacuo} H_4B_2O_4 + \underset{20\%}{H_3BO_3}$$

Acidic, alkaline, as well as neutral solutions of the ester intermediate have been observed to decolorize a solution of permanganate, and to reduce aqueous solutions of silver nitrate. A solution of iodine could not be reduced by it however.

V. Structural Considerations. Lennard-Jones has stated that any chemical bond is not the resultant of a pair of electrons, not even of all the electrons associated with a pair of bonded atoms, but of all the electronic forces present in the molecule (8). In the case of carbon, this idea can be expected to hold and yet conform to the principle that chemical bonds are closely related to paired electron orbits (7). However, in the case of boron, this conformity does not seem to hold, and structural representations of the compounds of boron are at best difficult, using the conventions applicable to carbon compounds.

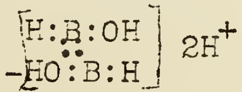
The application of some of the hypotheses which have been advanced to describe boron hydrides in particular often are of little value in indicating structure in the boronhydrate series. According to Ray, the bridge structure (19) as proposed by Pitzer (11), Dilthey (10), Cole and others (12), fails to explain to any degree of satisfaction the formation of stable borohydrates. Considering the possible resonance forms, it would be expected that the removal of hydrogen atoms would lead to a disruption of the boron-to boron bonds, especially when these hydrogen atoms are removed by acid or halogen. For example, in the case of tetraboron borohydrate, the compound loses hydrogen when treated with acid, and more hydrogen when treated with iodine; however, the degration proceeds only to the $H_2B_4O_6$ stage. From such a degradation it would seem that the borons are joined directly by the elimination of hydrogen. However, if the bridge structure is correct, it would be expected that the products would be boron compounds with fewer boron atoms in the chain.

Ray has postulated several structures to explain the isomerism found in $H_6B_2O_2$:



$$\left[\begin{array}{l} H:\underset{\cdot\cdot}{B}:OH \\ H:\overset{\cdot\cdot}{B}:OH \end{array}\right]^{-} 2H^+$$

α Form



$$\left[\begin{array}{l} H:\underset{\cdot\cdot}{B}:OH \\ HO:B:H \end{array}\right]^{-} 2H^+$$

β Form

He seems to think that the configuration he has assigned to the alpha isomer would permit hydrogen to be more easily lost than would the configuration which he has given to the beta isomer.

Ray has stated that since all the hypothese for boron structur seem to be more or less consistent with the facts, this is at least an indication of our ignorance concerning all the factors involved in chemical bonding. In the case of the borohydrates, because of the simple stiochiometry involved in the various reactions of the compounds with acid, Ray thinks that further efforts to assign configurations to the isomers of $H_6B_2O_2$ are completely justified. Possibly further studies into the mechanism of this elimination of hydrogen may clarify problems associated with the dissociation of ethane and ethylene, to which the process is doubtlessly related.

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THE CHEMISTRY OF THE TRANSURANIUM ELEMENTS

Theodore H. Dexter March 2, 1948

McMillan and Abelson (1) gave the first conclusive evidence that a transuranium element could be prepared when they isolated neptunium 239, element 93, and demonstrated some of its properties by tracer techniques. This result was followed during World War II by the isolation of plutonium 94 (2,3), americium 95 (4,5), and curium 96 (4,5). The properties of these elements and their compounds have been carefully studied. The chemistry of plutonium is now as well understood as that of most of the elements in the periodic system (6).

Because of their short half-lives in relation to geological time, and such mechanisms as the bombardment of uranium by neutrons from various sources, the transuranium elements probably exist naturally only in extremely small traces. Seaborg and Perlman estimated by chemical separation that the amount of plutonium in pitchblende is about one part in 10^{14}. Even smaller concentrations are anticipated for the other transuranium elements (7).

Neptunium exhibits the oxidation states VI, V, IV, and III and requires a stronger agent to oxidize it from the lower state to the upper state than does uranium (5,8). Also, the most stable oxidation state of neptunium tends to be lower than that of uranium. Throughout the transuranium series of elements, the lower oxidation state tends to be the most stable state as the atomic number increases.

Neptunium is carried from solution by lanthanum fluoride under reducing conditions but not under oxidizing conditions. This action indicates that the fluoride of the lower oxidation is insoluble while the fluoride of the higher state is soluble in aqueous solution (9).

Dark purple neptunium trifluoride and light green neptunium tetrafluoride may be prepared by the reactions:

$$NpO_2 + 1/2H_2 + 3HF \longrightarrow NpF_3 + 2H_2O$$
$$NpF_3 + 1/4O_2 + HF \longrightarrow NpF_4 + 1/2H_2O$$

The reaction of carbon tetrachloride vapor on neptunium (IV) oxalate or neptunium dioxide at 500°C produces yellow $NpCl_4$ while hydrogen reduction of $NpCl_4$ at 250°C produces $NpCl_3$. Aluminum tribromide reacts with neptunium dioxide to produce neptunium tetrabromide. Neptunium dioxide, excess metallic aluminum, and the appropriate aluminum halide form neptunium tribromide and triiodide. Neptunium oxysulfide is formed by passing an H_2S-CS_2 mixture over NpO_2 at 1000°C for two hours while prolonged treatment produces Np_2S_3 (10).

Like neptunium, plutonium exhibits the oxidation states VI, V, IV, and III but shows a greater trend toward the III state than neptunium. A stronger agent is necessary to oxidize plutonium from the lower to the higher state than is required for neptunium (5,8). However, the IV state of plutonium is the most stable state toward mild oxidizing and reducing agents in aqueous solution (11).

While no potential of the Pu-Pu (IV) couple has been obtained, the potential for the couple Pu (III) -Pu(IV), as de-

termined directly and polarographically, was found to be a function of the acid used. The potentials measured were 0.72v. at 23°C in N H_2SO_4, 0.92v. at 30°C in N HCl and 0.86v. at 23°C in N $HClO_4$ (11).

Further polarographic studies have shown that Pu (IV) ion is reduced to Pu (III) ion by U (IV) ion, SO_2, $NH_2OH.HCl$, $N_2H_2.HCl$, I^-, and by Hg in the presence of Cl^-. Plutonium ions are oxidized to the VI state by hot $KMnO_4$ solutions, $K_2Cr_2O_7$, argentic salts (including $Na_2S_2O_8$ in the presence of Ag (I)), Ce (IV) ion, and hot bromate solutions in nitric acid (11).

Aqueous solutions of Pu (III) salts are bright blue. The chloride, sulfate, and perchlorate are soluble in dilute acid solutions from which ammonium hydroxide will precipitate dirty blue plutonium (III) hydroxide. The fluoride is insoluble in dilute acids.

According to tracer evidence the oxalate is sparingly soluble in cold oxalic acid but appreciably soluble in a hot solution. Pu (III) has less tendency to hydrolyze and to form insoluble complexes with organic reagents than Pu (IV) (11).

Aqueous plutonium (IV) solutions are pale pink with the exception of the green nitrate. Solid plutonium oxide is brown, appearing yellow in thin layers. If only gentle ignition is used in preparing PuO_2 from the iodate, nitrate, or hydroxide, the oxide is readily soluble in concentrated sulfuric or nitric acid. The pale green gelatinous hydroxide may be precipitated from solution by ammonium hydroxide (11).

The composition of the bulky green peroxide precipitated from plutonium (IV) solutions by hydrogen peroxide has not been completely established (11).

Plutonium (IV) is precipitated on both zirconium phenylarsonate and zirconium m-nitrobenzoate while Pu (III) is not. This difference affords a good method for the separation of the two states (11).

Compounds of plutonium (VI) have been characterized principally by analogy to the corresponding uranium (VI) compounds. Thus brownish-yellow ammonium plutonate, orange to pink (depending on pH) plutonyl nitrate solution, and pale yellow sodium plutonyl acetate have been prepared. Since plutonium (VI) is not carried down by lanthanum fluoride, plutonium which has been carried in the IV state by lanthanum fluoride can be separated by oxidation to plutonium (VI) which is soluble and not precipitable on the lanthanum fluoride carrier.

On the basis of analyzed percentages of plutonium and analogy to the uranyl complex, plutonyl oxinate has been given the following structural formula:

A number of organic complexing reagents have been qualitatively combined with solutions of plutonium salts, generally resulting in the formation of a precipitate with plutonium (IV) and not with plutonium (III). Very few complexes of plutonium (VI) have been reported.

Further indications of complex formation are the various oxidation-reduction potentials for the Pu(III)-Pu(IV) couple in different acid media, and the inhibition of coprecipitation on carriers by the presence of high concentrations of chloride or thiocyanate ions (11).

Very few chemical data for americium, element 95, have been reported. However, deduction from tracer and ultramicrochemical techniques indicate that the III oxidation state is the most stable and most predominant state of americium (5,8).

As shown by extensive investigation with both tracer and ultramicrochemical techniques, curium element 96, exists exclusively in the trivalent state in aqueous solution (5,12). While it is carried by rare earth fluorides in precipitation reactions it cannot be oxidized or reduced to states which are not precipitable (12).

Like gadolinium, curium does not absorb light in the visible region. Strong absorption was found for curium in the ultraviolet region but none from 450-1100 mμ (12).

Among the various proposals (13,14,15,16,17,18) of a second rare-earth type series in the periodic table, a series suggested by Seaborg (6,9) beginning with actinium in analogy to lanthanum appears to be the most plausible in the light of present chemical evidence. The tendency toward stabilization of the lower oxidation states resulting in curium with a single oxidation state of III seems to indicate that the 5f shell rather than the 6d shell is being filled as the atomic number is increased. The transuranium elements show a great similarity among themselves and to uranium. Also, precipitation phenomena (11), biochemical data (19), and X-ray data (20) indicate a marked similarity in the crystal cheristry of the compounds of the transuranium elements and the first rare earth series.

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PRODUCTION, INDUSTRIAL APPLICATIONS, AND PROPERTIES OF FLUORSPAR

Oren F. Williams March 9, 1948

Fluorspar or fluorite, the simplest naturally occurring fluoride, is a fairly heavy (sp.g. 3.0-3.25), medium hard, brittle, glassy mineral composed chiefly of calcium fluoride. It crystallizes in the isometric system with a face-centered cubic lattice, each fluorine atom surrounded by four calcium atoms and each calcium atom by eight fluorine atoms (1). The mineral ranges from transparent to a translucent white and occurs in various shades, blood red, pink, yellow and deep purple being the most prevalent(2). Flawless transparent crystals of fluorspar have a very low index of refraction, disperse light faintly and display no double refraction. These properties along with the great transparency of the crystal to ultraviolet and infrared light make fluorspar suitable as apochromatic objectives for microscopes and as prisms for spectrographs employed in ultraviolet work (3). Some varieties of fluorspar fluoresce and the color of a specimen may be green or blue depending upon whether or not it is observed in transmitted or reflected light. The color of fluorspar has been determined to be due to the presence of colloidal particles of compounds of manganese, rare earths and radioactive materials (4).

Fluorspar is widely distributed in igneous rocks throughout the world but occurrence in commercial quantities is rather limited. The United States, Germany, France, Spain and Africa provide the largest quantities of fluorspar. In this country, fluorspar is mined to some extent in the states of Colorado, New Mexico, and Arizona, but by far the largest center of production is located in an area about 40 miles wide and 70 miles long in southern Illinois and in northern Kentucky (5). Recent statistics show that Illinois has supplied about 59 percent and Kentucky about 34 percent of the total fluorspar produced in the United States. In 1946, Illinois supplied 56 percent of the total U.S. production of 276,986 net tons (6).

In the past, considerable quantities of fluorspar have been mined at shallow depths but inasmuch as most of these easily accessible deposits are depleted, most of the ore remaining to be exploited lies in veins and is mined by shaft mines varying in depth from 300 to 600 feet. Prospecting for new fluorspar deposits is carried out by both surface and subsurface work. Surface prospecting involves observation of gravel-spar showings in the soil and subsoil. Subsurface prospecting is usually carried out by diamond drilling to obtain ore samples (7). Mining methods in general vary from simple pick and shovel operations to more modern methods of drilling and blasting.

Crude fluorspar ore as delivered from the mine contains such impurities as galena, sphalerite, calcite, silica, and barite. Actual fluorspar content varies with the character of the ore body. Milling operations separate mineral impurities and reduces the fluorspar to proper size for ultimate consumption in industry. Milling operations usually involve the following steps: crushing,

separation of acid-grade spar by hand picking, grinding, washing with water, gravity concentration by jigs and tables, flotation, and the recently developed heavy media process (8). The Heavy-Media Separation process, frequently referred to as the float-sink method, utilizes differences in specific gravity of minerals to effect their separation. The process was developed as a result of the observation that a suspension of fine solid particles in water possesses many of the properties of a heavy liquid, particulary with respect to the ability to float increments of low specifi gravity and to allow denser particles to sink. As applied to the separation of fluorspar from its mineral impurities, crushed fluorspar ore is added to a tank containing fine particles of ferrosilicon maintained in suspension by agitation in water. The heavy medium causes the lighter mineral impurities to float and the heavier fluorspar to sink. Fluorspar and the mineral impurities delivered from the float-sink. Fluorspar and the mineral impurities delivered from the float-sink tank by belt converyors are washed to remove particles of ferrosilicon and the washings are passed over an electromagnet to recover the ferrosilicon (9).

The largest consumer of fluorspar is the steel industry where it is used to lower the viscosity of the slag in the basic open-hearth process. A low slag viscosity is necessary to render the slag more fluid so that the contents of the molten iron bath will come into more intimate contact with the oxidizing slag. The pronounced effect of fluorspar on the slag-viscosity is due to depolymerization by the fluoride of silicate aggregates present in the slag. The mechanism of silicate depolymerization has been explained as being due to the substitution of fluorine atoms for the bridge oxygens connecting silica tetrahedra in the polymer-like structure of silicate aggregates. Formation of fluorine - silicon bonds reduces the number of silicon atoms available for oxygen bridge formation and in so doing causes depolymerization (10).

The chemical industry accounts for the second largest but most stable consumption of fluorspar. Anhydrous and aqueous hydrofluoric acid are manufactured by the reaction of fluorspar with sulfuric acid. To prepare the anhydrous acid, hydrogen fluoride gas from the reactor is passed through refrigeration coild (11) Aqueous hydrofluoric acid is made by absorbing hydrogen fluoride in water in lead cooling and absorbing towers (12). Fluorspar and hydrofluoric acid provide the chief if not the only source of fluorine for fluorine compounds. In considering fluorspar as a source of fluorine, there are two other sources, fluorapatite ($CaFCa_4(PO_4)_2$) and cryolite (Na_3AlF_6), neither of which offer any competition with fluorspar due to the difficulty of recovering fluorine in a usable form from the former and the high cost and limited amount available of the latter (13).

The third largest consumer of fluorspar is the ceramic industry where it finds application as an opacifying agent in the manufacture of opal glass and enamels. Opacity is thought to be due to the separation of fluorides as solid crystallites (14).

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ION EXCHANGE

A. E. Taylor March 16, 1948

Definition: Ion exchange may be defined as a reversible interchange between a liquid and a solid phase which does not involve any radical change in the solid structure, or as a process of double decomposition in which all of the salts of the cation exchanger and all of the salts of the anion exchanger are insoluble and filterable. Hence the Catex may be regarded as an insoluble acid, the Anex an insoluble base (1) (2).

General procedures:

(1) static system - batch process
(2) dynamic system - semi-continuous column operation

Theory of static systems

The cation exchanger can operate in either of two cycles, the sodium or salt cycle, and the hydrogen or acid cycle:-

(1) $n\mathrm{Na}_m\mathrm{R} + m\mathrm{M}^{+n} \rightleftharpoons m\mathrm{M\,R}_n + nm\,\mathrm{Na}^+$

(2) $n\mathrm{H}_m\mathrm{R} + m\mathrm{M}^{+n} \rightleftharpoons m\mathrm{M\,R}_n + nm\,\mathrm{H}^+$

where R^{-m} represents the exchanger anion and M represents a cation of valence n.

Reactions of the anion exchanger may be represented in the following ways:

(3) $\mathrm{X\,N}{<}^{\mathrm{H}}_{\mathrm{OH}} + \mathrm{H\,Cl} \rightleftharpoons \mathrm{X\,N \cdot H\,Cl} + \mathrm{H_2O}$

(4) $\mathrm{XN} + \mathrm{HCl} \rightleftharpoons \mathrm{X\,N \cdot HCl}$

(5) $2\,\mathrm{X\,N \cdot H\,Cl} + \mathrm{Ca\,SO_4} \rightleftharpoons (\mathrm{XN})_2\cdot \mathrm{H_2SO_4} + \mathrm{CaCl_2}$

where xN represents the anion exchanger showing nitrogen as the functional group.

Anion exchange takes place to a slight degree only in neutral solution, whereas effective exchange occurs in acid solution. Therefore anion exchange is considered by some to be nothing other than acid adsorption as indicated in equation 4. Adams and Holmes (3) cite reaction 5 as proof of true anion exchanger. Kunin and Myers (4) explain the inactivity of the Anex resins by the supposition that OH^- ions are already strongly adsorbed on the resin. Thus H^+ ions are required to displace these before other anions may be adsorbed (equation 3). They list the order of displacement of a number of anions from the resin. Nachod and Wood (5) have evidence to show that the rate of reaction of anion exchange is slower than that of cation exchange.

The mass law expression is approximated in most instances of cation exchange. The results will satisfy the empirical formula

$$\left[\frac{C_1}{C_2}\right]_s = K\left[\frac{C_1}{C_2}\right]_l^p$$

where C_1 and C_2 are the respective concentrations of ions having the same charge.

"S" and "l" refer respectively to the solid and liquid phases.

p is a constant less than unity. At true equilibrium

$$\left[\frac{C_1}{C_2}\right]_s = K\left[\frac{C_1}{C_2}\right]_l.$$

For the synthetic resins the expression becomes quantitative:-

$$\mathrm{Na}_m\mathrm{R} + m\mathrm{H}^+ \rightleftharpoons \mathrm{H}_m\mathrm{R} + n\,\mathrm{Na}^+$$

$$K = \left(\frac{A_{\mathrm{Na}^+}}{A_{\mathrm{H}^+}}\right)^m \left[\frac{\mathrm{H}_m\mathrm{R}}{\mathrm{Na}_m\mathrm{R}}\right]$$

from which "m" is proportional to the ratio of the logarithms and represents the valence of the resin. The graph is linear, with m = 1.

The rate of reaction has been studied by Nachod and Wood (5) and by Levesque and Craig (6) who conclude that the phenomenon is a second order reaction governed by various factors. Temperature had no effect on the rate between 27-60°C although a slower rate was observed at 0°.

Comparison of the types of exchangers.

Inorganic exchangers consist mainly of natural and synthetic zeolites. Organic exchangers include a variety of natural protein-like substances and synthetic resins of several types.

The cost of exchangers increases from the zeolites to the cation resins, the most expensive being the anion resins.

Synthetic resins have distinct advantages:-

(a) uniform composition
(b) higher capacity
(c) efficient operation over a wide range in pH.

Applications:-

A. Purifications
  1. water
    silica removal (7,8)
    sea water (9)
  2. sugar and sugar containing juices (10,112,12,13,14,15)
  3. pectin purification (16,17,18)
  4. miscellaneous
    wines; vitamins C (19); penicillin (20), streptomycin (21); organic acids; preparation and purification of various hydrous oxide gels by anion exchange (22); purification of $ZrO_2 . xH_2O$ (23).

B. Recovery or extraction processes
  1. Citric and malic acid from pineapple juice and wastes (11), malic acid from apple juice (24), aconitic acid from cane juices (12).
  2. Tartrates from grape wastes (25)
  3. Extraction and purification of alkaloids (26,27)
  4. Vitamin B 6 (28), thiamine and riboflavin (29)
  5. Amino acids
  6. Copper from rayon wastes and other liquors (29, 30).
  7. Adsorption of complex metal anions (31).

C. Catalysis (6,33,34).

D. Separation processes and applications to analytical and inorganic chemistry.
  1. Colorimetric determination of ammonia in urine (35)
  2. Phosphoric acid separation
  3. Determination of trace elements in plants (36)
  4. Titration of salts (37, 38, 39)
  5. H_2S reservoir in qualitative analysis (40)
  6. Amino acid recovery and spearation (41-46)
  7. Semi micro ion exchange column (47)
  8. Various analytical determinations, and studies of complex salts by ion exchange (48,49,50)
  9. Fractionation of lithium isotopes (51)
  10. Fractionation of Ra-Ba (52
  11. Seperation of the rare earths (53-58

Miscellaneous Applications
  1. Copper removal from gasoline
  2. Conversion of $CaCl_2$ and $MgCl_2$ to NaCl in petroleum
  3. Zeolitic adsorption of acids in exhaust gases
  4. Organic exchangers as ammonia adsorbants in gas masks
  5. Production of calcium and sodium nitrates from lime, air and sea water.

6. Antacids for the neutralization of gastric acidity (59)- treatment of peptic ulcers.
7. Instrument for the study of putrifactive chemicals in the body and their effect on disease such as old age (60)
8. Future possibilities in the study of the properties of very dilute solutions.

Postulates on the mechanism of ion exchange in dynamic systems.

The diversified opinions outlined by R Kunin serve to show the complexity of the problem. While many facts are being uncovered, no hypothesis has yet been evolved to explain and predict fully the course of the process.

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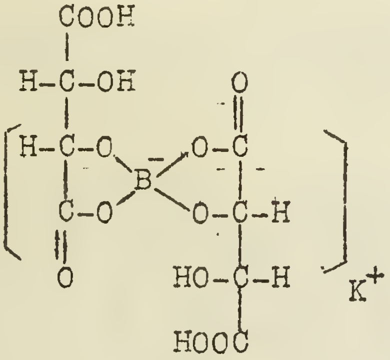
Complex Formation Between Boric Acid And Organic Polyoxy Compounds

Sister Mary Martinette March 23, 1948

The unexpected optical behavior of certain polyoxy compounds in the presence of boric acid and salts of boric acid indicates complex formation. A number of investigators have studied the phenomena and their observations are discussed here. In a limited number of cases the complexes have been isolated. Tsuzuki, a Japanese worker, extensively investigated the conditions under which certain of these complexes form (1).

For more than a century borotartrates of different compositions have been used in pharmacy but there has been some question as to the existence of the compounds proposed (2),(3),(4),(8),(5),(6),(7). Lowry (9) isolated a compound having the composition $KB(C_4H_4O_6)_2$ for which he proposed the structure:

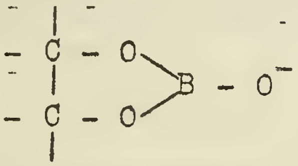


Tsuzuki studied the optical behavior of mannitol, glucose, tartaric acid and calcium gluconate (10) and found consistent evidence of complex formation.

Mannitol is normally weakly levo-rotatory and on addition of boric acid (HBO_2) there is scarcely any change in rotation (11), (12). However, if an alkali borate is added a marked change in rotation results (13). Böeseken and Vermas (14) report the reaction:

$$\text{mannitol} + NaBO_2 \rightleftharpoons BD' + BD_2'$$

where D is a molecule of polyhydric alcohol. Tsuzuki has graphically indicated the observed changes in the optical rotation of mannitol with changes in the BO_2^- concentration in a mannitol-boric acid system. (Figure I). These data indicate the complex formation proceeds with an increase in borate ion concentration. The borate ion increases the rotation of mannitol because it gives a complex having the cyclic structure:



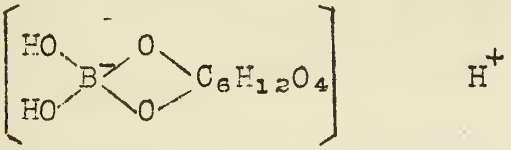
which is assumed to have a large optical rotation since the free rotation of the OH groups in the molecule is inhibited. The quantity of complex increases as the BO_2^- concentration increases

as the BO_2^- concentration increases as seen by the reaction:

$$\underset{\text{(small rotation)}}{C_6H_{12}O_6} + BO_2^- \rightleftharpoons \underset{\text{(large rotation)}}{\text{mannito-borate complex}} + H_2O$$

From the equation and the graph it is obvious the KBO_2 has a stronger effect than $Na_2B_4O_7$ of the same molar concentration with respect to the boron atoms.

Apparently free boric acid can form complexes of a strongly acid character with polyhydric alcohols. Boric acid can be titrated with alkali in the presence of mannitol (as well as glycerol), altho it is in itself a weak acid. In the titration of HBO_2 in the presence of mannitol the strongly acid mannito-boric acid complex forms. Lowry (15) proposed the quadricovalent complex:



This complex forms only after addition of a certain amount of alkali, however, once it begins to form the complex concentration steadily increases and all the acid is converted to the strongly acidic complex.

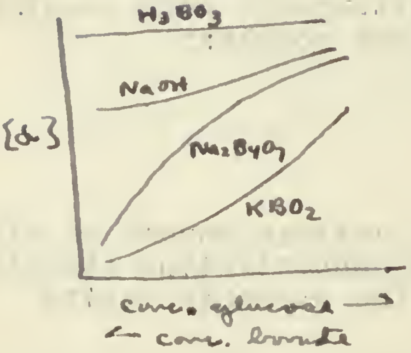
Like mannitol glucose is little affected by boric acid but greatly affected by $NaBO_2$ (16). Experimental evidence indicates that hexoses in general form small amounts of complex with H_3BO_3 but a well characterized complex with $NaBO_2$ (17). The specific rotation of glucose is high due to its cyclic glucoside structure. The change in the presence of alkali borates is very great, even to the point of negative rotation. Possibly the cyclic structure is modified some by the alkalinity of the borate salts, however, the actual effect of weak and even of strong alkali as such does not exercise a marked influence. (Figure II) Therefore, Tsuzuki assigns the radical change in rotation to the formation of a glucose-borate complex. The cyclic nature of the complex is believed to be responsible for the depression of the specific rotation of glucose. The general behavior of glucose with respect to change of specific rotation is similar to that of mannitol but in the opposite direction.

Doisy and Levy (18) published a study made on <u>alpha</u> and <u>beta</u> glucose rotatory changes for which they obtained interesting data. (Figure III) Time-specific rotation studies indicated that in borax-glucose solution there is present the sodium salt of a complex acid formed by glucose and H_3BO_3. The resulting complex has a lower optical rotation than s free glucose. On acidification the complex acid is liberated and its hydrolysis to a mixture containing <u>alpha</u>-glucose causes an initial rise in optical activity. A fall to normal is seen as the <u>alpha</u>-glucose undergoes mutarotation. Darmois and Peyroux propose the formula

$$\left[2\ B\ \text{Glucose}\right] Na_2$$

but they do not show a structure.

Tartaric acid and its salts of the alkali metals are strongly influenced by boric acid. Complex formation results due to the union of the COO^- and the $B(OH)_3$. The $B(OH)_3$ molecule acts not as


H_3BO_3
NaOH
[α]
$Na_2B_4O_7$
KBO_2
conc. glucose →
← conc. borate

an ionic compound but as an undissociated polyoxycompound. Darmois proposes the complex, $B(OH)_3.2C_4H_6O_6$ to exist in a tartaric -boric acid mixture (20).

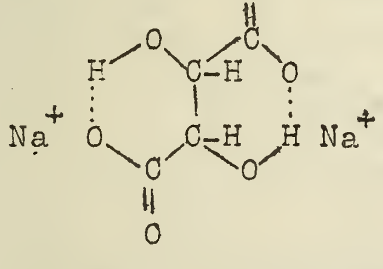
The rotation of d-tartaric acid is elevated as the ratio $\frac{H_3BO_3}{C_4H_6O_6}$ increases. This is explained as due to the cyclic structure complex which results as the H_3BO_3 combines with the COO^- group of tartaric acid. All the cyclic derivatives of tartaric acid which are known to be formed by fixing its carboxyl groups are strongly dextrorotatory. Therefore the borotartaric acid formed would be expected to show increased dextro-rotation.

According to Tsuzuki's view (21) the COOH group of d-tartaric acid is a contributor to its levo partial rotation and this effect is cut down when the acid forms a cyclic structure, hence the dextro partial rotation originating in the OH groups predominates. The action of borax on the rotation of tartaric acid is similar to that of boric acid on sodium tartrate. This is to be expected because of the reaction:

$$Na_2B_4O_7 + C_4H_6O_6 + 5H_2O \rightleftharpoons 4H_3BO_3 + C_4H_4O_6Na_2$$

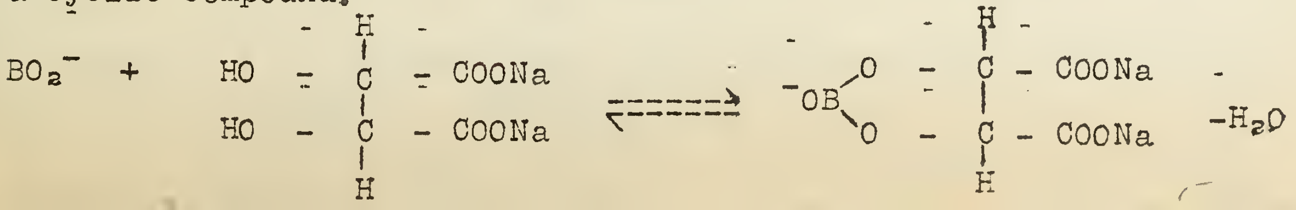
Obviously this mixture is always acidic and the undissociated OH group is present either in tartaric acid or in boric acid. A combination between the anion and this OH group leads to the formation of complexes similar in structure to those of the free tartrate-boric acid system. (Figure IV) The complexes dissociate more strongly than those of the free tartaric-boric acid system so complex formation proceeds further and strong dextrorotation appears. Increase of the $\frac{\overset{\text{Borax}}{\cancel{H_3BO_3}}}{C_4H_6O_6}$ ratio brings about an increase in the concentration of alkali consequently the concentration of borate will be raised and dextro rotation increased.

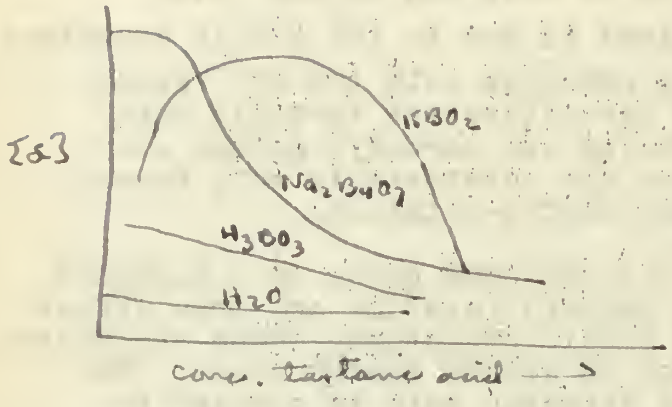
Unlike the acid the alkali tartrates show no optical anamolies (22). They exhibit a higher specific rotation which may be due to the formation of a fixed cyclic structure:



In a ring compound of this sort the negative partial rotation of the COOH group is diminished and the positive partial rotation of the OH group predominates; consequently the molecule shows strong dextro rotation. (Figures V and VI)

The rotation of alkali tartrates is depressed by KBO_2 and the effect becomes stronger as the concentration of BO_2 increases. Since the BO_2^- cannot unite with the COO^- this is explained as due to the BO_2^- uniting with the OH group of the tartrate to form a cyclic compound.




[α]
KBO$_2$
Na$_2$B$_4$O$_7$
H$_3$BO$_3$
H$_2$O
conc. tartaric acid →

The compounds of this type show strong levo-rotation (23); therefore with increasing KBO_2 the concentration of the complex with levo-rotation will be raised and the system will become less dextro-rotatory. This is seen in the system:

(Figure IV) $\frac{KBO_2}{C_4H_6O_6} = \frac{20}{10}$ which is equivalent to $\frac{H_3BO_3}{C_4H_4O_6K_2} = \frac{20}{10}$ (Fig.VI

The specific rotation reaches a maximum after which further addition of BO_2^- lowers the high dextro-rotation.

The indifference of alkali tartrates to borax is a curious phenomenon which Tsuzuki explains as follows:

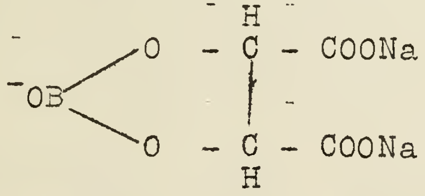
borax + tart~~aric acid~~ rate ion
undissoc $B(OH)_3$ in borax soln. combines with COO^- — strong d-complex
dissoc. BO_2^- in borax soln. Combines with alcoholic OH groups — levo-complex

andthe effects cancel one another.

As seen with tartaric acid the polyoxy compounds with COOH are strongly influenced by boric acid. Calcium gluconate further demonstrates this. The influence is again attributed to the complexes formed between COO^- and H_3BO_3. The unusual behavior seen with tartaric acid and its salts toward alkali borates is seen also with Ca gluconate. Dextro rotation is lowered with increased KBO_2 concentration and may be explained as due to the failure of BO_2^- to react with COO^- in an alkaline medium and consequently its reaction with OH. (Figure VII) As observed earlier this would cause the rotation to proceed in the opposite direction.

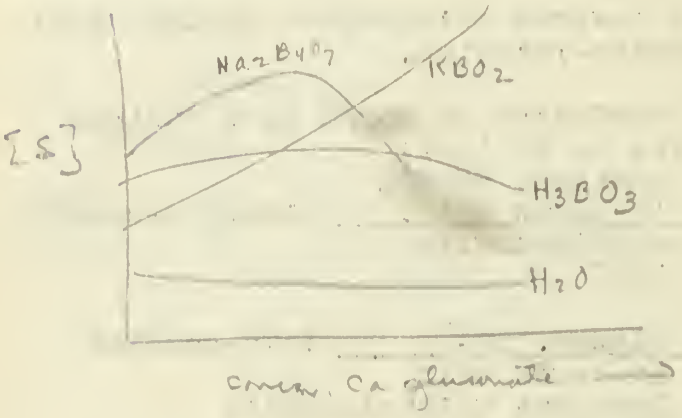
SUMMARY

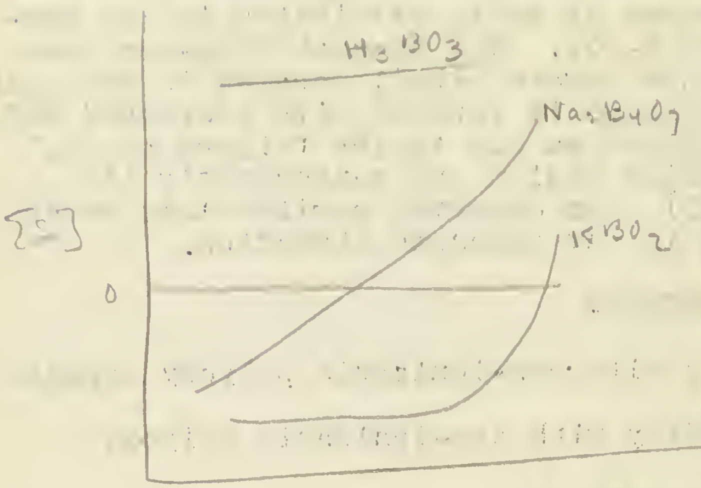
1. Boric acid complexes poorly with non-ionizable polyoxy organic compounds.
2. Alkali borates complex readily with non-ionizable polyoxy organic compounds.
3. The order of complexing strength is:
   $KBO_2 > Na_2B_4O_7 > H_3BO_3$
4. The complex ion concentration increases with increase in BO_2^- concentration.
5. With ionizable polyoxy organic compounds, e.g. tartaric acid, two types of complexes form.
   Complex I forms between free boric acid and free tartaric acid.
   Complex II forms between alkali borates and alkali tartrates.
   Complex II is formed by the action between BO_2^- and alcoholic OH e.g.



Complex I is formed by the action between $B(OH)_3$ molecule and COO^- e.g. $B(OH)_3 . 2C_4H_6O_6$.

The general statement may be made that complex formation is based upon the reaction between molecules and ions rather than between neutral molecules or between ions.


$Na_2B_4O_7$
KBO_2
[S]
H_3BO_3
H_2O
concn. Ca gluconate


H_3BO_3
$Na_2B_4O_7$
[S]
KBO_2
0
concn. diethyl tartrate

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POLONIUM

Edward Onstott April 6, 1948

I. Occurrence

Polonium is found in nature with radium in uranium ores as the decay product of U^{238}.

II. Recovery (1)

In the separation of radium from uranium, polonium is carried down with the insoluble sulfates. By treating the sulfate residue with dilute hydrochloric acid, the polonium is extracted and may be precipitated as the sulfide along with several other heavy metal sulfide impurities. Further concentration by chemical means is necessary before the final electrochemical separation.

Radon ampules contain polonium which results from decay of the radon; it may be separated electrolytically after ammonium hydroxide and sulfide precipitations for removal of alkali metals, copper, and mercury.

III. Isotopes

A large number of isotopes of polonium is known, most of which are very short lived. Isotopes of mass numbers 218, 216, 215, 214, 213, 212, 211, and 210 are formed as decay products of the thorium, neptumium, uranium, and actinium series. Only the Po^{210} isotope is available in sufficient quantity for chemical study (half-life 136 days).

The Po^{210} and Po^{211} isotopes have been made artificially by deuteron bombardment of Bi^{209} (2), (3), (4). These transmutations may be represented as follows:

a). $d + {}_{83}Bi^{209} \longrightarrow {}_{83}RaE^{210} + p$; ${}_{83}RaE^{210} \longrightarrow {}_{84}Po^{210}$

b). $d + {}_{83}Bi^{209} \longrightarrow {}_{84}Po^{211} \longrightarrow {}_{83}RaE^{210} + p$

c). $d + {}_{83}Bi^{209} \longrightarrow {}_{84}Po^{211} \longrightarrow {}_{84}Po^{210} + n$

Both a). and b). are (d,p) reactions, but a). is an Oppenheimer-Phillips reaction, whereas b). represents the formation of a compound nucleus. c). is a (d,n) reaction where a compound nuclues is formed.

Recently, three new isotopes of polonium have been reported (5). They are formed artificially by alpha particle bombardment of lead isotopes. Below are listed the reactions, half-life periods, and modes of decay:

Reaction	Half-life	Mode of Decay
${}_{82}Pb^{204}$ (,2n) ${}_{84}Po^{206}$	9 days	K -- 90% -- 10%
${}_{82}Pb^{206}$ (,3n) ${}_{84}Po^{207}$	5.7 hours	K -- 100% -- .01%
${}_{82}Pb^{207}$ (,3n) ${}_{84}Po^{208}$	--3 years	-- 100%

IV. Properties of polonium

A. Physical properties

The melting point and boiling point of polonium are not known accurately, but numerous investigators (1) have reported the temperatures at which polonium starts to vaporize. Apparently the nature of the metal from which the deposited polonium is vaporized determines largely the temperature at which the vapor pressure of polonium becomes appreciable.

The crystal structure of polonium was determined by Roller, Hendricks, and L. R. Maxwell to be monoclinic (6) but more recently Beamer and C. R. Maxwell reported that two crystal forms exist (7). They found that polonium undergoes a phase change at about 75°C. with an abrupt decrease in electrical conductivity. By x-ray analysis they found that the structure of the high temperature form is a simple rhombohedron, but at -10°C., a simple cubic lattice exists.

B. Chemical Properties

1). Methods of study (1)

Because of the unabailability of polonium and its radioaceivity, special techniques have been worked out for the study of its chemical properties. Co-precipitation and the principle of isomprphism have been largely responsible for the present knowledge. Insoluble compounds have been verified by centrifugation, and dialysis and photographic methods have been employed. Electrochemical studies have proved valuable.

2). Oxidation states

Compounds of polonium in which the polonium has a valence of -2,+2,+3,+4, and +6 are known.

3). Potentials of polonium couples

Polonium is readily displaced from solution by silver or metals that are less noble. Below are the couples for the various oxidation states:

$Po = Po^{++} + 2c^-$ $E° = -0.65$ (Latimer)
E normal $= -0.85$ (Haissinsky)
$Po = Po^{+++} + 3c^-$ $E° = -0.53$ "
$Po = Po^{++++} + 4\cancel{2}e^-$ $E° = -0.77$ "
$2H_2O + Po^{++} = PoO_2 + 4H^+ + 2e^-$ $E° = -0.8$ (Latimer)
$6OH^- + Po = PoO_3^{=} + 3H_2O + 4c^-$ $E°_B = 0.5$ "

4) Compounds (1),(8)

The hydride of polonium and sodium polonide have been prepared. In these compounds polonium has a valence of -2. There is some evidence that polonium may form a carbonyl compound (9). Many of the salts of divalent polonium are known; this is its most common oxidation state. Trivalent polonium has been reported, and apparently is stabilized only by complex formation of insoluble compounds . Complex compounds of quadrivalent polonium are known, as well as the oxide and hydroxide, $PoO(OH)_2$. The existence of the polonate ion, the polonium being hexivalent, has been reported (10). Whether polonium in PoO_3 is hexivalent is questionable.

Polonium has a great tendency to form complex compounds. Electrochemical studies show that all of the simple anions complex Quadrivalent polonium, and in addition, the simple salts are practically insoluble in water, but dissolve readily when an electrolyte is added. Both trivalent and tetravalent polonium complex compounds have the coordination number of six.

V. Position of polonium in the periodic table (1),(8).

From the following considerations, polonium logically should be placed below tellurium (Bohr table):

1. Its electronic configuration is similar to that of tellurium, selenium, sulfur, and oxygen.
2. It forms the polorides H_2Po and Na_2Po
3. It forms PoO_2 corresponding to TeO_2
4. It is precipitated from acid solution as the metal with $SnCl_2$ as is tellurium.
5. $(NH_4)_2\ PoCl_6$ is isomorphous with $(NH_4)_2\ PbCl_6$, $(NH_4)_2\ SnCl_6$, $(NH_4)_2\ PtCl_6$ with decreasing magnitude in the order listed.

However, many polonium compounds behave chemically as do those of bismuth, which indicates that the polorium is trivalent in these compounds.

VI. Uses

The alpha particles from the decay of polonium have sufficient energy so that it may be used as a source of alpha particles for nuclear reactions. It has also been used in physiological research (1)

Polonium has been used as an alloy in spark plugs for improving starting performance (11)

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SULFUR NITRIDE

John R. Mills March 30, 1948

I. Physical Properties

Sulfur nitride, N_4S_4, is an orange-red crystalline substance, insoluble in water, but soluble in benzene, carbon disulfide, and liquid ammonia. In powder form it readily explodes.

Molecular weight	Melting point	Specific Gravity	Dipole Moment	Crystal System
184	178-80°C	2.2(20°C)	$\mu = 0.72 \times 10^{-18}$ e.s.u.	Monoclinic

X-ray diffraction data (1):- space group C^5_{2h} $P2_1/n$; cell constants.- $a_0 = 8.74Å$, $b_0 = 7.14Å$, $C_0 = 8.645Å$, $\beta = 92°21'$ $Z = 4(N_4S_4)$.

II. Preparation

The preparation of N_4S_4 depends on the reaction of NH_3 with various sulfur compounds, S_2Cl_2, SCl_2, $SOCl_2$, CS_2, and sulfur itself. Gregory (2) first prepared the compound by dropping S_2Cl_2 slowly into an excess of aqueous ammonia, and allowing the mixture to stand until the red product became yellow. The yellow substance was extracted with boiling alcohol. This method yielded an impure compound for he reported an analysis corresponding to the composition NS_6. Subsequent workers have improved the methods of preparation, by utilizing dry ammonia gas or anhydrous liquid ammonia, in reactions with the above sulfur compounds either directly or dissolved in various solvents such as benzene, ether, chloroform, etc.(3-12)

III. Reactions

1. With amines - N_4S_4 reacts with primary amines to form the so-called thioamides R-N=S, and with secondary amines to form thioamines $(R)_2\text{-N-S-N}(R)_2$ (R = aryl or alkyl group).

2. With phenylhydrazine - N_4S_4 yields benzene and nitrogen.

3. With Grignard Reagents - Meuwsen (13) studied this reaction and believed that the Grignard adds to the sulfur atom. $2\ EtMgBr + N_4S_4 \longrightarrow 2EtSN_2\ SH + MgBr_2$.

4. With aromatic aldehydes - These react vigorously at the boiling point with N_4S_4 to give $(ArCN)_3$ and some lophin $(C_3N_2HAr)_3$.

5. Addition compounds (14,15,16). These are formed with salts of some amphoteric elements in inert solvents. e.g. $N_4S_4.TiCl_4$; $N_4S_4.SbCl_5$. The best solvent is carbon tetrachloride. At low temperatures N_4S_4 forms addition compounds with SCl_2 and SBr_2 in carbon disulfide.

6. Reactions in liquid ammonia

Ammonia adds to N_4S_4 to form a compound with the formula $N_4S_4.2NH_3$(9). Goehring (17) found 2.5 moles of ammonia per mole of N_4S_4 in the freshly prepared compound, and did not observe a fixed stoichiometric compound.

PbI_2 and HgI_2 react with solutions of N_4S_4 in liquid ammonia to give precipitates of the composition $PbN_2S_2.NH_3$ and $HgN_2S.NH_3$ (11,18).

7. Thiotrithiazyl Salts (16,19)

Demarçay obtained what appeared to be the chloride of a univalent radical N_3S_4 (which he called the thiotrithiazyl radicle) upon heating N_4S_4 with sulfur dichloride. It is also formed by heating with CH_3 COCl (19). The bromide, iodide, nitrate, and thiocyanate can also be made.

8. With halogens (9,11,19)

When chlorine is passed through a suspension of N_4S_4 in chloroform, $(NSCl)_3$ is formed. Bromine reacts similarly. These compounds are soluble in benzene, chloroform, carbon tetrachloride, and carbon disulfide.

9. With nitrogen dioxide (20)

When NO_2 gas is passed through a suspension of finely divided N_4S_4 in CCl_4; the compound $N_2S_2O_9$, the anhydride of nitrosylsulfuric acid is slowly formed.

10. Reduction with stannous chloride and alcohol

Wölbling (14) discovered that this reagent reacts with N_4S_4 to form the tetrahydrosulfur nitride $(HNS)_4$. Meuwsen (18) determined the molecular complexity to be four and showed the hydrogen atoms to be equivalent by its reaction with formaldehyde to give $(SNCH_3O)_4$. Arnold (21) prepared the tetra-acetate and tetra-p-nitrobenzoate derivatives of this compound showing the functional group to be an alcohol $(SNCH_2OH)_4$. $(HNS)_4$ forms an addition compound with $AgNO_3$ when dissolved in acetone $(HNS)_4 \cdot 2AgNO_3$ (13). When treated with a solution of potassium in liquid ammonia the compound $KNH_2.KSN$ is formed. Further reduction with alcoholic stannous chloride yields NH_4HS, while reaction with sodium and alcohol give sodium sulfide and ammonia.

11. Hydrolysis

This reaction proceeds readily in alkaline solution to yield thiosulfate and sulfite as the chief products.

$$N_4S_4 + 6NaOH + 3H_2O \longrightarrow Na_2S_2O_3 + 2Na_2SO_3 + 4NH_3.$$

V. Uses

1. Sulfur nitride mixed with iminosulfur (S_7NH) and diluents such as talc, bentonite, and chalk to prevent detonation is used for controlling fungi, plant diseases, insects, and repelling birds from freshly planted seeds. (22)

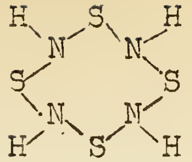
2. A hydrocarbon Diesel fuel oil mixed with 0.1-5% N_4S_4, serving to facilitate ignition, and with 0.001-0.005% of 1-mercaptobenzothiazole to inhibit deterioration of the N_4S_4 has been patented by Paulsen and Collins (23).

VI. Structure

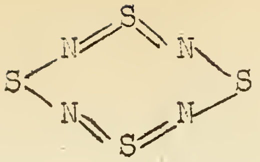
Although early workers regarded N_4S_4 as a complex sulfide, Goehring (17) points out that if such a compound were a sulfide it would hydrolyze to give hydrogen sulfide and oxygen acids of nitrogen, whereas it yields ammonia and oxygen acids of sulfur. N_4S_4 should therefore be regarded as a nitride.

Ruff and Geisel (11) as well as Meuwsen (18) believed that S-S bonds exist in the compound and the latter attempted to support this idea by postulating a dithionite as a primary hydrolysis product of N_4S_4.

Arnold (21) believes that tetrahydro sulfur nitride has the structural formula I and the observation that this compound reacts with phenylisocyanate like an amine supports this view.



I



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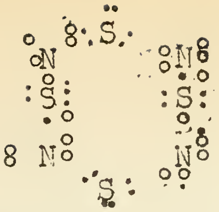


III

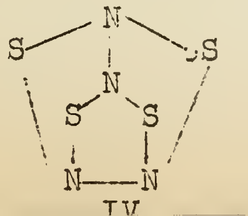
Goehring (17) has recently made a detailed study of the hydrolysis products of N_4S_4 and is able to account satisfactorily for her observations by postulating that the primary products of hydrolysis are sulfur (II) hydroxide, sulfurous acid, and ammonia. $S(OH)_2$ is also believed to be a primary product of the hydrolysis of $(HNS)_4$. As a result of these studies "reaction" formula II is proposed.

All the derivatives of this hypothetical intermediate such as the esters, amines, and halogenides oxidize I^- to I_2. Therefore both $S(OH)_2 + 2HI \longrightarrow S + I_2 + 2H_2O$ $(HNS)_4$ and N_4S_4 in formic acid solution were allowed to react with KI to test this oxidizing action. Each mole of $(HNS)_4$ liberated four moles of iodine, and each mole of N_4S_4 gave six moles of iodine. This indicates that $(HNS)_4$ has sulfur in the oxidation state of two, a further support for formula I, whereas N_4S_4 has sulfur in the oxidation state of three which corresponds to the average oxidation state for formula II.

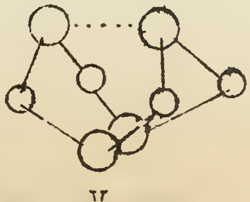
Faessler and Goehring (24) have utilized the fact that the position of the K-α doublets in the X-ray emission spectra of sulfur compounds depends on the type of bonding, to show that both N_4S_4 and $(HNS)_4$ have the outer electron shell of sulfur strained just as much as that of sulfur in $S(NC_5H_{10})_2$, a derivative of $S(OH)_2$. Hence formula II is altered to give the electronic formula III in which all of the sulfur atoms have the same oxidation state. This formula has two of the sulfur atoms with single bonds and two with a double bond and a semipolar bond. Goehring considers this as only a mesomeric form, and assumes that the π-electrons of the double bond are not rigidly fixed, so that the electrons are equally distributed about the whole ring in the resultant resonance hybrid.

The diamagnetic value of $(HNS)_4$ (X mol $= -88 \times 10^{-6}$) agrees well with that calculated for formula I (X mol $= -90 \times 10^{-6}$) while that for N_4S_4 (X mol $= -102 \times 10^{-6}$) shows a strong exaltation above the calculated value for formula II (X mol $= -72 \times 10^{-6}$) a further indication of the mesomerism.

Both X-ray diffraction (25) and electron diffraction (26) studies show that N_4S_4 does not have a planar structure. The X-ray diffraction investigation led to the proposal of the structure which is represented in the plane by IV. The N-N distance was determined to be 1.47Å, which is greater than twice the single bond radius of the N atoms, and the N-S distance is 1.74Å, just equal to the sum of the single bond radii of the two atoms. The cradle-shaped model V in which the sulfur atoms occupy the four corners of a bisphenoid, and the nitrogen atoms form a square lying in a plane midway between the sulfur atoms, fits the electron diffraction intensity curve better than any of several structures considered by Lu and Donohue. The N-S distance is 1.62 ± 0.02 Å, the S-S distance 2.69Å, the ∠S-N-S=112°, and the ∠N-S-N = 106° in this model.



IV



V

◯ - sulfur atom
○ - nitrogen atom

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THE HALOGEN OXIDES AND NITRATES

Leo F. Heneghan April 13, 1948

Nomenclature

In view of the electronegativity values for oxygen and the halogens the compounds of chlorine, bromine, and iodine with oxygen should be named as the corresponding halogen oxides. Oxygen, being the more electronegative, is named as the anion. However the compounds of fluorine and oxygen should be named as oxygen fluorides since fluorine is the more electronegative.

The Oxygen Fluorides

OF_2

Preparation

Oxygen difluoride was first prepared by Lebeau and Damiens (1) by the electrolysis of potassium acid fluoride containing a trace of water. Fluorine gas, of course, was the main product. OF_2 is best prepared by bubbling fluoride gas through dilute sodium hydroxide.

$$2F_2 + 2NaOH \longrightarrow 2NaF + OF_2 + H_2O \qquad (2)$$

Properties

OF_2 melts at -223.8°C and boils at -144.8°C. It is colorless in the gaseous state, yellow as a liquid, and yellow in the solid state. It is an oxidizing agent in aqueous media and an active fluorinating agent when anhydrous. The compound shows no characteristics of an acid anhydride.

Structure

The O-F distance was measured by electron diffraction methods and found to be 1.4±0.1 A (3) as compared to the calculated distance of 1.30Å. The bond was estimated to be approximately 6% ionic. The bond angle was found to be 105±0.5°; consequently the compound has an angular structure similar to that of water.

O_2F_2

Preparation

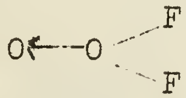
O_2F_2 was prepared by the action of a glow discharge on a mixture of oxygen and fluorine at low temperature and pressure(4).

Properties

The melting point was found to be -163.5°C and the boiling point (by extrapolation) was -57°C. O_2F_2 is orange colored in the solid state and pale brown in the gaseous state, becoming colorless at higher temperatures. The change in color at higher temperature was originally thought to be due to the formation of a new fluoride, OF, but is now believed to be the result of decomposition into oxygen and fluorine. (5)

Structure

Vapor density measurements indicate the composition to be O_2F_2. On the basis of its decomposition at higher temperature Ruff and Menzel (4) postulate the structure to be



The interatomic distances and bond angles were not reported.

O_3F_2

Aryama and Sakuraba (6-7) reported the preparation of O_3F_2 by the inter-action of liquid OF_2 and liquid O_2.

$$OF_2\,(l) + O_2\,(l) \longrightarrow O_3F_2(s)$$

The structure was not determined.

The Chlorine Oxides

Of the four oxides of chlorine--Cl_2O, ClO_2, Cl_2O_6 (ClO_3), and Cl_2O_7--- all except the hexoxide have been known for some time. Only recently has the existance of the hexoxide been clearly established. For this reason Cl_2O_6 will be discussed in some detail. The remaining oxides will be discussed only with respect to their structures.

Cl_2O_6

Preparation

Cl_2O_6 was prepared by Booth (8) by the action of sunlight on ClO_2 and by Goodeve and Richardson (9) by the action of ozone on ClO_2.

Properties

Cl_2O_6 melts at 3.50 ± 0.05°C with decomposition.

$$Cl_2O_6 \longrightarrow 2ClO_2 + O_2$$

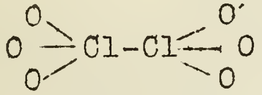
The molecular weight was determined by the freezing point depression of carbon tetrachloride and found to correspond to the formula Cl_2O_6. The hexoxide has the highest melting point, the highest density, the highest latent heat of evaporation and the lowest vapor pressure of any oxide of chlorine. This is particularly well illustrated by comparison with Cl_2O_7.

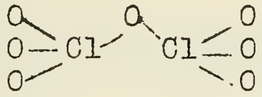
Table I

	Cl_2O	ClO_2	Cl_2O_6	Cl_2O_7
Molecular weight	87	67.5	167	183
Melting point °C	-116	-59	3.5	-19.5
Boiling point °C	2	11.0	203(calc.)	80
Latent heat, evap'n	6.20	6.52	9.5	8.29
Vapor Press. mm 0 °C	699	490	0.31	23.7
Density 0 °C	---	1.64	2.02 3.5°C	1.86

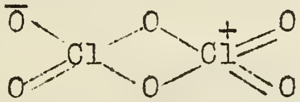
Structure

The abnormal properties of Cl_2O_6 indicate a symmetrical, non-planar structure leading to close packed crystals. Sidgwick assumes that the structures of Cl_2O_6 and Cl_2O_7 are similar to those of aliphatic alcohols and ethers.

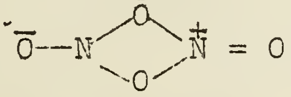




According to this concept, Cl_2O_6 consists of two trigonal pyramids joined at the apices. Recently Longuet-Higgins (10) proposed the structure



This structure is based on a presumed similarity to the compound, N_2O_4, to which he assigns the following configuration



Dissociation of Cl_2O_6

In CCl_4 solution the hexoxide exists principally as Cl_2O_6; however, in the liquid state small concentrations of ClO_3 are present (11). In the gaseous state Cl_2O_6 is almost entirely dissociated into ClO_3 (12). The extent of dissociation in the liquid state was determined at various temperatures by magnetic measurements as indicated in Table II.

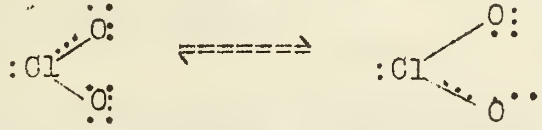
Table II

Temp. °C	% ClO_3 by wt.	Mole % ClO_3	$K_{eq} \times 10^3$
-40	0.721	1.46	2.54
-30	0.775	1.54	2.94
-20	0.826	1.64	3.34
-10	0.886	1.77	3.85
0	0.943	1.87	4.36
10	1.001	1.99	4.91

ClO_2

Structure

The structure of ClO_2 was studied in the vapor state by electron diffraction. The Cl-O distance was found to be 1.53 Å as compared to the calculated value of 1.65 Å. These values indicate the existence of 2- and 3- electron bonds; two resonance structures were postulated. (13)



The bond angle was found to be 137 ± 15°.

ClO_4

Preparation

This compound would be better classified as a free radical rather than as an oxide. ClO_4 was prepared by Gomberg (14) by the action of I_2 on $AgClO_4$ in ether solution.

$$2AgClO_4 + I_2 \dashrightarrow 2AgI + 2ClO_4 \dashrightarrow (ClO_4)_2$$

Properties

$(ClO_4)_2$ reacts quantitatively with Zn, Cu, Mg, Sn, Fe, Cd, Bi, and Ag to give the corresponding perchlorates. Addition compounds are formed when $(ClO_4)_2$ is allowed to react with triaryl methyl. On the basis of ebullioscopic measurements in ether, the composition was found to correspond to the formula $(ClO_4)_2$.

Many investigators feel that $(ClO_4)_2$ does not exist, but that perchloric acid is the main product.

Cl_2O

Structure

The O-Cl distance was found to be 1.71 ± 0.02 Å as compared to the calculated distance of 1.65 Å. The bond angle was found to be 111 ± 2°. (3)

The Bromine Oxides

Three oxides of bromine have definitely been characterized. There is some evidence for the existance of a fourth

$$Br_2O,\ Br_3O_8,\ BrO_2,\ (Br_2O_7)?$$

The structures of these oxides have not been studied. For a discussion of the properties and preparation of these and other halogen oxides reference is made to general reference one.

The Iodine Oxides

I_2O_5 is the only true oxide of iodine. Two other compounds of iodine and oxygen, I_2O_4 and I_4O_9, often called iodine oxides, are now believed to exist as iodate compounds of trivalent iodine. Therefore, they are more correctly represented as $IO(IO_3)$ and $I(IO_3)_3$, respectively. I_2O_3 and I_2O are unknown in the free state. They exist only in the form of their derivatives; e.g. $I_2O_3 \cdot SO_3$ or $(IO)_2SO_4$.

The structures of these compounds have not been investigated.

The Halogen Nitrates

Nomenclature

Compounds between the halogens and the nitrate radical are commonly called halogen nitrates; however, the name, nitrogen trioxyfluoride, has been proposed for FNO_3.

FNO_3

Preparation

Nitrogen tri-oxyfluoride was first prepared by Cady (15) by bubbling fluorine gas through nitric acid. It was later prepared by the action of fluorine gas on KNO_3 (16).

Properties

FNO_3 explodes violently upon heating. The melting point was found to be ca. -42 °C. It is moderately soluble in water with liberation of oxygen. It is adsorbed completely by KI solution

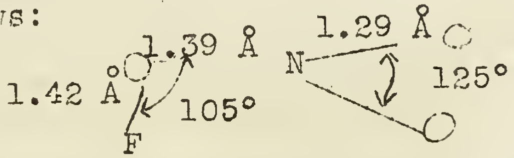
$$FNO_3 + 3I^- \longrightarrow I_3^- + F^- + NO_3^-$$

and liberates oxygen from KOH solution

$$FNO_3 + 2OH^- \longrightarrow 1/2O_2 + F^- + NO_3 + H_2O$$

Structure

Molecular structure, inter-atomic distances, and bond angles were determined by Pauling and Brockway (17); the structure is depected as follows:



This picture would account for the two resonance structures of the FNO_3 molecule.

Similar compounds of the other halogens are known only in the form of their pyridine derivatives.

$ClNO_3$. 2Py, $BrNO_3$. Py, and INO_3. Py, $BrNO_3$. 2Py

Preparation e.g. $ClNO_3$. 2Py

$AgNO_3$ is treated with chlorine solution in the presence of pyridine

$$Cl_2 + AgNO_3 \longrightarrow ClNO_3 + \underline{AgCl}$$

The silver chloride is filtered off and the product is crystallized from the filtrate.

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THE PROPERTIES OF GLASS

Warren W. Brandt April 27, 1948

The history of manufactured glass dates back to 1550 B.C. Its main development has occurred within the past 150 years. This development has by no means ended, but is still accelerating. The definition of glass is a problem, but Morey (1) has presented the following, quite generally accepted one: "a glass is an inorganic substance in a condition which is continuous with, and analagous to, the liquid state of that substance; but which, as a result of having been cooled from a fused condition, has attained so high a degree of viscosity as to be, for all practical purposes, rigid".

All glasses, on cooling from their melting temperature, pass through a temperature range in which the liquid is unstable with respect to one or more crystalline compounds; and, at and below this temperature the glass can be devitrified, i.e., crystallized, by appropriate heat treatment. The temperature where devitrification can begin is called the liquidus temperature. Devitrification is the chief factor limiting the composition range of practical glasses. In general, the lower the liquidus temperature and the higher the silica content, the higher the resulting viscosity, and therefore the less chance for devitrification. An example is Pyrex 774, which has the lowest liquidus of any glass with as high a silica content, and has an exceptional resistance to devitrification. Homogeneity is of considerable importance since a mix of the correct overall composition might contain regions of widely different composition which might devitrify and spoil the batch.

The glass-forming oxides are SiO_2, B_2O_3, P_2O_5, GeO_2, and occasionally V_2O_5 and As_2O_3. Natural glasses are of an igneous nature or the result of lightning striking sand. They are generally highly resistant glasses, but cannot be duplicated practically, due to their high viscosities. (Yellowsone Obsidian = 10^7 poises at 1200°C compared to 300 poises for ordinary soda-lime-silica glass at the same temp.)

Silica glass would be the most desirable if it were not for the difficulty in melting, working, and removing bubbles. Na_2O is the best flux for silica, but it decreases the resistance to attack by water. Durability is increased by CaO, MgO, and Al_2O_3. Pyrex is different in that the "melting point" of silica glass has been lowered by B_2O_3 and Al_2O_3 using the least possible Na_2O.

When glass is heated, gases are given off. The surface adsorbed come off first and then the dissolved. The form of these "dissolved" gases in glass is not known, but the amount is known to vary with the conditions under which the glass is made.

The durability of glass refers to the corroding action of solutions. Solubility is not generally involved, but rather, a penetration of water into the complex silicate structure forming new substances (2,3). Durability is tested by the dimming of optical glasses (4), the iodeosine test on surfaces (5), and the evaporation tests of powdered samples in solutions.

Viscosity is an important property in many stages of glass manufacture, since it governs the workability and the ease of devitrification. The most applicable method of its determination is that of Margules. The glass is placed between two concentric cylinders, one of which is rotated at a constant speed, and the resulting torque of the other is measured. This method has been applied over a range of $10-10^8$ poises. Equilibrium is very slowly attained with respect to viscosity, requiring years at 400-500°C.

Many other properties of glass have been studied extensively. Annealing and strain have been the subject of related studies. Surface tension measurements which are important in coloring and bonding require special methods. Heat capacity, coeffieient of expansion, elastic properties, strength, thermal endurance, and hardness, have been studies with the idea of preparing glasses of certain special properties. Optical characteristics (index of refraction, etc.) have received extensive study for effects of varying composition (6). Coloring methods and materials have been studied in detail under the leadership fo Dr. Weyl of Penn State. Assorted electrical properties such as conductivity, dielectric, and magnetic, have been studied in connection with the uses of glasses in this field (7).

The constitution of glass is not completely known. X-ray measurements have provided our present concept of a tetrahedron of oxygen atoms around each silicon, but that there is an overall lack of any regularity or repetition in three dimensions (8).

It may be said that the chemistry of glass embodies interesting and worthwhile problems for the research worker interested in almost any phase of inorganic chemistry.

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THE CHEMISTRY OF BERYLLIUM

Jennie C. I. Liu May 4, 1948

I. Discovery (1)

Beryllium (Be), which has been prepared commercially only within the last twenty years, is rapidly growing in industrial importance. In 1798, the Frenchman L. N. Vanquelin (2) discovered this new element in the mineral beryl. A. Bussy and F. Wohler (3) independently obtained it by reduction of the chloride with metallic potassium in 1828. It was not until 1898 that a large enough sample was prepared to study some of its properties. This was done by P. Lebeau (4) by electrolysis of fused sodium beryllium fluoride, using a nickel crucible as cathode and a graphite rod as anode.

II. Occurrence (5)

Beryllium compounds do not occur in large deposits, but small quantities are formed in many minerals and granitic rocks, usually as complex silicates and aluminates. The most important mineral is beryl, $3BeO.Al_2O_3.6SiO_2$.

III. Recovery (6)

In commercial practice, there are three different ore processes: The first two involve fusion of the ore at about 1500°C. Then sulfuric acid is added. The sulfate solution is separated from the solid silica. From this point, the two processes differ.

(A) In the one, aluminum is crystallized out as alum by adding ammonium sulfate. Evaporate beryllium sulfate solution and ignite the crystals at 1000°C to decompose beryllium sulfate into beryllium oxide.

(B) The second process separates beryllium from aluminum in the sulfate solution by careful control of pH value. Aluminum and iron hydroxides precipitate out before the beryllium does.

(C) The third or fluoride process renders beryllium ore into a reactive condition by briquetting with Na_3FeF_6. Then heat it for about one hour at 750°C. Beryllium oxide content of the ore, attacked by the reagent, gives Na_2BeF_4, the only soluble portion of the sinter. Again, add sodium hydroxide to precipitate beryllium hydroxide. Finally, ignite it into oxide.

IV. Metallurgy

There are also three chief electrolytic processes for the preparation of this metal. They are the German, English and American methods.

Comparison of the Chief methods of producing beryllium

	German (7)	English (8)	American (9)
temperature	1400°C	1200°C	800°C
anode	graphite crucible	graphite crucible	carbon rod
cathode	iron pipe	iron pipe	graphite crucibl
electrolyte	$5BeF_2.2BeO$	BeF_2, NaF, BaF_2	$BeCl_2$
flux	NaF, BaF_2		5NaCl
yield from ore	60%		75%
purity of metal	98%	99.5-99.9%	99.25-99.5%
cost	high	highest	higher

Degussa Company in Germany has modified the American procedure by using 50% $BeCl_2$ and 50% NaCl at 350°C with graphite as anode and nickel as cathode. Details of the procedure are not well known.

V. Properties (10)

(A) Physical properties

Atomic no.	Atomic wt.	Atomic vol.	Atomic radius	Ionic radius
4	9.02	5.5c.c.	1.11Å	0.32Å
m.p.	**b.p.**	**density**	**E°in $Be \rightarrow Be^{++} + 2e$**	**Isotopes**
1278°C	1500°C	1.84	+1.7 volts	8 and 9

(B) Chemical properties

In all its compounds, beryllium is present in the +2 oxidation state. It burns brilliantly when heated in air. It dissolves in acids as well as in alkali. It reacts with halogens, sulfur and nitrogen. Beryllium halides and complicated compounds give some complexes. In some respects, it resembles aluminum.

VI. Applications (11)

(A) Alloys

(1) Be-Cu alloys

The most important uses of beryllium are in the production of Be-Cu alloys. Some unusual properties of the alloys formed by the addition of only 2.25% Be are claimed: corrosion and fatigue resistant, exceptional hardness, high strength, superior electrical and thermal conductivity, non-magnetic, non-sparking and a lower elastic hysteresis than any other commercially available alloy. Because of these properties, there is a growing use of Be-Cu alloys for springs of all kinds in electrical devices, aviation instruments, etc.

Cu-Be alloys may be prepared by (6)

a) Electrolysis of $BeF_2.NaF$ at 950°C. This temperature is intermediate between melting point of copper and that of the alloy. As beryllium diffuses on copper cathode, it melts copper and the alloy is made.

b) Thermal reduction

$$BeO + CuO + C \xrightarrow{1900°C} 3\text{-}4\%\ Be \text{ (master alloy)}$$

(2) Be-Al alloys

These alloys show heat strength above that of other aluminum alloys. The thermal conductivity is high and thermal expansion is low. These properties seem favorable for aircraft pistons and certain other engine parts.

(3) Be-Mg alloys

Very small percentages of beryllium are added to magnesium alloys to prevent drossing and burning during melting, as well as to make the metal less susceptible to ignition.

(4) Alloys of beryllium with nickel, cobalt, iron and silver are known. They have good physical properties but none that are obtained at low cost.

(B) X-ray tube construction

A permeability of x-ray 17 times greater than that of aluminum has led to the application of beryllium in its pure state as the windows of X-ray tubes.

(C) Refractories

Beryllia (BeO) with a melting point of 2570°C is admirably adapted for refractories in ceramic industry. Articles made from it are characterized by resistance to their shock and high electrical resistance, even at high temperature.

(D) Deoxidizing agent

$Be\ (solid) + 1/2\ O_2\ (gas) \dashrightarrow BeO\ (solid) + 136,000$ cal. Upon heating, beryllium reveals its greater affinity for oxygen. This makes it an extremely effective deoxidizing agent when added to other metals.

(E) Target for neutron production (12)

In bombarding beryllium targets with protons and deuterons, neutrons are produced from the disintegration of beryllium.

$${}_{4}Be^{9} + {}_{1}H^{1} \longrightarrow {}_{5}B^{9} + {}_{0}n^{1} + hN$$

$${}_{4}Be^{9} + {}_{1}H^{2} \longrightarrow {}_{5}B^{10} + {}_{0}n^{1} + hN^{1}$$

$${}_{5}B^{10} \longrightarrow {}_{3}Li^{6} + {}_{2}He^{4} + hN^{11}$$

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STUDIES OF CHLORINE AS A DONOR TO BORONTRICHLORIDE

David H. Campbell May 4, 1948

The acid HBF_4 as well as the salts of HBF_4 are known to be stable, but the analogous chloro-salts have not been reported. Ephraim (1) suggests that the atomic volume of boron is too small for the requisite number of four chlorine atoms to arrange themselves around it so as to be sufficiently close to the central atom.

In a review of the coordination compounds of boron trichloride, Martin (2) points out the fact that boron trichloride forms fewer coordination compounds than boron trifluoride. The larger size of the chlorine atom and the greater electronegativity of the fluorine atom are given as reasons. There are only seven elements which in their compounds have been reported to be donors to the boron atom of boron trichloride. These are nitrogen, phosphorus, arsenic, oxygen, sulfur, fluorine and chlorine. Chlorine is the donor element with which this study has been concerned.

In a later review, Martin (3) postulates that there is a correlation between the dipole moments of alkyl chlorides and their ability to form coordination compounds with boron trichloride, the lower limit of dipole moment being about 2.00 D. That is to say, the donor molecule must have a certain minimum ionic character before coordination can take place. In addition to the alkyl chlorides, PCl_3, PCl_5, SCl_4, $FeCl_3$, $FeCl_2$ and $MnCl_2$ have been reported as donor molecules to boron trichloride, although the evidence for the last three is not conclusive.

If the ionic character of the bond between the chlorine and the central atom of the donor molecule is the determining factor, it seems reasonable to expect some of the metal chlorides to donate to the boron trichloride. In order to test this hypothesis three metal chlorides of varying ionic character were chosen to act as donors. These were sodium chloride, chromic chloride and mercuric chloride.

The first investigation was carried out at a temperature of 30°C. Since the systems were gas-solid equilibria, the vapor pressure was plotted versus the composition. A baro-buret similar to the one described by Booth and Jones (4) was used to measure the pressure, volume and temperature of the gas. The formation of a coordination compound should give a phase diagram analogous to the vapor pressure versus composition curve for a salt hydrate. The three systems studied gave curves that indicated only slight surface adsorption of BCl_3.

Since the baro-buret was not suitable for work at high temperature and pressure, a second apparatus was constructed. This consisted of a 34 mm. glass tube about three feet long, surrounded by an electric furnace at the middle, and connected to the gas manifold through standard taper glass joints. A procelain boat containing a weighed quantity of the metal chloride was placed inside the tube within the furnace; the system was closed, evacuated, then filled with BCl_3 gas. The boat and its contents were heated for several hours, then cooled to room temperature. The excess gas was removed and dry air admitted. The boat was then removed and re-weighed, and any gain in weight assumed to be due to the addition of BCl_3. These reactions were run at temperatures up to 600° C, but no gain in weight was observed for any of the systems.

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The next reactions were carried out in sealed tubes to permit the application of higher pressures. Specially designed reaction tubes were made in such a way that they could be attached to the gas manifold before and after the reaction without BCl_3 being exposed to the atmosphere. A small amount of solid was placed in the tube which was then attached to the manifold and evacuated. A small amount of BCl_3 was condensed into the tube and the tube was sealed off. The sealed tube was then placed inside an iron pipe fitted with a cap at each end and placed in the electric furnace. These systems were heated for several hours to temperatures as high as 600°C. When the tube had cooled to room temperature it was attached to the manifold and the excess BCl_3 drawn off. The tube was broken and the solid residue dissolved in a known excess of standard NaOH solution. The solution was titrated with standard HCl to the methyl orange end point to determine the total chloride. Mannitol was then added and the solution titrated to the phenolphthalein and point to determine the boron.

The last method is the only one that has given any indication of the formation of a coordination compound, and at the present time this evidence is only slight. The analysis of one $CrCl_3$-BCl_3 system indicates that a 1:1 compound may be formed. There is no evidence that the chloride ion of sodium chloride acts as a donor to the BCl_3.

The results of these studies indicate that there may be an upper limit to the ionic character of the donor molecule if coordination with boron trichloride is to occur. This could be explained by the increase in size of the chlorine as the bond between it an the central atom of the donor group becomes more ionic. The radius of a singly bonded boron atom in a covalent compound is 0.88 A.U., and that of a singly bonded chlorine atom in a covalent compound is 0.99 A. U. It would be easily possible for a boron atom to accommodate four chloride atoms about it in a covalent compound. However, the radius of the boron ion is only 0.20 A. U., while the radius of the chlorine ion is 1.81 A. U. Thus, if the boron trichloride has any ionic character there might not be room for a chloride ion to fit in closely enough to be held in a stable condition, but a chlorine in a more covalent compound would be small enough to do so.

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METHODS OF MEASURING MAGNETIC SUSCEPTIBILITY

J. E. Brown May 18, 1948

Since the work of Faraday was published in 1845, all types of materials have been divided magnetically into three classes:

1. Diamagnetic materials which are less permeable to magnetic lines of flux than is a vacuum, and which therefore tend to move toward the lowest field intensity;
2. Para magnetic materials which are more permeable to the magnetic lines of flux than a vacuum, and therefore tend to move toward the highest field intensity;
3. Ferromagnetic substances which are many times more permeable to lines of flux than para magnetic materials.

Diamagnetism is a universal property. All substances, even though they may be para magnetic, have an underlying diamagnetism which must be corrected for to achieve precise magnetic moment data.

Paramagnetism arises only where a molecule of a substance has a permanent magnetic moment, such as might be caused by the motion of an unpaired orbital electron. Ferromagnetism is an example of intense paramagnetism. At some elevated temperature, all ferromagnetic materials become paramagnetic.

Particular types of data require highly specialized techniques, so that only very general methods may be treated here.

GOUY METHOD

In the Gouy method a cylindrical sample, long enough to reach beyond the effective magnetic field, is suspended from an accurate balance so that one end is between the poles of a rather strong magnet. The sample is weighed both with andwithout the magnetic field. The volume susceptibility is then:

$$k = \frac{2g}{H^2A} \Delta W$$

where k is the volume susceptibility, g is the gravitational constant, H is the field strength of the magnet at one end of the sample, A is the cross-sectional area, and Δw is the change in weight. (This formula assumes a negligible susceptibility for the surrounding atmosphere.)

The Gouy method is readily adaptable to measurements to determine variations of susceptibility with temperature. It has been used successfully on solids, powdered solids, liquids, and with some trouble, on gases. Recently the method has been adapted to microtechnique. (4)

QUINCKE METHOD

In the Quincke method, the sample is placed in a U tube, one arm of which is very narrow with respect to the other. A magnetic field is then applied across the meniscus of the narrow arm, and the rise or fall of the meniscus is accurately measured.

$$\chi = \frac{2\Delta h\, g}{H^2}$$

where χ is the mass susceptibility, and Δh is the change in height due to applying field H.

This method is best used for liquids or solutions, but it has been adapted to the measurement of the susceptibility of gases.

FARADAY METHOD

Faraday made use of non-homogeneous magnetic fields to produce a force on the sample under investigation. Such fields are produced by inclining the magnets toward each other. If the sample is then put equidistant from the poles,

$$\chi = \frac{f}{mH\,\frac{dH}{dX}}$$

where H is the field, m is the mass of the sample, $\frac{dH}{dX}$ is the rate of change of field strength along the line equidistant from the poles, and f is the measured force. f can be conveniently measured by mounting the sample on a torsion arm.

Weiss developed the Faraday equipment to include a bi-filar suspension, and Foex improved on this equipment by using an electrical current flowing through a coil to return the sample to its rest position; thus, the ratio of susceptibilities of two materials would be the ratio of the currents used for restoring the sample.

SUCKSMITH METHOD

The Sucksmith method uses the same principle as the Faraday, but employs a verticle rather than horizontal force. The sample is suspended from a ring of phosphor bronze which is fixed at the upper side. Two small mirrors fastened to the ring at optimum positions magnify the movement of the sample as much as 150 times. Thus an accurate comparison can be made between the susceptibilities of two substances. The method is readily adaptable to temperature and atmosphere control.

CURIE-CHENEVEAU METHOD

The substance under investigation is placed in a glass tube which hangs from one end of a torsion balance arm between the poles of a magnet. The magnet can be rotated about an axis collinear with the suspension wire. The force on the tube will be zero when it is between the poles or when the poles are removed a large distance, but there will be a maximum force when the magnet is at a certain distance on either side of the tube. The mass susceptibility of two substances may be compared by:

$$\frac{\chi}{\chi_o} = \frac{m_o}{m}\quad\frac{d - d_t}{d_o - d_t}$$

where X and X_0 are mass susceptibilities, m and m_0 are masses measured, d and d_0 are the differences in maximum deflections, and d_t is the difference for the empty tube.

This method is useful for solids, powdered solids, or liquids, but the same volume of each must be used.

CALIBRATING SUBSTANCES

Many substances have been used to calibrate the various apparatuses. Probably the most common is water. This is useful for low susceptibilities, its susceptibility being accepted as -0.720×10^{-6}. Various investigators have reported values ranging from -0 71992 to -0.7218×10^{-6} for the value. Water shows a marked change in susceptibility with temperature.

A carefully prepared solution of nickel chloride is a useful calibrating agent with a higher susceptibility than water. The susceptibility of such a solution is given fairly accurately by:

$$X = \left[\frac{4433}{129.6} p - 0.720 (1-p)\right] \times 10^{-6}$$

where p is the proportion by weight of $NiCl_2$.

For even higher susceptibility, hydrated ferrous ammonium sulfate is used. The susceptibility per gram is given by:

$$X = \frac{9500 \times 10^{-6}}{(T + 1)}$$

where T is the absolute temperature.

For gases, oxygen is a suitable calibration agent, with a volume susceptibility at 20°C and 760mm. pressure of 0.1434×10^{-6}.

For work at very low temperatures, helium vapor has been used as a standard.

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ORGANIC COMPOUNDS OF GOLD

Ruth C. Pierle May 25, 1948

In 1907, Pope and Gibson (1) reported the preparation of the first alkylgold compound, Et_2AuBr. Since that time, numerous unsuccessful attempts have been made to obtain a compound in which all the valencies of gold are attached to carbon. Recently, Gilman and Woods (20,22) have described the preparation of such a compound, Me_3Au.

Compounds of Au(I):

No organogold compounds of the type RAu have been isolated. Gilman (19) and Kharasch (24) have postulated their existence as unstable intermediates in the linking of organic radicals by means of aurous chloride carbonyl, AuClCO. When this reagent is allowed to react with a Grignard reagent, gold is deposited, and coupling occurs: $AuClCO + RMgBr \longrightarrow Au + R\text{-}R + MgBrCl + CO$, where R is benzyl, phenyl, tolyl, or naphthyl. The postulated intermediate, RAu, should be most stable when R is most strongly electronegative. It was found that α-naphthylmagnesium bromide gave a red solution, which had to be warmed to cause decomposition into gold and dinaphthyl. In the cases of phenyl and benzyl, gold was precipitated instantly.

While this reaction does not give organogold compounds, it is a good method of coupling organic radicals. Aurous chloride carbonyl is a useful reagent for this purpose, since it is soluble in organic solvents.

Compounds of Au (III):

Organic compounds of gold (III) are well known. Numerous examples have been prepared and studied, particularly by Gibson, Kharasch, and Gilman.

$RAuX_2$:

Preparation from R_2AuX: These compounds have been prepared by Gibson and others by treatment of R_2AuBr with Br_2 in $CHCl_3$ or CCl_4 at room temperature. This method has been used to prepare compounds in which R is methyl, ethyl, n-propyl, benzyl, phenylethyl and cyclohexyl. (2,6,8,14,21).

$EtAuBr_2$ has been prepared from Et_2AuBr and $AuBr_3$ (6).

$MeAuBr_2$ is formed in the disproportionation of Me_2AuBr (21):

$$Me_2AuBr \xrightarrow[\text{reflux 48 hours.}]{\text{ether}} C_2H_6 + Au + MeAuBr_2 + AuBr_3.$$

Preparation by direct auration: Kharasch (25, 26, 27) found that the auration of aromatic compounds with anhydrous $AuCl_3$ is a very general reaction. Due to the instability of the product, $ArAuCl_2$, the reaction proceeds rapidly to form AuCl, HCl, and aromatic chloro compounds, unless ether is added to stop the reaction at $ArAuCl_2$. The electronegativity of the organic radical is important in determining the stability of the product. This reaction has been applied by Kharasch to the preparation of many dichlorogold derivatives of substituted aromatic compounds, particularly nitriles.

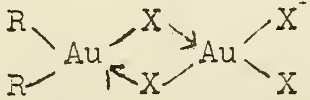
The monoalkyldibromogold compounds are dark red crystalline substances, melting with decomposition, relatively insoluble in water and organic solvents. They are less stable than the dialkylmonobromo compounds, and are readily decomposed by solvents which are easily brominated or oxidized. The aryldichlorogold compounds differ in being bright yellow to almost colorless.

The monoalkyl compounds do not form compounds with coordinating agents such as ethylenediamine and pyridine. These reagents cause decomposition into derivatives of dialkylmonohalogold compounds and AuX_3 complexes.

The decomposition of $RAuBr_2$ on heating is a good method of preparing AuBr:

$$(EtAuBr_2)_2 \xrightarrow[\text{quant.}]{\text{heat}} 2EtBr + 2AuBr.$$

Molecular weight determinations on the ethyl and n-propyl compounds indicate that these compounds are dimeric. The structure (I)


(I)

is favored on the basis of chemical reactions and measurements of dipole moments (6,8,9). If this structure is correct, the monoalkyl compounds should be considered as dialkylmonohalogold coordinated with AuX_3.

R_2AuX

Dialkylgold halides are the commonest and most readily prepared organic compounds of gold.

When a gold trihalide is allowed to react with a Grignard reagent in ether at a low temperature, dialkylmonohalogold is produced in about 20% yield.

$$RMgX + AuX_3 \xrightarrow[\text{2. } H_2O,\ H^+]{\text{1. ether, } 0°} R_2AuX$$

Anhydrous AuX_3 is less satisfactory than bromoauric acid or coordination compounds of AuX_3 with amines such as pyridine. The dialkyl compound may be obtained directly, but it may be isolated more conveniently as an amine complex such as $[R_2Au.en]Br$. The free R_2AuX may be recovered by treatment with acid.

Derivatives of R_2AuX are formed when monoalkyldihalogold compounds are treated with amines, e.g.:

$$(PrAuBr_2)_2 + 2\ py \xrightarrow{\text{quant.}} Pr_2AuBr.py + pyAuBr_3.$$

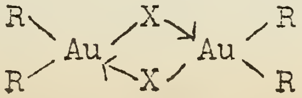
Recently, Gilman and Woods (20,22) have recommended preparation of dialkylgold halides by the cleavage of trialkygold compounds with hydrogen chloride at -65°:

$$Me_3Au + HCl \xrightarrow{Et_2O} Me_2AuCl + CH_4.$$

The dialkylgold halides and their derivatives are colorless cyrstalline materials, soluble in organic solvents, but insoluble in water, with an odor similar to that of bromocamphor. As the size of the alkyl group increase, the melting point decreases to a minimum, then increases. Many of the compounds explode on heating.

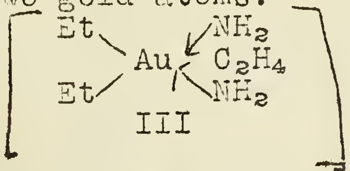
The dialkylmonohalogold compounds are more stable to reducing agents than are most other Au (III) compounds. Those examples in which R is a weakly electronegative group are the most stable. Compounds in which R is strongly electronegative have not been prepared.

Molecular weight determinations indicate that the dialkylgold halides are dimeric. The accepted structure is (II).

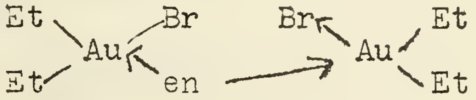

(II)

The four valences of gold lie at right angles in a planar confiruration. (12)

The dialkylgold halides react readily to form coordination compounds with ethylenediamine, pyridine, dipyridyl, acetylacetone, dibasic acids, dibenzyl sulfide, etc. These derivatives have properties similar to those of the parent substances, but are in general more stable. Most of these compounds may be divided into two classes, depending on whether the coordination sphere contains one or two gold atoms:



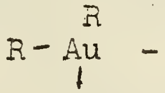
III



IV

Dialkylgold halides may be treated with AgCN or Ag_2SO_4 to prepare the corresponding cyanide (10,12,15,25) and sulfate (17, 18,25) compounds. These products have more complex structures than do the halogen compounds.

The sulfate has a molecular weight corresponding to $(R_4Au_2SO_4)_2$ Possible structures for the ethyl compound have been discussed (18). All of the possibilities are complex, and none has been established experimentally.

Molecular weight determinations indicate that the cyano compound is a tetramer, $(R_2AuCN)_4$. The crystal structure of the n-propyl compound has been studied. The molecule consists of four Au atoms at the corners of a square, connected by $-C{\equiv}N \dashrightarrow$ groups. The ends of the propyl groups extend out of the plane of square. When this compound is heated, it loses half its alkyl groups, forming $R_2Au_2(CN)_2$ (10,16). This compound is of interest because it contains both aurous and auric gold. The molecular weight has not been determined, but the structure is believed to be a zig-zag chain in which linear $-C{\equiv}N \dashrightarrow Au-C{\equiv}N \dashrightarrow$ groups alternate with planar  $R-\overset{R}{\underset{|}{Au}}-$ groups.

R₃Au

All trivalent gold compounds which have been investigated have been shown to be four-covalent. It has therefore been postulated by Gibson that compounds of the type R_3Au are incapable of existence, since they cannot contain 4-covalent gold (III). Trialkylgold compounds have now been prepared, but their structure has not been determined.

In 1933, a method for preparing Et_3Au appeared in the patent literature (23), but no details were given.

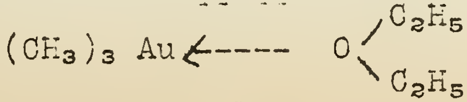
More recently, Gilman and Woods (20,22) have prepared solutions of trimethyl and triethylgold by the reaction of methyl or ethyllithium with $AuBr_3$ or R_2AuBr in ether solution at -65°. The resulting solution of Me_3Au decomposed on warming, with the formation of Au, ethane, and methane.

Ether solutions of R_3Au may be cleaved by hydrogen chloride at -65°, with the formation of R_2AuCl and RH.

Relatively stable derivatives of trimethylgold were prepared by treating the ether solution at -65° with ethylenediamine, α-aminopyridine, and benzylamine. Other amines appeared not to form coordination compounds with Me_3Au. The products obtained were analyzed, and appear to have structures of the type

$(CH_3)_3\,Au \dashleftarrow en \dashrightarrow Au(CH_3)_3$

Gilman suggests that trimethylgold may exist in ether solution as a coordination compound with the solvent:



V

In this case, the tetracovalency of Au (III) is maintained.

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SILICON PSEUDO-HALIDES

W. H. Libby June 1, 1948

Within the last eight years a series of papers by H. H. Anderson at Harvard (several in conjunction with G. S. Forbes) has appeared on the subject of halogenoid derivatives of silicon. Aside from the obvious problem of preparing these compounds this research has dealt with the stability of silicon pseudo-halides and the effect on stability of substituting various alkyl, aryl and alkoxy groups into the molecule. In general, these investigations of stability are concerned with the rate of hydrolysis with water or decomposition by alcohol.

This work was begun in 1940 when Forbes and Anderson (1) reported the preparation of silicon cyanate and silicon isocyanate by reaction of silicon tetrachloride with silver (iso) cyanate. The resultant reaction mixture was fractionally distilled to yield two main fractions boiling at 185.6° and 247.2°, representing 98% and 2% of the total yield respectively. The physical properties of the two are sufficiently different to indicate two different structural entities and both give identical analyses (within the limits of allowable experimental error).

Property	$Si(NCO)_4$	$Si(OCN)_4$
Bp., °c. (760mm.)	185.6	247.2
Mp., °c.	26.0	34.5
density (g./cc.)	1.409,1.413	1.414
n (white light)	1.4610	1.4646

On the basis of these physical properties and by analogy to work done by Anschutz (2) on ethyl cyanate and isocyanate the 186° fraction was assigned the isocyanate structure and the 247° fraction that of the cyanate. Further evidence for this choice was based on the hydrolysis of these materials. The equations as written by Anderson and Forbes are:

$$Si(NCO)_4 + 4\ H_2O \longrightarrow H_4SiO_4 + 4\ HNCO$$

$$Si(OCN)_4 + 12\ H_2O \longrightarrow H_4SiO_4 + 4\ NH_4HCO_3.$$

The first reaction was vigorous and yielded coagulated silica (stated as evidence for formation in acid solution) while the second proceeded slowly and the product was a sol which was extremely difficult to dehydrate.

The authors admit that this is rather weak evidence on which to base a structure proof and suggest that an investigation of the Raman spectra would offer better proof. Such work, however, has not been carried out. The physical properties of the two fractions would indicate that two structurally different forms of the same empirical formula are actually obtained, but nothing definite can be said on the basis of present evidence regarding the true structures of these two isomers. Since the 247° fraction is obtained in only 2% yield and since no true organic cyanates are known it seems reasonable to accept this research only as the preparation of silicon isocyanate, disregarding until further evidence is presented the postulated cyanate.

Subsequent work consists of the preparation and separation of a number of series of organosilicon pseudo-halides and the elucidation of their properties. In general these were prepared by reaction of the corresponding organosilicon halide with the silver pseudo-halide. The synthesis of chloroisocyanates (3) was performed by three different methods:

1. hot tube reaction (600°) of $SiCl_4$ and $Si(NCO)_4$ to yield all products
2. sealed tube reaction of $SiCl_4$ and $Si(NCO)_4$ at 135° for one week to yield all products
3. treatment of $SiCl_4$ with AgNCO to yield all products except $SiCl(NCO)_3$.

All of these materials are liquids and the boiling points increase with each replacement of chloride by the isocyanate group. Densities decrease in the same order. All are vigorously decomposed by water and react with alcohols. Oxidation by air at 200° is negligible. It was found that these substances undergo redistribution of the attached groups when heated to 600°. The following table gives the results of the thermal rearrangement of the individual members of this series.

	Per Cent Compound Formed				
	$SiCl_4$	$SiCl_3NCO$	$SiCl_2(NCO)_2$	$SiCl(NCO)_3$	$Si(NCO)_4$
1/2 $SiCl_4$ +1/2$Si(NCO)_4$	8	25	34	25	8
$SiCl_2(NCO)_2$	8	25	34	26	7
$SiCl_3NCO$	33	38	24	5	(0)
$SiCl(NCO)_3$	0	5	26	36	33

These values are in accord with those which would be predicted by random distribution.

Silicon fluoroisocyanates were prepared by heating antimony trifluoride with silicon isocyanate (4). As would be expected, excess isocyanate and low pressure favor the formation of $SiF(NCO)_3$. Silicon trifluoroisocyanate is unstable at room temperature; all three are vigorously hydrolyzed by water and rapidly decomposed by absolute methanol. The mono- and difluoro compounds are soluble in benzene, carbon tetrachloride, bromobenzene and dioxane.

Complete series of methyl isocyanates (5), phenyl isocyanates (6) and ethoxy isocyanates (6) were prepared by the action of excess silver isocyanate on the corresponding substituted silicon chloride. n-Butyl silicon triisocyanate was prepared similarly (5). The phenyl substituted materials are solids at room temperature or slightly below while the methyl and ethoxy compounds are relatively high boiling liquids. In all cases replacement of isocyanate groups by the organic radical decreases the rate and vigor of hydrolysis. All of the methyl isocyanates show sharp freezing points on cooling; however, n-butyl silicon triisocyanate shows the tendency to supercool to form a glass to such an extent that liquid nitrogen and vigorous stirring were necessary to obtain this compound as a crystalline solid. The methoxy isocyanates, as well as the ethoxy compounds, were prepared by the alcoholysis of silicon isocyanate (7).

Two silicon oxyisocyanates and silicon oxyisothiocyanate were prepared by treating the corresponding oxychloride in benzene solution with an excess of AgNCO or AgNCS (8). Those prepared were $Si_2O(NCO)_6$, $Si_3O_2(NCO)_8$ and $Si_2O(NCS)_6$ which fall in the general classification $Si_nO_{n-1}X_{2n+2}$. Hexaisocyanatodisiloxane was also prepared by the partial hydrolysis of silicon isocyanate in anhydrous ether, benzene or acetone solutions. $Si_2O(NCO)_6$ and $Si_2O(NCS)_6$ are white solids having melting points of 44.5° and 120-121° respectively, while $Si_3O_2(NCO)_8$ is a yellowish liquid boiling at 170° (2mm.).

Silicon thiocyanate was first prepared in 1906 by Reynolds (9) by the action of $Pb(SCN)_2$ on a benzene solution of silicon tetrachloride. This solid material melts at 143.8° and is quite stable to heat in the absence of water or oxygen. Anderson synthesized this same compound along with $SiCl_3SCN$ by the reaction of silver thiocyanate with $SiCl_4$ (10). There was no evidence for the formation of the mono- or dichloro thiocyanate. When heated at 140° for twenty hours, silicon trichlorothiocyanate yeilds $SiCl_4$ and $Si(SCN)_4$ exclusively.

Only two complete organosilicon isothiocyanate series have been prepared, i.e., the methyl (11) and phenyl (12) derivatives. Both series were obtained by heating silver isothiocyanate with the proper organosilicon chloride at 80-90° in benzene. Again the rate of hydrolysis is decreased by substitution of an organic radical for the NCS group. In spite of the relatively large size of the phenyl group as compared to the isothiocyanate radical no steric effects were encountered. The only alkoxy thiocyanates for which syntheses have been attempted are the methoxy derivatives and of this series it was possible to prepare only $(CH_3O)_3SiSCN$ (13). This substance (Bp. 170.5°) was obtained by the vigorous reaction of absolute methanol with silicon thiocyanate at 145°.

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RADIOACTIVE EXCHANGE REACTIONS IN INORGANIC CHEMISTRY

J. C. Brantley June 24, 1948

I. While ordinary reactions can be detected by chemical means, a reaction involving exchange, corresponding to

$$AB + B^{*} \rightleftharpoons AB^{*} + B$$

can be detected only if B and B^{*} can be distinguished. Since this reaction can be of great value in determining structures, bond strengths and their reactivity, types of bonds, and reactivity of ions and compounds, it is of interest to have a suitable method for differentiating B and B^{*}. The use of radioactive isotopes has made this possible, and because of the large number of isotopes now available, the study of exchange reactions in inorganic chemistry has become very common.

Exchange reactions involving radioactive isotopes have been shown to be first order reactions (18). Therefore it is possible to measure a half-life of the equilibrium reaction as an indication of the rapidity and ease of the reactions. The following examples of exchange reactions have been chosen for their applications to inorganic chemistry and as evidence of the uses to which exchange reactions can be put.

References to any of the general references in the bibliography will give the techniques and methods of radioactivity measurements which must be used in evaluating the results of the exchange reactions.

II. 1. Halogen exchange reactions.

A great deal of work has been done on halogen exchange (4), but only three examples have been included here.

Exchange between the halogens of the phosphorous halides and radioactive halogens in carbon tetrachloride solution at room temperatures has been studied by Koskosky and Fowler (5). The distribution of the radioactive element takes place rapidly in all cases; and the authors conclude that all of the halogen atoms in the pentahalides are equivalent and equally reactive. This result is of interest, since the pentahalides are known to dissociate in solution according to

$$PX_5 \rightleftharpoons PX_3 + X_2$$

the pentabromide being dissociated to a larger extent than the pentachloride. The exchange is considered to proceed by virtue of this equilibrium; and, if the five phosphorous-halogen bonds were not equivalent, it might be expected, as an extreme case, that complete exchange with two halogen atoms of the pentachloride might occur, and little or none with the other three; at any rate, that two of the halogen atoms would exchange at a different rate than the other three. This equivalence of all five bonds is in accord with the view of Pauling (6) and others of the presence in phosphorous pentachloride of five equivalent hybrid covalent bonds.

Roginsky and Gopstein (7) conducted exchange experiments between radioactive bromine vapor and solid cupric bromide; finding that after the radioactive exchange has been carried out, one atom of radioactive bromine tends to remain in the molecule even though carried through a dissociation and recombination. They say that this shows a disymmetry between the two bromines in cupric bromide.

Kolthoff and others have studied the exchange between radioactive halogen vapors and solid silver halides as a characteristic of the aging of the silver halide precipitates (8)(9). In both the bromide and the chloride they find that complete exchange takes place between the vapor and the solid halide when the solid precipitate is fresh. Exchange takes place less rapidly as the precipitate is aged, until as the end case no exchange takes place with the drastically aged precipitate.

2. Sulfur exchange reactions.

Andersen (10) has shown that there is no exchange between the two sulfur atoms of the thiosulfate ion, and thus proved that the sulfur atoms in thiosulfate are not equivalent. He also shows that there is no exchange between sulfide and sulfate between sulfite and sulfate, or between sulfur dioxide and sulfur trioxide below the dissociation temperature of sulfur trioxide.

Vogue and Libby (11)(12) have shown that there is no exchange between aqueous thiosulfate and sulfite within twenty hours at 20° although there is an exchange between thiosulfate and sulfide ion (one sulfur completely exchanged) within one hour at 100°. This is in agreement with the findings of Andersen

Cooley and Yost (13) have studied the exchange between liquid sulfur monochloride and elemental sulfur. They find the rate to be very slow at room temperatures but measurably rapid at 100°. Since they show the rate to be directly proportional to the concentration of sulfur, they consider a satisfactory mechanism for the reaction to consist of a slow dissociation

$$S_8 \longrightarrow S_6 + S_2$$

followed by the rapid reversible reaction

$$S_2 + S_2Cl_4 \rightleftharpoons 2S_2Cl_2$$

3. Phosphorous exchange reactions.

Actually there has yet to be shown that there are any exchange reactions in phosphorous compounds. Perrier and Segre (14) have shown that there is no exchange in neutral or acid solutions between phosphate and hypophosphate, while Wilson (15) has shown that there is no exchange between phosphate and phosphite either in acid or alkaline solution. Hull (16) has made a study of the exchange between ortho, meta, and pyro phosphoric acids in dilute solution and found that there is no exchange in any equilibrium mixture under the conditions he used.

4. Iron exchange reactions.

Kennedy, Ruben and Seaborg (4) state that exchange between ferrous and ferric ions, in an equilibrium of the type

$$Fe^{*+3} \quad Fe^{+2} \rightleftharpoons Fe^{+3} + Fe^{*+2}$$

occurs instantaneously, the radioactivity being distributed equally between the two valence forms.

5. Exchange reactions applied to complex compounds.

Exchange reactions offer a method of determing many interesting facts about the structures and bonding involved in complex compounds. The following examples show some of these possibilities.

Thompson (17) using radioactive iron has studied the exchange reactions between the hexacyanoferrates and iron. He first shows that contrary to the reports of Kennedy, Ruben and Seaborg (4) there is a rapid exchange between the hexacyanoferrate (II) ion and the hexacyanoferrate (III) ion in solution. This exchange apparently involves the same oxidation-reduction equilibrium that is established in the exchange between iron (II) and iron (III).

However, he did not find any exchange between ferrous or ferric iron and the hexacyanoferrates. Failure to observe interchange in these examples adds to the evidence for the non-equivalence of the irons in the iron hexacyanoferrates. It is also further evidence for the postulate that half the irons are linked by covalent bonds (presumably those of iron-carbon) and half are linked by ionic bonds (those of iron-nitrogen).

Ruben, Kamen, Allen and Nahinsky (23) have studied exchange reactions of iron complexes, especially those in which the iron is bonded to nitrogen. It was found that radioactive ferric iron does not exchange with ferriprotoporphyrin or ferripheophytin wich supposedly have ionic linkages. On the other hand they found exchange between ferrious iron and ferrous orthophenanthroline and ferrous , dipyridil sulfate in which the bonds are covalent. Their conclusions are that in the cases in which no exchange is observed the complex is formed by a "fused ring" about the central ion requiring that the exchange take place by all four iron-nitrogen bonds being broken simultaneously. In those compounds which undergo exchange the ring is made up of two or more molecules so that exchange may take place by stepwise dissociation.

Studies of copper chelate compounds carried out by Duffield and Calvin (18) indicate a similar phenomenon with these compounds. They studied a series of copper salicylaldehydes plus nitrogen complexing agents. It was found that for such compounds as cupric salicylaldehyde methylimine the exchange is very rapid (less than one minute). However, in compounds in which the chelate ring is closed about the central ion (ie, cupric acetylacetone ethylenediimine) the exchange is slowed down greatly or is non-existent.

Exchange reactions have been used by Grinberg (19)(20) to show that the bromine positions in tetrabromo and hexabromo platinum complexes are equivalent. He also shows that no exchange takes place between the platinum of different complexes.

Long (21)(22) has shown by means of radioactive exchange studies that the potassium chromioxalate and potassium cobaltioxalate compounds must have covalent bonds while the corresponding iron and aluminum compounds have ionic linkages. When the metal complex is introduced into a solution of free oxalate ions containing radioactive carbon, rapid exchange takes place when the metal is iron or aluminum but not when the metal is cobalt or chromium.

Since no exchange takes place with the potassium chromioxalate he concludes that the racemization of the optical isomer is achieved by internal rearrangements rather than ionic dissociation. Further, he concludes that under the conditions of his experiments there should be no stable optically active isomers of the iron or aluminum complexes since they should be very unstable in solution. The fact that no stable isomers have been found would substantiate this.

These examples of exchange reactions have been cited as an indication of the possibilities of their use now that radioactive isotopes of most of the elements are available. It may be evident from them that exchange reactions offer new methods for determing chemical behavior.

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CATALYTIC HYDROGENATION

A. H. Anderegg July 1, 1948

INTRODUCTION: By catalytic hydrogenation (1) is understood the chemical addition of hydrogen to a compound in the presence of a catalyst. By this process, carbon, nitrogen, sulfur and halogens may be eliminated from a compound as methane, ammonia, hydrogen sulfide and hydrogen halides respectively. The substance to be hydrogenated is brought into contact with finely divided metals, oxides, or a fixed catalytic surface, and hydrogen at a proper temperature. The commonly accepted picture (2,9) of the surface of the catalyst is one in which active centers for adsorption are distributed over the surface. The active centers presumably consist of atoms whose valence forces are not entirely satisfied by other atoms in the surface of the catalyst. These active centers vary in activity.

No attempt will be made in this paper to mention the exceptionally numerous mechanisms of catalysis which have been offered to account for catalytic hydrogenation. The generally accepted views of Adkins of the University of Wisconsin serve as basis of this paper.

HYDROGEN: Hydrogen mixes faster with other gases than any other gas and it diffuses through porous bodies and many metals, the latter at temperatures of 300° to 400°C and higher. Diffusion through palladium (one volume of palladium adsorbs approximately 900 volumes of hydrogen) takes place considerably below 200°C. Molecular hydrogen diffuses through nickel at about 450°C, and through copper at about 640°C and higher (1). Commercial copper reduced with hydrogen at approximately 600°C becomes brittle, but not pure copper. Chromium does not adsorb hydrogen. The increase of stability of platinum and steels containing chromium is due to this property as it lowers the adsorbing power of these metals when alloyed with them.

CATALYST: A catalyst here is defined as a substance which accelerates or causes a reaction to take place. Catalysis is concerned with the influence of one molecule on another. This definition assumes that two molecules, such as those of hydrogen and ethylene do not react with each other except under the influence of a third substance, such as nickel. The catalysts for hydrogenation apparently function by combining with the hydrogen and with the compound to be hydrogenated (hydrogen acceptor). The result of this combination with the catalyst is that the hydrogen and hydrogen acceptor react with each other. It may be said that molecules of hydrogen and molecules of ethylene are inert toward each other, but that hydrogen attached to nickel may react with ethylene attached to nickel to give ethane. The ethane then leaves the nickel, permitting the metal to react with more ethylene and hydrogen and so repeat the process of hydrogenation.

The following, and/or various compounds and combinations of the following comprise the catalysts used in hydrogenation: Cu, Zn, Al halides, Ce, C, Pb, Cr, Mo, W, Re, Co, Ni, Pd, Pt, and Rh. Of these the Pt, Pd, Cu, and Ni catalysts are probably the best known. It is established (3) that the activity of a

catalyst greatly depends on the method by which it is prepared. The activity of platinum is wholly dependent on the form in which it is used, i.e., whether as a powder, such as platinum black, as sponge, as platinized asbestos, or as platinum wire. According to Adams and Vorhees (4) in the preparation of platinum black the most important physical factors to be considered are temperature, media in which reduction of platinum oxide proceeds to platinum black, and retarding influences of traces of inorganic salts and spent solvents. The catalytic action of palladium and nickel likewise is dependent on methods of preparation of the catalyst. The activity of nickel depends on the reduction temperature of nickel oxide. Surface properties of nickel reducible at different temperatures vary, as indicated by its color. Nickel prepared at 300°C is black with a highly developed surface and correspondingly is a very good catalyst, whereas nickel prepared at 500°C is grey with a white metallic luster and wholly unsuitable for catalytic purposes. At 600°C reduction with carbon renders nickel active, and at 650°C practically inactive (6). Copper chromite, an excellent catalyst for hydrogenation in the liquid phase, in many cases is not so satisfactory in the gas phase. This is because the divalent copper in the active catalyst is more readily reduced by hydrogen if the copper chromite is not wet.

PROMOTERS: The activity of the catalyst may in many cases be enhanced by the use of promoters, sometimes referred to as "co-activators". As an example, the synthesis of ammonia may be considered, where an iron-molybdenum mixture is used as the catalyst. This mixture of equal parts of Fe and Mo is more effective than either alone (1,7).

CARRIERS: In general the term "carrier" means an inert material which acts as a support for the catalyst. When this so-called carrier increases or decreases the rate of the reaction, or directs the latter, it is no longer a carrier. A few of many uses of these are:

1. To yield a cheaper substitute for the unexposed mass of an expensive catalyst such as platinum or palladium. Experimental data point out that there is always a comparatively large mass of the catalyst which does not take part in the reaction.
2. To provide a larger contact surface, and at the same time, a more equal distribution of the catalyst.
3. To influence indirectly the activity of a catalyst by protecting it from poisons. (3)

Examples of carriers are Al_2O_3, kieselguhr, silica gel, $MgSO_4$, asbestos, $CaCO_3$, $ZnCO_3$, and gelatin colloids.

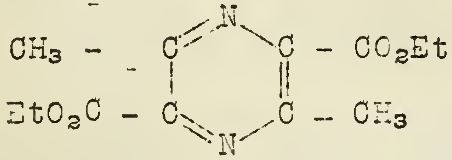
REQUIREMENTS OF A GOOD CATALYST: According to Adkins (2) a good catalyst must:

1. Be stable in the presence of reactants.
2. Adsorb and activate hydrogen.
3. Adsorb and activate the hydrogen acceptor.
4. Hold the activated hydrogen and hydrogen acceptor in the proper ratio and space relationship.
5. Desorb the desired product.

He concludes that the rate of hydrogenation over a catalyst is dependent on: amount of catalyst, acceptor of hydrogen, impurities in the hydrogen, temperature of hydrogenation, pressure of hydrogen, amount and kind of solvent, ratio of catalyst to hydrogen acceptor, time, thoroughness of mixing, and the activity and selectivity of the catalyst.

An example of the results of a variation in the proportion of the hydrogen and hydrögen acceptor on the surface of the catalyst is shown in the Fisher-Tropsch synthesis of hydrocarbons. In this process carbon monoxide and hydrogen at atmospheric pressure are passed over a cobalt, iron or nickel catalyst held at about 200°C. During the first few hours after the catalyst is put into service there is a large amount of hydrogen on the catalyst and methane is the chief product. After a time the amount of hydrogen on the catalyst is much less than in the early stages, and hydrocarbons containing many carbon atoms in each molecule are produced.

The effect of variations in pressure may be illustrated by the hydrogenation of alpha-oximinoacetoacetic ester ($CH_3COC = NOH\ CO_2Et$) over nickel. At 80°C and under a pressure of 120 atmospheres, the pyrazine I below is obtained. Under a pressure of 320 atmospheres structure II results:

I 

II $CH_3CHOHCHNH_2CO_2Et$

At the higher pressure there would be more hydrogen on the catalyst and therefore less probability that two molecules of the oximino ester would be near enough to each other on the surface of the catalyst so that interaction would be possible. It is of interest that platinum and palladium are active at pressures near atmospheric. Copper chromite requires pressure of 50-300 atmospheres, and nickel is somewhat intermediate in its pressure requirements.

One of the most striking facts about catalytic hydrogenation is the selectivity shown by the catalyst and hydrogen acceptor. For example, nickel is more active against a carbon-carbon than it is toward a carbon-oxygen double bond, whereas copper chromite is more active to the carbon-oxygen than toward the carbon-carbon double bond. However, both catalysts will cause the hydrogenation of both types of unsaturation so that the difference between the catalysts is quantitative rather than qualitative. The higher the temperature the less selective the catalyst, and the more the probability that the hydrogenation will go to the ultimate stage of the saturated hydrocarbon.

The possible variations in the structure of a given reactant should be considered in the role of the catalyst. As an example, a catalyst such as copper chromite which is rather inactive toward the benzenoid nucleus may bring about such a hydrogenation through a tautomeric form the the hydrogen acceptor. The ethyl ether of beta-naphthol does not react with hydrogen over copper chromite at 200°C (10). However, betanaphthol is readily converted to 1,2,3,4-tetrahydro-2-naphthol at 200°C over copper chromite. Presumably this is because naphthol may tautomerize to an unsaturated ketone, a type of compound which is rapidly hydrogenated over this catalyst.

A great number of substances, in minute quantities, possess the property of partly or wholly destroying the activity of the catalyst. This is called poisoning. The most common poisons are Pb, Cu, cyanide, arsenates, Hg, H_2O, ethyl alcohol, amyl alcohol, CO, CO_2, H_2S, S, Cl_2, and O_2. (1)

In some cases a very specific role is played by the solvent. For example, in the presence of ethanol only two of the three phenyl groups in triphenylmethane are hydrogenated, whereas in the presence of methylcyclohexane the hydrogenation goes to completion. In other cases solvents may be beneficial only because they facilitate the dispersion of the catalyst and the contact of the three essential materials, hydrogen, catalyst, and organic compound.

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RELATIONSHIPS BETWEEN THE STRUCTURE AND THE COLOR OF INORGANIC COMPOUNDS

Alvin J. Cohen June 29, 1948

I. Introduction

At the present time, inorganic chemists are beginning to have renewed interest in this fascinating problem. The Office of Naval Research has recently announced the sponsorship of a project to study the structural basis of color in inorganic compounds (4).

This seminar will briefly outline some of the more interesting aspects and problems in this field in a descriptive and non-mathematical manner.

II. Color of Inorganic Compounds

The visible color in inorganic compounds is caused by the electrons in the outer electron shells. Maxted (5) gives the following table of energy relationships of various radiations absorbed or emitted:

Nature of Energy	Order of magnitude of Quanta involved in changes of level within given energy form.		Nature of radiation absorbed or emitted
	a) Ergs. per molecule.	b) Kcal. per mole	
Molecular rotation	10^{-14} to 10^{-13}	0.1 to 1	Far infra-red
Vibrations of atoms	10^{-13} to 10^{-12}	1 to 10	Near infra-red
Levels in Outer Electron Shells	10^{-11}	100	Visible or ultra-violet
Levels in Inner Electron Shells	10^{-10} to 10^{-8}	10^3 to 10^5	X-rays
Nuclear energy levels	10^{-7} to 10^{-6}	10^6 to 10^7	Gamma-rays

The color of an inorganic compound depends on the quality, intensity, and spectral distribution of the incident radiant energy; the luminous reflectance or transmittance of the object; the principle wavelength and purity of the reflected light; and the visual sensations of the human observer. If a substance absorbs radiation unequally in the region 3000-7000Å color will result. The substance has absorbed a certain quantity of the visible light and transmitted or reflected the remainder (6).

III. Earlier Work

A. Matthew Carey Lea (7) wrote on "the color relations of atoms, ions, and molecules" in 1895. He stated "color belongs essentially to the metallic atom whether it exists in a free state or as an ion or combined with a dissimilar atom or atoms to form a molecule". His criteria for color: (1) If dilute solution of electrolyte is colorless, both anion and "kathion" are colorless. (2) If solution is colored then color is due to "kathion" only. Oxides, fluorides, chlorides, bromides, etc., have colorless anions, many composite anions are colorless ($SO_4^=$ etc.). (3) Color or non-color is a function of atomic weight. Formulated Law of Color:

"No element having ions colored at all valences can belong to the same natural group with elements having colorless ions only". Lea believed the periodic law to be "a singular mixture of truth and error". The proposed a periodic table based on color.

B. Edwin Ray Watson (8) in his book "Color In Relation to Chemical Constitution" gives a brief survey of the earlier work and includes a useful bibliography of color. He considers Lea's paper to be of sufficient importance, 23 years after its publication, that he discusses it in some detail.

Watson showed by means of colored charts that it was unnecessary for Lea to propose an original classification of the elements in order to show that color depends in a systematic way on atomic weight. He deduced that the elements in the middle of the long periods show selective absorption of the least refrangible rays of the visible spectrum and increase of atomic weight causes increased general absorption, starting from the blue end of the spectrum and extending further and further towards the red.

C. F. Russell V. Bichowsky wrote a paper entitled "The Color of Inorganic Compounds" (1) in 1918. This was the first modern approach to the theory of color of inorganic compounds and was a result of G. N. Lewis's publication (3) two years earlier. He formulated the following rules: (1) Since the valence color may be defined as that part of the color of a compound which is due to one nucleus alone, the color of a free ion will obviously be the valence color. (2) In the case where the ion color is unknown, i.e. in cases where the substance does not ionize or is not stable in solution or has its color masked by other substances present, we have to depend on general rules, (a) the valence color of its atoms (b) on the amount of interference the forces due to one nucleus have on the stability of arrangement of the electrons belonging to another atom.

Valence colors of Bichowsky:
(incomplete table)

Subscripts:
° = oxide and sulfide colorless
* = one or both are colored.

Element	N	N+2	N+1	N	N-1	N-2	N-3	N-4	N-5	N-6
Σ	-			$0_{\circ}$						
Cu	1		Blue$_*$	0_*						
Ag	1		Brown$_*$	0_*						
Au	1	Yel$_*$	Red	0_*						
Cd	2			0_*						
Hg	2			0_*	0_*					
Ga	3			$0_{\circ}$		0				
In	3			$0_{\circ}$		0_*?				
Tl	3			0_*		0_*				
⋮	⋮	⋮	⋮	⋮		⋮	⋮			
V	5	Yel		0_*	blue$_*$	green$_*$	?violet$_*$			
⋮	⋮	⋮	⋮	⋮	⋮					
Cr	6		Blue?*	yel$_*$		...*	"$_*$	yel$_*$		
Mo	6			$0_{\circ}$	blue$_*$	yel$_*$	"$_*$	yel$_*$		
W	6			0_*	dark?$_*$	yel$_*$	...*	yel		

(table continued on next page)

U	6			0	brown?*	grn*	purp.*	yel.*		
⋮	⋮			⋮	⋮	⋮	⋮	⋮		
Mn	8				purp.	grn*		yel.*	red?*	pink*
Fe	8					?			purp*	yel?*
⋮	⋮					⋮		⋮	⋮	⋮
Ir	8					grn?		yel	blue	orange

where 0 = colorless
where N = group in periodic system.

where Σ= elements of invarient valence, including H, He, Ne, Ar, Kr, Xe, Nt, Li, Na, K, Rb, Cs, Be, Mg, Ca, Lu, Sr, Ba, Ra, B, Al, Sc, Si, Zr, F.

D. G. N. Lewis (9) stated that an electron in a position of constraint possesses a natural period of vibration, the frequency being proportional to the magnitude of constraint. Light which has the same period of vibration is capable of imparting energy to this electron resonator and thus the electron absorbs light in that part of the spectrum which corresponds to its own natural frequency. Most electrons are so tightly held that the natural frequency is in the UV region.

The newer theory of the discontinuity of chemical states furnishes a similar and equally satisfactory explanation of color. Any process where a colorless substance is converted into a colored substance may be regarded as one in which the molecule may be changed from one energy state to another state of only slightly different energy.

An illustration of the Lewis theory:

Halogen	bond Pair Strength	Absorption of	(10) HX bond energy in $\frac{K.Cal}{Mol.}$
F	strongest	extreme violet	147.5
Cl	strong	↓ λ	102.7
Br	weaker		87.3
I	weakest	red	71.4

Halide Colors

Cation → Anion ↓	Ag^+	Tl^+	Cu^+	Cu^{++}
F^-	yellow	colorless	red	blue($2H_2O$)
Cl^-	white	white	white	bright yellow
Br^-	pale yellow	yellowish-white	white	black
I^-	yellow (3xtaline forms)	bright yellow (red on heating)	pale yellow	unstable

E. Wilhelm Biltz (11) in 1923 wrote of "Mischverbindungen" where the same element is present in more than one valence state in the same compound. He distinguished these from the simple parent compound by the color deepening. He gave the following sequence for color deepening: greenish yellow, yellow, orange, red, purple, violet, indigo, cyanblue, blue-green, green. Many of his

examples, in the light of present knowledge are incorrect. A few examples from his paper:

Compound I	"Mischverbundung"	Compound II
$TlCl$ colorless	$Tl_3^{I}[Tl^{III}Cl_6]$ yellow	$TlCl_3$ colorless
$TlBr$ colorless	$Tl_3^{I}[Tl^{III}Br_6]$, $Tl^{I}[Tl^{III}Br_4]$ red yellow	$TlBr_3.H_2O$ colorless
UO_2 black to reddish	U_3O_8 black to green	UO_3 orange
$Na_2[Pt(C_2O_4)_2]$ yel.	$Na_4[Pt^{II}(C_2O_4)_2][Pt^{IV}(C_2O_4)_2Cl_2]$ copper red	$Na_2[Pt(C_2O_4)_2Cl_2]$ bright yellow

F. L. F. Yntema of this laboratory proposed (12) in 1926, a theory of color for the Rare Earths. He stated that the striking similarity in chemical properties is due to the similarity in arrangement of the outer, or valence electrons while differences in physical properties such as color must be due to differences in the arrangement in inner levels. The facts indicate that the origin of the characteristic lines for each element is in the fourth level (4f). When the shell is incomplete, there is a shift of electrons from orbit to orbit within the unfilled shell and each shift is accompanied by giving off or absorption of energy equal to h/ν , where ν represents the frequency of the resulting band.

IV. Recent Work

A. Consideration of color and structure in ordinary complexes (not involving intermediate oxidation states) has recently led Linus Pauling to formulate a new rule (2), to the effect that half-full and full electronic shells in an atom are closely similar in properties. This rule applies to not only ordinary shells such as the 3d subgroup of 5 orbitals in an isolated atom, but also to special subgroups of orbitals in atoms which form covalent bonds. Examples are (1) terpositive gadolinium ion with seven 4f electrons and terpositive lutecuim ion with fourteen 4f electrons.

Many earlier workers have remarked on the similarity of La, Gd and Lu (13). The rule might be modified in this case to empty, half-full, and full shells. (2) Bipositive europium ion and bipositive ytterbium ion, (3) terpositive cobalt and terpositive chromium (4) K_3RhCl_6 and K_3MoCl_6 are both red xtaline materials.

B. Relationships of Lanthanide and Actinide Series in regards to color and structure:

COLORS OF THE HALIDES OF THE LANTHANIDE AND ACTINIDE SERIES

Element	MCl_2	MBr_2	MI_2	MF_3	MCl_3	MBr_3	MI_3	MF_4	MCl_4	MBr_4	MI_4	Element	MCl_2	MBr_2	MI_2	MF_3	MCl_3	MBr_3	MI_3
La				W	W							Tb					W		
Ce				W	C	W	R-W	W				Dy					Y		
Pr					Bl-g	g						Ho							
Nd					Ro-V	g	Bk					Er					C		
Sm		R-Br			y-W	y	O-y					Tm					g		
Eu	W		Br-g		y							Yb					g		
Gd				W	C	C						Lu							

Element	MF_2	MCl_2	MBr_2	MI_2	MF_3	MCl_3	MBr_3	MI_3	MF_4	MCl_4	MBr_4	MI_4	MF_5	MCl_5	MI_5	MF_6	MCl_6	MBr_6	MI_6
Ac					X	X	X												
Th									W	W	C	W							
U						Dk-R	Dk-Br		g	Dk gn-gr	Br	Bk	E [illegible]	Dk gn-gr			Pa-y	E	
Np	E				Dk-Pu	E	E	E	Lt-g	y	E						E		
Pu					E	E			E				E						
Am					Pk														
Cm					W	E	E	E											

Key: Bl = Blue
Bk = Black
Br = Brown
C = Colorless
Dk = Dark
E = Exists
g = green
gr = gray
Lt = light
O = orange
Pa= pale
Pk = pink
Pu = purple
R = red
Ro = Rose
V = violet
W = white
x = x-rays
y = yellow

Ion	Z	e	Color	Me	M_2O_3	MO_2	Other Oxides
La^{+3}	57	0	C	0.00	W		
Ce^{+3}	58	1	C	2.56	gr-g		
Ce^{+4}	58	0	O-R			Pa-Y	
Pr^{+3}	59	2	Y-g	3.62	Y-g		Pr_6O_{11} Bk
Pr^{+4}	59	1	?			Br-Bk	
Nd^{+3}	60	3	R-V	3.68	Bl-Gr		NdO_2
Il^{+3}	61	4	Y(?)	2.83			
Sm^{+3}	62	5	Pa-Y	1.55-1.65	W		
Sm^{+2}	62	5	R-Br O-Y				
Eu^{+3}	63	6	Pa-Pk	3.40-3.51	Pa-Pk to W		
Eu^{+2}	63	6	Pa-straw				
Gd^{+3}	64	7	C	7.94	W		
Tb^{+3}	65	8	C to O Pa-Pk	9.7	W		Tb_4O_7 dk-br or Bk TbO_2
Tb^{+4}	65	7	?				

Ion	Z	e	Color	Me	MO	M_2O_3	MO_2	M_2O_5	MO_3	Other oxides
Ac^{+3}	89	0	-----			X				
Th^{+4}	90	0	C				W			
Pa^{+5}	91	0	C				E	E		
U^{+2}	92	3		2.95	E					
U^{+3}	92	3	Pu	3.22						
U^{+4}	92	2	g	2.97			Br-Bk			
U^{+6}	92	0	Y	0				E	Y-R	U_3O_8 g.
Np^{+3}	93	4	Pu							
Np^{+4}	93	3	g		E(?)		E			
Np^{+5}	93	2	---							
Np^{+6}	93	1	---							Np_3O_8
Pu^{+3}	94	5	Bl							
Pu^{+4}	94	4	Pk (g)				Dk-Br (y)			
Pu^{+5}	94	3	---							
Pu^{+6}	94	2	Br-y, y,o.							
AM^{+3}	95	6	Pk				Bk			
Am^{+2}	95	6	----		Bk					
Cm^{+3}	96	7	Pa-Y							

C. Deepening of color in complexes where the same element is present in two valence states. An exception is Sb(III) Sb(V)O_4 which is white in color.

D. Color changes in oxides associated with reversible loss of oxygen atoms from the crystal lattice:

Oxide	Color	
	Cold	Hot
Cu_2O	bright red	carmine
ZnO	white	yellow
CeO_2	pale yel.	yellow
In_2O_3	straw yel.	brown
Tl_2O	yellow	red
PbO	yellow	red
Pb_3O_4	scarlet	violet, then black
Cr_2O_3	green	brown
MnO	green	yellow
Mn_3O_4	reddish brown	black
NiO	yellowish green	yellow

E. Color in species having no unpaired electrons:

(1) $CrO_4^=$ is yellow, the potassium salt has a small temperature independent paramagnetism (14)

(2) MnO_4^- is purple, TcO_4^- is pink, and ReO_4^- is colorless. The potassium salts of Mn and Re both have a small temperature independent paramagnetism (14).

(3) $FeO_4^=$ is red in solution

F. "F" centers

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URANIUM AND ITS CHEMISTRY

W. B. Schaap July 6, 1948

I. DISTRIBUTION, OCCURRENCE AND MINERALS

A. DISTRIBUTION[1,2,3,4]

Uranium in low concentrations is widely distributed. It occurs in practically all rocks, sedimentary formations and in sea water. The estimated percentage of uranium in the earths crust is 8×10^{-5}, which is remarkably high in comparison to most other heavy metals.[5] Commercial deposits (in probable order of importance) are found at Great Bear Lake, Canada; Katanga, Belgian Congo; Colorado and Utah; St. Joachismsthal, Czechoslovakia; the Kirgiz Republic, U.S.S.R.; and Cornwall, England.[7]

B. OCCURRENCE[1,4]

Over 100 uranium minerals are described in mineralogical literature, and contain uranium in many different compounds--oxides, phosphates, carbonates, vanadates, and sulfates. For example, the most important of these minerals are pitchblende (uraninite) (uranosic oxide), carnotite (potassium uranium vanadate) and perhaps autunite (calcium uranyl phosphate).

C. ORES AND MINERALS

Uranium minerals have been classified by the U. S. Bureau of Mines into three types.[4] (1) The uraninites, oxides of uranium which occur as primary minerals deposited in granite rock formation, (2) Complex crystalline minerals which also occur as primary minerals --not important, (3) Secondary minerals obtained by dissolution and redeposition of primary ores. These occur in fissures and cracks in rocks and are usually yellow since the uranium is commonly present in the oxidized (VI) state.

The uraninites[1,2,4] contain uranium as U_3O_8. The term "uraninite" is often restricted to the crystalline modifications while "pitchblende" refers to the amorphous forms of the mineral. The mineral has a black, pitchy luster (brown or dark green in a few cases) with density varying from 6.4 to 9.7 and a hardness of 5.5. The impurities generally associated with these minerals are rare earths, Pb, Ca, Fe, Bi, Mn, Cu, Si, and Al. The percentage purity of the natural pitchblende may be as high as 90%. The chief deposits occur at Great Bear Lake, Canada, Belgian Congo, and Czechoslovakia. Many other scattered, small deposits occur, but are not commercially important. The mines at St. Joachimsthal, Czech. have been worked since 1517, but not for uranium until about 1900 when the medicinal values of radioactive elements were recognized. After World War I most of the world's production of uranium (and radium) bearing ores came from the Congo. This continued until 1930 when the Canadian deposits were discovered. A cartel arrangement between these two sources controlled production and prices until the second world war. The Canadian government bought out the Canadian mines in 1944.

Carnotite[1,2,4] is a soft, canary-yellow mineral with a sp. grav. of about 4. Its composition is given as $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$.

It is found extensively in Colorado and Utah and in south Australia. Typical carnotite ores from the Colorado region contain about 2-4% uranium calculated as U_3O_8 and 5-10% V_2O_5, although some rich veins and pockets have yielded ores with over 20% uranium. Theoretical mineral values in a ton of average (3% U_3O_8) carnstite were listed by the Bur. of Mines (1914) as $150 for uranium, $60 for vanadium and $729 for radium. (Uranium was actually a by-product in radium recovery.) Carnotite is not fluorescent, thus the uranium is probably not present as the uranyl ion, since uranyl salts are strongly fluorescent.

D. PROSPECTING FOR U ORES[4]

In addition to the usual methods of mineral recognition by crystalline form and appearance and by chemical analysis, several other convenient methods are available based on the properties of fluorescence and radioactivity that uranium ores exhibit.

Ultraviolet light is used for night prospecting. Fluorescent secondary uranium minerals are indicative of richer primary ores in the vicinity. Not all uranium minerals are fluorescent, for the primary ores and some secondary ores (principly cornotite) do not exhibit this phenomenon. However, practically all non-fluorescent ores contain fluorescent secondary ores on their surfaces or on adjacent rocks hence the method is of real value.

Radiation detectors such as the electroscope, Geiger counters and even photographic plates have proved useful for location of ores, tracing veins, and even in analytical estimation of uranium (and radium) present[1]. Radioactive thorium ores will similarly affect the detectors.

II. RECOVERY FROM ORES[1,3,4,7]

About 20 different procedures were found concerning the extraction of mineral values from uranium ores. Some generalizations obtained are listed.

(1) Carnotite is soluble in cold dilute acids and this presents the easiest and most convenient method of ore treatment. Sulfuric[8] acid is often used because of its low cost, although if HCl or HNO_3 acid is used the radium may be precipitated as the sulfate after the ore is dissolved. A Na_2CO_3 leach is sometimes used to dissolve the uranium directly.

(2) The primary uranium ores[9] require digestion or fusion to enable a complete recovery. The fusions are usually preceded by roasting to remove volatile matter. The usual fusion media are sodium sulfate, sodium bisulfate or sodium carbonate. The effect of fusion is to "crack" the ore and solubilize (in acids or carbonates) the uranium as sodium uranate, while leaving the radium in the leached residue. A disadvantage is the high cost of fusions, necessitating rather rich ores be used.

(3) Other uranium minerals may require special methods; for example, the presence of phosphate interferes with recovery and separations by the usual procedures.[10]

(4) Separations and purifications for various elements are accomplished by recourse to some combination of the following reactions.

(a) U and V are soluble in dilute H_2SO_4, Pb, Ra, Ag are not
(b) U forms a soluble carbonate complex in presence of excess ammonium or sodium carbonate to give a separation from insoluble carbonates and hydroxides.
(c) NaOH leach dissolves V, leaves U and Ra.
(d) U does not ppt. as sulfide in acidic UO_2^{++} solutions.
(e) Ag is recovered from U and Ra as insoluble chloride
(f) U is usually finally pptd. as $Na_2U_2O_2$ or better as $(NH_4)_2U_2O_7$, which ignites to U_3O_8.
((g) The introduction of ether extraction of uranyl nitrate provides a one-step separation from practically all impurities.)

III. PROPERTIES AND PRODUCTION OF U METAL, INDUSTRIAL USES OF THE METAL AND SALTS.

A. PROPERTIES OF THE METAL [3,4,5,11,13]

Uranium, when pure and in massive form is a silvery-white metal with a bluish tinge, (tarnishes in air) sp. gravity is 18.4, atomic volume 12.53 cc. Its melting point is now known to be about 1150°C.[12] The metal is rather soft, can be scratched with a file, is ductile, malleable, non-magnetic and if carbon is present can be tempered. It sparks when struck or cut and is pyrophoric when finely divided, sp. heat is 0.02765 and av. coeff. of expansion is 4×10^{-5}. The electrical resistivity is high, being 62×10^{-6} ohms at 18°, emissivity below m.p. is 0.51 ($\lambda = 0.67$), thermionic work function is 3.27 to 0.05 with a Richardson A of about 6. Its permeability to X-rays is low.

B. INDUSTRIAL USES OF THE METAL AND SALTS[3,4,7,11,14]

The industrial demand for uranium has never been great, and the supply (in the past) was more than adequate for the demands. Uranium has been used in ceramics as a coloring agent, in alloys, X-ray tubes, photocells, in photography for toning prints, for staining leather and wood, in dyeing of silk, in photometry, and as a hydrogenation catalyst in organic chemistry. Prior to 1940 the chief use was in ceramics, where uranium compounds gave glasses and glazes of various colors[15]--fluorescent yellow, non-fluorescent yellow and orange, non-fluorescent brown and green and even a red glass. (The use of uranium as a coloring agent in ceramics was prohibited by WPB Order M 285, Jan. 26, 1943). Uranium in steel[16] alloys increases hardness, strength and durability, in nickel alloys increases corrossion resistance, in cobalt alloys hardness is increased to such an extent that the alloy serves for cutting tools. U-W alloys are refractory.

C. PREPARATION OF THE METAL[4,17]

Although uranium was discovered by Klaproth in 1789, it was over 50 years later when Peligot first prepared the metal by heating the tetrachloride with sodium. The metal may be obtained by reductions of oxides or halides and by electrolysis from fused baths.

Oxides[18] may be reduced by heating with an alkaline earth metal in the presence of an alk. earth halide. Other metals, such as Mg, Al and Misch metal have been used. At very high temperatures (induction furnace) C will reduce oxides to metallic U.

Halides[19] are reduced by an alkali or alkaline earth metal. Ca is usually used if UF_4 or KUF_5 are to be reduced.

Electrolysis[20] of fused halides yield the metal. KUF_5 or UF_4 in fused NaCl-$CaCl_2$ baths was used by Westinghouse to prepare the initial U metal for the atomic project.

Massive metal[21] is prepared by heating the metal powder in an induction furnace. The buttons of metal can be made into wire by cold rolling and annealing at 900-1000°.

D. PRODUCTION AND PRICES[1,2,7,14]

The price of U_3O_8 remained nearly constant from 1913 to 1940 selling at about $250 per lb. Figures on the cost of the pure metal are not available over those years since practically none was made before 1940. In 1943 Westinghouse was producing pure metal at a rate of 500 lbs./day and a cost of $22 per pound[20]. This process was replaced by a more economical process (unspecified). U salts were produced much more extensively than the metal as evidenced by the fact that in 1938 Canada alone produced 800,000 lbs. of U salts.

E. STRUCTURE OF URANIUM METAL[22]

Uranium metal crystallizes into a distorted hexagonal close-packed structure with 4 of the atoms closer to an atom than the other 8 of its 12 nearest neighbors. This structure is not typically metallic because the 4 nearer neighbors to an atom indicate a tendency to form covalent bonds. The high electrical resistivity (about 11 times that of tungsten and about 35 times that of Cu and Ag) also indicates the psuedo metallic character of uranium. The bond directions are curious. Two bonds go in the direction of the North and South poles while the other two go toward the equator making an angle of 127° with each other.

IV. THE URANIUM ATOM

A. ISOTOPES AND RADIOACTIVITY[1,12,23,24]

Isotope	Decay	Range	Half-life	Natural Occurrence	Properties
232	α	5.36cm.	30y		
233	α	4.83	1.63×10^5y		fissionable
234	α	4.76	2.35×10^5y	0.006%	
235	α	4.52	7.13×10^8y	0.71	fissionable
237	$\beta^-\gamma$	--	7d		
238	α	4.18	4.56×10^9	99.28	fissionable (fast n)
239	β^-, γ	--	23.5M		

(Disintegration rate of natural uranium is 24,300 ± 700 α's / sec. / gram.)

B. ELECTRONIC STRUCTURE AND POSITION OF U IN PERIODIC TABLE[25,26,27]

The discovery of the transuranium elements and their dissimilarity to Os, Re, etc., focused attention on the correct placement of all the heavy elements. Although uranium possesses remarkable chemical similarity to the Group VI elements, its similarity to the transuranium elements is even greater. There appears to be no alternative to the existance of a second transition

series and for the inclusion of U in it, the only question which has not been definitely settled is where the series begins. At present most authorities regard the series as an "Actinide Series" beginning with element 89, actininm. Accordingly, uranium would have three-5f electrons, one-6d and two-7s electrons, a total of six, available for its valency states. Reasons supporting these views are listed below.

1. Physical: a. Recent interpretations of uranium emission spectra show the probable presence of 5f electrons[25,25] and the Zeeman effect in some well resolved lines indicate certain levels which appear only when f electrons are present.[28] b. A shift in position of absorption lines of all valences with changing anions indicates that, like the rare earths, U has an incomplete lower electron orbital, probably the 5f. c.[29] The absorption bands are sharp and similar in position to those of the first rare earth series. d. Magnetic susceptibilities agree well with predicted values invloving f electrons and the shape of the curve is similar to that of the first R.E. series.[30]

2. Chemical: a. The transuranium elements do not correspond at all to predicted properties for eka-Re and eka-Os, where they would go if no transition series occurred. b. A gradual shift in stability of the +3 valence state occurs with increasing atomic number. This is expected as the 5f shell approaches a half-filled condition. c. Chemical similarities and isomorphism exist among[26] the elements from U to Am. (Some U^{+4} and Th^{+4} compounds are isomorphous.) d. The crystal radii for the +3, +4 and MO_2^{++} salts show the characteristic decreases expected from electrons going into the 5f shell. e. Oxidation states are better explained.[31]

C. MAGNETIC PROPERTIES OF U ATOMS

U Metal[32] shows temp. dependent paramagnetism. Atomic suscept. at room temp. is 620×10^{-6} abs. units.

U^{+3} [4] is paramagnetic: moment of UCl_3 is 3.22 Bohr magnetons.

U^{+4} [4,32] is paramagnetic: moment of UCl_4 is 2.97 B. mag., moments for sulfate and perchlorate of U^{+4} are 2.95, for UO_2, 2.83. Above 25°, UCl_4 follows the Curie Weiss law, $\Theta = 50°$ (moment is 2.7).

U^{+6} [4,33] exhibits paramagnetism indep. of temp. Specific mag. suscep. of UF_6 were found to be +0.12 and 43×10^{-6}. UO_3 has weak paramagnetism indep't. of temp., X_{mol} is $+157 \times 10^{-6}$. UO_2^{++} has a magnetic moment of 2.73 B. mag and is paramagnetic.

V. VALENCE STATES AND THEIR CHARACTERISTICS

Oxidation numbers of +2, +3, +4, +5 and +6 have been reported for uranium. Of these only the +3, +4 and +6 are readily obtainable.

+2.[34] Uranium does not exist in the +2 state in solution, and compounds cannot be prepared by usual dry reactions. Only reliably reported compounds are UO, UC and UN, all reported since the war.

+3. U (III) may be prepared by vigorous reduction of U(IV) salts. Its aqueous solutions are deep red and are not stable, H_2 being slowly liberated. Oxidation potential for $U^{+3} \dashrightarrow U^{+4} + e$ is

+0.5 volts. Some compounds are UH_3, UX_3 (X = Cl, Br, I) and U_2N_3. The strongly ionic hadides are most easily prepared by vapor-phase reaction of the hydride with the corresponding hydrogen halide.

+4. Uranous (U IV) solutions are green in color, stable in aqueous solution, although slowly oxidized by air. ($UO_2 \dashrightarrow UO_2^{++} + 2e$; E° = -0.33v). U(IV) exists in two forms, the usual U^{+4} and also the UO^{++} ion. Some insoluble compounds of U^{+4} are UF_4, UO_2, UN_2, $U(HPO_4)_2$, UP_2O_7, $U(C_2O_4)$, U (cupferron)$_4$. Compounds containing UO^{++} are exemplified by $(UO)_2P_2O_7$, $UOF_2.2H_2O$(?), $UO(IO_3)_2$.[3] The normal U^{+4} compounds are all rather ionic.

+5. Only two known compounds contain (apparently) uranium (V) they are the halides UCl_5 and UF_5.[36] Molecular weight measurements in organic solvents indicate UCl_5 to be dimeric, U_2Cl_{10}. This together with its ease of disproportionation and other evidence indicate that the compound may actually be $UCl_4.UCl_6$. (UCl_6 and UF_6 are the only U(VI) halides that exist). Evidence for the occurrence of U(V) in solutions have appeared recently from polarographic work. Kolthoff and Harris[37] proposed a U(V) ion to account for the one-electron reduction of uranyl ions. At the recent A.C.S. meeting,[38] the preparation of millimolar solutions of U(V) were reported as a result of electrolysis of U(VI) in perchlorate media.

+6. U(VI) exists in two forms, the bare U^{+6} compounds and the UO_2^{++} (uranyl) salts. The two known U^{+6} compounds[35] (UCl_6 and UF_6) are covalent compounds, soluble in organic solvents, readily hydrolyzed by water or moisture to the more stable uranyl compounds, and highly reactive ($UF_6 + CCl_4 \dashrightarrow UF_4 + CCl_2F_2 + Cl_2$ at 770°). The uranyl ion represents uranium in its most stable state. Its salts, usually ionic, yellow, strongly fluorescent are soluble in water or acids. Typical compounds are the halides, UO_2X_2, $UO_2(NO_3)_2$, UO_2SO_4, and $UO_2(C_2H_3O_2)_2$. Some water insoluble compounds are $UO_2NH_4PO_4$ (or $AsO_4^{\equiv}$), and $(NH_4)_2U_2O_7$ (ammonium diuranate). $UO_2(OH)_2$ ppts. at pH 4.1. Uranyl ions complex readily in basic solutions. Examples, are the soluble basic carbonate complex and complexes with anions of organic acids such as tartrate, utrate, etc. The compound $UO_4 \cdot 2H_2O$ is a peroxide and also contains U(VI).

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FLUORINATION OF INORGANIC HALIDES

P. J. Pizzolato July 8, 1948

In recent applications of fluorination methods the emphasis appears to have been on finding the conditions under which better control of the reaction can be achieved. It has been known for a long time that fluorination of inorganic non-polar halides may be accomplished by interaction of the halide with anhydrous hydrogen fluoride or a metallic fluoride, the strongest being silver fluoride. Strong fluorinating agents such as silver and mercuric fluorides produce only the completely fluorinated compounds, however, and when the partially fluorinated products are desired a milder reagent such as antimony trifluoride or anhydrous hydrogen fluoride must be employed.

After Booth and Swinehart (12) successfully applied the Swarts method to silicon tetrachloride to obtain a series of mixed chlorofluorides of silicon, the method was applied to other inorganic non-polar halides and pseudo-halides. Although stepwise fluorination of such halides as $POCl_3$ and PCl_3 has been carried out with anhydrous hydrogen fluoride (17), the difficulties involved in handling hydrogen fluoride have apparently limited the study of that method.

Fluorination of $RSiCl_3$ Type Compounds. A compound of this type when fluorinated with SbF_3 in the presence of halogens or $SbCl_5$ (Swarts method) might be expected to yield three products: alkyl dichloromonofluorosilane ($RSiCl_2F$), alkyl monochlorodifluorosilane ($RSiClF_2$), and alkyl trifluorosilane ($RSiF_3$).

The monoalkyl chlorosilanes fluorinated by Booth and coworkers included the methyl, ethyl, n-propyl, isopropyl, and n-butyl compounds, some of which underwent the reaction more readily than others. Since the investigators were interested in the intermediate partially fluorinated products as well as the completely fluorinated compounds, one of the main objectives was to establish the conditions under which these intermediates might be obtained in good yields. Complete fluorination, however, was apparently the favored reaction for in no case was the yield of intermediate chlorofluoride anything but small.

The fluorination of ethyl trichlorosilane by means of SbF_3 without a catalyst produced small yields of the intermediate chlorofluorides (3). The corresponding n-propyl compound, with or without the catalyst, normally yielded only traces of the intermediate compounds (5), the use of tetrachloroethylene as a diluent in the reaction mixture increasing the yields slightly. Methyl trichlorosilane was best fluorinated by SbF_3 in the presence of $SbCl_5$, at 45° and 760 mm., yielding mostly the trifluoro derivative with some of the monofluoro compound and a trace of the difluoro compound. Attempts to improve the yield of the difluoro derivative by the use of special conditions were unsuccessful. By a different method which involves passing the vapor of methyl trichlorosilane over CaF_2 powder heated to 200° at 700 - 750mm. in a rotating copper tube and collecting the products in the usual manner, equal amounts of all three fluorination products were obtained but the yields were still very small.

For the fluorination of the i-propyl and n-butyl chlorosilanes, SbF_3 with $SbCl_5$ as catalyst was used, the technique being more or less the same as that used on the other monoalkyl

chlorosilanes except that the reaction was "forced" to favor the preparation of partially fluorinated products (9,8). In place of the usual reflux condenser surmounting the flask together with an automatic take-off to bleed off higher-boiling products as they were formed, the generator flask was connected directly to a trap and through a large-bore stopcock to ampules and to the vacuum line so that everything that could be withdrawn from the flask was collected as rapidly as possible.

For the i-propyl compound estimated average yields of several different fluorinations were:

i-$C_3H_7SiF_3$	75 - 70%
i-$C_3H_7SiF_2Cl$	8 - 10%
i-$C_3H_7SiFCl_2$	17 - 20%

The yields of intermediate chlorofluorides here are surprisingly high considering the difficulty encountered in getting the corresponding intermediates from the fluorination of the n-propyl compound even at diminished operating pressures.

Among the series of products obtained in the fluorination of any given alkyl trichlorosilane, the chlorofluoride in which all but one of the chlorine atoms had been replaced was almost always obtained in the smallest amount. This behavior was consistent with previous experience (10,12) and was explained in terms of a definite threshold temperature for the fluorination of each covalent chlorofluoride or chloride. Since, with increasing fluorine content the threshold temperature is lowered, the rate of fluorination increases as the fluorine content of the halide is increased. If the threshold temperature for the fluorination of a given alkyl chlorodifluorosilane were extremely low, then at the temperature needed to initiate the fluorination of the trichlorosilane, the former reaction may be so extremely rapid as to prevent the removal from the reaction zone of any appreciable yield of this intermediate.

Several factors tend to increase the production of the two intermediate chlorofluorides of any given series: (1) The temperature and pressure should be kept as low as possible, consistent with a smooth yet fairly vigorous reaction. (2) The use of a catalyst is of great importance as it lowers considerably the threshold temperature of fluorination. (3) In certain cases, as in the fluorination of n-butyl trichlorosilane, excessive localized action of the fluorinating agent must be prevented if appreciable yields of the intermediate chlorofluorides are to be obtained. This is accomplished by rapid stirring of the reaction mixture and by slow addition of the fluorinating agent.

Fluorination of R_2SiCl_2 and R_3SiCl Types by the Swarts Method.

Highest yield of the intermediate chlorofluoride, $(CH_3)_2SiClF$, was obtained in the presence of a catalyst, and using the "forcing" technique used in the fluorination of i-propyl and n-butyl trichlorosilanes (11). No pressure control was used, that is, the SbF_3 was fed into the generator rapidly, and the products were condensed into ampules as fast as possible, regardless of pressure, which, however, was never above 300 mm.

Trimethyl chlorosilane, $(CH_3)_3SiCl$ added dropwise to antimony trifluoride at one atmosphere pressure, reacted immediately to form the corresponding fluoro compound, no heating of the reaction vessel being necessary (11).

Fluorination of $RXHal_3$, R_2XHal_2, and R_3XHal, where X = S, Se, or Te

Fluorination of these compounds was accomplished in many cases by the interaction of another halide with the metallic fluoride, AgF,

and in other cases less directly by the action of aqueous hydrogen fluoride on the appropriate oxide or hydroxide. The fluorination of the non-polar types required silver fluoride in the anhydrous form, while for the double decomposition type reaction which occurs with salt-like halides, aqueous silver fluoride was used (13).

Results indicated that substituted halides are generally rather resistant to conversion into fluorides, only vigorous reagents such as silver fluoride being effective. The halides of bivalent sulfur and selenium were the most reactive, although C_6H_5SCl and other similar aryl substituted compounds could not be fluorinated. The mono- and disubstituted tetrahalides of quadrivalent tellurium were moderately reactive as indicated by the formation of CH_3TeF_3, $(CH_3)_2TeF_2$ and $(C_6H_5)_2TeF_2$ by the action of silver fluoride in organic solvents.

Mono- and disubstituted tetrahalides of sulfur and selenium were resistant to fluorination.

The trisubstituted tetrahalides are salt-like and nearly all the fluorides can be prepared. Typical preparations were the following:

$$(CH_3)_3SF \xleftarrow[AgF]{\text{aqueous}} \left[(CH_3)_3S\right]^+ I^-$$

$$(CH_3)_3SeF.H_2O \xleftarrow[\text{aq. HF}]{\text{dil.}} \left[(CH_3)_3Se\right]^+ OH^- \xleftarrow[H_2O]{Ag_2O} (CH_3)_3SeI$$

$$\begin{matrix}(CH_3)_3TeF \\ C_6H_5IF\end{matrix} \xleftarrow[\text{aq. HF}]{\text{dil.}} \text{free base}$$

Fluorination of the Pseudo-halides $Si(NCO)_4$ and $P(NCO)_3$.

For the preparation of silicon fluoroisocyanates, Forbes and Anderson (14) adapted the method previously developed for the preparation of silicon fluorobromide (15), sublimed SbF_3 being added slowly to boiling silicon isocyanate, a mercury-sealed stirrer relieving pressure temporarily greater than atmospheric, and the silicon tetrafluoride being allowed to escape without condensation. The three well-defined fractions obtained were identified as the following: SiF_3NCO (2 parts), $SiF_2(NCO)_2$ (3 pts.), and $SiF(NCO)_3$ (6 1/2 pts.). As was expected by analogy to similar fluorinations (4,7), operating at diminished pressure and temperature favored the formation of monofluoro derivative, silicon fluorotriisocyanate

The action of antimony trifluoride without catalyst on $P(NCO)_3$ produced both phosphorus fluoroisocyanates (1). The difluoroisocyanate, PF_2NCO, however, was best prepared by the fluorination of the monofluoro derivative, $PF(NCO)_2$.

Phosphorus isothiocyanate, $P(NCS)_3$, and antimony trifluoride yielded only one mixed "halide", phosphorus difluoroisothiocyanate, PF_2NCS (1).

Rearrangements and Glass Formation of Fluorination Products.

Rearrangements of the type observed by Booth and Morris (7) among the chlorofluorides of germanium, were noted only for certain of the mixed compounds of the silicon and phosphorus pseudo-halide series. No rearrangement of the mono- or di-fluoro silicon isocyanate was noted, but the trifluoro compound, SiF_3NCO disproportionated rapidly at its boiling point, mainly to SiF_4. In the corresponding phosphorus isocyanate series, PF_2NCO decomposed rapidly at its boiling point to PF_3.

The freezing points of many of these compounds could not be determined because of the tendency for glass formation on cooling. This behavior was shown most often by the mixed halides or pseudo-halides but in certain cases also by the fully fluorinated compounds. It is believed that irregularity of molecular form contributes toward a tendency for glass formation (16). Thus, although the symmetrical $SiCl_4$ crystallizes readily, groups introduced into the molecule which destroy its symmetry tend to cause the resulting substances to solidify as glasses.

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THE STRUCTURE OF GLASS

Dr. Scott Anderson

July 13, 1948

Zacharisen has given a theory of the structure of oxide glasses. This theory resulted in a list of cations which could be considered as the "glass former". The list was based upon four rules. 1) An oxygen atom is linked to not more than two atoms A. 2) The number of oxygen atoms surrounding atoms A must be small. 3) The oxygen polyhedra share corners with each other. 4) At least three corners in each oxygen polyhedron must be shared. These rules produced the following list of glass formers. B^{3+}, Si^{4+}, Ge^{4+}, P^{5+}, As^{3+}, P^{3+}, Sb^{3+}, V^{5+}, Cb^{5+}, Ta^{5+} and Al^{3+}. (Al_2O_3 does not form a glass but may substitute isomorphously for Si^{4+}.) Any oxide glass must have at least 1/3 of its oxides from one of these cations.

By Fourier analysis of X-ray scattering data Warren and co-workers have given some proof of the theory in the cases of silicate borate, and phosphate glasses, although it will be pointed out that the conclusion of this school with regard to borate glasses is not justified on the basis of their own data. Moreover, the X-ray method is limited to the study of simple glasses.

The author has carried out certain infra red studies on glasses. These will be discussed. These data agree with both Zacharisen and Warren in the case of soda-lime-silicate glasses. Certain points of departure will be indicated. Evidence will be presented to show that when two or more polymeric forms are present these polymers are cross linked with certain atoms. Moreover, it appears that Barium should be included in some way with the list of "glass formers."

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CHEMICAL APPLICATIONS OF PUNCHED CARD TECHNIQUES

Alan L. McClelland July 15, 1948

In recent years punched card techniques, long used in other fields, have been successfully applied to chemical problems. These applications have shown the advantages of these methods, and point to further use as more chemists become acquainted with them. These methods have three general types of use: (a) carrying out long and laborious mathematical calculations, (b) correlating large amounts of data, and (c) filing information in an easily accesible form. Two types of equipment are available; electrically sorted cards, requiring considerable complicated equipment, and manually sorted cards, requiring very little auxiliary equipment.

Electrically Sorted Cards

This type of equipment, originally developed by Dr. Herman Hollerith in the late 19th century, and often referred to by his name, is manufactured in this country by the International Business Machines Co. and, in recent years, by Remington Rand. Since these machines are quite complex, they are expensive to obtain and require experienced operators. Therefore they are hardly practical for one individual, but since most large industrial firms and many colleges and universities have the equipment for accounting purposes, it is often available to the chemist. This university maintains a completely equipped office which will carry out problems for any department of the university.

A brief description of the International Business Machines Co. equipment will illustrate the operations which can be carried out. The standard card used in these machines is 3 1/4 x 7 3/8 inches, and contains 80 vertical columns with 12 punching positions in each column. The positions desired are punched by machines; machines are available which punch out one card at a time or which punch the same pattern on a large number of cards at the same time. The cards are sorted by a machine which separates the cards into thirteen groups corresponding to the twelve punching positions and to no punch in any vertical column. This machine will sort 25,000 cards per hour. The collator is a machine which compares two decks of cards and is especially valuable in correlation studies. Various calculating machines are available which add, subtract, multiply, and divide, and print the results on a sheet of paper or punch them into cards. A machine is available which will print on paper the data punched in the cards.

Use in Mathematical Calculations.

These machines are very useful in long mathematical calculation since they are much faster and more accurate than any other availabl method. The extensive use made of these machines in astronomical calculations show the advantages of this method (1). King has illustrated its use in physical chemistry calculations, (2), and has applied the method to the analysis of the band spectra of asymmetric rotor molecules. (3). Pauling and co-workers have used the method for years in the Fourier methods of crystal structure analysis and in the calculation of the structure of molecules from electron diffraction data. They report that greater speed, greater accuracy, and greater density of calculated points are obtained than are possible by any other method (4). Jeffrey, et al, also describe a system for using punch cards for Fourier syntheses (5).

Correlation Studies

Punch cards are especially well adapted for correlation studies and have often been used in that way in other fields. Frear studied

the relation of structure to toxicity for 8,000 insecticides and fungicides, though in this case he used manually sorted cards (6). Bailar, Heumann, and Seiferle have described a system for indexing inorganic compounds on IBM cards (7), and Morgan and Frear have described a similar system for organic compounds (8). With these codes it would be very easy to make correlation studies between structure and any desired property.

Filing.

Large amounts of information can easily be classified with IBM cards, since numerous subjects can be classified on the same card. One of the machines available will print on paper the information punched which is on the card, thereby allowing the mechanical printing of a bibliography. Such systems have often been proposed but so far have been tried very seldom. A system of this type has been put into use in the Socony-Vacuum research laboratory, and has apparently been successful (9). The patent office also has this type of set-up for searching patent files(10).

Manually Sorted Cards.

The manually sorted cards are punched with holes around the edge of the card, and are coded by cutting out the margin between the hole and the edge of the card. The cards are then sorted by passing a long needle through a given hole and the cards which have been slotted will drop off.

These cards are sold by the Charles R. Hadley Co., Los Angeles Calif., and the McBee Co., Athens, Ohio. Cards can be obtained in any size, though only a few sizes are carried in stock, and any desired coding system can be printed on the face of each card. The only equipment necessary is the cards, needles for sorting (knitting needles work perfectly well), and a punch or pair of scissors for notching the cards. Thus the use of this type of cards is not much more expensive than the use of the ordinary filing cards, and so is practical for the individual chemist.

One of the advantages of this type of card over the IBM card is that the center of the card is available for writing the information or abstract being filed, while in the IBM card this is not as convenient, since holes may be punched anywhere throughout the body of the card.

Uses.

The manually sorted cards are primarily for filing information and for correlation studies, since they are not applicable to mathematical calculations. Since there are fewer holes per card, they will not handle as large a volume of information as the IBM cards, and since they must be handled manually the total number of cards in the file cannot be as great, but for many purposes they are much more efficient and convenient than the electrically sorted cards. Frear found the manually sorted cards gave excellent results in his correlation study of 8,000 insecticides, previously mentioned (6). Murphy has found punch cards the most convenient way of keeping data on isotopes (11). Each card contains the data on one isotope, and is punched according to half life, atomic number, mass number, type of decay, and type of nuclear reactions which produce the isotope. Bausch and Lomb Co. maintains a record of all experimental glass melts on punch cards, enabling sorting for a melt of any given composition or properties (12)

Coding.

The most important consideration in setting up a manually sorted system is the preparation of a suitable code. There are three main types: (a) direct coding, (b) numerical coding, and (c) random coding. Direct coding gives each hole a specific

meaning independent of the other holes on the card. This is the best method of coding if it can possible be used; its main disadvantage is that it severely limits the total number of subjects that may be coded. It has the advantages of allowing as many of the different subjects as necessary to be coded on one card, and of cutting down sorting time.

Numerical coding uses various combinations of holes to indicate numbers, and then each number is assigned a meaning. Usually the basic unit of the numerical coding system is a group of four holes numbered 7-4-2-1. By combinations of these four numbers any number from one to fourteen may be obtained. Thus these four holes can be used to indicate any of fourteen subjects, but the important limitation is that only of those fourteen subjects may be put on one card. By using two sets of four holes, but going only from 1-9 in each set, any number from 1 to 99 may be obtained. This same technique can be continued for more digits, thereby increasing the number of possible coded subjects considerably, but the advantage of the larger number of possibilities is largely lost because only one of the possibilities can be used.

Random coding involves giving each subject to be coded a random designation, and then superimposing the codes for any subjects to be indexed on the same card on the same group of holes. Mooers has developed this sytem, on which he has applied for a patent, and given it the name "Zatocoding" (13). He has shown that the number of extra cards obtained in sorting for a given subject is controlled by statistical probability, and that the number can be kept below any desired average by proper coding. He gives a mathematical proof showing that if the sum of the number of holes required for coding each of the subjects to be put on one card is not greater than 69% of the total number of holes on the card, the ratio of extra cards obtained to the total number of cards sorted will average less than $(1/2)^x$, where x is the number of holes used to code the subject being sorted for. This system increases greatly the number of different subjects that can be coded, but does not allow very many subjects to be put on the same card. It required a fairly large number of passes of the needle in sorting for each subject, and makes it necessary to look up the code number for subjects desired. However, it would appear to be a good system for a file containing information on numerous unrelated topics.

Coding authors and elements.

Elements are most easily coded by the atomic number, using four holes for each digit, but this allows only one element to be coded on one card. If two or more elements must be coded on the same card, as is often the case, it is usually best to code them directly, assigning one hole to each of the elements which will appear most frequently and grouping the rest into groups or subgroups.

Authors are usually coded with some type of numerical code to minimize the number of holes used. This ordinarily allows coding of only one author's name; if desired, other authors can be coded on a separate card with a reference to the card containing the abstract or information.

The most economical use of holes is obtained by dividing the alphabet into sixteen groups, based on the frequency of occurrence of initial latters in authors' names. The following groups are of approximately equal size:

0	- A	4	- F-G	8	- L	12	- S-Si
1	- B	5	- H	9	- M	13	- SJ-SZ
2	- C	6	- I-J	10	- N-O-P	14	- T-U-V
3	- D-E	7	- K	11	- Q-R	15	- W-X-Y-Z

These are coded in four holes by using no punch for 0, and coding the rest by numbers (by substituting 8 for 7 in the 7-4-2-1 series any number from 1 to 15 may be coded in four holes). For further subdivision, the second letter of the name can be coded in another four hole field (for names beginning with S the third letter is coded, since the first two letters are considered in coding the initial letter). The groups above will no longer be of equal frequency for the second letter, but it is probably an unnecessary complication to have a separate coding system for the second letter.

A more easily remembered coding system requiring five holes per letter is obtained by giving the letters from A to N the numbers 1 to 13, and then repeating these numbers for the second half of the alphabet. The numbers corresponding to the letter can be punched in a four hole area, and a fifth hole is used to indicate whether the hole is in the first or last half of the alphabet.

Other variations in the coding of authors and a table of the frequency of letters in names are given by Cox (14).

Choice of code.

In general, direct coding is most practical if it will handle all the information desired. If more possibilities are need either random coding or a combination of direct and numerical coding can be used. If random coding is used it is usually best to use all the holes on the card for the random code, and not combine it with another type of coding.

Two general rules should be remembered in setting up a code:

(a) Include in the code only those subjects known to be of importance when the code is set up, and leave plenty of spaces in the code blank for future expansion.

(b) Put material on completely unrelated topics in separate files with separate codes, thereby allowing each code to be much more specific.

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VALENCE STABILIZATION THROUGH COORDINATION

Edward I. Onstott July 20, 1948

Quantitative Measurement of Valence Stabilization.

Valence stabilization is generally defined as the stabilization of a particular oxidation state of an ion to reduction to a lower oxidation state or oxidation to a higher state. A quantitative measure of the stability of an ion to reduction (or oxidation) is the oxidation-reduction potential. The stability of comples ions which dissociate into simpler constituents is quantitatively expressed as an equilibrium constant, which is termed a dissociation or instability constant or complexity constant.

Anions Which Effect Stability of Ions.

If oxide ion may be considered to be a coordinating agent, then undoubtedly it is the most common and most effective agent for stabilizing the higher oxidation states of the elements. Maximum valence oxy ions are known for the elements of groups V, VI, and VII, as well as some other transition and representative elements. A look at potential values (1) will demonstrate the dependence of the stability of the oxy ions on the oxide ion concentration of the solution. In acid solution, where the oxide ion concentration is low, these ions are much more powerful oxidizing agents than in alkaline solution where the oxide ion concentration is considerably higher. Unstable ions such as manganate ion (2) and rhenate ion (3) exist only in alkaline solution.

Halide ions form complexes with a large number of metal ions. Thus, gold forms chloride and bromide complexes in both the monovalent and trivalent state, while monovalent and divalent copper forms complexes with these same halide ions. (Copper does not exist in solution as the simple cuprous ion). Thallic ion, which is a good oxidizing agent, is stabilized markedly by complex formation with chloride ion. The platinium metals form chloride complexes in the tetravalent state, and some complexes of divalent and trivalent metals also are known. The complex of divalent palladium is more stable than the tetravalent palladium complex (4), but in general the higher oxidation states of the metals in these complexes are more stable. Potassium hexachlororhenate (IV) is so stable that it is formed either by heating $ReCl_5$ with KCl, in which case chlorine is evolved, or by heating $ReCl_3$ with KCl, in which case metallic rhenium is formed as the reduction product (5).

Cyanide ion forms stable complexes with most of the transition metals, as well as the coinage metals and zinc, cadmium, and mercury. It stabilizes trivalent cobalt, the simple ion of which is a powerful oxidizing agent. On the other hand, cuprous ion is stabilized by cyanide ion, and the cupric complex does not exist, as cyanide ion is oxidized by cupric ion to cyanogen. Mercuric ion, unstable to reduction as the simple ion, is made

quite stable by complexing with cyanide ion. Other unusual compounds are the molybdenum and tungsten (IV) cyanide complexes, which show the coordination number of eight (6), (7). Pentavalent rhenium is stabilized by cyanide ion in $K_3 ReO_2(CN)_4$ (8).

Several other anions coordinate to metal ions to stabilize particular oxidation states. Nitrite ion stabilizes trivalent cobalt, while thiosulfate ion stabilizes monovalent copper (9) and silver (10). Oxalate ion forms stable complexes with many metal ions. Carbonate ion and thiocyanate ion likewise form numerous stable coordination compounds.

Polydentate Groups Which Effect Stabilization Through Chelation.

Molecules or ions which are capable of occupying two or more coordinating positions and forming rings (preferably five-membered) with metal ions generally effect more stable compounds than coordinating groups occupying single positions. Organic amines such as ethylenediamine, dipyridyl, and diethylenetriamine, and oxalate ion are examples of this type of coordinating group (11). Trivalent cobalt and chromium compounds containing polydentate groups are quite stable, as are compounds of divalent and trivalent ion. Divalent silver, a powerful oxidizing agent as the simple ion, is stabilized by certain chelate forming groups (12). Dipyridyl complexes of cuprous and cupric copper are known (13), although ethylenediamine stabilizes only cupric copper (14).

Other Stabilizing Groups

Ammonia and monodentate amines form stable coordination compounds, although these compounds are less stable than chelate compounds. Derivatives of trivalent cobalt, monovalent copper, and the same general type of compounds previously mentioned are known. Thiourea and some of its derivatives form complexes with monovalent copper (15) and silver (9).

Structure Considerations.

The tendency for a complex compound to attain the octahedral tetrahedral, or planar configuration involving respectively d^2sp^3 (or sp^3d^2), sp^3, or dsp^2 orbitals (16) undoubtedly is the most important reason for the stabilization of a particular oxidation state of a metal. Divalent cobalt complexes are unstable and trivalent cobalt complexes very stable because the single electron of a divalent cobalt must be promoted to the 4d level if the octahedral configuration is to be attained, and is consequently easily lost to form the trivalent cobalt complex (17). (A cobaltous complex may be compared to rubidium metal, which is a very good reducing agent.) Complex compounds of divalent iron and monovalent manganese are isoelectronic with the cobaltic complexes. Divalent nickel, palladium, platinium, and copper form stable planar compounds, as well as trivalent gold, while monovalent copper, divalent zinc, cadmium, mercury, and nickel form tetrahedral complexes. Linear complexes of monovalent copper, silver, and gold, involving sp orbitals (16) also are quite stable. Several instances of stable complexes are known where d or p orbitals are singly occupied, but few cases where inner d orbitals are vacant.

The configuration of the complex cyanides of molybdenum and tungsten which show the coordination number of eight was not predicted theoretically (18), but it is of interest to note that both have the electronic configurations of rare gases, the bond orbitals being d^4sp^3.

Conditions Which Favor Valence Stabilization.

A particular oxidation state will be more stable if the configuration is one of those outlined in the section above, and does not contain unpaired electrons or vacant orbitals, and is not far removed from its normal valence state.

The stability of complex compounds is generally greater when five-membered chelate rings are present.

The type of donor group determines largely the stability of complex compounds.

Use of the Concept of Valence Stabilization.

The need for oxidizing and reducing agents in chemical reactions is great. Coordinating agents afford unlimited possibilities for controlling oxidation-reduction potentials.

Practically all of the plating baths used today contain some type of coordinating agent, which effects a good metal deposit.

The study of the stereochemistry of complex ions is made possible when very stable complexes are available.

Many colored complex compounds can be used for the colorimetric determination of a particular constituent of the complex.

Polarographic analyses of metal ions are often made possible by using complexing agents which separate the polarographic waves.

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COMPOUNDS AND OXIDATION STATES OF RHENIUM

Aaron B. Herrick July 22, 1948

A. Introduction to the Chemistry of Rhenium Compounds.

Oxidation States and their Stability: Oxidation States from -1 to +7 are known, although only the +4, +7, and metallic states are stable. Rhenium does not exist as a stable, positive ion in solution, generally occurring in the anion or in covalent compounds. The -1 state (rhenide ion) exists only in cold, air-free, strongly reducing solutions. The +1 and +2 states have been obtained as oxide hydrates by reduction with zinc and cadmium, respectively. The +3 state is shown by an oxide and by covalent halides. The other states (+4 to +7) occur more frequently and are discussed with their characteristic compounds.

Disproportionation of Unstable Oxidation States: Rhenium compounds disproportionate to a greater extent than the compounds of any other element. Typical of the many disproportionations encountered are the following:

a. Rhenate (ReO_4^{-2}) in acid goes to ReO_4^- (Re^{VII}) and ReO_3^{-2} (Re^{IV}).
b. Rhenium dioxide and ReO_4^{-1} under drastic conditions exhibit reverse disproportionation to $Re_2O_7^{-4}$ (Re^V). This is reversed by water, acids, or ammonia.
c. Rhenium trioxide at 400° in vacuo goes to ReO_2 and Re_2O_7.
d. Pentachlororhenate (III) ($ReCl_5^{-1}$) on standing gives $ReCl_6^{-2}$ and rhenium metal.

Position of Rhenium in the Periodic Table: Rhenium is a member of the manganese (VIIA) family, but at times behaves like the halogens or like osmium and tungsten. Potassium perrhenate is a weak oxidizing agent (cf. $KMnO_4$). Alkali perrhenates are similar to perchlorates in solubility. The existence of two forms of perrhenate (ReO_4^{-1} and ReO_5^{-3}) is somewhat analogous to periodate. The rhenide ion (Re^{-1}) suggests halide ions.

Hexachlororhenate (IV) ion ($ReCl_6^{-2}$), sometimes called rhenichloride or chlororhenate, is similar to $PtCl_6^{-2}$, and $[Re(CO)_5]_2$, although dimeric, suggests $Os(CO)_5$. The C.N. of rhenium in coordination compounds is six, reminiscent of certain of the platinum metals. Rhenium disulfide, like OsS_2, is more stable than the higher sulfides of these elements. Like tungsten, rhenium forms oxyhalides.

B. Familiar Compounds of Rhenium

Oxides, Oxyacids, and their Salts: Oxides of all positive oxidation states exist, with the exception of +5. Oxyacids for states +4 to +7 are known. Re_2O_7 is the most stable oxide, and is the anhydride of $HReO_4$, the salts of which, the perrenates, are the most common compounds of rhenium. Alkali fusion of ReO_4^- in the absence of oxygen gives ReO_5^{-3} (mesoperrhenate). Rhenium trioxide is prepared by heating ReO_2 and Re_2O_7 together. It is the parent compound of the rhenates (ReO_4^{-2}), unstable salts which are green in color like the manganates. Rhenium pentoxide does not exist, but its salts, the hyporhenates, are prepared by the reverse disproportionation previously mentioned. Rhenium dioxide (ReO_2), prepared by reduction of Re VII, is the anhydride of

the rhenites, analogous to the manganites. This oxide, like all the lower oxides is reducing in character. The lower oxides Re_2O_3, $ReO \cdot H_2O$, and $Re_2O \cdot 2H_2O$ are prepared by reductions in the absence of oxygen, and are not anhydrides.

Halides, haloacids, and Oxyhalides: The known halides of rhenium are ReF_6, ReF_4, $ReCl_5$, $ReCl_3$, $ReBr_3$. Decreased attraction for halogens as the halogen group is descended is attested by the failure of rhenium to form an iodide. Derivatives of ReX_4 exist for all halogens, although the halides themselves do not. Potassium hexahalorhenate (IV) is prepared by treating a $KReO_4$ - KI mixture with HX. These salts hydrolyze to ReO_2. The weak acids $HReCl_4$, $HReI_5$, H_2ReBr_6 and H_2ReCl_6 are known. The oxyhalides of rhenium are $ReOF_2$(Re IV), $ReOF_4$ and ReO_2F_2 (Re VI), ReO_3F (Re VII), and $ReOCl_4$ and ReO_3F. Oxybromides have not been isolated.

Sulfides, selenides, and thioacids: Only two sulfides of rhenium exist. Rhenium disulfide (the more stable) is obtained by heating the heptasulfide. The latter is prepared by treating perrhenate in acid with hydrogen sulfide. The selenides are exactly analogous to the sulfides. Thioperrhenates from ReO_3S^{-1} to ReS_4^{-1} have been prepared.

Miscellaneous rhenium compounds: Rhenium forms a carbide of undetermined structure only with great difficulty. A high temperature reaction with phosphorus yields a series of refractory phosphides. Intermetallic compounds with tungsten and zirconium have been reported.

C. Complex Rhenium Compounds

Alkoxides and alkyls: When $ReCl_3$ is treated with $NaOC_2H_5$ and $NaOCH(CH_3)_2$, $Re(OC_2H_5)_3$ and $Re[OCH(CH_3)_2]_3$ respectively are obtained. From the reaction between $ReCl_3$ and CH_3MgI rhenium trimethyl ($Re(CH_3)_3$ is isolated.

Oxythiocyanate and oxycyanides: The formation of the oxythiocyanate, $ReO(CNS)_4$, under certain conditions constitutes a good test for ReO_4^{-1}. It is prepared by stannous chloride reduction of the reaction product obtained when ReO_4^-, KCNS, and dilute hydrochloric acid are mixed. Double salts like $(C_5H_5NH)_2[ReO(CNS)_6]$ have been isolated. The complex oxycyano derivatives (3) of rhenium, $M'_3[ReO_2(CN)_4]$, where M = K, Na, phenanthridine, or 2,2'-dipyridyl, are prepared in two ways, (1) H_2O_2 oxidation of M_2ReCl_6-KCN mixtures, or (2) N_2H_4 reduction of $MReO_4$-KCN mixtures. Hot, 4N hydrochloric acid converts the amine derivatives to acid salts, $M'_2H[ReO_2(CN)_4]$. These complex cyano compounds are very stable. In all of these compounds rhenium is pentavalent.

Oxyhalo salts: By treating $ReOCl_4$ in acid with potassium chloride K_2ReOCl_6 is obtained. Jezowska (4) prepared $M'_4[Re_2OCl_{10}]$ and $M'_2[ReCl_5OH]$ (M = K, NH_4, Rb, quinoline) by treating $HReO_4$ in 30% HCl with MI in a carbon dioxide atmosphere.

Halopentacarbonyls, pentacarbonyl, carbonyl hydride, and amine-substituted carbonyls: The rhenium halopentacarbonyls have been prepared by Hieber (5) in three ways, all involving high temperatures and pressures.

(1) Potassium hexahalorhenate (IV) in the presence of a halogen acceptor (Cu) is heated under high carbon monoxide pressure.

(2) Active rhenium plus a halogen donor (eg. $CuBr_2$) is heated under high carbon monoxide pressure.
(3) Potassium perrhenate plus a compound serving both as halogen donor and oxygen acceptor (like CCl_4) is heated under high carbon monoxide pressure.

Rhenium iodopentacarbonyl, $Re(CO)_5I$ is more easily prepared, less stable, and more covalent than the corresponding bromo and chloro compounds, and is readily converted to them by the action of bromine or chlorine at a temperature below 100°.

Rhenium pentacarbonyl, $[Re(CO)_5]_2$ was obtained (6) by heating Re_2O_7 with carbon monoxide under pressure. No oxycarbonyls were obtained if lower oxides were subjected to the same treatment. Rhenium pentacarbonyl is dimeric, differing from $Os(CO)_5$ and $Re(CO)_5X$ which are monomeric. A carbonyl hydride, probably $ReH(CO)_5$, was obtained but could not be purified.

Amine-substituted halocarbonyls and carbonyls were prepared by a high temperature sealed tube reaction (7). Pyridine and o-phenanthroline derivatives, $ReX(CO)_3py_2$, $Re(CO)_3py_2$, $ReX(CO)_3\ (C_{12}H_8N_2)$, and $Re(CO)_3(C_{12}H_8N_2)$ were obtained. However, ethylenediamine gave no reaction.

Ethylenediamine complexes: If K_2ReCl_6 is treated with a large excess of ethylenediamine, $[ReO_2en_2]Cl$ is produced (8). It is transformed into $[ReO(OH)en_2]Cl_2$ and $[Re(OH)_2en_2]Cl_3$ by successive treatments with hydrochloric acid. The corresponding iodides, chloroplatinates and cobaltinitrites are obtained by metatheses. These compounds comprise some of the very few instances of rhenium occurring in the cation.

D. Recent Investigations Concerning less Stable Oxidation States.

Tribalat (9) has recently demonstrated the existence of Re(V) in solution by following the reduction of perrhenic acid potentiometically. The +5 state is unstable in acid and disproportionates to +4 and +7.

Lingane (10) concludes from the polarographic oxidation of Re^{-1} that the oxidation proceeds $Re^{-1} \dashrightarrow Re^{+2} \dashrightarrow Re^{+3} \dashrightarrow Re^{+5} \dashrightarrow Re^{+7}$. He also notes that no +1 state is obtained upon heating Re^{-1} solutions, contrary to previous reports. He suggests that the electronic configuration of Re^{-1} is $5S^2\ 5p^6\ 6S^2\ 6p^6$.

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I.) $K_2ReI_6 + x's\ CO \xrightarrow[\substack{125^0 \\ \text{or } 200^0,\ Cu \\ 1\ atm.}]{\substack{200^0,\ \text{no } Cu \\ \text{or } 50\ atm}} Re(CO)_5I$

$K_2ReBr_6 + CO \xrightarrow[200-300^0]{10\ atm} Re(CO)_5Br$

$K_2ReCl_6 + CO \xrightarrow[30\ atm.]{230^0,\ Cu} Re(CO)_5Cl$

II.)

$Re + CuCl_2 + CO \xrightarrow[250^0]{210\ atm.} Re(CO)_5Cl + CuCl(CO)$

$Re + CuBr_2 + CO \xrightarrow{''} Re(CO)_5Br$

$Re + NiI_2 + CO \longrightarrow \underset{46\%}{Re(CO)_5I} + Ni(CO)_4$

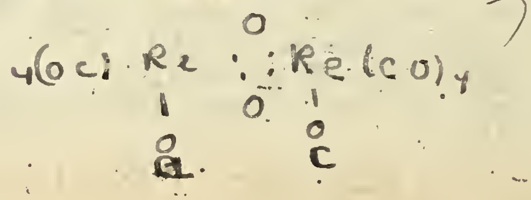
III. $KReO_4 + CCl_4 + CO \xrightarrow[230]{200\ atm} Re(CO)_5Cl + KCl + COCl_2 + CO_2$

CBr_4 or $CHBr_3 \longrightarrow Re(CO)_5Br$

$CHI_3 \xrightarrow[200^0]{} Re(CO)_5I$

IV. $Re_2O_7 + CO \xrightarrow[250^0;\ 16\ hr]{200\ atm} [Re(CO)_5]_2$

thus, according to ~~the~~ Hieber



NON-STOICHIOMETRIC COMPOUNDS

R. Keith Osterheld July 22, 1948

The distinction between solid solutions, interstitial compounds and non-stoichiometric compounds is rather arbitrary. Kurnakow (7) proposed the term "Berthollide compounds" to describe homogeneous solid phases for which the maxima or minima of properties (melting point, conductivity, lattice order, etc.) do not coincide with a rational atomic ratio of the components and which may exist over an appreciable composition range.

The Daltonian laws of constant and multiple proportions depend on either definitely directed electron-sharing bonds (true only of covalent molecules) or upon the necessary equality of positive and negative charges (which gives simple relationships only if all the ions of each sign are of the same kind and not of readily varied valence).

A stoichiometric excess of element B causing deviations of a crystal phase from an ideal formula AB_n can be due to one of three factors: 1) Substitutional solid solution, in which B atoms replace A atoms in A's lattice sites; 2) Interstitial solid solution, where additional B atoms are located in inter-lattice positions; and 3) Subtractive solid solution, in which all B atoms are in proper positions but a number of A lattice sites are vacant. The first of these, substitutional solid solution is likely to occur only in the case of intermetallic compounds where ionic repulsions do not preclude it. Cases two and three may be distinguished because two increases and three decreases the average weight per unit cell.

These departures from stoichiometry obviously involve a valence change. Excess metal may be incorporated into the lattice by effecively lowering the valence of the cations. This decrease is apparently possible for any metal since alkali halides, heated in the vapor of the corresponding metal, will take up as much as several atoms per thousand of excess metal (10). The presence of excess non-metal involves the raising of the valence of the cations or the lowering of valence of the anions.

If a compound is to be stable over an appreciable range of composition several conditions must be fulfilled (1): 1) The energy expenditure to produce lattice defects must not be large, 2) the energy difference between the two valence states must be small, and 3) the difference in size between the ions in the two valency states must be small so that the lattice is not distorted to the point where it will collapse. It is apparent that the heavier metals fill these requirements particularly well so it is not surprising that the marked variations from stoichiometric balance have been found with them.

<u>Detection of Non-Stoichiometry</u> Departures from stoichiometric balance may be detected in the more pronounced cases by ordinary chemical analysis. Much of the evidence for non-stoichiometric compounds comes from binary phase diagrams and from x-ray studies. Departures of a degree too small to be detected by these means may be indicated by the electronic semi-conducting properties they

induce in otherwise non-conducting crystals. Color changes such as zinc oxide, indium oxide, and ceric oxide undergo upon heating are associated with the reversible loss of oxygen from the crystal lattice and consequent non-stoichiometry.

Notation In recording non-stoichiometric phases most of the literature simply adjusts the subscript of the more negative element: FeS-$FeS_{1.14}$. For cases in which the cause of the stoichiometric departure is known there is a tendency to make the subscripts represent the true state of affairs. Here the cause is a certain deficiency and would be shown by: FeS-$Fe_{0.88}S$.

Examples of Non-Stoichiometric Compounds - Intermetallic Systems

In the thallium-bismuth system there is a melting point maximum at 62.8 atom percent bismuth with well-defined eutectic systems on each side of this maximum. An unlikely formula, Tl_3Bi_5, has been suggested which would lie close to this composition. However, there is a homogeneous region termed the γ-phase which exists over the composition range 55-64 atom percent bismuth. The electrical conductivity and the hardness have sharp maxima at 64 atom percent bismuth. It was to cover this example of a homogeneous phase of variable composition exhibiting characteristics of a compound that Kurnakow first proposed the term "Berthollide."

As would be expected, iron is a participant in a good number of the non-stoichiometric compounds described in the literature. The wüstite phase (FeO) in the iron-oxygen system has a range of composition ($FeO_{1.05}$-$FeO_{1.19}$) on the oxygen rich side of ferrous oxide. According to ordinary interpretation of the thermal diagram this would be considered as a solid solution of Fe_3O_4 in FeO. Jette and Foote (6) state that x-ray data do not show lines which would be expected from such a solid solution. They consider it to be a case of omission of iron from the lattice. A truer representation of the composition range would then be $Fe_{0.94}O$-$Fe_{0.84}O$. Insofar as these workers were able to determine, the homogeneous region does not include the actual chemical compound ferrous oxide (77.73 percent iron). All homogeneous samples prepared contained excess oxygen. Samples containing 77.69 or even 77.4 percent iron were found to be non-homogeneous, giving lines corresponding to metallic iron in the x-ray patters even after prolonged annealing. They believe that if ferrous oxide itself is stable it will only be above 1300°.

It has also been shown that in pyrrhotite, FeS-$FeS_{1.14}$; and ferrous selenide, $FeSe$-$FeSe_{1.15}$; the non stoichiometric condition is due to cation deficiency as the anion lattice is essentially complete (5,4). A pyrrhotite such as Fe_8S_9 would then be best formulated as $Fe_{0.89}S$. According to Phragmen (9) stoichiometric $FeSi_2$ is non-existent, the homogeneous phase in this system varying from 68.8 to 70.7 atom percent silicon. The maximum occurs at about 69.8 atom percent silicon. At this point there is a 10 percent deficiency of cations.

Various Oxides The semi-conducting properties of cuprous oxide depend upon a small excess of oxygen (11). At high temperatures

this excess is present in equilibrium with the gaseous phase. The composition of cuprous oxide in equilibrium with 0.7 mm and 33 mm. of oxygen at 1000° was reported to be $Cu_2O_{1.00052}$ and $Cu_2O_{1.00114}$ respectively. The conductivity was found to decrease as the oxygen pressure was decreased (as the stoichiometric excess of oxygen was decreased).

A number of non-stoichiometric tungsten oxide phases appear to exist: WO_3-$WO_{2.95}$, $WO_{2.92}$-$WO_{2.88}$, $WO_{2.75}$-$WO_{2.65}$, and $WO_{2.05}$-$WO_{2.00}$. The tungsten bronzes Na_xWO_3 may have compositions ranging from x=0.95-0.30. Apparently the stoichiometric compound (x=1) does not exist. Molybdenum oxides have been reported to have the homogeneous phases: $MoO_{2.92}$-$MoO_{2.85}$ and $MoO_{2.85}$-$MoO_{2.72}$ Oxides of titanium, vanadium, columbium, chromium, uranium, manganese, cobalt, nickel, zinc, and lead have been reported as existing in non-stoichiometric phases.

Cuprous Iodide At room temperature cuprous iodide will absorb iodine up to a composition of $CuI_{1.0045}$. Maurer (8) has shown that at 132° the concentration of absorbed iodine varies as the square root of the pressure of iodine vapor in equilibrium with the sample while the electronic conductivity varies approximately as the 4/3 power of the concentration of the absorbed iodine.

Non-Stoichiometric Compounds in Solid Phase Reactions The rate of reaction between solids will be determined by the rate of transport of the reactants through the reaction product if the formation of the new compound on the surface of the reactants is fast enough. The rate then is connected with the mobility of ions and electrons in the reaction product. The semi-conducting property of the reaction product is an indication of this mobility.

Under reducing conditions both aluminum oxide and magnesium oxide become semi-conductors, losing oxygen and leaving excess metal behind. Castell, Dilnot, and Warrington (2) claim to have shown that this is also true of spinel ($MgAl_2O_4$) and that consequently heating magnesium oxide and aluminum oxide together under reducing conditions favors the diffusion of reactants through the product, increasing the rate of reaction. In other reactions, such as the tarnish of metals, stoichiometric variations provide a composition gradient through the layer of reaction product. This facilitates the migration of metal to the solid-gas interface.

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ELECTRONEGATIVITY AND THE ABILITY TO CHAIN

George R. Coraor July 29, 1948

Although the study of hydrides and certain organometallic compounds has yielded considerable information about chain compounds, the phenomenon of chaining itself has received little attention from modern investigators. Few attempts have been made to determine or account for the relative ability of the elements in groups 3B through 7B to form chains. The chains in question are those in which the element bonds with itself in a manner somewhat analogous to carbon bonding in the hydrocarbons.

There is no absolute standard for determing the relative ability of elements to chain. If the hydrides alone are considered the following difficulty is encountered. The ionic character of the H-E (hydrogen to "element") bond varies considerably in the range of elements studied. An Si-H bond, for example, is only about 4% ionic with H at the negative end of the dipole. A P-H bond is a "normal" covalent bond possessing no ionic character; whereas a N-H bond is roughly 20% ionic with H at the positive end of the dipole. (1) That the character of these bonds would affect the nature of the adjacent E-E bonds and consequently the ability of E to chain will become apparent later in the discussion. If the largest known chain compound of the element is considered, other factors such as the added resonance of attached groups makes such a criterion equally unreliable.

A further consideration should be mentioned. All elements have not received the same amount of attention in fields which yield the types of compounds in which we are interested. The chain compounds of silicon, for example, have been investigated far more exhaustively than those of selenium. Silicon, because of its position directly below carbon in group 4, has been compared with carbon whereas selenium has been examined as an element which will form many organometallic compounds analogous to those of oxygen and sulfur.

Table I lists the largest known hydride and the largest known chain of each element with the elements' covalent bond radii and electronegativities.

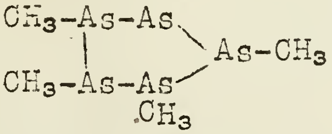
Table I (2)

	B	C	N	O	F
Hydrides	10		5	2	1
All Cpds.	10		5	3	2
Covalent radius (A)	.88	.77	.70	.66	.64
Electronegativity (x)	2.0	2.5	3.0	3.5	4.0
	Al	Si	P	S	Cl
Hydrides	1	6	12?(2or5)	2	1
All Cpds.	1	6	12? "	11	2
Covalent radius		1.17	1.10	1.04	.99
electronegativity (x)	1.5	1.8	2.1	2.5	3.0
		Ge	As	Se	Br
Hydrides		3	2	1	1
All Cpds.		3	5	2	2 or 3
Covalent radius		1.22	1.21	1.17	1.14
Electronegativity (x)		1.7	2.0	2.4	2.8
		Sn	Sb	Te	I
Hydrides		1	1	1	1
All Cpds		5	2	2 or 5	8 or 9
Covalent radius		1.40	1.41	1.37	1.33
Electronegativity (x)		1.7	1.8	2.1	2.5
		Pb	Bi	Po	
Hydrides		1	1	?	
All Cpds.		2	2	?	

The structures of the boron hydrides are still in question; however, the structures favored at present contain B-B bonds, not hydrogen bridges as were previously proposed. (3) Aluminum shows no tendency to chain.

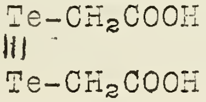
Carbon, of course, chains most extensively. Silicon forms stable hydrides through Si_3; however, the higher silanes through Si_6, the largest, are increasingly unstable. (4) Organic derivatives through Si_4 have been isolated plus several polymers of undetermined length with the formula $(\text{Ø}_2Si)_n$. (5) Germanes through Ge_3 have been prepared. (6). Kraüs and coworkers have reported such organotin compounds as: $(CH_3)_3Sn\left[Sn(CH_3)_2\right]_nSn(CH_3)_3$ where n is 2 or 3. (7)

A few aromatic derivatives of the hypothetical hydronitrogens triazane, NH_2NHNH_2, and tetrazane, $NH_2NHNHNH_2$ exist and more numerous triazenes and tetrazenes, the corresponding unsaturated compounds are described. Besides PH_2PH_2, there have been mentioned in the literature a P_5H_5 and a $P_{12}H_5$ (8) Several arsenic compounds such as HOOC-CH_2-As:As-As:As-CH_2-COOH and

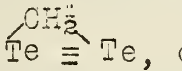


have received attention. (9) $(CH_3)_2Sb-Sb(CH_3)_2$ and the tetraamyl derivative are the only antimony compounds described except for the stibeno compounds which are analogous to the azo compounds. (10) Paneth and Lolert report a bismuth compound, $(CH_3)_2Bi-Br(CH_3)_2$. (11).

Ozone represents the limit of oxygen chaining. Sulfur, however, chains very readily. Numerous organic polysulfides have been isolated and identified as definite compounds. (12) Selenium has received less attention, but several compounds of the general type R-Se-Se-R where R is either aromatic or aliphatic are known. (13) Tellurium forms several ditellurides such as



$$\begin{array}{l}Te-CH_2COOH\\ \quad\equiv\\ Te-CH_2COOH\end{array}$$

ditelluroacetic acid, and  ditelluromethane. The following reaction has also been briefly mentioned:

$$CH_3I + Te \dashrightarrow I_2Te(CHI)_2 \dashrightarrow Te(CHI)_2 + ICH_2\left[\begin{array}{l}I\\Te\\CH_2I\end{array}\right]_5 CH_2I \quad (14)$$

No polonium chain compounds are known.

The halogens as a group would not be expected to chain because of their electronic structures. The existance of the polyhalides, however, indicates that chaining possibly does take place. Iodine is by far the most extensive polyhalide former. Only the triiodide ion has been studied crystallographically. It has been shown to be linear. (15) I_4^-, I_5^-, I_7^- and I_9^- have been reported. (16) Evidence indicates that CsI_4 probably is actually Cs_2I_8. A structure has been suggested by Hubard. $Cs^+ (I_3-I_2-I_3) Cs^+$. (17)

It is evident that elements with x values equal to 2.5 (C,S, and I) chain exceedingly well in relation to those around them in the periodic table. This observation invites the suggestion that all "Normal" covalent bonds are not identical in nature. Inasmuch as an electronegativity value is a measure of the attraction of the atom for additional electrons when the valence requirements of the element are satisfied, it is a measure of: a) the tendency to attract the bonding electron pair causing the bond (with an element of lower x) to be polar; and b) the tendency to attract, distort and in small part neutralize the other electrons which are outermost in the adjacent bonded atom. (the valence shell). In the case where a highly electronegative atom is bonded to a second atom of the same species, the following situation exists. The

electrons of both atoms are highly concentrated in the direction of the bond. That is to say, the electron density of one atom in the direction of the second bonded atom is far greater than the density in any other direction. The "Scarcity" of electrons in the other directions prevents or impedes further bonding with another atom of the same element. This accounts in part for fluoriness inability to chain, oxygen's best attempt, a very unstable O_3 and nitrogen's reluctance as typified by the unstable derivatives of tetrazane and its maximum multiple bond chain of N_4.

For elements with x values less than 2.5 the tendency is in the following direction. The atom has less tendency to attract additional electrons. In fact, the atom is beginning to lose the ability to hold its own valence electrons in their formally assigned orbitals. In short, it is approaching the metallic state in which the electrons are loosely held. In an extreme case, with electrons quite free, bonding becomes indistinct and the situation can best be explained by saying that the energy of the system is reduced by the electrons' being free in the lattice in the same way that the energy of a system consisting of a charge on a small sphere is reduced when that charge is allowed to pass to a larger sphere. It is possibly this tendency which complicates the problem of determining the structure of decaborane. More generally, the lack of attraction for electrons renders normal covalent bonding a relatively poor way to reduce the energy of the system. Consequently, the length of the chains decreases as the electronegativity drops below 2.5.

Other factors undoubtedly are involved. Although no other set of values corresponds as closely to the ability to chain as do the x values, it can be shown that covalent bond radii can be used as a supplement to electronegativity to explain such cases as that of Sn and Ge which have the same electronegativity but one, Ge, chains more readily than the other. Electronegativities being equal, the smaller element will chain more extensively if x is below 2.5 and the larger if x is above 2.5. The ability to bond through specific orbitals is the criterion on which such an argument must be based.

A more important consideration is electronic configuration. Carbon forms tetrahedral, sp^3 bonds as proved by the bond angles. In such compounds as NH_3 and H_2S, however, bond angles are smaller, approaching the 90° of pure p bonds. Inasmuch as bonds are considerably weaker than sp^3 hybrid bonds, chaining would be less likely to occur. In the case of the halogens, of course, d orbitals must be used to house electrons supposedly donated from the p orbitals of the neighboring atoms.

Finally, thermodynamic considerations can not be neglected. The most obvious case is that of nitrogen. The exceptional energy of the N-N triple bond, 225 Kcal/Mole at 0°K., makes other relatively less exothermic compounds unstable. An N-N single bond would be included in this category. (N-N single bond energy 37Kcal./Mole) (18)

In conclusion it may be said: (a) only with considerably more research can the relative ability to chain be precisely determined (b) from data now available it appears that the deviation of electronegativity from 2.5 bears a logical inverse relationship with the ability to chain (c). Other factors involved in decreasing order of importance are thermodynamic considerations, electronic configuration and the length of the element's covalent bond radius.

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CHEMICAL MINEROLOGY OF ROCKS AND MINERALS

A. G. Buyers July 29, 1948

1. CLASSIFICATION OF COMMON MINERALS

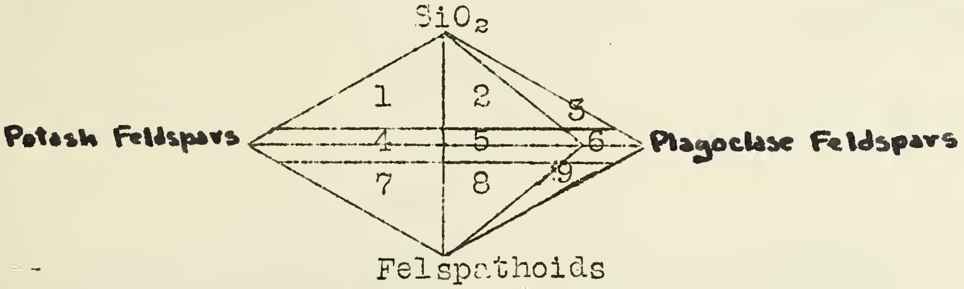
- a. Silica group
- b. Feldspars
  - 1. Potash feldspars
  - 2. Plagoclaise feldspars-calcic to sodic (continuous series)
- c. Felspathoids
- d. Pyroxene
- e. Amphibole
- f. Olivine
- g. Mica
- h. Accessory
- i. Other common minerals

2. CLASSIFICATION OF COMMON ROCKS

a. Igneous rocks formed from a moltent mass, composed of glassy or crystalline material depending upon composition and cooling conditions of the original moltent body.

Plutonic rocks formed at great depths

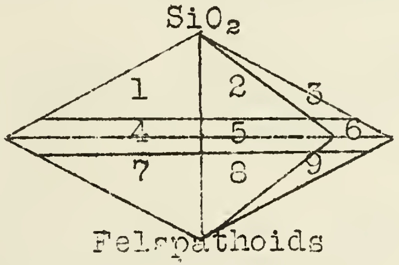
An_0 -- An_{50}
1 Granite
2 Granodiorite
3 Quartz Diorite
4 Syenite
5 Monzonite
6 Diorite
7 Nepheline Syenite
8 Nepheline Monzonite
9 Nepheline Diorite



An_{50} -- An_{100} More than 5% quartz--Quartz Gabbro
Less than 5% quartz
and felspathoids -- Gabbro

Volcanic rocks formed at the surface

An_0 -- An_{50}
1 Rhyolite
2 Quartz Latite
3 Dacite
4 Trachyte
5 Latite
6 Andesite
7 Phonolite
8 ---------
9 Nepheline Andesite



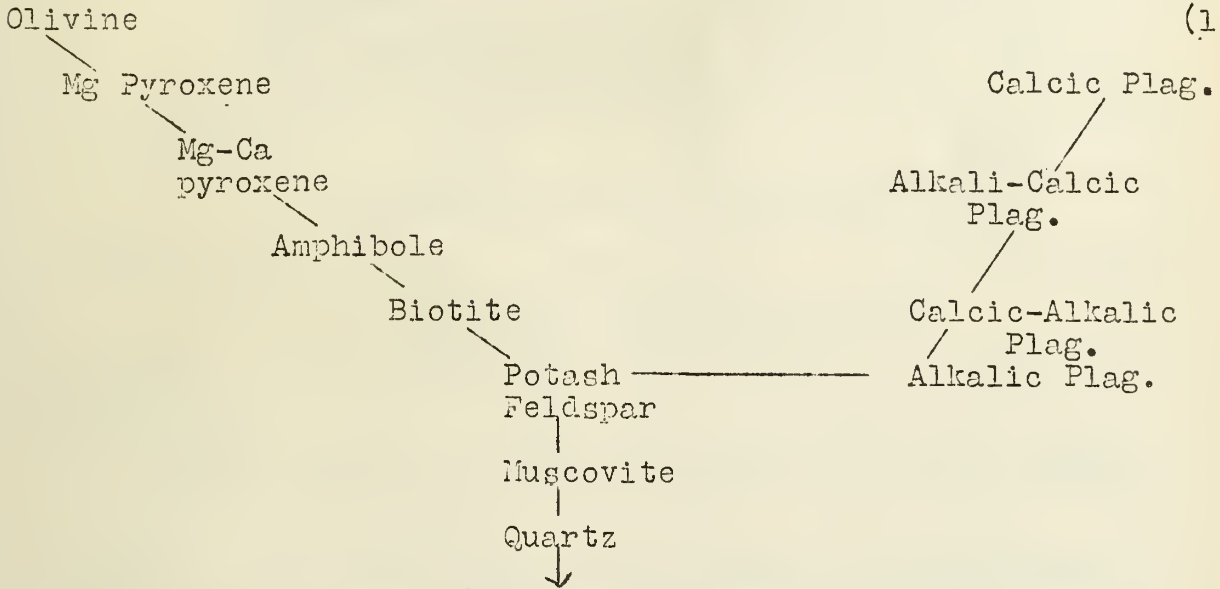
An_{50} -- An_{100} More than 5% quartz - Quartz Basalt
Less than 5% quartz
and or felspathoids - Basalt

Hyperbyssal rocks or dike rocks- formed at more or less intermediate depths between plutonic and volcanic rocks.

Plag. Feld An_0 -- An_{50}	Feldspar	Quartz>5%	Quartz < 5% Felsp. < 5%	Nepheline
	Potash Feld > 50% Feldspar	Granite Quartz-Bostonite Quartz-Monzonite	Syenite Bostonite Minette (bi) Vogesite (hbd)	Nepheline-Syenite Nepheline-Minette

Potash Feld 5-50% of Feldspar	Granodiorite	Monzonite
Potash Feld <5% of Feldspar	Quartz-diorite Malachite	Diorite Kersantite
An_{50} =- An_{100}		Gabbro Beerbachite
No Feldspar		Peridotite Pyroxenite (Ultra basic)

3. ORDER OF MINERAL CRYSTALIZATION IN THE FORMATION OF IGNEOUS ROCKS (1)



Zoning in plagoclaise feldspar
Reactionrims of pyroxene surrounding cores of olivine

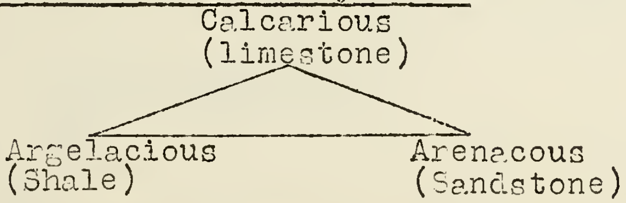
b. SEDIMENTARY rocks

Origin and formation processes

These rocks are the product of weathering of older formations and seldom result from direct formation. Older rocks are broken down mechanically or chemically by air, water and the organic and inorganic acids present in the earth. The processes involved in the chemical decomposition of older rock formations are:

1. Solution - affecting primarily feldspars and mafics(basic)
2. Oxidation - affecting primarily iron constituents, i.e., hematite and limonite
3. Hydration - olivine, biotite and hornblende, feldspars affected most
4. Carbonation-alkalis, lime and magnesium constituents are the most affected

Classification of sedimentary rocks



Cements - calcarious, silicous, ferruginous

c. METAMORPHIC rocks

Regional extensive area and deformation of the earths crust (oragenic belts)

1. Gradés of regional metamorphism
   LOW - fine grained
   conditions- low temperature, low press, high shearing stress (mechanical processes predominant)
   characteristic minerals- sericite, chlorite, talc, epidote, albite.
   MED- medium grain size
   conditions-intermediate temperature, press, less shearing stress(mechanical and chemical i.e., recrystalization)
   characteristic minerals - muscovite, biotite garnet, staurolite, kyanite, hornblende, oligoclase, andescine
   HIGH- coarse grained
   conditions- high temp., high press, low shearing stress(chemical recrystalization dominant)
   characteristic minerals- sillimanite, pyroxene, micas, biotite and garnet.
2. Typical changes in the metamorphism of an argellaceous sediment.

	LOW	MED	HIGH
Hyd Al sil --->	sericite --->	muscovite--->	microcline+Al_2O_3
	chlorite --->	biotite --->	garnet
rutile ----->	rutile (req xs) (Al_2O_3)	garnet staurolite kyanite	sillimanite
organic material	----------->	------------>	graphite
iron oxides	----------->	------------>	magnetite

3. Typical changes in the metamorphism of an acid igneous rock

quartz ------>	quartz------>	quartz ------>	quartz
potash feldspar ------>	sericite----->	muscovite----->	microcline Al_2O_3
plagoclase feldspar--->	albite------>	oligoclase--->	plagoclase feldspar
biotite------>	chlorite---->	biotite------>	microcline biotite

Contact Metamorphic rocks

Types of contact metamorphism
1. Thermal - heat is the principle factor in bringing about the metamorphic changes
2. Hydrothermal - hot solutions are primarily responsible for the metamorphic changes
3. Ultra metamorphism - complete recrystalization country rock heated

Typical changes due to contact metamorphism are: sandstone recyrstalized yields quartzite, impure sandstone recrystalized yields granulite, hornfels (flint and mica), shale recrystalized yields hornfels and spotted slate and chloratoid, limestone recrystalized yields marble, impure limstone recrystalized yields calcium, aluminum and calcium, magnesium silicates, Wollastonite and garnet.

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THE TERNARY SYSTEM N_2H_4-H_2O-NaOH

P. H. Mohr August 3, 1948

Until recent years hydrazine has been considered mainly a chemical curiousity of little commercial value. However, its use as a jet propulsion fuel directed attention to its unusual chemical and physical properties. Hydrazine is one of the simpler hydronitrogens. It is somewhat unstable and difficult to prepare, but its organic derivatives can be prepared more easily. Accordingly, alkyl and aryl hydrazines were prepared and studied before the parent compound. (1)

While many methods have been suggested for the synthesis of hydrazine (2) (3) only the Raschig method (4) (5) involving oxidation of ammonia by hypochlorite has been adapted technically. The overall reaction may be represented as follows:

$$NaOCl + 2NH_3 \longrightarrow N_2H_4 + NaCl + H_2O$$

It proceeds in a stepwise fashion in accordance with equations:

1) $NaOCl + 2NH_3 \longrightarrow NH_2Cl + NaOH$
2) $NH_2Cl + NH_3 + NaOH \longrightarrow NaCl + N_2H_4 + H_2O$

An undesirable side reaction appreciably diminishes the yield:

3) $2NH_2Cl + N_2H_4 \longrightarrow 2NH_4Cl + N_2$

According to German procedures, as developed during World War II (6) (7), good yields are obtained if a solution of chloramine is heated with an excess of ammonia under pressure at temperatures of 150-300°C and if the process is carried out as rapidly as possible. The yield is usually 70-75% (based on the active chlorine) and the product is a solution containing approximately 3% hydrazine hydrate. This crude hydrazine hydrate solution also contains 10-11% sodium chloride and some sodium hydroxide. These materials are removed in a salt evaporator from which the dilute hydrazine hydrate vapors are passed through a fractionating column. Two additional fractionations, the latter under nitrogen, yield 40-50% and 85-90% $N_2H_4.H_2O$, respectively.

The 85-90% $N_2H_4.H_2O$ made by this process has generally been the starting material for the manufacture of the anhydrous base. Long refluxing with dehydrating reagents such as potassium hydroxide, (8), sodium hydroxide (9) (10), calcium oxide (11), and barium oxide (12)(13)(10)(14) has usually been recommended, followed by distillation in an inert atmosphere or under vacuum. Sodium hydroxide appears to be the best dehydrating agent. Calcium oxide and barium hydroxide form heterogeneous systems which result in poor heat transfer and entrapment. Potassium hydroxide and sodium hydroxide do not suffer from this disadvantage. However, sodium hydroxide has the advantage of forming a hydrate of lower vapor pressure than potassium hydroxide. Penneman (15) has made an extensive and successful investigation of a process for the preparation of anhydrous hydrazine involving fractional distillation under reduced pressure from a hydrazine hydrate - sodium hydroxide mixture. Concentrations up to 99.9% N_2H_4 have been achieved by this method.

The Ternary System N_2H_4 - H_2O - NaOH

The melting points of $NaOH.H_2O$ and N_2H_4 are 64.3° (16) and 2.0°C (17), respectively. It is conceivable that solid sodium hydroxide monohydrate might precipitate from a solution containing hydrazine hydrate and sodium hydroxide. Such a phenomenon was observed by Penneman (15). Above 64.3°C two liquid phases are formed, while below this temperature a solid phase ($NaOH.H_2O$) separates out. The upper liquid phase was found to be rich in hydrazine, and the value of this finding was at once apparent and subsequently led to the investigation of the ternary system N_2H_4 - H_2O - NaOH.

It is not unexpected that hydrazine might be salted out of water by sodium hydroxide, since the same phenomenon is exibited by the simple organic diamine ethylenediamine ($NH_2CH_2CH_2NH_2$) (18) and also by ammonia (above atmospheric pressure) (19).

The system N_2H_4 - H_2O - NaOH was studied at 50, 60, 70, 90, and 100°C. to determine the area of limited miscibility and the phase relationships which characterize varying mixtures of the three components at these temperatures. At temperatures above 60°C. this ternary system exhibits two liquid phases within certain concentration ranges. At 50°C a simple solubility curve is observed with $NaOH.H_2O$ in equilibrium with a saturated solution containing hydrazine, water, and sodium hydroxide.

Since the pressure was held constant in these experiments, the use of triangular coordinates allowed the representation of all three components in one plane while the temperature may be represented by the third dimension. Such a representation shows that there is little change in the limiting compositions of the conjugate liquid phases between 70 and 100°C. At 60°C, however, the area of limited miscibility is considerably smaller. Furthermore, the crystalline phase $NaOH.H_2O$ is obtained under certain conditions at this temperature, whereas at higher temperatures, anhydrous sodium hydroxide appears as the solid stable phase.

One very important practical application resulting from this work is found in the fact that a hydrazine rich material can be separated from a dilute hydrazine solution by the addition of sodium hydroxide.

It was hoped that other dehydrating agents might also exhibit this two phase phenomenon. Negative results were obtained using potassium hydroxide, potassium carbonate and sodium sulfate over a temperature range of 25 - 100°C.

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RADIOACTIVE TIME CLOCK

P. A. Zimmerman August 5, 1948

The radioactive time clock method of determing geologic ages, as developed from Boltwood's original concept (1915), depends on the systematic generation of lead isotope end products and of helium as a by-product of the parent radioactive elements. Other radioactive degeneration processes have also been used. All methods agree in determining geologic time by the fundamental equation:

$$\text{Age} = \frac{\text{Amount of disintegration product}}{\text{Rate of production of product}}$$

Fundamental Assumptions:

1. All isotopes of all atoms were created with their existing abundance ratios except the radioactive isotopes whose relative ratio to each other or to a stable isotope has changed only because of radioactive decay.
2. The disintegration constants of the radioactive elements have never varied from their present values.
3. The mineral examined is of homogeneous character and has neither lost nor gained any atoms of any series since its formation.
4. Amounts of UI, AcU, Th, Pb, He, etc. are present in quantities large enough to be determined accurately by analysis.
5. The isotopic ratios of the lead or any other end product of a series can be determined accurately and a correction made for any common lead or corresponding material which is non-radiogenic
6. Non-radiogenic lead, non-radiogenic strontium etc. today have a constant isotopic composition.

Radioactive Process of Use in Estimating Geologic Time:

1. Lead methods: The generation of RaG, AcD, and ThD, by UI, AcU, Th.
2. Helium method: The generation of 8,7,6 atoms of Helium by UI, AcU, Th.
3. Strontium method: Generation of ^{87}Sr by ^{87}Rb
4. Potassium methods: Generation of ^{40}Ca by ^{40}K, generation of A by ^{40}K This method is impractical.

The Lead Method:

In setting up equations for computing "t", the age of the mineral, the time required for the disintegration of the intermediate members of the radioactive families is neglected, since they have comparatively short half lives. (33)

Basic Equations: (3)

$$(1)\quad N(Pb^{206}) = N(RaG) = N(UI)(EXP[\lambda(UI)t] -1)$$
$$(2)\quad N(Pb^{207}) = N(AcD) = N(AcU)(EXP[\lambda(AcU)t] -1)$$
$$(3)\quad N(Pb^{208}) = N(ThD) = N(Th)EXP[\lambda(Th)t] -1)$$

Equation (2) is applied indirectly by dividing (2) by (1) to give

$$(4)\quad \frac{AcD}{RaG} = \frac{N(AcU)}{N(UI)} \cdot \frac{EXP[\lambda(AcU)t] -1}{EXP[\lambda(UI)t] -1}$$

(AcU) is not known directly, and is evaluated by the equation:

(5) $R = \lambda(AcU)N(AcU) / \lambda(UI)N(UI)$ where R is the present-day ratio of the actinium and uranium series. Since $\frac{N(UI)}{N(AcU)}$ has been shown by Nier to be 139.0, eq. (4) becomes:

$$(6)\quad \frac{AcD}{RaG} = \frac{1}{139} \cdot \frac{EXP[139 R\lambda(UI)t] -1}{EXP[\lambda(UI)t] -1} \qquad (33)$$

Difficulties Encountered in Using the Lead Method:

1. Alteration of Minerals: Goodman and Evans indicate that alteration is to be expected in view of the continual bombardment of the mineral and its surroundings by high energy particles and of the atomic and molecular rearrangements necessitated from the finite recoil of the active atoms with each disintegration. The resulting heating effect and internal pressure of helium together effect the

[illegible] active atoms [illegible]

[illegible] different [illegible]

[illegible] (5) [illegible]

development of stresses sufficient to cause fractures throughout the mineral in a relatively short time. (8) This exposes the members of the radioactive series to oxidation, leaching, etc. Hahn states that unaltered throium minerals are practically unknown. (11) Mattauch judges that of the many lead determinations made in America at the most 8 are free from objectionable features. (32) Goodman and Evans concur in this. (8).

3. Correction for "common lead." Since Nier's determination of lead isotope ratios by the mass spectrograph this problem has been reduced to determining what values to use for the composition of common lead. Nier has shown that although atomic weight determinations for common lead vary less than 0.02%, the isotopic composition may vary considerably. Thus for two samples of non-radiogenic lead he obtained the values: (29)

	Isotopes	204	206	207	208
Percent in sample	1	1.48	23.59	22.64	52.29
	7	1.26	27.31	20.00	51.43

The Alpha-Helium Method:
Despite inherent difficulties, this method has appealed to many investigators because of its applicability to a much greater variety of geological materials than the lead method. In these minerals it is merely necessary to measure their alpha activity, estimate the amount of uranium and thorium present from that, and extract the helium from the mineral in a high temperature vacuum furnace.

Basic Equations: (6)

$$(7)\quad t_o = 30.7\,\frac{He}{(8\,N_{U^1} + 7\,N_{A^1} + 6\,N_{T^1}}$$

where t_o equals the approximate age of the specimen in 10^9 years; N_{U_1} N_{A^1} and N_{T^1} represent the rate of production of alpha rays per 10^9 years per gram of source. "He" represents the total helium per gram of specimen. (8)

$$\frac{t_o}{t} = 1 + t\,(0.0249 + 0.0675F) + t^2\,(0.000414 + 0.00952\,F) + t^3\,(0.00166F) + t^4\,(0.000302F) + \dots$$

where "t" equals the "true age" of the specimen in 10^9 years and "F" is the fraction of the total alpha rays produced in the source due to UI and AcU.

Difficulties: Ordinarily it is impossible to check helium age determinations directly with lead, since the two methods apply essentially to different type minerals. But whenever it is possible to check indirectly, it is usually found that helium ages are lower than lead ages. It has been postulated that this is due to the loss of helium from the mineral. Keevil (20) has shown that the helium indexes are not consistent in this variation from the lead index. A survey of 150 helium determinations has shown that there is only a one to one chance of finding the age of a basic rock within one geological period, a still smaller chance of determining the age of a granite rock, and that the results obtained from porphyries and lavas are meaningless from the point of view of age. It is extremely interesting that some minerals have been reported as having excess helium. Keevil reports 14 such instances. Urry (30) reports other instances, while two Russians report further cases. (21) These latter indicate the most probably source of the excess as either the absorption by the mineral during crystallization of considerable amounts of shortlived radioactive elements or the selective occlusion of helium from that left in the magma. The first supposition will cause one to wonder how much doubt this possibility may throw on all age determinations based on radioactivity.

Rubidium-Strontium Method.

Within the last decade Hahn and Mattauch in particular have advocated the estimation of geologic ages by calculations based

on the radioactive decay process ^{87}Rb ------ ^{87}Sr. The simplicity of the transformation makes possible the calculation of the age of the mineral by the simple equation: (8) $t = \frac{1}{\lambda} \cdot \frac{N^1}{N}$ where "t" is the age, "N" is the number of ^{87}Rb atoms present at the time of the analysis, "Ni" is the number of ^{87}Sr atoms present in excess of those due to the presence of non-radiogenic strontium, and lambda is the disintegration constant of ^{87}Rb.

Speaking also for this method is the fact that the rather slight quantities of rubidium in minerals, and the fact that no gas is released means that one may expect to find these rocks less altered than uranium and thorium rocks. However, the rather small rubidium content renders analysis more difficult. Further, rubidium-bearing minerals are much less common than minerals suitable for lead age and helium age determinations. Another difficulty lies in the lack of precise knowledge of the half-life period of ^{87}R

What Does the Clock Say?

Goodman and Evans present the table of radioactive time scales given below. Although it selects the best results from each method and elminates much dissenting data, it is obvious that the various methods do not give concordant results. Further, there is a lack of consistency within a given column. Cf. circled ages. Again, the estimate of Holmes (14) of 3.35 x 10^9 years for the age of the earth on the basis of these data compares oddly with the 3 x 10^9 years set as the age of the solar system by Chrandrasekhar, Jeans, and other notable astronomers. Moreover, more emphasis should be placed on the possibility that the liquors from which crystallization took place may have contained not only uranium and thorium, but also considerable quantities of short-lived members of the various series. If such were the case, the earth may not be as ole as these calculations may cause it to appear. Further, one may speculate whether the tremendous forces attendant on the birth of the earth may not have effected a change in the now extremely stable decay constants of the longer-lived radioactive elements.

RADIOACTIVE TIME SCALES(8)
in millions of years

Helium Acidic Rocks	Helium Basic Rocks	Geol.Era	Lead Ratios	Lead Isotope Ratios	Helium A Rocks	Helium B Rocks	Geol.Era	Lead Ratios	Lead Isotope Ratios
5	5	Tertiary			60		Devonian		
8	5				88	54		269	
22	9				100	81		278	
	11				109	160	------		
	17						Silurian		
	22						-------		
			34				Ordovacian	349	300
	37							366	
	36	---------					-------	371	
	58	Cretaceous	70		150	190	Cambrian	400	770
		---------			280	290			
					195	250		580-995	610-665
		Jurassic	123		250	500	-------	531	485
		---------					Pre-Cambrian		
	57	Triassic				600		765	825
		---------						803	595
		Permian	220	140		860		882	905
		---------				1050		900	
45	196	Carboniferous	232					1085	1090
66						1830		1077	1035
72	83							1251	1420
								1500	
	105	---------						1570	2200
								1850	

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THE COORDINATION NUMBER EIGHT

Theodore H. Dexter

August 5, 1948

While the majority of known inorganic complex compounds exhibit coordination numbers of four or six, there is a group of compounds in which the coordination number appears to be eight. Examples of these compounds have been reported in which the central atom is Ca, Sr, Ba, Ce, Zr, Hf, Th, Ta, Cr, Mo, W, U, Ru, Os, Sn, Pb, and Po (8).

Conclusive evidence for eight coordination in the form of conductivity data (15), chemical reactions (1), and X-ray measurements (4) has been reported for $Mo(CN)_8^{-4}$. The eight cyanide radicals are located at the eight points of a dodecahedron with triangular faces. Since all of the cyanide radicals are equidistant from the central molybdenum atom, four of the intercarbon distances are longer that the remaining fourteen.

The compound $Sr(OH)_2.8H_2O$ has been shown by X-ray data to crystallize in the tetragonal system, the strontium atom being surrounded symmetrically by the eight water molecules (10).

By fractional crystallization of the strychnine salt, tetra-strychnine tetra-oxalato-uranium-IV, Marchi and McReynolds (9) resolved $K_4[U(C_2O_4)_4].5H_2O$ into four optically active isomers. According to present theories of optical activity, this resolution implies an asymmetrical structure for the tetra-oxalato-uranium-IV ion. Therefore highly symmetrical structures such as the arrangement of the four oxalato chelate groups between adjacent vertices of a cube are eliminated for this compound. However, the method of isomer count does not distinguish among the arrangements which may give rise to optical isomers.

From the geometrical standpoint the orientation of ligands about an eight-coordinated central atom might be represented by any conceivable arrangement of eight points in the vicinity of a common center. However, by analogy to the majority of investigated coordination compounds, the eight points of coordination should tend to be nearly equidistant from the common center. Although similar groups should repel each other, there is evidence, even for coordination number eight (4), that the points of coordination do not necessarily lie equidistant from each nearest neighbor.

Examples of solid geometrical figures in which eight vertices are equidistant from the center are the (1) cube, (2) Archimedean antiprism, (3) dodecahedron with triangular faces and symmetry V_d, (4) hexagonal bipyramid, (5) trigonal prism with two extra vertices along the unique axis, (6) trigonal prism with two extra vertices located along normals to two rectangular faces and having symmetry C_{2v}.

Marchi et al. (6,7,8,9) have calculated the number of possible isomers for different combinations of monodentate and bidentate coordinating groups arranged in any of five different configurations about a central atom. Their results for the cube (C), Archimedean antiprism (A), dodecahedron (D), trigonal prism with two extra bonds along the unique axis (P), and trigonal prism with two extra bonds normal to two rectangular faces (T) are given in Table I for two different classes of compounds. Capital letters indicate ligand atoms in bidentate groups; small letters indicate ligand atoms of monodentate groups.

Table I

Class	Configuration	Optically Active	Optically Inactive	Total
abcdefgh	C	1680	0	1,680
	A	5040	0	5,040
	P	6720	0	6,720
	D	10080	0	10,080
	T	20160	0	20,160
4AA	C	0	2	2
	P	0	1	1
	A	6	0	6
	D	10	1	11
	T	10	1	11

Application of the theory of directed valence bonds (5) shows that the type of eight-coordination structure is dependent upon the available orbitals. Least common should be the cubic structure, which requires the use of f orbitals in the two possible configurations d^3fsp^3 and d^3f^4s. The antiprismatic and dodecahedral arrangements are stable for the configuration d^4sp^3 while the face-centered prismatic structure has the configuration d^5sp^2. Kimball (5) predicted the latter structure for OsF_8 and TaF_8^{-3}, but Hoard (3) reported the antiprism for TaF_8^{-3}. Penney and Anderson (12) originally proposed that Na_3TaF_8 was a lattice compound, $NaTaF_6.2NaF$, and not an example of eight coordination.

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PHOTOCHEMICAL DECOMPOSITION OF THE ALKALI AND SILVER HALIDES

Bodie Douglas August 10, 1948

I. HISTORICAL

The influence of light on the formation of the green color of plants was probably noted by Aristotle (384-321 B.C.). Vitruvius (30 B.C.) reported on the bleaching of pigments by light and the writings of the alchemists contain vague references to the action of light. Stephen Hales (1677-1721), who regarded light as a material substance, was probably the first to suggest the influence of light in plant nutrition.

The darkening of silver compounds was probably known as early as the thirteenth century, but J. H. Schulze in 1727 was the first to make a distinct statement concerning the darkening of a silver compound by the action of light.

The first generalizations on the chemical action of light were given by Grotthus in 1818. The most important of these generalizations is the photochemical absorption law, which states that only those rays which are absorbed are effective in producing photochemical changes. This and his other observations helped to correlate the information available and opened the way to many new researches concerning photochemical reactions.

II. THE ALKALI METAL HALIDES

In the solid state, where recombination is impaired, ultraviolet light causes permanent changes in the alkali halides. Rock salt crystals become yellow on exposure to ultraviolet light and the coloration of glass in desert sunlight is due to a similar cause.

The process of absorption can be pictured as bringing about the liberation of an electron from the halide ion. The electron is free to wander through the crystal until it comes to a hole surrounded by positive charges, into which it sinks. High energy photons are required to bring about the liberation of the electron, but once it occupies a "hole", it absorbs light in the blue region, giving a yellow color. The "electron in a hole" is referred to as an F center (Farbzentren).

F centers may also be produced by exposing the crystals to alkali vapors at high temperature and then suddenly quenching them (1), or by introducing electrons into a hot crystal from a pointed cathode (2). In the latter case, halogen is simultaneously ejected. The color produced by the alkali vapor can be discharged by heating in hydrogen. The resulting crystal shows new absorption bands believed to be due to alkali hydride dispersed in the crystal.

III. SILVER HALIDES

The emulsions employed for the preparation of photographic plates and films consist of a colloidal suspension of silver halide in gelatin. The change in the photographic emulsion on short illumination is invisible. This image, which can be intensified by suitable development, is called the latent image. The nature of the latent image has been the subject of much controversy and many theories have been proposed. In 1925, Koch and Vögler (3) showed that if silver bromide is exposed to light, its x-ray powder pattern shows lines characteristic of metallic silver. Moreover, if the exposed silver bromide is fixed with sodium thiosulfate, the remaining material shows only the silver lattice.

A. The Development Centers

Since prolonged exposure of silver bromide to light produces metallic silver and this occurs in the form of definite specks on the surface of the grain, it seems reasonable to assume that the latent image is of similar nature. The tiny specks are believed to consist of metallic silver, which is located in patches rather than disseminated through the mass of the crystal. A single grain which contains a development center is completely developable, and the effect of exposure in increasing the density must be due to an increase in the number of grains possessing development centers.

B. The Nature of Sensitivity Specks

It is well known that the developer acts on the grain at local points which represent discontinuities in the grain structure. Sheppard (4) discovered the presence of isothiocyanates in the photographic gelatin and showed that at low concentrations small specks are formed on silver halide crystals. Under alkaline conditions, these specks consist of silver sulfide, The use of gelatin free from sulfur compounds produced emulsions of very low sensitivity. Clark (5) showed that the sensitivity specks probably contain some free silver, because oxidizing agents not only destroyed the latent image, but also decreased the sensitivity somewhat.

C. The Function of the Sensitivity Specks

Some writers (6) claim that the function of the sensitivity specks is to facilitate, catalytically, the decomposition by litht. Sheppard and co-workers (7) disproved this and showed that the foreign nuclei do not affect: a) the relative spectral sensitivity, b) the number of quanta absorbed, or c) the number of silver atoms formed per quantum absorbed. These authors propose that once a speck is formed, it will grow, because in its immediate neighborhood the number of inelastic collisions and fruitful encounters will be relatively greater. These specks serve to "concentrate the silver atoms reduced by the light absorbed by silver bromide".

D. The Gurney-Mott Theory

Gurney and Mott (8) porposed a theory of the latent image process which consists of two parts: a) a primary process, in which electrons are released in the crystal and trapped by the

sensitivity specks; and b) a secondary process, in which there is an electrolytic migration of silver ions to the negatively charged sensitivity specks. The primary process is independent of the temperature, while the secondary process is highly dependent on temperature.

E. "F" Center Theory

Pohl (9) proposed a mechanism, similar to that for the coloration of alkali halides, for the formation of the latent image. The mean free path of the electron is much greater in silver halides (10) than in the alkali halides and there is a greater probability that the electron will reach a disturbed portion of the crystal where it may discharge a silver ion and form an atom.

Although the presence of flocculated particles of silver has been shown, the F centers may exist simultaneously with or prior to the formation of such particles. Tanmann and Bandel (11) found that, when the silver halide crystals are distorted _after_ exposure to light, ultramicroscopic examination shows that agglomerates of silver are formed in the places of the fracture. Lohle (12) indicates the improbability that such aggregates are formed by migration of atoms, for the size of the aggregates seems to be independent of the temperature at which they are formed or of the time between exposure and ultramicroscopic examination.

F. Solarization

If areas of a photographic plate are exposed to increasing amounts of light, the densities produced after development reach a maximum and then diminish somewhat. This is known as reversal or solarization. Prolonged exposure may produce re-reversal. Two main groups of theories have been proposed to explain solarization:

1. Liesegang (13) suggested that a layer of silver so surrounds the silver halide grain in the overexposure region that the developer is prevented from reaching it. The fact that the first reversal can be obtained after fixation by means of physical development is in disagreement with this theory. According to the gelatin-coagulation theory of Luther (14), the cause of the first reversal is a coagulation of a gelatin around the grain by the photochemically liberated halogen. It is difficult on the basis of his hypothesis to picture how a reversal of solarization by prolonged exposure is possible. Solarization also appears in the absence of gelatin.

2. The theories which ascribe solarization to a change in the latent image itself consider the effect to be due to a coagulation of the image or to a destruction of the image.

The coagulation effect is supposed to be due to the formation of more compact particles on long exposure with a lessening of their catalytic properties.

A more likely theory is that the effect is due to recombination of the halogen liberated with the silver of the latent image. For low exposures, the gelatin can absorb the amall amount of halogen liberated. With high exposures, high concentrations of halogen may result in the region surrounding the grain surface and the silver of the latent image may be attacked. This would form a layer of silver halide on the surface of the speck and render it inaccesible to the developer. Silver halide solvents destroy the protective layer and render the grains developable without a trace of solarization. Further evidence for this theory is that a delay or complete destruction of the solarization effect is produced by the addition of substances which readily accept halogens.

G. The Herschel Effect

If an emulsion which has been exposed to blue light is subsequently exposed to long-wave radiation before it is developed, some of the effect of the original exposure is erased. This is known as the Herschel effect and has been attributed to a dispersion or some other physical alteration of the latent image nuclei by the direct action of infrared light. Gurney and Mott (8) propose that the speck is broken up by the ejection of electrons from the silver nuclei as the result of the absorption of quanta of infrared light, followed by the loss of silver ions. The ions are supposed to be pushed after the electrons by the excess charge on the nuclei. This process continues to break up the original nuclei.

H. The Sabattier Effect

If a film which has been exposed, developed, and washed, but not fixed, is given a second uniform exposure and developed again, a reversal of the original image will be obtained. This effect was discovered by Sabattier (15) in 1950. It probably results partly from a physical screening effect of the first image and partly from a chemical desensitizing effect resulting from the first exposure and development.

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BASIC SALTS

J. R. Mills

August 12, 1948

I. Introduction

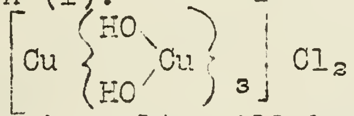
A discussion of the nature of basic salts may perhaps best be commenced by considering a few of the more familiar examples of such substances. Some of these are as follows.

1. "Trouble-makers" in analytical procedures
   - a. Formation of BiOCl, SbOCl
   - b. Formation of insoluble basic salts upon evaporation of solutions to remove solvents, excess acid, etc. Interference of Bi with Pb when precipitating as sulfate due to formation of $(BiO)_2SO_4$.
2. Useful basic salts
   - a. Basic acetate separation in qualitative analysis schemes when phosphate is present.
   - b. Separation of beryllium as basic acetate.
   - c. Many important and well-known minerals e.g. zeolites, asbestos, micas, talc, and many of the complex silicates and aluminates utilized in the ceramics industry are basic in nature.

II. Definition of the Term "Basic Salt"

Originally, basic salts were considered to be those substances which resulted when part of the hydroxyl groups or oxygen atoms of a polybasic hydroxide or oxide reacted with acid. In this way such basic salts as Cd(OH)Cl and BiOCl were formed. They were thus to be regarded as the opposite of acid salts such as $NaHCO_3$ and $CaHPO_4$.

More complex basic salts such as $CuCl_2 \cdot 3\,Cu(OH)_2$ could not be explained readily on this basis. Werner proposed that these salts contained complex cations in which molecules of the metal hydroxide were coordinated through the hydroxyl group to the metal ion (1).



$$\left[\mathrm{Cu}\left\{\begin{matrix}\mathrm{HO}\\ \mathrm{HO}\end{matrix}\right\}\mathrm{Cu}\Big)_3\right]\mathrm{Cl}_2$$

For our purposes, basic salts will be defined as "salts in which the proportion of base to acid is greater than in the normal salts."

III. The Composition and Structure of Basic Salts

1. General considerations: The relative insolubility of most basic salts renders the study of their composition by phase-rule methods rather difficult. X-ray examination has been of great value in sorting out the various basic salts in impure mixtures. The application of X-ray diffraction methods to the determination of the structures of these substances has resulted in many significant advances in our understanding of this group of compounds.

In order to better understand the structural considerations which are deal with below, the following facts and concepts should be kept in mind.

- a. The interatomic distance in a covalent link is longer than that of an ionic link for the same pair of elements, and the covalent linkage is directed. For these reasons a crystal formed by covalent links has a more open structure than one formed only by ionic links.

b. It is easy to realize that crystal lattices made up of isolated groups of atoms, or of chain, bond, sheet, or meshwork structures may result when the bonding is covalent. The fact that similar types of structures may result when the crystal is ionic is not so commonly recognized.

c. The presence of hydroxyl groups or ions in a crystal lead to complications due to the formation of hydroxyl bonds (2,3)

IV. Classification of Basic Salts on Structural Basis

The knowledge of the structure of basic salts is now sufficiently advanced that the following classification has been made (4). Examples of each of the types are also given.

1. Salts derived from poly-acid bases in which only some of the O or OH groups have reacted with acid and in which the remainder are covalently attached to the metal.
   a. The mineral autunite $Ca[(UO_2)_2(PO_4)_2] \cdot nH_2O$. A two dimensional sheet anion structure similar to mica, having large interstices containing the calcium ion as well as water molecules, which are both zeolitic in character (5,6)
   b. $K_2[OsO_2Cl_4]$ (7), $(NO)ClO_4$, $(NO)BF_4$ (8).
   c. Werner complexes containing hydroxyl groups
2. Basic salts with an infinite three-dimensional lattice of an ionic type.
   a. Lanthanum oxyfluoride, LaOF, has the cubic fluorite structure. (9)
   b. Libethenite, $Cu_2(OH)PO_4$; (10) olivenite $Cu_2(OH)AsO_4$; (11) and adamite, $Zn_2(OH)AsO_4$ (12) are isomorphous and all have the three dimensional ionic type structure. Half of the metal ions are surrounded, approximately octahedrally, by four oxygen atoms of AsO_4 (or PO_4) ions and by two OH ions, while the other half are surrounded by four oxygen atoms of AsO_4 (or PO_4) ions and one OH ion, the five oxygens being at the corners of a deformed trigonal bipyramid. The polymorphic forms of the orthosilicate $Al_2(O)SiO_4$, andalusite (13), sillimanite and cyanite (14) have closely related structure to the above, as do higginsite $CaCu(OH)AsO_4$, descloisite, $(Pb,Zn)Pb(OH)VO_4$, tilasite $CaMg(OH,F(AsO_4$, titanite, $CaTi(O)SiO_4$, (15) durangite, $NaAlFAsO_4$, (16) topaz, $Al_2(F,OH)_2SiO_4$ (17) linarite, $CuPb(OH)_2SO_4$, and malachite $Cu_2(OH)_2CO_3$.
   c. Hydroxyapatite, $Ca_5(OH)(PO_4)_3$ (18) and $Pb_5(OH)(PO_4)_3$(18

   Although these minerals have OH ions adjacent to each other in their structure, a temperature of 1200°C is needed for expulsion of water. The ionic strength of the OH, and the formation of OH bonds affect this property.
3. Basic salts with layer lattices ofthe Ionic Type and without hydroxyl.
   a. FeOCl (20), forms a layer lattice structure.
   b. The bismuth oxyhalides BiOCl, BiO Br, and BiOI (21).
4. Basic salts with Layer Lattices of the ionic type and containing hydroxyl.
   a. These include many of the basic salts of bivalent metals, especially zinc, magnesium, and cadmium. In the case of the halides for example each metal ion is surrounded octahedrally by six halogen or hydroxyl ions, each of which is common to three octahedra. The structures of Cd(OH)Cl and Mg(OH)Cl differ in an interesting manner.

Although both $Mg(OH)_2$ and $Cd(OH)_2$ crystallize with the same lattice as do $MgCl_2$ and $CdCl_2$ and the general arrangement of the ions in the lattices of Mg(OH)Cl and Cd(OH)Cl are fundamentally similar, the OH and Cl are distributed randomly in the case of the magnesium compound but are fixed in a very definite way in the cadmium compound.

b. Brucite - olivine series, $Mg(OH)_2$ ---- Mg_2SiO_4.

c. Staurolite, $2Al_2SiO_4$, $Fe(OH)_2$ has layers of cyanite interleaved with ferrous hydroxide layers.

5. Basic salts containing complex silicate and aluminosilicate anions.
    a. The amphiboles - e.g. hornblende, chrysotile, asbestos form band anions.
    b. The clay minerals (kaolinite, dickite, nacrite, etc.) the micas, and chlorites form sheet anions.
    c. Epidote, $Ca_2(OH)\,[(Al,Fe)_3\,Si_3O_{12}]$ is a representative of the three dimensional network types of basic silicate.
6. Basic Salts consisting of discrete molecules.
    The only basic salts in this category are the remarkable basic beryllium salts. Their structure is truly molecular and the links are essentially covalent (22).

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