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The electron-sharing ability of organic radicals: organic mercurials

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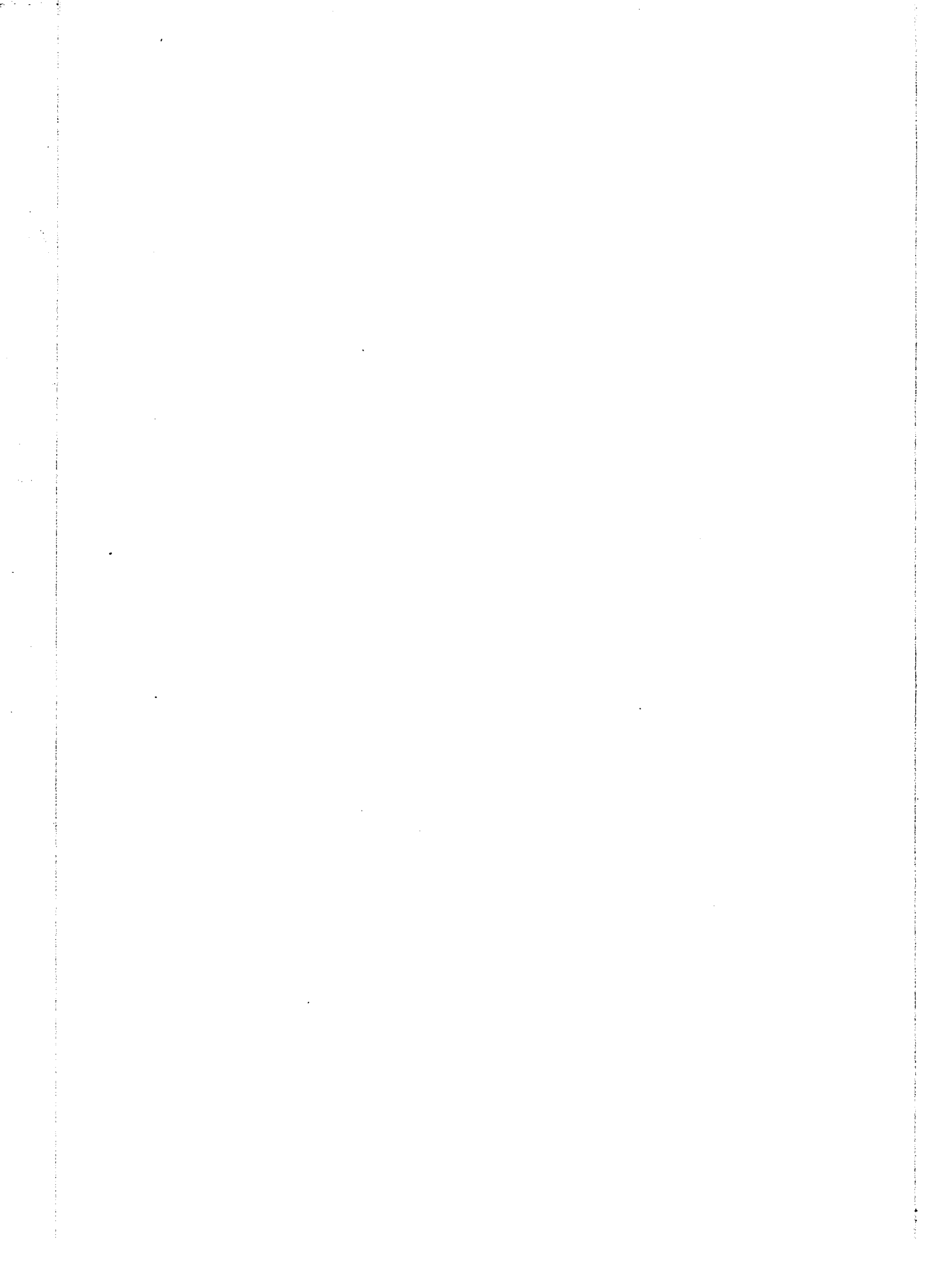
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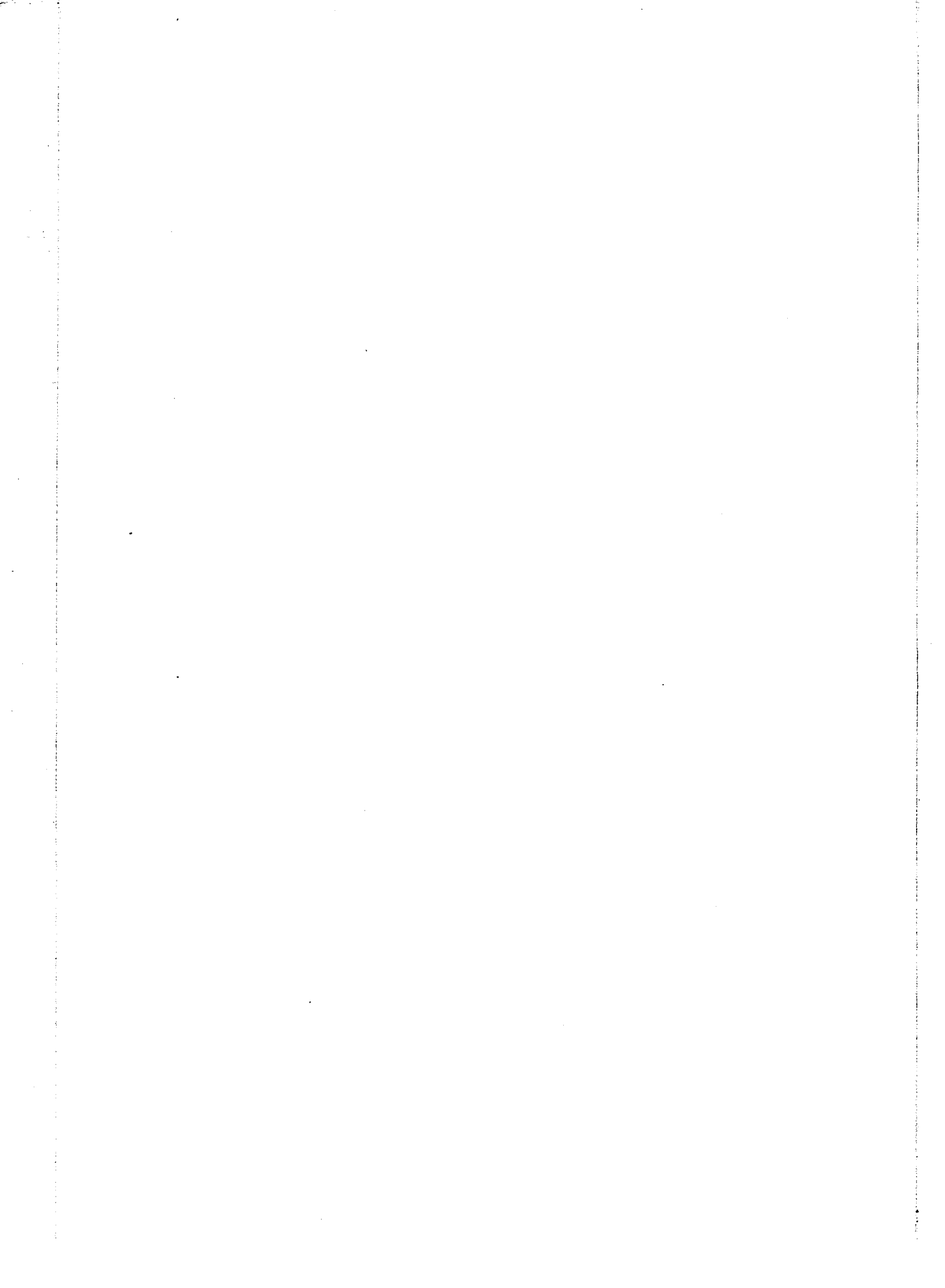
THE ELECTRON-SHARING ABILITY OF ORGANIC

RADICALS: ORGANIC MERCURIALS

By

Iral Brown Johns

A Thesis Submitted to the Graduate Faculty
for the Degree of

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INTRODUCTION

One of the very important problems that have stimulated
speculation and experimentation in organic chemistry has been
the relation of the constitution of molecules to their proper-
ties. A singular advance was made in this line when Van't
Hoff and Le Bel proposed the tetrahedral form for the carbon
atom and thus laid a logical foundation for the treatment of
the yet unexplained phenomenon of optical activity. The other
properties of substances, such as reactivity, degree of ioniza-
tion, orientation in substitution reactions, physiological ef-
fects and in fact nearly every known characteristic except
molecular weight, have eluded all efforts at complete system-
atic treatment. Many efforts have been made to correlate the
properties of compounds with the positive or negative
character of the radicals of which they are composed.

Ostwald[1] pointed out that certain elements or radicals,
when substituents in organic acids, affected the dissociation
constant in a uniform manner. Those elements, or radicals,
which when substituted into acetic acid caused an increase in
the dissociation constant, he called negative, and those

1. Ostwald, J. prakt. Chem., 31, 433 (1885);
Z. physik. Chem., 3, 170, 418 (1889).

which caused a decrease, positive. Wegscheider[2] summarizes the available data and puts them into a tabulated form from which it is possible to calculate the dissociation constants of various substituted acids. Many limitations to these generalizations, such as those of Bader[3] and Hantzsch[4] have been pointed out.

In 1901, Noyes and Lyon[5] pointed out that if all reactions involving the decomposition of molecules are preceded by an ionization of the parts of the molecules, it would follow that elementary molecules as well must ionize into positive and negative parts. A few years later, Abegg[6] stated that all elements are amphoteric, that is, exhibit both positive and negative electricity. We may interpret the generalizations of these pioneers to mean that the electron-sharing ability of any atom depends upon the strength of the other groups to which it is linked.

This generalization is involved in all of the recent theories which attempt to explain the distribution of affinity in the carbon compounds. All of these theories are qualitative in nature and the success of the manipulation de-

2. Wegscheider, Monatsh., 23, 287 (1902).
3. Bader, Z. physik. Chem., 6, 295 (1890).
4. Hantzsch, Ber., 32, 3071 (1899).
5. Noyes and Lyon, J. Am. Chem. Soc., 23, 460 (1901).
6. Abegg, Z. anorg. Chem., 39, 330 (1904).
7. Henrich, Johnson and Hahn, Theories of Organic Chemistry, John Wiley and Sons, New York, 1922, pp. 75-168.

pends upon ones ability to read into them a degree of stress or strain which can only be acquired by experience.

The confusion is due mostly to the lack of a quantitative measure of the "electron-sharing ability" of the various carbon radicals. Derick[8] attempted to establish such a standard by means of the acidic and basic dissociation constants of the various hydroxides. We may use the following electronic explanation for Derick's reasoning. (a) In water, hydrogen and oxygen are balanced. There is an equal tendency for the formation of hydrogen and hydroxyl ions. (b) If one hydrogen is replaced by an element or radical R with a greater tendency than hydrogen to take on an electron, the compound tends to ionize into $RO^- + H^+$. Furthermore, the degree of the ionization would be a measure of the "negativity" of R. (c) If one hydrogen is replaced by an element or radical R with a greater tendency than hydrogen to give up an electron, the compound tends to ionize into $R^+ + OH^-$. Furthermore, the degree of this ionization would be a measure of the "positivity" of R. He then uses the following mathematical value for these terms. Positivity = $-1000/\log K_{basic}$; negativity = $-1000/\log K_{acidic}$. Ostwald had previously considered this standard but had re-

8. Derick, J. Am. Chem. Soc., 33, 1152, 1162, 1181 (1911); 34, 74 (1912).

jected it in favor of the standard mentioned above, based on acetic acid, because the "non-ionization" of such a large group of compounds makes this standard impossible to apply experimentally. For this very reason, Derick's treatment of the subject is limited to the organic acids, and is not applied without difficulty even here.

Some of the factors other than negativity that affect the ionization of acids are, the mass, the structure, and the spatial configuration of the molecule. Thus the methyl substituted acrylic acids are known to exist in geometrically isomeric forms. Ostwald[9] has shown that their ionization constants are not alike.

A.

$$H \quad H$$
$$C = C - C \underset{}{\overset{O}{\lessgtr}} OH$$
$$H$$

K = 0.0056

acrylic acid

B.

$$H \quad H$$
$$C = C$$
$$| \quad | \overset{O}{\diagup}$$
$$CH_3 \quad C$$
$$\diagdown OH$$

K = 0.0020

cis-crotonic acid

C.

$$CH_3$$
$$| \quad H$$
$$HC = C$$
$$| \overset{O}{\diagup}$$
$$C$$
$$\diagdown OH$$

K = 0.0036
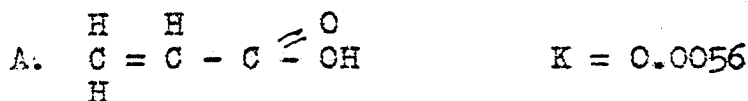
trans-crotonic acid

9. Ostwald, Z. physik. Chem., 3, 241 (1889).

One would expect the ethyl substituted acrylic acids to show a similar difference butthis was not considered by Fichter and Pfister[10] who determined the constant for 2-pentenoic acid.

$$C_2H_5C \overset{H}{=} \overset{H}{C} - C\overset{O}{\diagdown_{OH}} \qquad K = 0.00148$$
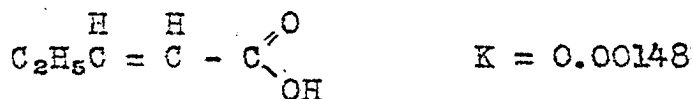
With the isomeric tartaric acids no difference in the constants has been found, though they can be separated into pure forms.

$$
\begin{array}{ccc}
C\overset{O}{\diagdown_{OH}} & C\overset{O}{\diagdown_{OH}} & C\overset{O}{\diagdown_{OH}} \\
| & | & | \\
HOCH & HCOH & HCOH \\
| & | & | \\
HCOH & HOCH & HCOH \\
C\overset{O}{\diagdown_{OH}} & C\overset{O}{\diagdown_{OH}} & C\overset{O}{\diagdown_{OH}}
\end{array}
$$

(l-tartaric acid) (d-tartaric acid)   (meso-tartaric acid)

It is only by a severe rounding off of the constants recorded in the literature that such confusing effects can be eliminated. It must also be borne in mind that the solvent plays a large and poorly understood role in ionizations. The data obtained in ionization measurements have been found satisfactory in arranging the radicals in the order of their electron-sharing ability, but not without some slight irregularities.

10. Fichter and Pfister, Ann., 334, 201 (1904).

THEORETICAL DISCUSSION

The method of approach to this problem proposed by
Hixon and Johns in 1927[11] involves a reasoning on the basis
of the electron theory of valency. It excluded from con-
sideration for the time being, all radicals which themselves
have polar linkages, as well as those compounds which exist
in more than one isomeric form. We may assume two extremes
of electron transfer: the first, total extraction of the
electron from a neutral atom resulting in a positively charged
ion, the second, total impression of an electron into a
neutral atom resulting in a negatively charged ion. Between
these two extremes which according to Lewis[12] exist in the so-
called "polar" compounds, there may be gradations in the trans-
fer of the electron, resulting in more or less non-polar
linkages of the atom concerned.

This change in the relation of the electrons to the nucle-
us in an atom can be calculated for the case of the more simple
atoms, if we assume some law of force between these units of
electricity that allows stability in the molecule. For con-
venience we will follow Thompson's reasoning[13].

11. Hixon and Johns,   J. Am. Chem. Soc., 49, 1786 (1927).
12. Lewis,   Valence and the Structure of Atoms and
Molecules,   Chemical Catalog Co., 1923, Chapter I.
13. Thompson,   The Electron in Chemistry,   Franklin
Institute, 1923, Chapter I.

Let the law of force between a positive charge and an electron be expressed by the equation

$$F = \frac{Ee}{r^2} \left(1 - \frac{c}{r}\right)$$

where F is the attracting force between the charges,

E and e the + and - charges respectively,

r the distance between them, and

c a constant characteristic of the kind of atom considered and is the distance at which the force changes from attraction to repulsion. Let the law of force between two electrons be expressed by the equation

$$F' = \frac{e^2}{d^2}$$

where F' is the repulsive force between the charges,

e the negative charge on the electron, and

d the distance between the electrons

In a neutral atom F = F'

Let us consider the case of a two-electron atom, in which the positive charge is midway between the electrons. Then E = 2e, d = 2r, and

$$\frac{Ee}{r^2} \left(1 - \frac{c}{r}\right) = \frac{e^2}{4r^2}$$

from which r = 1.14c.

Now consider the case in which one of these electrons is used in chemical combination with another atom and in so doing is drawn farther away from the positive nucleus of its

own atom. Let this electron be twice as far from the nucleus as the other uncombined electron. Then for the uncombined electron

$$\frac{Ee}{r^2} \left(1 - \frac{c}{r}\right) = \frac{e^2}{(3r)^2}$$

From which we find $\qquad r = \frac{18}{17} c$

While previously $\qquad r_0 = \frac{8}{7} c$

In the extreme case of complete removal of one electron the other will be at equilibrium when $F = 0$, and $r = c$.

Thus if the law of force at atomic dimensions is like that proposed by Thompson, the electrons of an atom should move in closer to the nucleus when one of them is partly or completely removed. If completely removed the new radius r_1 is given by the relation $r_1 = 0.875 \, r_0$ for a two-electron atom.

In the 4 electron atom the radius of the neutral atom is found to be $1.29 \, c_4$. If one electron is entirely removed the radius is found to be

$$\frac{4e^2}{r^2} \left(1 - \frac{c}{r}\right) = \frac{2e^2}{3r^2} \frac{1}{2} \sqrt{3}$$

$$r_1 = 1.168 \, c_4$$

$$r_1 = 0.905 \, r_0$$

Thus the effect is less pronounced in the more complex atoms.

These ideas are in agreement with the results obtained by Davey[14] in his study of the radii of atoms and ions. He

14. Davey, Chem. Rev., 2, 349 (1925).

finds that with the alkali metals of large atomic weight (Cs, Rb, K) the radius of the ion seems to be constant regardless of whether the atom is combined with Cl, Br, or I. With the alkali metals of lower atomic weight the radius is not constant and is least when the atom is combined with Cl and greatest when combined with I. Table I reproduces a portion of his calculations.

TABLE I

Radii of Alkali Ions

Cs^+ - 1.974 X 10^{-8} cm.
Rb^+ 1.696
K^+ 1.548
Na^+ Li^+
  In NaI 1.257   in LiI 1.03
    NaBr 1.231   LiBr 1.01
    NaCl 1.225   LiCl 0.98
    NaF < 1.15   LiF < 0.86(?)

These are in strict agreement with predictions from the ionizing potential. The greater the work done in removing an electron, the greater the change in the atom as a result of its removal and the stronger the force necessary to remove it. A comparison of the radii of the neutral atoms of Li, Na and K with the radii of their ions in their chlorides is given in Table II.

In this series of atoms the percent decrease in radius of the atom in changing from the neutral atom to the ion is in the same order as the ionizing potential. Also from

TABLE II

		:R atom	:R ion in RCl	:% decrease in R	: I. P.,volts:
:	Li	: 1.51	: 0.98	: 35.1	: 5.37 :
:	Na	: 1.86	: 1.225	: 34.1	: 5.13 :
:	K	: 2.25	: 1.548	: 31.2	: 4.1 :

Table I it is seen that for the same atom the change in radius
is in the same order as the negative nature of the ion with
which it is combined. (This reasoning is not limited to the
metallic ion, for as Davey shows, the radius of the fluorine
ion varies with the alkali metal ion with which it is combined.
The effects are entirely mutual.)

Now if the atom has two valences occupied in holding it
in combination with two other atoms or groups, any change in
the relation of this central atom to one of the groups must
necessarily produce a change in its relation to the others.
This change should be most marked when the central atom is
small and relatively simple, i.e., contains few electrons.
It is less marked in atoms that are larger and more complex.
This concept is capable of experimental verification. We
may use various atoms or groups for the so-called "central
atom", such as:

$$-(NH_3)-, \quad -(C=O)-, \quad -(S)-, \quad -(O)-, \quad -(Hg)-, \quad -(As\overset{O}{\underset{OH}{\diagup}})-,$$
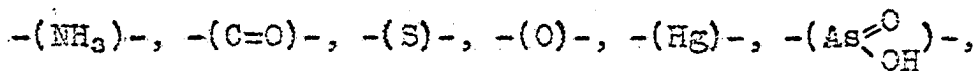
etc. If in any given case we use a polar group such as $-OH^-$,

$-\overset{+}{H}$, $-\overset{-}{I}$, $-N\overset{-}{O_3}$, etc. at one valence and a non-polar group, R, at the other, we obtain a number of series of compounds, such as:
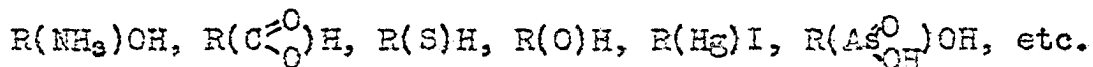
$R(NH_3)OH$, $R(C\overset{O}{\underset{O}{\lessgtr}})H$, $R(S)H$, $R(O)H$, $R(Hg)I$, $R(As\overset{O}{\underset{OH}{\lessgtr}})OH$, etc. In each series any change in the relation of R to the central atom must produce a change in the relation of the nucleus of this atom to its electrons and consequently a change in its relation to the polar group.

The affinity of the bond between the polar group and the central atom can be measured by a number of physico-chemical methods all of which depend upon determining the equilibrium constant for a reversible reaction involving that bond. Some of the commonly used methods are:

(1) Measurement of vapor pressures, in the case of gaseous substances or easily vaporized liquids.

(2) Measurement of electromotive force, for reactions that can be made to proceed with the production of electric current.

(3) Any analytical method that determines the equilibrium concentration of reacting substances. This includes conductance measurements, which indirectly determine the concentration of the ions and the molecules in solution.

The third method is the most convenient way of determining the ionization constant of an ionization reaction such as:

$$R(C\overset{O}{\underset{O}{\lessgtr}})H \rightleftharpoons R(C\overset{O}{\underset{O}{\lessgtr}})^- + H^+$$

From the constant obtained, the free energy of separation of
the molecules at unit concentration into the ions, each at
unit concentration, is given by the equation

$$-\Delta F = RT \ln K$$

Then by arranging the compounds of the series in the order of
their ionization constants we will have the radicals in the
order of their electron-sharing ability. In the case of non-
polar compounds, i.e. those which are not usually considered
as undergoing electrolytic dissociation, similar methods may
be used, provided a reversible reaction is involved and the
equilibrium constant for the reaction determined.

An examination of all of the values given in Landolt-
Börnstein for the dissociation constants of the acids and
amines makes possible the comparison shown in Table III for
the dissociation constants of $R(NH_2)$, $R(COOH)$, $R(CH_2COOH)$,
$R(CH_3CH_2COOH)$ and ROH.

Representative values from Table I are plotted in Figure
I against an arbitrary abscissa designated as "electron-shar-
ing ability of various radicals." In plotting these results,
it was observed that the curves were exponential no matter
what units were chosen for the x axis. Accordingly, an arbi-
trary curve $y = \log K = -20(e^{0.05X}-0.75)$ was drawn and the
dissociation constants for the various amines $R(NH_2 \cdot H_2O)$ were
located on the curve, thereby fixing the position of R along

TABLE III

Dissociation Constants of Corresponding Polar Compounds of Various Radicals in Water at 25°

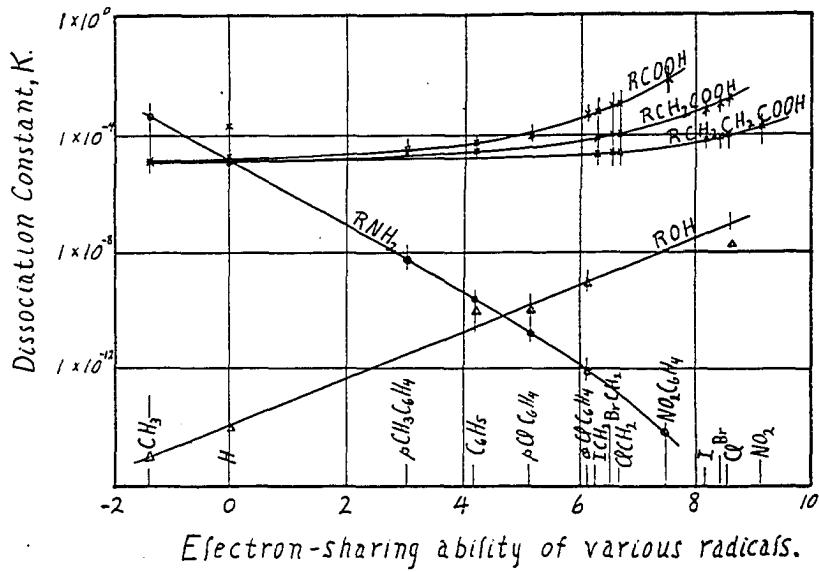| Radical	Amine $R.NH_2H_2O$	Acid $R.COOH$	Acid $R.CH_2COOH$	Acid $R.CH_2.CH_2CCOH$	Hydroxide ROH
$(CH_3)_3C-$	3×10^{-4}	1×10^{-5}			
CH_3-	5×10^{-4}	1×10^{-5}	1×10^{-5}	1×10^{-5}	
CH_3CH_2-	5×10^{-4}	1×10^{-5}	1×10^{-5}	1×10^{-5}	10^{-15}
$CH_3CH_2CH_2-$	5×10^{-4}	1×10^{-5}	1×10^{-5}	1×10^{-5}	
$CH_3CH=CHCH_2-$	4×10^{-4}	5×10^{-5}	3×10^{-5}		
$C_6H_5CH_2-$	2×10^{-5}	5×10^{-5}	2×10^{-5}		
$CH_2=CH-$	6×10^{-5}	6×10^{-5}	4×10^{-5}	2×10^{-5}	
$H-$	2×10^{-5}	2×10^{-4}	2×10^{-5}	1×10^{-5}	10^{-14}
$C_6H_4CH_3-p$	2×10^{-9}	5×10^{-5}			
$C_6H_4OCH_3-p$	6×10^{-7}	3×10^{-5}			
$C_6H_4CH_3-m$	6×10^{-10}	5×10^{-5}			
$C_6H_4OCH_3-o$	2×10^{-10}	8×10^{-5}			
C_6H_5-	3×10^{-10}	7×10^{-5}	5×10^{-5}	2×10^{-5}	10^{-10}
$C_6H_4CH_3-o$	3×10^{-10}	1×10^{-4}			
C_6H_4Br-p	2×10^{-10}				
C_6H_4Cl-p	1×10^{-11}	9×10^{-5}			10^{-10}
C_6H_4Br-m	9×10^{-11}				
$C_{10}H_7-\alpha$	9×10^{-11}	2×10^{-4}			
C_6H_4Cl-m	6×10^{-12}	2×10^{-4}			
$C_6H_4NO_2-p$	1×10^{-12}	4×10^{-4}			10^{-8}
$C_6H_4NO_2-m$	4×10^{-12}	3×10^{-4}			
H_2IC-		7×10^{-4}	9×10^{-5}	2×10^{-5}	
C_6H_4Cl-o	9×10^{-13}	1×10^{-3}			10^{-9}
CH_3CHCl-		2×10^{-3}	9×10^{-5}		
H_2CBr-		1×10^{-3}	1×10^{-4}	3×10^{-5}	
H_2CCl-		1×10^{-3}	9×10^{-5}	3×10^{-5}	
$C_6H_4NO_2-o$	1×10^{-14}	6×10^{-3}			
$H_2C(NO_2)-$			2×10^{-4}		
$CH_3-C\equiv C-$		3×10^{-3}			
$H_2C(CN)-$		4×10^{-3}			
C_2H_5OOC-			5×10^{-4}	3×10^{-5}	
$HCCl_2-$		5×10^{-2}			
$I-$			8×10^{-4}	9×10^{-5}	
$Br-$			1×10^{-3}	1×10^{-4}	
$Cl-$			1×10^{-3}	9×10^{-5}	10^{-8}
$CN-$			4×10^{-3}		
NO_2-				2×10^{-4}	

Fig. I.   Relation between the dissociation constants of different polar derivatives of various radicals.

the x axis. The corresponding values for the other derivatives of R were then located and a smooth curve was drawn through them. It was found that the following mathematical expressions held for the dissociation constants of the various polar compounds listed.

$$R(NH_2 \cdot H_2O), \quad y = \log K_b = -20(e^{0.05X} - 0.75)$$

$$R(COOH), \quad y = \log K_a = 20(e^{0.5X - 5.6} - 0.24)$$

$$R(CH_2COOH), \quad y = \log K_a = 20(e^{0.5X - 6.6} - 0.24)$$

$$R(CH_2CH_2COOH), \quad y = \log K_a = 20(e^{0.5X - 7.6} - 0.24)$$

Since the slope of the ROH curve is questionable, no equation has been derived.

As was expected from the theoretical considerations, none of the curves are erratic. That is to say, the same change in R that is expressed by the spacing of the radicals along the axis of abscissae and can be said to cause the progressive change in the ionization of the amines (RNH_2), is also the cause of the equally orderly change in the ionization of the acids (RCOOH) and alcohols (ROH). One might with considerable confidence pass to the general case and say that the equilibrium constants for a given reversible reaction of any series of compounds is a function of the electron-sharing ability of the radicals attached to the central atom or group.

The above mechanistic view of valence offers a tangible explanation of the changes in properties of the compounds

throughout a series and also gives an explanation of the steepness of the curve for the amines, which have a small central group $-(NH_3)-$ compared to the more flat curve for the acids which have a larger central group $-(C\stackrel{O}{\underset{\backslash}{\diagdown}})$. However the method of determining the electron-sharing ability of the radicals is quite independent of such a theory and places the radicals, by an experimental method, in a series analogous to the electro-chemical series of the elements.

STATEMENT OF THE PROBLEM

The preceding discussion has brought out the following points:

1. The radius of an atom must decrease when an electron is removed from it, and must increase when an electron is added to it.

2. The radius will undergo intermediate changes when an electron is partially removed or partially added, as is assumed to be the case in the non-polar linkages of atoms.

3. The effect is most marked with the smaller and more simple atoms.

4. It is possible to arrange the non-polar organic radicals, R, in a series analogous to the electro-chemical series of the elements, the order of the arrangement representing the degree of sharing of the electrons involved in the valence bond.

5. As a consequence of the above the order in which the radicals are placed must be preserved, no matter what series is investigated.

The first three points seem to have been fairly well established by the data already quoted. To test the validity of the last two points is the purpose of the present work.

A series of organo-mercury derivatives was chosen be-

cause these compounds, involving a great variety of radicals R, can be easily prepared and offer a central atom, Hg, having one valence occupied in a typical non-polar lingake R-Hg, and the other in a typical polar linkage $Hg-NO_3$ or $Hg-I$.

The experimental part divides itself into five main sections:

A. The preparation of compounds used.

B. Methods of analysis devised for the analysis of pure compounds and of dilute solutions of these compounds.

C. The determination of the ionization constants of compounds of the type $RHgNO_3$ and $RHgCl$.

D. The determination of the equilibrium constants for the type reaction $2RHgI \rightleftharpoons R_2Hg + HgI_2$.

E. The determination of decomposition voltages and decomposition temperatures of compounds of the type $RHgNO_3$.

EXPERIMENTAL PART

The Preparation of Compounds Used

Organo-mercuric Halides:

Compounds of the type RHgX, where R is methyl, ethyl, butyl, benzyl, p-tolyl, and phenyl, and X is Cl, Br, or I, were all prepared by means of the Grignard reaction in the way suggested by Marvel, Gauerke and Hill[15] for the alkyl-mercuric halides. The reactions are illustrated by the following equations:

$$RX + Mg \longrightarrow RMgX$$

$$RMgX + HgX_2 \longrightarrow RHgX + MgX_2$$
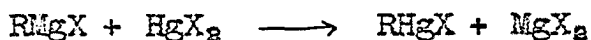
The reactions are carried out in anhydrous ether. In the first reaction the magnesium is activated by means of a crystal of iodine and a few drops of the halide before adding dropwise the main portion of the halide. During the reaction the suspension of magnesium is stirred vigorously. The second reaction is carried out by adding the halide of mercury in the form of a fine powder to the solution obtained in the first reaction. There is usually considerable heat of reaction and the mercuric halide must be added in small portions with constant agitation. After the calculated quantity has been added and the reaction has been completed the magnesium salts

15. Marvel, Gauerke and Hill,   J. Am. Chem. Soc., 47, 3009   (1925).

are dissolved in dilute (5%) acetic acid and the residue consisting mostly of the organomercuric halide is recrystallized from alcohol. The ether solution on evaporation yields a small amount of the pure compound.

Methylmercuric nitrate:

To a weighed quantity of $AgNO_3$, a slight excess of methylmercuric iodide is added in ethyl alcohol. After shaking for three hours, or until the filtrate gives no test for Ag ions, the solution is diluted with three times its volume of water, warmed, and filtered with suction - best through a Gooch crucible adapter filled with alternate layers of asbestos and glass wool. This removes the silver iodide and the excess methylmercuric iodide which was thrown out when the water was added. The solution is evaporated by drawing a stream of air over it, while on a water bath. It first concentrates to a thick oil which suddenly crystallizes. To obtain pure, it must be recrystallized at least twice from water, each time concentrating the solution until a crystalline mush is obtained, then removing the mother liquor by absorption in filter paper in a press. The crystals are dried in vacuo. This purification reduces the yield very considerably, but gives a pure product that is white, stable in light, strongly deliquescent, and causing painful blisters if applied to the skin. Samples have been kept for two years with-

out becoming discolored.

The melting point, unlike that given in the literature[16], is 59°, obtained in two independent preparations and constant through successive recrystallizations.

Anal. Calc. for CH_3HgNO_3: Hg, 72.26   Found: 72.24, 72.72. The conductivity in water checks the values reported by Maynard and Howard[17], though they gave no melting point. It is deliquescent and extremely soluble in water.

Ethylmercuric nitrate:

This compound was prepared in the same way as the methyl- compound. It is less soluble and recrystallizes more easily, giving a better yield. The melting point, not reported by Strecher[16] who first prepared it, is 87°.

Anal. Calc. for $C_2H_5HgNO_3$: Hg, 68.79   Found: 68.85, 68.42. Samples kept for two years have not become discolored. Solubility in water is 6.96 g. per L.

Butylmercuric nitrate.

This compound is much more difficult to prepare than the ethyl- and methyl- compounds. 17 g. n-butylmercuric bromide and 10 g. $AgNO_3$ were shaken with 150 cc. alcohol for 1 hour in a long necked flask, to prevent contact with the stopper,

16. Strecher,   Ann., 92, 79 (1854).
17. Maynard and Howard,   J. Chem. Soc., 123, 960 (1923).

then warmed and filtered. Dilution with 800 cc. water gave
only an opalescence. When concentrated under reduced pres-
sure on a water bath, an oil separated when the volume
reached 200 cc. The evaporation was completed and the oil
dried by evaporating 10 cc. portions of alcohol from it and
finally 10 cc. of ether. On cooling, the residue solidified.
The melting point, after 3 recrystallizations from ether, was
39.5-40° with some preliminary softening. Yield 12 g.

Anal. Calcd. for $C_4H_9HgNO_3$:

	C	H	N
Anal. Calcd. for $C_4H_9HgNO_3$:	15.02	2.84	4.38
Found:	14.80	2.89	4.44

Solubility in water: 0.956 g. per L.

It was later found better to use exactly equivalent
quantities of butylmercuric bromide and silver nitrate, and
after filtering off the silver bromide formed, to evaporate
the alcoholic solution without diluting with water. The
first solid substance obtained is yellow in color, and can be
purified to a certain extent by recrystallizing from ether.
Until this purification and drying, the preparation is very
unstable, breaking down to a yellow oil and a dark insoluble
residue of mercury and inorganic mercury salts, exactly as
happens more rapidly, when heated to 150°-160°. It was never
obtained entirely colorless, always retaining a gray color.

Benzylmercuric nitrate.

This compound is about as difficult to prepare as the butyl- compound. If the reaction between the halide and the silver nitrate is carried out in alcohol, decomposition of the resulting benzylmercury nitrate takes place on warming to evaporate the solvent, giving a yellow solid, free from carbon, and containing mercury (probably a basic mercury nitrate). If a solution of the previously prepared nitrate in 95% alcohol is heated to boiling, all the mercury will precipitate in the form of inorganic compounds. In ether the reaction between the halide and silver nitrate takes place very slowly. It is best carried out by dissolving the benzylmercuric chloride in ether and the silver nitrate in alcohol and mixing the two solutions. After shaking for an hour, filter off the precipitated silver halide, and evaporate the solvent by warming in a crystallizing dish over a small electric hot plate within a vacuum desiccator.

In this way 11.35 g. benzylmercuric chloride and 5.89 g. $AgNO_3$ gave 4.95 g. AgCl (theoretical 4.97 g.). The resulting benzylmercuric nitrate was a gray crystalline mass. Recrystallized 3 times from ether, it gave large pure white rhombic needles. Melting point 90-91° with decomposition.

Anal. Calcd. for $C_6H_5CH_2HgNO_3$: Hg 56.71.

Found: 56.64, 57.05.

Solubility in water 0.93 g. per L.

In spite of all care in preparation and preservation, the compound slowly decomposes and after several months appears dark though still crystalline.

Para-tolylmercuric nitrate and phenylmercuric nitrate[18] were prepared in the same way as those just described. They are very stable white solids.

Solubility in water at 25°,

para-tolylmercuric nitrate, 0.2017 g. per L.

phenylmercuric nitrate, 0.799 g. per L.

Absolute alcohol.

The alcohol used was prepared by fractionating through a three-bulb distilling head three gallons of 96% alcohol to which had been added 100 cc. of 50% sulfuric acid, rejecting the first and last half gallon. The middle fraction was refluxed for twenty-four hours with freshly dehydrated lime and distilled. It was then treated with a slight excess of metallic calcium and again distilled. The conductance of such alcohol varies from 3×10^{-7} to 8×10^{-8}. The conductance of a 0.05 molal solution of potassium iodide in such alcohol varied from 1.02×10^{-3} to 1.15×10^{-3}. This variation has not been accounted for. It cannot be due to water in the alcohol for with a solution whose conductance was 1.02

18. Whitmore, Organic Compounds of Mercury, The Chemical Catalog Co., (1921) pp. 177, 184.

x 10^{-3}, the addition of 2.5% water by volume raised the conductance only to 1.07 x 10^{-3}. It cannot be due to variations of concentration for in preparing 1500 g. batches, the weighing of the alcohol was accurate to one part in thirty thousand, and the weighing of the potassium iodide to one part in fifty thousand. These variations in conductance produced no noticeable variation in the E.M.F. of the cells.

Potassium iodide.

A c.p. grade of KI was recrystallized once from water and once from alcohol and dried at $200°$ for three hours. It was then powdered and dried again at $200°$ for three hours.

Mercuric iodide.

The mother liquors from the purification of potassium iodide were added to a saturated mercuric chloride solution to precipitate mercuric iodide. The precipitate was washed several times by decantation and then boiled with water three times. It was then dried and distilled. The yellow lustrous crystals, which soon turn red, were finely powdered.

Conductivity water.

The water used in preparing solutions for conductivity measurements was prepared in the usual way by distilling from alkaline permanganate. The specific conductance of the various preparations of water came within the limits 1.4 to 3×10^{-6}.

Methods of Analysis for Mercury in Organo-mercuric Halides and Nitrates

It has been found more convenient to decompose the organic compounds with bromine in aqueous solution than to use concentrated acids, since the lower temperature causes less danger of volatilization of mercury halides. This also serves for the analysis of dilute solutions for which the use of concentrated acids is obviously impossible.

In analyzing a solid compound, sufficient sample to give 0.25 g. HgS is covered with 100 cc. water in a flask provided with a long air condenser connected through a ground glass joint. About 5 cc. bromine is added and the flask heated to give constant reflux of bromine in the condenser, the escaping fumes being removed by a loosely fitting cap connected to the water pump. Heating is continued until the excess bromine is expelled, the condenser being finally removed and the last traces of bromine destroyed by a few drops of sodium and sulfite solution[19]. The decomposition can also be carried out without the use of a condenser, larger quantities of bromine being necessary and some loss of volatile mercury derivatives being possible under such conditions. In case the organic radical forms oily bromination products, as in the

19. Contrary to statements in text books, SO_2 has not been found to reduce mercury in solution, a slight excess of $NaHSO_3$ doing no harm. A large excess will sometimes produce some reduction.

case of many aromatic mercury derivatives, these may be removed by filtration through a paper filter.

After decomposition, the clear colorless solution is made more acid with HCl and saturated with H_2S. The precipitate is allowed to settle and the supernatant liquid filtered through a Gooch crucible. The precipitate is then transferred to the crucible, washed with water, followed by alcohol and ether. The crucible is then allowed to stand filled with CS_2 in a small covered beaker, for at least two hours to remove free sulfur. The CS_2 is then filtered off, the crucible washed with alcohol and dried at 110°. The success of this method is indicated by the data in Table IV.

Table IV

Compound	Sample	HgS Found	HgS Calculated
C_4H_9HgBr	0.2283	0.1580	0.1574
	0.2551	0.1763	0.1758
CH_3HgNO_3	0.3504	0.2935	0.2936
	0.2736	0.2307	0.2292
$C_2H_5HgNO_3$	0.1428	0.1140	0.1139
	0.1573	0.1248	0.1255
$C_6H_5CH_2HgNO_3$	0.1614	0.1060	0.1062
	0.1693	0.1120	0.1114

In analyzing a dilute solution, a sample sufficient to give 0.2-0.3 g. HgS is used and treated in the same way as

above. That all the mercury is obtained by this procedure

has been shown by analyzing 100 cc. samples of a dilute solu-

tion of ethylmercuric nitrate, which was prepared by dissolv-

ing a weighed sample. A sample weighing 1.5882 g. was made

up to 500 cc. and two separate 100 cc. portions were analyzed.

The weights of mercuric sulfide obtained were 0.2538 g. and

0.2530 g., while the calculated weight is 0.2534 g.

The quantitative precipitation of mercury as the sulfide

is difficult when iodides are present. Dunning and Farinholt[20]

report the necessity of removing iodine, while Reinders[21] con-

siders digestion of the precipitated HgS with NH_4Cl solution

sufficient to remove this difficulty. This difficulty was en-

countered in determining mercuric iodide concentration in half

cells of HgI_2 in KI solution, which were being used as refer-

ence cells in the E.M.F. measurements described later. It can

be eliminated by applying a modification of the double precip-

itation method used by Scott[22] in separating mercuric sulfide

from lead sulfide. The following method was used to obtain

the results reported in Table V.

A sample of HgI_2 equivalent to 0.25-0.30 g. HgS is dis-

solved in 50 cc. 0.1 N KI solution and treated with enough

20. Dunning and Farinholt,   J. Am. Chem. Soc., 51, 807
(1929).
21. Reinders,   Z. physik. Chem., 32, 498   (1900).
22. Scott,   Standard Methods of Chemical Analysis,
4th Ed.   (1927) p. 310.

1 M KSH solution just to redissolve the HgS that first precipitates. Then 1 M NH$_4$NO$_3$ solution is added to precipitate the HgS. After boiling to remove most of the ammonia, the solution is filtered and the precipitate redissolved by pouring warm KSH solution over the filter. The paper must be removed and boiled in a small amount of KSH solution to remove the last traces of mercury, the resulting solution being filtered into the same flask with the first solution. NH$_4$NO$_3$ is then added a second time to precipitate the HgS. After some digestion, the precipitate is filtered on a Gooch crucible, washed with water and alcohol and allowed to stand filled with CS$_2$ in a small beaker for two hours to remove free sulfur. The CS$_2$ is then filtered off and the crucible washed with alcohol and dried at 110°.

In analyzing 0.025 molal HgI$_2$ solutions in absolute alcohol that was 0.05 molal in KI, the first precipitate when weighed was found to be approximately 4% too heavy, while when reprecipitated the weight was found to agree with that calculated. In Table V, the first three samples were analyzed by a single precipitation. The second two samples of the same solution were analyzed by double precipitation.

TABLE V

Analysis of 0.025 molal HgI_2 in Alcohol 0.05 molal in KI			
By single pre-cipitation	g. Solution	g. HgS Found	g. HgS Calcd.
1	47.265	0.2821	0.2696
2	55.108	0.3288	0.3143
3	65.612	0.3889	0.3742
By double pre-cipitation			
4	58.815	0.3351	0.3354
5	56.234	0.3203	0.3207
Analysis of pure HgI_2 dissolved in 50 cc. 1/10 N KI			
By double pre-cipitation	g. Sample	g. HgS Found	g. HgS Calcd.
6	0.5000	0.2556	0.2559
7	0.5000	0.2554	0.2559
Analysis of pure CH_3HgI decomposed by aqueous bromine			
By double pre-cipitation	g. Sample	g. HgS Found	g. HgS Calcd.
8	0.4000	0.2712	0.2717
9	0.4000	0.2714	0.2717

The Determination of Ionization Constants of
Compounds of the Type RHgNO₃ and RHgCl

In extending the generalization pointed out in the
Theoretical Discussion, page 18, to the organic derivatives
of mercury, a general reaction was sought which would permit
a comparison of the radicals. Conductivity determinations
were selected as the most rapid and convenient measurements
for a preliminary examination of this field, though it was
obvious that such data could not be used to calculate ac-
curately free energy of ionization. Salts of the type $RHgNO_3$
hydrolyze in water, their aqueous solutions being acid to
litmus. The extent of this effect could be calculated if the
basic strength of the corresponding hydroxides were known or
could be estimated. Furthermore, the reaction:

$$2 \text{ RHgX} \rightleftharpoons R_2Hg + HgX_2 \qquad (I)$$
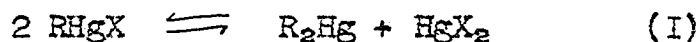
known to take place with the halogen derivatives, would be
expected to occur with the nitrates. The conductance in this
case would be the sum of the conductances of the unchanged
$RHgNO_3$ and of the $Hg(NO_3)_2$ formed. As R increases in nega-
tivity from the methyl to the nitrate radical, i.e., as we
change from CH_3HgNO_3 through a series of more negative radi-
cals to NO_3HgNO_3, the ionization will change progressively
from $RHg^+ + NO_3^-$ to $R^- + Hg^{++} + NO_3^-$. There is no evidence
to indicate that this latter type of ionization would take
place with phenylmercuric nitrate, which is the nearest ap-

proach to this extreme in the compounds investigated. For the aliphatic compounds, the principal ions are known to be RHg^+ and NO_3^- from the electrolytic isolation of the free radical RHg by Kraus[23], and it is significant that the corresponding aromatic radicals could not be isolated.

If the generalization mentioned earlier is correct, the basic strength of compounds of the type RHgOH, which governs the degree of hydrolysis of the salts, should change from radical to radical in the series in an orderly way, resulting in an augmentation or diminution of the relative differences between the various salts. Likewise the extent of Reaction I should be an orderly function of the radicals and should have the same orderly effect on the conductivity measurements[24]. The conductance measurements would then be a measure of all of these effects.

Study of the Nitrates in Aqueous Solution.

The compounds were prepared as previously described and were very carefully recrystallized and analyzed for purity immediately before use.

The limited solubility of the compounds with the larger organic radicals necessitated the measurement of solutions as dilute as 0.0001 molar. Although this dilution would in-

23. Kraus, J. Am. Chem. Soc., 35, 1732 (1913).
24. This is proven for the compounds RHgI, in the following section.

troduce considerable error, the results serve for comparative purposes. The values for the conductance at infinite dilution were obtained by Washburn's[25] method of extrapolation.

The molecular conductances at various dilutions and the ionization constants for the organo-mercuric nitrates in aqueous solution are reported in Table VI.

TABLE VI

Conductances of Organic-mercuric Nitrates

T. = 25°. Specific Conductance of Water 1.4 to 3x10⁻⁶

								μ_∞	
Methyl-	:c #	.01077	.00539	.00269	.00134	.00067	.00034:		
mercuric	:μ_c #	123.5	126.7	133.0	140.5	146.8	152.8:	159	
nitrate	:Kx10⁻³	29.2	17.4	11.5	9.0	7.47	7.95:		
Ethyl-	:c	.01475	.00738	.00369	.00184	.00092	.00046:		
mercuric	:μ_c	111.5	117.0	120.3	126.0	131.8	137.5:	146	
nitrate	:Kx10⁻³	36.4	23.8	14.4	10.0	7.2	7.0:		
Butyl-	:c	.00191	.00143	.00107	.00081	.00060	.00025:		
mercuric	:μ_c	126.2	128.5	132.2	137.0	141.2	157.0:	185	
nitrate*	:Kx10⁻³	2.8	2.2	1.9	1.7	1.5	1.2:		
Benzyl-	:c	.00263	.00131	.00066	.00033	.00016			
mercuric	:μ_c	135.0	147.0	160.0	174.0	187.0		200	
nitrate	:Kx10⁻³	3.6	2.7	2.1	1.9	2.2	:		
p-Tolyl-	:c	.00057	.00043	.00032	.00024				
mercuric	:μ_c	74.4	77.5	81.5	83.7		:	96	
nitrate	:Kx10⁻³	1.5	1.4	1.5	1.4		:		
Phenyl-	:c	.00128	.00064	.00032	.00016				
mercuric	:μ_c	99.0	120.0	139.0	155.0		:	180	
nitrate	:Kx10⁻⁴	8.6	8.6	8.5	8.5		:		

\# Compares favorably with data by Maynard and Howard[1] .
* The butylmercuric nitrate remained grey in color and could not be further purified. These values are accordingly approximations only.

25. Washburn, J. Am. Chem. Soc., 40, 122 (1918).

A comparison of the apparent dissociation constants for like concentrations of these compounds is given in Table VII. The constants for the corresponding acids, RCOOH, and amines RNH_2H_2O are included. It will be seen that although the highly dissociated aliphatic mercury derivatives have a K that varies with concentration, still the values are in the same order at all dilutions as are the values of the corresponding acids and amines. These relations are shown graphically in Figure II.

TABLE VII

Comparison of Physical Constants as Measured By Conductivity Methods for the Type Compounds R-NH$_2$, RCOOH and RHgNO$_3$

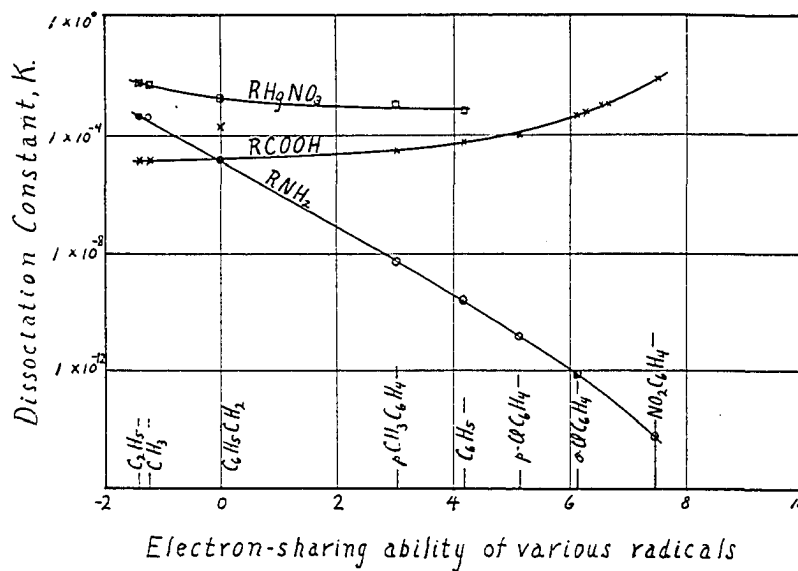| Composition of R	Value of K for:		Comparative values of K for RHgNO$_3$ at concentrations:			
	R-NH$_2$	R.COOH	.00195M	.00097M	.00049M	0.0M
CH$_3$-	5×10^{-4}	1×10^{-5}	1×10^{-2}	8×10^{-3}	7×10^{-3}	7×10^{-3}
C$_2$H$_5$-	5×10^{-4}	1×10^{-5}	1×10^{-2}	7×10^{-3}	7×10^{-3}	7×10^{-3}
C$_4$H$_9$- #	5×10^{-4}	1×10^{-5}	3×10^{-3}	2×10^{-3}	1×10^{-3}	1×10^{-3}
C$_6$H$_5$CH$_2$-	2×10^{-5}	5×10^{-5}	3×10^{-3}	2×10^{-3}	2×10^{-3}	2×10^{-3}
p-CH$_3$C$_6$H$_4$-	2×10^{-9}	5×10^{-5}	Not soluble	Not soluble	1×10^{-3}	1×10^{-3}
C$_6$H$_5$-	3×10^{-10}	7×10^{-5}	Not soluble	8×10^{-4}	8×10^{-4}	8×10^{-4}

#See statement as to purity.

Fig. II. Relation between the dissociation constants of some organomercuric nitrates, acids and amines.

Study of the Nitrates and Chlorides in Alcoholic Solutions.

In the study of alcoholic solutions, it was hoped that ionization constants could be obtained unaffected by hydrolysis. The measurements on three compounds of the type $RHgNO_3$ and three of the type $RHgCl$ in absolute alcohol and in mixtures of alcohol and water, were made to test this possibility. The conductances were very low, indicating an extremely low degree of ionization. The variation between members of the series was so slight that the method was considered inadequate for the desired purpose.

The alcohol used was prepared by fractionating from dilute sulfuric acid and then repeatedly distilling from fresh lime until the specific conductance fell within the limits 2×10^{-7} - 8×10^{-8}. A dilute solution (0.05 molal) of potassium iodide in this alcohol had a specific conductance of 1.05×10^{-3}, while a 0.0335 molal solution of methylmercuric iodide has a specific conductance of only 2.9×10^{-6}, and a 0.0528 molal solution of methylmercuric chloride only 5.8×10^{-7}.

The conductances are recorded in Table VIII. The rate at which the molecular conductance increases at high dilutions indicates that complete ionization is not approached even in 0.0001 molar solutions.

On adding water to an alcohol solution of these compounds, the conductance is increased slightly for small quantities of water, but very greatly for larger quantities. The conductance

TABLE VIII

Molecular Conductances of Some Organo-mercuric Nitrates and Chlorides in Absolute Alcohol. $T = 25°$

$C_2H_5HgNO_3$					
c : 0.01262	0.00631	0.003155	0.001578	0.000789	0.000394
μc: 6.05	8.27	11.38	16.05	22.70	32.2
$C_6H_5CH_2HgNO_3$					
c : 0.004531	0.002265	0.001132	0.000566	0.000283	0.000141
μc: 11.5	18.4	29.9	36.4	38.9	41.1
$C_6H_5HgNO_3$					
c : 0.006416	0.003208	0.001604	0.000802	0.000401	
μc: 8.34	9.85	11.78	14.85	18.4	
CH_3HgCl					
c : 0.04194	0.02097	0.01048	0.00524	0.001	
μc: 0.0162	0.0200	0.0258	0.0324	0.18	
$C_6H_5CH_2HgCl$					
c : 0.001					
μc: 0.15					
C_6H_5HgCl					
c : 0.005	0.0025	0.001	0.0005		
μc: 0.154	0.159	0.300	0.438		

c = mols per liter.

in 20 volume-percent alcohol is more than fifty times as great as in absolute alcohol. The mixtures of alcohol and water were prepared by introducing into a volumetric flask a quantity of absolute alcohol from a pipette calibrated to deliver a known volume of alcohol, and then filling the flask to the mark with water. The resulting mixture was then used in preparing 0.001 molar solutions of the organo-mercuric chlorides. The

molar conductance in absolute alcohol and mixtures of alcohol and water are reported in Table IX.

TABLE IX

Molecular Conductances of 0.001 Molar Solutions of
Some Organo-mercuric Chlorides in Absolute
Alcohol and in Alcohol-Water Mixtures

Volume % Alcohol	100	80	60	40	20
CH_3HgCl	0.18	0.70	2.15	4.1	9.0
$C_6H_5CH_2HgCl$	0.15	0.73	1.5	3.4	8.3
C_6H_5HgCl	0.30	1.22	2.55		
Specific conductance of solvent	8×10^{-8}	2×10^{-7}	6×10^{-7}	9×10^{-7}	1.2×10^{-6}

The Determination of the Equilibrium Constants
for the Type Reaction 2RHgI ⇌ R_2Hg + HgI_2

The preceding conductance data indicate that the ionization of the organo-mercuric nitrates in water can be correlated with the dissociation constants of the corresponding organic acids and amines as was to be expected if the concepts of valence mentioned in the theoretical discussion are correct. The ionization values of the organo-mercuric nitrates can not be used to calculate free energy of ionization due to incident acid hydrolysis and variation of the ionization constant with dilution. To obtain data which can be used to calculate free energy relationships and therefore interpreted in terms of chemical affinity, a study of the reversible reaction,

$$2 \text{ RHgI} \rightleftharpoons R_2Hg + HgI_2 \qquad (I)$$
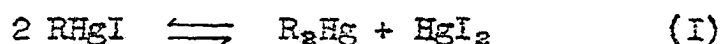
was undertaken.

This reaction is general for the organo-mercury halides and the fact that it is used for the preparation of either the compounds of type RHgI or R_2Hg from the other, demonstrates its reversibility. The reaction tends to go to the left with the aliphatic compounds and the complete removal of the mercuric iodide by reducing agents is necessary for the preparation of the dialkyl mercury compounds from the corresponding alkylmercury halides. With the aromatic mercury derivatives the reaction is easily carried to the right,

The removal of the mercuric halide by formation of the complex compound with potassium halide being sufficient for the preparation of some diaromatic mercury derivatives from the corresponding aromatic mercury halides.
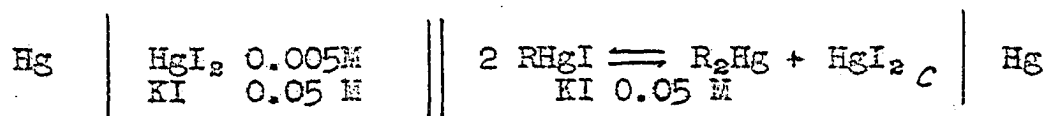
These relationships which suggest a correlation with the positively and negativity of the organic radicals, can be more readily observed if the mercuric iodide is qualitatively determined in the alcoholic solutions by means of diphenyl carbazide. This compound has been suggested by Skinner[26] as a reagent for detecting mercury, a blue color being formed with very slightly basic solutions of mercury salts, a blue precipitate slowly forming as the solutions stand. In alcoholic solutions of the alkylmercuric iodides, the blue color is very faint, its intensity increasing slowly on standing. With benzylmercuric iodide, the color develops quite quickly while with the tolyl- and phenylmercuric iodides, the color appears immediately on adding the reagent. The radicals are mentioned in the order of the dissociation constants of their amines and carboxylic acids and these color tests would indicate the same order in the formation of mercuric iodide according to reaction I. This colorimetric method was found inadequate for the accurate determination of the con-

26. Skinner, J. Chem. Soc., 53, 551 (1888).

centration of mercuric iodide since the compound formed with diphenyl carbazide soon precipitates displacing reaction I to the right. Also, the bis-organomercuric compounds produce colored compounds with the reagent[27]. These red shades of color interfere with the accurate estimation of the blue color produced by the mercuric halide. In very dilute solutions the blue compound does not precipitate and in such a case the reaction can be reversed by adding a large excess of the type compound R_2Hg with resulting decrease of the blue color.

The equilibrium represented by Equation I is so labile that the use of precipitating reagents for the determination of the concentration of the constituents is out of the question. Since the R_2Hg compounds do not ionize to form the free mercury ion, as evidenced by the failure of hydrogen sulfide to precipitate mercuric sulfide from their solutions, and since the RHgI compounds have been shown to be very slightly ionized, it seemed probable that the concentration of the mercuric iodide in the equilibrium could be determined by concentration cell methods. Preliminary experiments using 0.05 molal alcoholic potassium iodide as solvent showed that reproducible voltages could be obtained when known solutions of RHgI compounds were measured against a solution of HgI_2 in cells of the type,
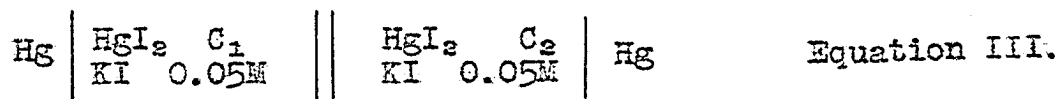
27. Fiegel and Lederer, Monatsh., 45, 115-32 (1924).

$$\text{Hg} \quad \left| \begin{array}{l} \text{HgI}_2 \ 0.005\text{M} \\ \text{KI} \quad 0.05 \text{ M} \end{array} \right| \left| \right| \quad \left| \begin{array}{c} 2 \text{ RHgI} \rightleftharpoons \text{R}_2\text{Hg} + \text{HgI}_2 \\ \text{KI} \ 0.05 \text{ M} \end{array} \right._c \quad \left| \quad \text{Hg} \right.$$

(Equation II)

Furthermore, identical voltages could be obtained quite in-dependent of whether the organo-mercury cell was made up by adding RHgI or equivalent quantities of R_2Hg and HgI_2 accord-ing to Equation I. This experiment quantitatively demon-strates the reversibility of the reaction represented by Equation I.

As indicated above, it seems probable that no appreciable voltage would be exerted between RHgI and Hg_0 or between R_2Hg and Hg_0. Accordingly, the voltage of the organo-mercury half-cell in Equation II has been interpreted as due to the concen- of HgI_2 only. Concentration cells of the type

$$\text{Hg} \quad \left| \begin{array}{l} \text{HgI}_2 \quad c_1 \\ \text{KI} \quad 0.05\text{M} \end{array} \right| \left| \right| \quad \left| \begin{array}{l} \text{HgI}_2 \quad c_2 \\ \text{KI} \quad 0.05\text{M} \end{array} \right| \quad \text{Hg} \qquad \text{Equation III.}$$

have been measured to determine the relationship between con-centration of HgI_2 and voltage. This relationship has then been used to translate the voltages obtained in the organo-mercury cells of Equation II into concentrations of HgI_2. Knowing the total concentration of organic mercury added and the concentration of mercuric iodide at equilibrium, the con-centration of all the members in Equation I can be calculated and the equilibrium constant for the various compounds de-rived. In the experimental studies reported, all solutions

were made in absolute alcohol 0.05 molal in potassium iodide.
The reference cell was in all cases 0.05 molal in potassium
iodide and 0.005 molal in mercuric iodide.

Apparatus and Method.

The potentiometer used was a Leeds and Northrup type K.
with galvanometer 2500-b with lamp and scale at 1 meter. The
standard cell (Weston) and the concentration cells were kept
in an air thermostat with temperature controlled to $25^\circ \pm 0.1$.
The half-cells were a modification of the type used in this
laboratory[28] in the studies on potassium and sodium amalgams.

At the beginning of the work a great deal of trouble was
experienced in getting satisfactory measurements, due to con-
densation of moisture on the cells and consequent leakage of
current. This was especially true in warm weather. This
trouble was entirely eliminated by the cell construction
shown in Figure III. All supports are of glass sufficiently
far removed from metallic contacts to insure proper insu-
lation. In use the tips of two such cells are put together.
The solutions join and drop from the tips into a beaker tall
enough to surround both cells and covered by a card through
which the cells pass.

The electromotive force is independent of the flow of
the solutions for all rates greater than two drops per

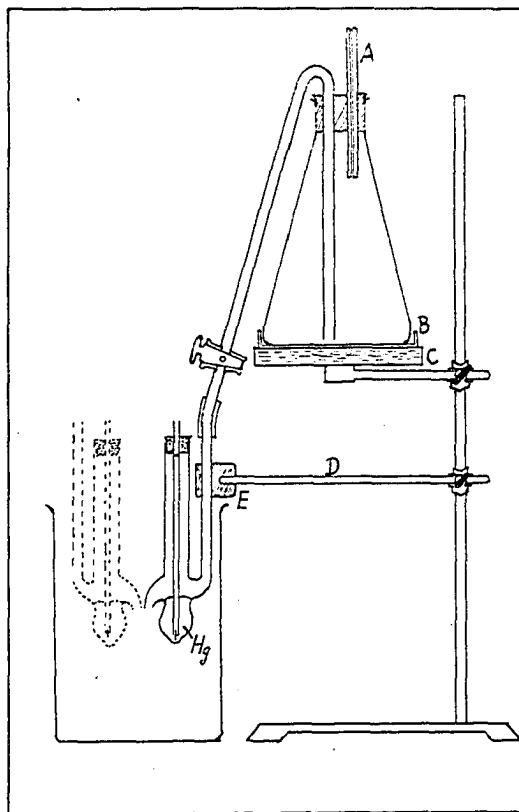28. Bird and Hixon,   J. Phys. Chem.,

Fig. III. Cell construction; A, capillary
tube; B, glass; C, paraffined wood; D, glass
rod; E, rubber.

second. At very low rates (one drop per second or less) the electromotive force becomes erratic but returns to a steady reproducible value on increasing the rate beyond two drops per second.
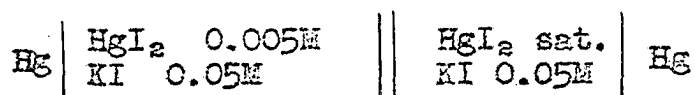
The resistance across two such half-cells is approximately 40,000 ohms when filled with alcohol 0.05 molal in potassium iodide. This high resistance forbids the use of the usual half-cells with long narrow limbs, when working with dilute alcoholic solutions.

Electromotive Force of Mercuric Iodide Concentration Cells.

In the study of cells of the type shown in Equation III, the concentration of mercuric iodide was varied from 0.0005 molal to saturation. In the absence of metallic mercury, an absolute alcohol solution 0.05 molal in potassium iodide will be 0.1136 molal in mercuric iodide when saturated with this salt. If metallic mercury is added, reduction takes place with the precipitation of mercurous iodide until the concentration is lowered to 0.05101 molal. If a solution is prepared from mercurous iodide, the concentration is 0.05101 molal (HgI_2) at saturation. At all concentrations of mercuric iodide lower than 0.05100 molal, no measurable reduction takes place as evidenced by the constancy of the weight of a globule of mercury placed in it. It is to be expected that an equi-

librium will always exist between mercuric and mercurous io-
dides in the presence of metallic mercury, but the amount of
the mercurous iodide in solution is too low to be determined.
For this reason, in all the cells of this study, the mercury
may be considered to be entirely in the higher valence form.

With all cells using solutions below saturation, a defi-
nite reproducible (to $\pm$ 0.0002 volts) E.M.F. was obtained im-
mediately after solution was effected. With the saturated
solutions, the voltage of the cell,

$$Hg \left| \begin{array}{l} HgI_2 \ \ 0.005M \\ KI \ \ \ \ 0.05M \end{array} \right| \left| \begin{array}{l} HgI_2 \ sat. \\ KI \ 0.05M \end{array} \right| Hg$$

becomes approximately -0.229 after fifteen days but could not
be checked within five millivolts.

The E.M.F. of the cells measured are reported in Table X.
The second column, headed "number of cells", gives the number
of times the cells were prepared from entirely new solutions.
The E.M.F. of each individual cell was measured at intervals
over a period of time ranging from two days to one month. At
least two reference cells were maintained at all times for
checking.

TABLE X

E.M.F. of Alcoholic Concentration Cells of the Type:

$$\text{Hg} \ \left| \ \begin{array}{l} \text{HgI}_2 \quad 0.005 \\ \text{KI} \quad\ \ 0.05 \end{array} \ \right|\!\!\left| \ \begin{array}{l} \text{HgI}_2 \quad C \\ \text{KI} \quad\ \ 0.05 \end{array} \ \right| \ \text{Hg}$$

C	No. of cells	E.M.F.	Max. Variation
0.025	5	+0.04850	±0.0002
0.010	5	+0.01455	±0.0001
0.0025	2	-0.01150	±0.0001
0.0010	2	-0.02260	±0.0002
0.0005	2	-0.02905	±0.0001

The relationship between voltage and concentration of HgI_2 is represented graphically in Figure IV. It is evident that the relation between E and $\ln \frac{c_1}{c_2}$ is far from linear. It is interesting to note that by plotting the data of M. S. Sherrill[29] for mercuric iodide in aqueous potassium iodide (1M) the same type of curve is obtained.

E.M.F. of Cells Containing Organo-mercuric Iodides.

The solutions for the organo-mercuric iodide half-cells were prepared by adding to the alcoholic potassium iodide the calculated amount of the organo-mercuric iodide, or equivalent quantities of the bisorgano-mercuric compound and mercuric iodide. With the higher concentrations, the amount of mercuric iodide present when equilibrium is reached is sufficient to

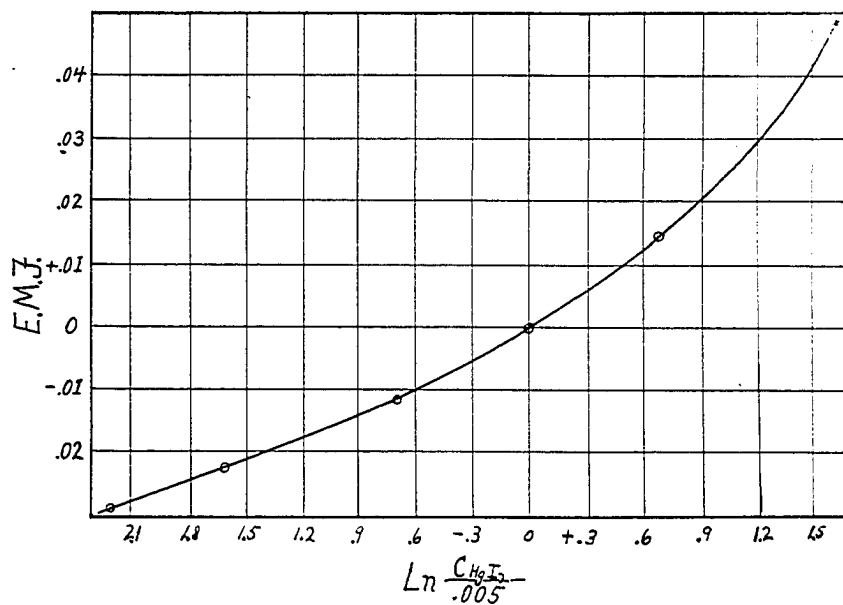29. Sherrill, Z. physik. Chem., 43, 731 (1903).

Fig. IV.   Relation between E.M.F. and $\ln \frac{c_1}{c_2}$ for mercuric iodide concentration cells in absolute alcohol.

give a characteristic greenish yellow tint to the solutions.
The E.M.F. of the organo-mercuric iodide half-cells against
the reference mercuric iodide half-cell as shown in Equation
II was determined. No difficulties were encountered in ob-
taining electromotive force measurements reproducible to
± 0.0003 volt over a period of from two to twelve days with
any of the compounds except methylmercuric iodide, which is
discussed below as a special case.

From the measured E.M.F., the concentration of mercuric
iodide in the cells was found from the curve, Figure IV. From
this, and the initial concentration of the organo-mercuric com-
pound, the concentrations of all the constituents of Reaction
I were calculated. These data, with the equilibrium constants
and free energy calculated from them, are presented in Table
XI.

Irregularities of the Methylmercuric Iodide Cells.

Solutions of methylmercuric iodide in alcoholic potassium
iodide deposit small quantities of metallic mercury on stand-
ing at 25°. After one week, the amount deposited is very
noticeable and during this time the E.M.F. of the cell changes
slowly in the direction of increasing concentration of mercur-
ic iodide. This change is not complete in two weeks.

Thus, a cell of 0.06 molal methylmercuric iodide had an
initial voltage of 0.0027, two days later the E.M.F. was

TABLE XI

Study of the Reaction $2RHgI \rightleftharpoons R_2Hg + HgI_2$, from E.M.F. Measurements of Concentration Cells of the Type:

$$\text{Hg} \left| \begin{array}{l} HgI_2 \ .005M \\ KI \ \ \ .05M \end{array} \right| \left| \begin{array}{l} RHgI \rightleftharpoons R_2Hg + HgI_2 \ C_1 \\ KI \ .05M \end{array} \right| \text{Hg}$$

RHgI Conc.	E in millivolts Max.	Min.	$HgI_2 C_1$ Average	RHgI Average	$K = \dfrac{(R_2Hg)(HgI_2)}{(RHgI)^2}$	$-\Delta F$ calcd.	
CH_3-							
0.06	+2.7 #		.00575	.0485	1.4×10^{-2}	-2540	Av.
0.03	-11.5 #		.0025	.025	1×10^{-2}	-2710	-2620
C_2H_5-							
0.02	-19.6	-19.3	.00134	.01732	5.97×10^{-3}	-3020	Av.
0.02593	-16.4	-16.0	.00174	.02245	6×10^{-3}	-3030	-3020
C_4H_9-							
0.02	-23.0	-22.8	.000983	.01803	2.97×10^{-3}	-3430	
0.02	-23.0	-22.8	.000983	.01803	2.97×10^{-3}	-3420	Av.
0.025	-19.6	-19.4	.00133	.02234	3.54×10^{-3}	-3330	-3390
0.03	-18.1	-18.0	.00149	.02702	3.04×10^{-3}	-3420	
$C_6H_5CH_2-$							
0.01	-11.0	-10.9	.00258	.00484	2.84×10^{-1}	-742	Av.
0.01	-11.4	-11.3	.00252	.00496	2.58×10^{-1}	-800	-768
$CH_3C_6H_4-$							
0.0025 +	-25.4	-25.3	.00078	.00094	6.9×10^{-1}	-219	Av.
0.0025	-26.0	-25.9	.00073	.00104	4.92×10^{-1}	-418	-212
0.003	-22.7	-22.6	.0010	.0010	10×10^{-1}	0	
C_6H_5-							
0.001 +	-36.8	-36.4					
0.001	-36.8	-36.4					
0.0025 +	-25.4	-25.3	.00078	.00094	6.9×10^{-1}	-219	
0.0025	-25.5	-25.1	.00078	.00094	6.9×10^{-1}	-219	Av.
0.0035 +	-20.6	-19.9	.00122	.00106	13.2×10^{-1}	+164	-28
0.0035	-20.5	-19.9	.00122	.00106	13.2×10^{-1}	+164	

\# Initial voltage of these cells is given due to slow decomposition of compound.

\+ Cell prepared from equivalent quantities of R_2Hg and HgI_2, reported concentration calculated on basis of RHgI.

0.0062, and at the end of ten days the E.M.F. was 0.0158. Because of this change, only the initial values of the E.M.F. of the cells containing methylmercuric iodide are included in Table XI.

The methylmercuric iodide is the only compound studied that has been found to decompose at 25° within the usual time of observation. Samples of all the solutions have been kept for two months without any visible separation of mercury and the original compound was removed and identified (by melting point) after evaporation of the alcohol and removal of potassium iodide with water. However, after six months at room temperature, solutions of ethylmercuric iodide were found to have deposited minute quantities of mercury, and solutions of benzylmercuric iodide had deposited mercury in quantity sufficient to be easily observed in the flasks.

This decomposition can be brought about quickly with all the compounds studied by heating them to 130°-160° in a saturated alcoholic potassium iodide solution in sealed tubes. The literature[30] reports that dibenzylmercury, when decomposed by heat, yields metallic mercury and dibenzyl. This can be represented by the equation,

$$R_2Hg \longrightarrow R-R + Hg \qquad \text{Equation IV.}$$

In an alcoholic potassium iodide solution of an organo-mer-

30. Whitmore, Organic Compounds of Mercury, The Chemical Catalog Co. 1921, p.185.

curic iodide this would be a secondary reaction added to the reaction shown in Equation I or the combined equations could be written,

$$2 \text{ RHgI} \rightleftharpoons \text{R}_2\text{Hg} + \text{HgI}_2$$
$$\longrightarrow \text{R}_2 + \text{Hg} \qquad \text{Equation V.}$$

The formation of metallic mercury and a hydrocarbon would render this reaction irreversible and if allowed to go to completion, one-half of the mercury in the organo-mercuric iodide should separate as metallic mercury. This conclusion was tested by heating 4.8296 g. benzylmercuric iodide in alcoholic potassium iodide to 160° for two hours in a sealed tube. The metallic mercury liberated weighed 1.1542 g. which is within 0.3% of the theoretical according to Equation V.

Methylmercuric iodide shows the shortest time factor for this side reaction of any of the compounds studied. The constancy of K calculated for Equation I from E.M.F. measurements on cells of varying concentration would indicate that even in this case, the speed of the side reaction is so slow that a reliable measure of the concentrations of the first equilibrium can be obtained.

The data presented in Table XI show that K is independent of concentration over the range of dilutions employed, with the possible exception of the cells containing tolyl- and phenylmercuric iodides. Even in these cases the variation in

E.M.F. equivalent to the variation of K is only ± 0.0004 volts

which is not much greater than the actual experimental error.

The marked variations in K produced by such slight variations

in E.M.F. results from the flatness of the curve in Figure IV

from which the concentration of HgI_2 is determined and from

the smallness of the concentration of RHgI, which enters the

denominator in the calculation of K. The cells cannot be

measured at higher concentrations so as to employ the part of

the curve with greater slope, due to the limited solubility of

these compounds.

In all of this work the electromotive force has been in-

terpreted as being due to and a measure of the concentration

of mercuric iodide resulting from the reaction represented in

Equation I. This assumption seems justified in view of the

approximate constancy of K with varying concentrations. As

the series were extended to the more negative radicals, com-

pounds would be reached which would not form an unionizable

radical RHg^+. This would be expected in the case of the ex-

tremely negative radicals such as $-NO_3$ or $-Cl$. Such compounds

as NO_3HgI or $ClHgI$, if obtainable, would undergo reaction I

to give

$$2 \ NO_3HgI \ \rightleftharpoons \ Hg(NO_3)_2 + HgI_2$$
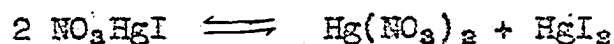
and in such a case both of the products of the reaction, as

well as the initial compound NO_3HgI, would be expected to contribute to the total E.M.F. of the cell containing this equilibrium mixture. As mentioned earlier, it does not seem likely that any of the organo-mercuric iodides or bisorgano-mercury compounds used in this work would contribute measurably to the E.M.F. of the cells though even a slight effect of this kind might be a factor influencing the change in K with dilution, found with the cells using tolyl- and phenylmercuric iodides.

If these conclusions be true, one would expect that the more negative radicals in the series, such as NO_3, Cl, Br, would cause Reaction I to proceed even more completely to the right. This is supported by the work of Reinders[21] on mixed halides of mercury.

The curves used in the theoretical discussion for showing the relationship between the dissociation constants of the RNH_2 and $RCOOH$ derivatives are reproduced in Figure V. Since the equilibrium constants K derived in Table XI are found to plot a smooth curve in Figure V, it is apparent that these mathematical relationships can also be extended to the type derivatives $RHgI$ and R_2Hg. The approximate ionization constants for the $RHgNO_3$ derivatives as reported in the preceding paper have also been plotted in Figure V to show that the mathematical relationship can be extended to cases in which the chemical factors do not permit the calculation of free energy.
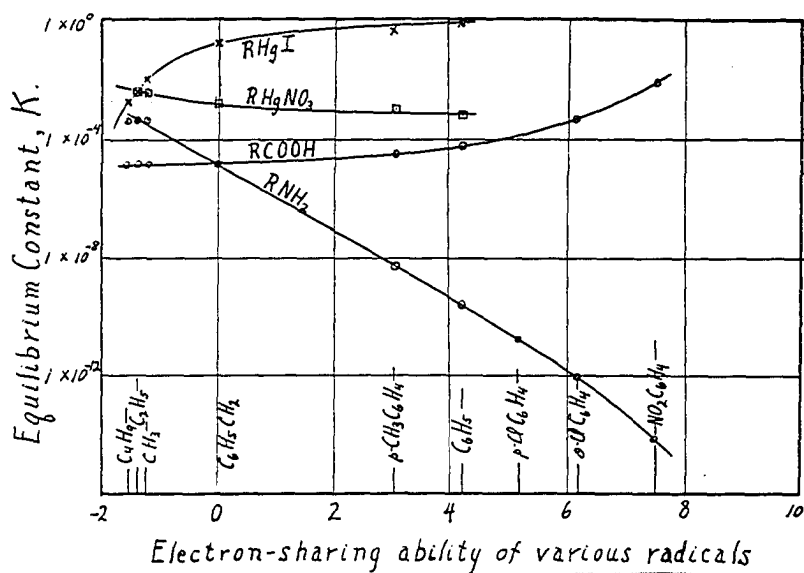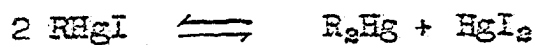
Fig. V. Relation between the equilibrium constants for the reaction,

$$2 \; RHgI \; \rightleftharpoons \; R_2Hg + HgI_2$$

and the ionization constants of the type compounds $RHgNO_3$, $RCOOH$, RNH_2.

The Determination of Decomposition Voltages of
Compounds of the Type RHgNO₃

Whenever an external electromotive force is applied be-
tween electrodes of an inert metal such as platinum immersed
in a solution of an electrolyte, the positive ions of the
electrolyte migrate toward the cathode and the negative ions
to the anode. If the positive ions lose their charges by re-
ceiving an electron from the cathode they may plate out on
the cathode. In case this happens the cathode is no longer
inert toward the solution and assumes a characteristic electro-
motive force due to the material that has plated out tending
to redissolve. The E.M.F. will be affected by similar con-
ditions at the anode. If the negative ion is the same for all
members of a series of compounds the E.M.F. at the anode should
be the same for all, and any variations in the measured E.M.F.
should be due to differences in the material that deposits on
the cathode. There are some confusing factors in the deter-
mination of decomposition voltages but in general, for solu-
tions of metallic salts, the voltages are fairly consistent
with the order of the metals in the electro-chemical series.

It has been found by Kraus[23] that the radicals RHg, where
R is aliphatic, can exist in the free state and have metallic
properties. He prepared methyl-, ethyl- and propylmercury by
electrolyzing the chlorides in liquid ammonia. From this one

might expect that the free radicals RHg could be arranged in a series analogous to the electro-chemical series of the metals, provided sufficiently accurate determinations of the decomposition voltages of compounds of the type $RHgNO_3$ can be made.

The apparatus used was similar to that used by Newberry[31] in his studies of overvoltage.

A cell (D, Figure VI) is connected by means of a commutator to two separate potentiometers (A and B). The voltage from source B is run through the cell during one-half of each revolution of the commutator and electrolyzes the solution. During the other half of each revolution, the electrodes are connected through a galvanometer (G) with the potentiometer (A) which is so adjusted that no current flows. This latter potentiometer measures the back voltage of the electrodes in the cell (D). The commutator is rotated from 1000 to 2400 r.p.m. and the rapid impulses through the galvanometer give it a steady deflection unless the potentiometer (A) exactly balances the back voltage.

The cell used is illustrated in Figure VII. The electrodes are platinum wires 1/2 mm. in diameter and 1/2 mm. long. The solution is circulated rapidly by means of a propeller, to prevent changes in concentration at the electrodes. No difference was observed when the electrodes shown were replaced by platinum plates 1 cm. square and 5 mm. apart.

31. Newberry, J. Chem. Soc., 105, 2419 (1914).

In determining the decomposition voltage of an electrolyte the cell is filled with the solution and while stirring rapidly the circuit (B) is adjusted to apply a certain low voltage to the cell. During half of each revolution of the commutator the back voltage is balanced against the circuit (A), which is adjusted till the galvanometer gives no diflection. For each value of the electrolyzing voltage (B) the cell offers a definite back electromotive force which is easily reproducible and constant over long periods (30 minutes) of continuous operation. The voltage (A) increases with B until the decomposition voltage is reached, when A ceases to increase or increases much less rapidly. It is convenient to plot the difference B-A as abscissae against A as ordinates.

In Figure VIII are given these data for silver nitrate and for copper sulfate in water solution. For the latter the curve has reached a maximum when the back E.M.F. is 1.50-1.54, which agrees well with the decomposition potential (1.49) obtained by Le Blanc[32]. For the former the maximum comes at 0.92 while Le Blanc gives 0.70. Measurements made upon the ethyl-, benzyl-, and phenylmercuric nitrates in alcoholic solution were much less satisfactory. The data are shown in Figure IX.
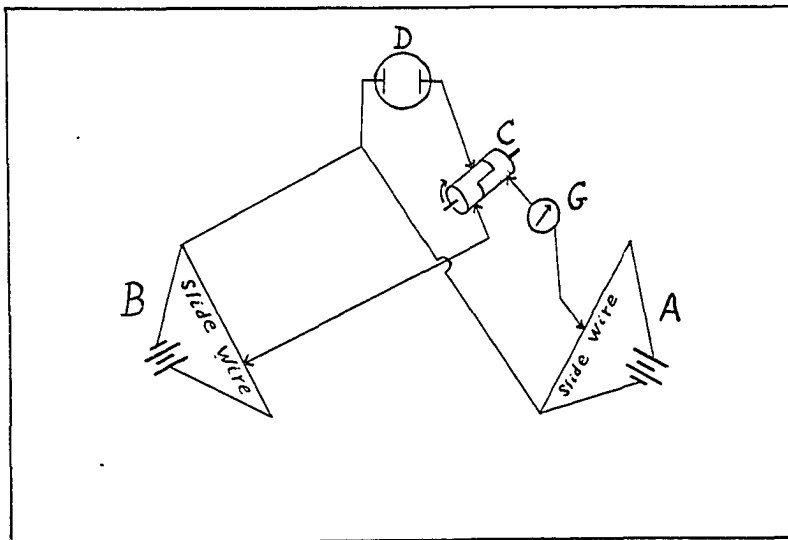
32. Le Blanc, Z. physik. Chem., 8, 299 (1891).

Fig. VI. Diagram of circuit used for measuring
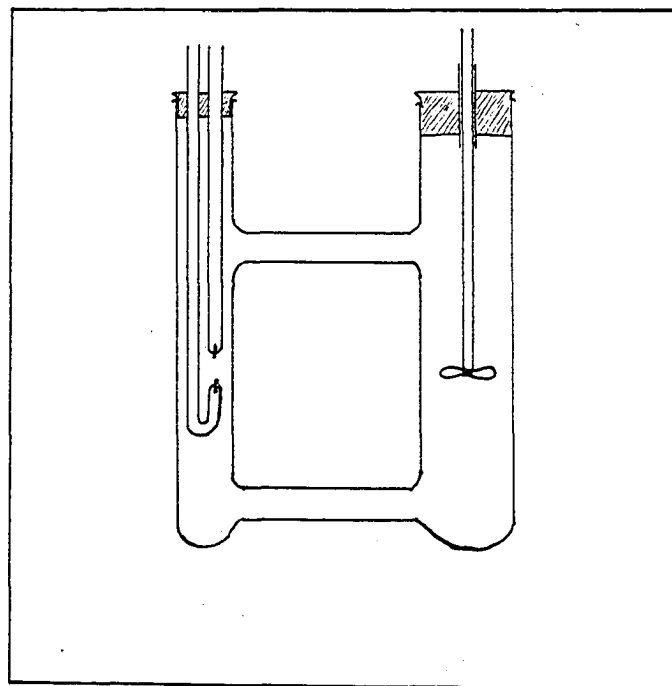decomposition voltage.

Fig. VII. Diagram of cell used for measuring de-
composition voltage.

The voltages are much less reproducible with these mercury derivatives than with silver nitrate or copper sulfate and do not show a very satisfactory distinction between the compounds. This is due partly to the decomposition of the free radical RHg at the cathode. In every case when the decomposition voltage had been reached free mercury deposited on the electrode. These complicating factors rendered the method unsuitable for distinguishing between the compounds. It was accordingly abandoned. It is probable that greater success would have been obtained had the measurements been made at lower temperatures since the free radicals would then have been more stable. This greater stability at low temperatures was reported by Kraus[23]. Even at -30°, however, some decomposition occurs.
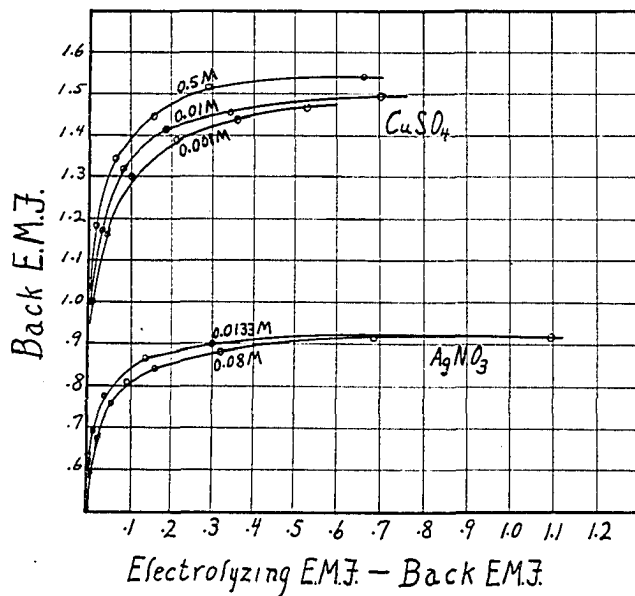
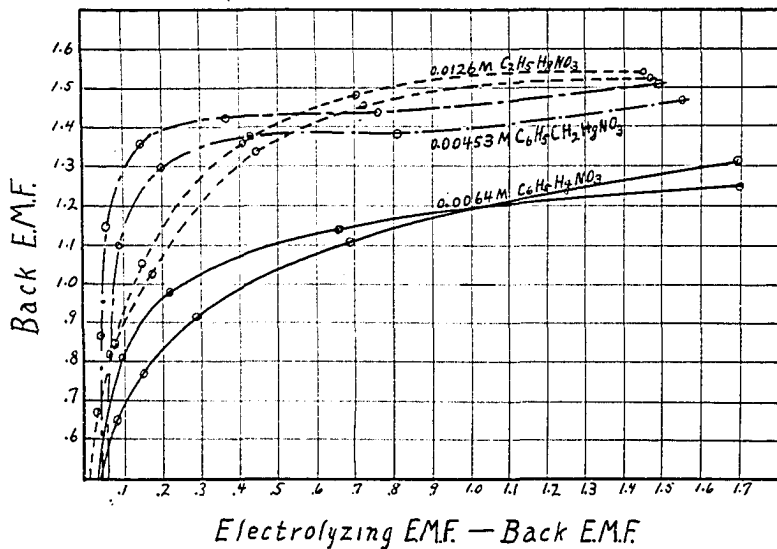Fig. VIII. Determination of decomposition voltage of copper sulfate and silver nitrate.

Fig. IX. Determination of decomposition voltage of ethyl-, benzyl-, and phenylmercuric nitrates.

Determination of Decomposition Temperatures of
Compounds of the Type RHgNO₃

It was recognized early in the progress of this work that the order in which the organo-mercuric derivatives had been arranged, from conductance and E.M.F. measurements, was not the same as the order of their stability or reactivity. Thus benzylmercuric nitrate is very unstable and reacts with water or alcohol when heated, precipitating a basic mercuric nitrate, while the methyl- and phenyl- derivatives which are placed at the two ends of the series are very inert to this treatment. They show the same order in their stability toward heat.

The approximate decomposition temperatures recorded in Table XII were determined by noting the temperature at which the compound decomposes when heated in a capillary tube such as is used for melting point determinations. The temperature of decomposition varies but slightly with the rate of heating and is very sharp.

The temperatures at which the compounds decompose would offer a rough comparison of the relative thermal stabilities of the compounds. The data for the organo-mercuric nitrates examined places the organic radicals in approximately the same order as that found by Kharasch[33] for the stability of

33. Kharasch and Macker, J. Am. Chem. Soc., 48, 3130 (1926).

the unsymmetrical mercuri-organic compounds when treated with hydrochloric acid; namely, tolyl- 190°, phenyl- 184°, methyl- 190°, ethyl- 155°, butyl- 150°, benzyl- 91°. The difficulties encountered in preparing the benzyl- and butylmercuric nitrates also would indicate that these two compounds are both the most reactive and unstable in the series investigated. In view of the fact that the conductivities of these unstable nitrates still place them in the same consecutive order as that found for the corresponding carboxy and amine derivatives, it seems probable that this is another case in which chemical stability cannot be directly interpreted in terms of "electronic potential" as Kharasch has done. A number of such cases for the elements have been discussed by Hildebrandt[34] as "discrepancies in the electro-chemical series".

TABLE XII

Melting Point, Approximate Decomposition
Temperature, and Solubility in Water at 25°
For Various Organo-Mercuric Nitrates

	Solubility Moles per L.	m.p.	Approximate Decomp. T.
Methylmercuric nitrate	deliquescent	59°	190°
Ethylmercuric nitrate	.0239	87	155
Butylmercuric nitrate #	(.00299)	(40°)	(150°)
Benzylmercuric nitrate	.00263	91	91
p-Tolylmercuric nitrate	.00057	187	190
Phenylmercuric nitrate	.00236	176-184	184

#Preparation was gray in color and could not be further purified.

34. Hildebrandt, Chem. Rev., II, 394 (1926).

DISCUSSION OF RESULTS

The considerations in the Theoretical Discussion indicated that the polar properties of any series of compounds containing one polar group should be a function of the electron-sharing ability of the radicals attached to the central atom or group, and that the magnitude of the change caused by substituting one radical for another will be inversely proportional to the size and complexity of that group. The results obtained in the Experimental Part are in fair agreement with these predictions, as the following statements indicate:

1. The ionization constants of the series of organo-mercuric nitrates change along the series in so orderly a way as to suggest a functional relation between these constants and the previously fixed order of the radicals.

2. The equilibrium constants for the reaction,

$$2 \ RHgI \ \Longrightarrow \ R_2Hg + HgI_2$$

change along the series in an equally orderly way.

3. The extent of the change in K, as shown in Figure II, for the ionization of the organo-mercuric nitrates is much less than for the ionization of the carboxylic acids and of the amines, as was expected. The change in K for the iodides cannot be compared with that of the acids and amines since an entirely different type of reaction is involved.

The effect of increased size and complexity of the central group on the variation in K along the series can be shown in another way. In the acid RCOOH, the central group is $-(C\overset{O}{\underset{O}{\lessgtr}})-$, while in the series RCH_2COOH the group is $-(CH_2-C\overset{O}{\underset{O}{\lessgtr}})-$. In this latter series the central group is considerably larger and there is accordingly a much smaller variation in K. In the series RCH_2CH_2COOH the variation is even less. When the radicals, R, are separated from the carboxyl group by more than four CH_2 units there ceases to be any noticeable change in K. The same relations are observed with the amines RNH_2 and RCH_2NH_2, etc. A graphical representation is given in Figure X, in which the distance between R- and -NH_2 or -COOH is measured by the number of intervening -CH_2- units. The magnitude of the effects shown would undoubtedly be different in case the intervening -CH_2- units form a branched chain instead of a straight one.

It has not been found possible to correlate quantitatively the magnitude of the change in K through the series with any one property of the central atom or group. The relation is doubtless very complex involving the radii of the atoms of the group, the number of atoms and their configuration in space. In spite of our inability to calculate, or even to explain these effects, the graphical method used in arranging
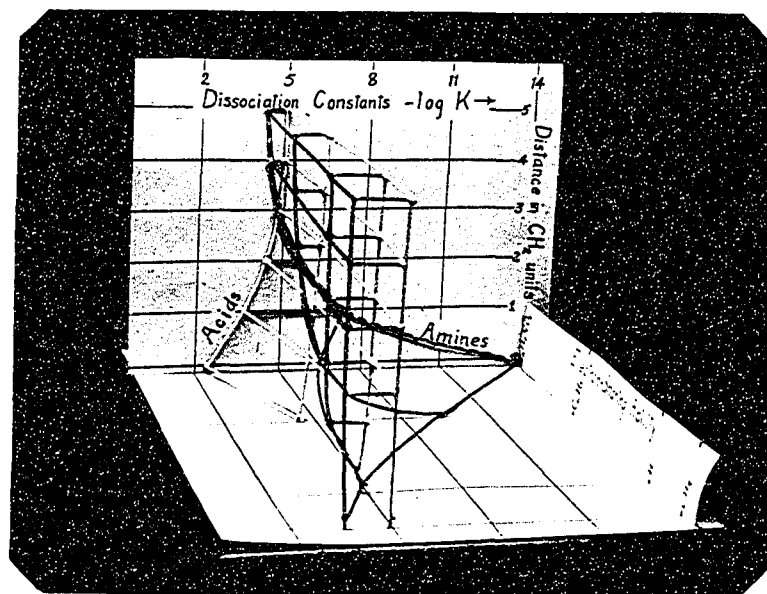
Fig. X. Photograph of a model, constructed to scale, showing the relationship between the dissociation constants of the acids and amines of radicals of different electron-sharing ability and the distance of the radicals from the polar group in CH_2 units.

the radicals in a series seems to place them in the true order of their electron-sharing ability, since that order has been found to control the polar properties of four series of compounds, without any marked discrepancies.

The method also offers a means of predicting with a fair degree of certainty, the constants for many other members of the two series of mercury derivatives. Since the ionization constants for parachlorobenzoic acid and parachloraniline place the radical ClC_6H_4- at about 4.6 on the axis of electron-sharing ability, the constants for parachlorophenylmercuric nitrate and iodide can be estimated from the curve, Figure V, to be 7×10^{-4} and 1×10^0 respectively.