SOME GENERAL ASPECTS OF MERCURY CHEMISTRY

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The element mercury, because of its ease of extraction from ores and its distinctive physical properties, has been known from the earliest times. Its fascination for the alchemists has found an echo in the continued interest of modern chemists in exploring the chemistry of the element. Since the number of publications concerning mercury must run to many thousands, it is impossible in a short review to do even rough justice to its detailed chemistry. We have therefore attempted to bring out certain features that seem to provide a framework on which the diverse studies of many disciplines can hang and be seen as a coherent whole.

I. The Mercury Atom

The mercury atom has the electronic ground state (Xe core)-$4f^{14}5d^{10}6s^2$. It may therefore be compared with Ba, (Xe core)$6s^2$, and the other Group IIB elements Zn, (Ar core)$3d^{10}4s^2$, and Cd, (Kr core)$4d^{10}5s^2$. The ionization potentials of the Group IIA, IIB, and IV elements are shown in Fig. 1. Two features are at once apparent: the overall higher values of the ionization potentials of the B subgroup elements than of the A subgroup elements, and the contrast between the steady fall in ionization potential with increasing atomic number in the A subgroups and the minimum at the second long period shown in the B subgroups. In quantum mechanical terms, this can be rationalized by noting that in the A subgroup the effect of increasing effective nuclear charge with atomic weight is a little more than offset by the increase in principal quantum number of the electron removed, leading to a steady but small decrease in ionization potential (I.P.) with atomic number. In going from Ca to Zn the 3*d* shell is filled. Because the radial distribution function of a 4*s* electron is such that it spends a portion of its time near the nucleus, while

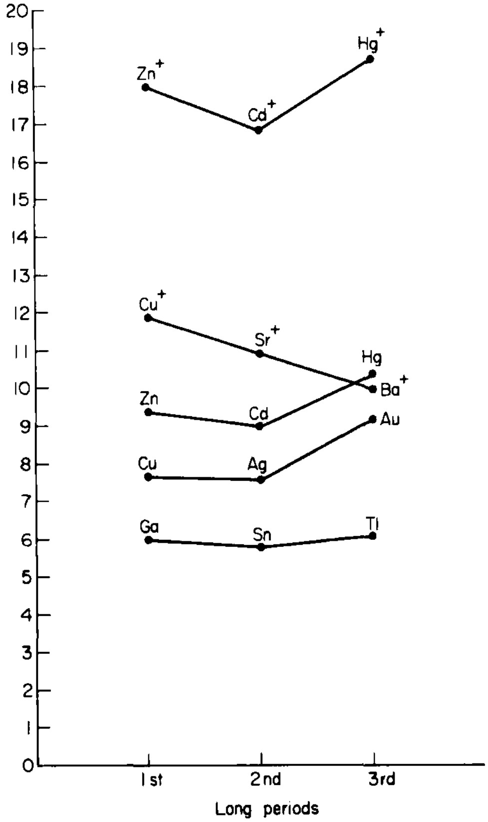


FIG. 1. Ionization potentials of Group IB, IIA, and IIB elements (C. E. Moore, Atomic Energy Levels, N.B.S., Washington, 1958).

the $3d$ electrons do not penetrate the Xe core to an appreciable extent, the $4s$ electrons in Zn experience a higher effective nuclear charge than in Ca and the first I.P. is 3.28 eV higher. Similarly, the first I.P. of Cd is 3.30 eV higher than that of strontium. However, between barium and mercury, in addition to the $5d^{10}$ electrons, there are the $4f^{14}$ electrons. The same arguments about the penetration of the $6s$ electrons through a $5d$ core apply to the $4f$ core, and the first I.P. of mercury exceeds that of Ba by 5.22 eV; indeed, the first I.P. of mercury is slightly greater than the second I.P. of barium. This effect of tighter binding of the external electrons results in smaller atomic and ionic radii for the B subgroup elements than for their A subgroup partners with external electrons of the same principal quantum number, and is the cause of the "lanthanide contraction" referred to by chemists in the 1930–1950 period. These effects are major causes of the distinctive differences between A and B subgroup chemistry, and are especially important in the chemistry of the B subgroup elements of the third long period where they operate together.

TABLE I

IONIZATION POTENTIALS AND VALENCE STATE PROMOTION ENERGIES OF GROUP IIB METALS

	Zn	Cd	Hg
I.P. of $M \rightarrow M^+$ (eV)	9.4	9.0	10.4
I.P. of $M^+ \rightarrow M^{++}$ (eV)	18.0	16.9	18.7
$ns^2 \rightarrow ns^1p^1$ (kcal)	103.2	97.4	125.3

The electron affinities of the Group IIB metals have not been measured directly and estimated values do not appear to be very reliable (*45*, *50*). The high values of 1.2, 1.0, and 2.2 eV for Cu, Ag, and Au, respectively, suggest that the order should be Hg > Zn >Cd, which is the order of the electron affinities of Hg^+, Zn^+, and Cd^+. However, addition of an electron to the uncharged atom is to the p orbital and, as will be seen later, this lies well above the s level for the Group IIB elements. It seems likely therefore that the electron affinities (E.A.) of the Group IIB atoms will be rather low. This means that the Mulliken electronegativity (I.P. + E.A.)/2 can be replaced by I.P. in making comparative studies in these cases. By this definition mercury is, after gold, the most electronegative metal.

Before mercury can form bonds to other elements it is necessary that the $6s^2$ ground state is reorganized to give $6s^16p^1$. The energies required for this promotion for the Group IIB elements are given in Table I. Just as the ionization potentials are high for Group IIB metals so are these promotion energies, and this is particularly true for mercury. It has important consequences in the chemistry of covalent compounds of mercury; in particular, the high energy of promotion of electrons from 5*d* or 6*s* to 6*p* means that mercury tends to form two covalent bonds and further ligands are added only with difficulty. This theme, to be examined in more detail later, runs through the whole of the chemistry of mercury. In contrast to this high $s \rightarrow p$ promotion energy, the $5d^{10} \rightarrow 5d^{9}6s^{1}$ transition in Hg^{++} requires very little energy, as can be seen from Table II. Dunitz and Orgel have shown that in these circumstances, an effect related to a Jahn-Teller effect can operate to distort an octahedral environment in such a way that four bonds in a plane would be lengthened, and two bonds perpendicular to this plane shortened (*21*). This emphasizes that in an ionic environment, too, mercury, like Cu^{+}, Ag^{+}, and Au^{+}, but unlike Zn^{++} and Cd^{++}, tends to have a special interaction with two ligands at 180°. The importance of the unit LHgL is therefore apparent in both the factors affecting reactivity of covalent compounds and the structure of crystalline ionic compounds.

TABLE II

PROMOTION ENERGY (eV) FOR GROUP IIB METALS

	Zn	Cd	Hg
$nd^{10} \rightarrow nd^{9}(n+1)s^{1}$	9.7	10.0	5.3
$nd^{10} \rightarrow nd^{9}(n+1)p^{1}$	17.1	17.3	14.7

II. Mercury Metal and Its Interaction with Other Metals

Mercury metal is unique in being a liquid at room temperature and is volatile and monatomic in the vapor. Nyholm (*45*) has suggested that this can be understood in terms of the high valence state promotion energy of mercury. If it is assumed that metals in their standard states exhibit their characteristic valency (i.e., 2 for the Group IIB metals), the effective binding energy of the metal is given by the sum of the heat of atomization and the valence state promotion energies. When this is done (see Table III), the "corrected" bonding energy is seen to follow the order of ionization potentials.

TABLE III

HEATS OF ATOMIZATION OF GROUP IIB METALS CORRECTED FOR VALENCE STATE PROMOTION

Metal	Heat of atomization (kcal)	Valence state correction (kcal)	Corrected heat of atomization (kcal)	I.P. (eV)
Zn	31.2	103.2	134.4	9.4
Cd	26.8	97.4	124.2	9.0
Hg	15.3	125.3	140.6	10.4

The physical properties of mercury metal have been studied in great detail (and can be found in any of the standard compilations of physical data). Attempts have been made to understand these properties in terms of various models (*32*, *33*).

It has already been noted that mercury is one of the most electronegative metals and, although there does not appear to be a mercury equivalent of saltlike CsAu, mercury does react exothermically with the alkali metals to give stable compounds. With the metals of higher lattice energy and higher ionization potential, compound formation has been demonstrated at higher temperatures. [A summary of the available phase diagrams can be found in metallurgical texts (*34*).]

Mercury-mercury covalent bonds in mercurous compounds were the first, and for long the only known covalent metal-metal bonds. Recent research has greatly altered this picture and the conditions for metal-metal bond formation are better understood. It is thought that, as the formal positive charge on a complex having an odd number of electrons is reduced, it becomes more like a free radical (*45*). That is, the orbital becomes larger and effective overlap with another orbital becomes possible. In the case of mercury the known mercurous compounds are ionic in nature, with the possible exceptions of $(CCl_3CO \cdot O)_2Hg_2$ (*55*) and $(CH_3CO)_2N_2Hg_2$ (*29*). These two compounds appear to be in a class of their own, and preparative studies to delineate the stability range of such compounds would be very valuable.

The thermodynamic factors governing the disproportionation in solution of Hg_2^{++} into Hg^{++} and Hg will be discussed later. The disproportionation is strongly influenced by the nature of the ligands present, so that mercurous compounds of ligands that interact strongly with Hg^{++} are not known. It was thought at one time that all ligands would tend to bind more strongly to Hg^{++} than to Hg_2^{++}, and that no genuine complexes of Hg_2^{++} would exist. Recent work, however, has demonstrated that ligands with oxygen as the donor atom do form complexes with Hg_2^{++}. The first evidence for mercurous complexes came from potentiometric studies on solutions containing Hg_2^{++} and $NO_3^=$, SO_4^-, ClO_4^-, and especially polyphosphate and oxalate. The first characterized compounds, however, contain ligands such as $(C_6H_5)_3PO$, C_6H_5NO, and $(CH_3)_2SO$ (*49*).

An interesting property of the Hg—Hg bond in the mercurous halides is the variation in bond length with the nature of the halogen (*29*):

	Hg_2F_2	Hg_2Cl_2	Hg_2Br_2	Hg_2I_2
d(Hg—Hg) (Å)	2.43	2.45	2.50	2.69

Various explanations have been advanced for this, but the most convincing is due to Ebsworth (*22*), who suggests that it is a lattice energy effect. For the small F^- ion, there is a large gain in lattice energy if the Hg—Hg bond is compressed. This factor becomes relatively less important as the size of the halogen increases. This factor could account also for the long Hg—Hg bond (2.90 Å) in $Hg_2N_2(COCH_3)_2$, which had always been a difficulty for the explanations based on electronegativity arguments. The importance of the coordination number of 2 in the chemistry of mercury compounds is shown in the structure of mercurous nitrate, in which the two water molecules of crystallization are positioned along the Hg—Hg axis (*29*),

$$[H_2O—Hg—Hg—OH_2]^{++}$$

as in the case of $[CH_3HgOH_2]^+$ the Hg—O stretching frequency can be detected in the Raman spectrum (*25*).

Compounds containing metal-metal bonds, in which one partner is a transition metal, occur mainly with transition metals in a low valency state, and particularly for d^6, d^8, and d^{10} systems. Mercury(II) is d^{10} and forms bonds to other d^6, d^8, and d^{10} systems. Some examples are shown in Table IV. King (*39*) and Hieber and co-workers (*36*) have prepared a number of derivatives of the type $Hg[Mn(CO)_5]_2$, where the metal may be Mn, Fe, or Co and the CO group can be replaced (e.g., by NO or PPh_3). Compounds containing metal-HgX systems have been prepared by Nyholm and Vrieze (*46*), Lewis and Wild (*41*), and Gamorkan and Stiddard (*26*). The metals involved are Rh^{III}, In^{III}, Fe^0, and W^{II}. It is probable that many more examples will be found. Examples are listed in Table IV.

TABLE IV

COMPOUNDS WITH MERCURY-METAL BONDS

Compound[a]	M.P. (°C)
$Hg[Mn(CO)_5]_2$	~155
$Hg[Fe(CO)_2C_5H_5]_2$	145–146
L_3Cl_2RhHgF	195
$L_3Cl_2RhHgCl$	205
$[(Ph)_3P_2COCl_2IrHgCl$	270
$(CO)_2py_2FeHgCl_2$	>340

[a] L = Ph_2AsMe.

III. Bond Energies of Mercury Hydrides, Halides, and Alkyls

As a result of spectroscopic (*35*) and kinetic (*56*) studies, the energies of a number of Hg—X bonds are known; these data are shown in Table V. The species exist as discrete molecules only in the gas phase. In Fig. 2 the bond energies of the compounds HgX (where X = halogen) are plotted against the sum (I.P. + E.A.) of the halogen. For comparison the bond energies of the corresponding HX are also shown. It can be seen that $\delta(HX - HgX)$ increases from iodine to fluorine, and at fluorine the difference in kcal is only slightly less than the valence state promotion energy of 107 kcal for mercury. The mercury-to-fluorine bond is therefore quite similar to the H—F bond, while the Hg—I bond, after allowing for the valence state promotion energy, is much stronger than the H—I. This has important consequences in the solution chemistry of mercury halides.

TABLE V

BOND ENERGIES OF HgX (g) → Hg (g) + X (g) (kcal)

HgF	HgCl	HgBr	HgI	HgCN
41	24	17	8	23 ± 6
$HgCH_3$	HgC_2H_5	$HgCH{=}CH_2$	HgH	HgH^+
7 ± 3	6 ± 4	19 ± 6	8.6	53

Unfortunately the available data for ZnX and CdX are of low accuracy (*14*) and it is therefore difficult to make useful comparisons. Better data are available for the metal hydrides and alkyls, of which CH_3 can be taken as typical. These are shown before and after correction

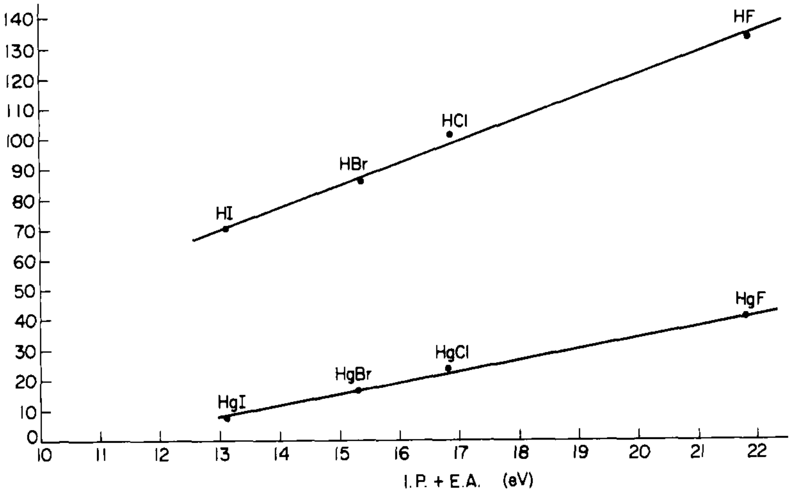


FIG. 2. Bond energies of mercury halides and hydrogen halides plotted against I.P. + E.A. of the halogen.

for valence state promotion in Table VI. The pattern of the corrected bond energies roughly follows the I.P.; a better comparison would be with I.P. + E.A., but E.A. data for Zn, Cd, and Hg are not available.

TABLE VI

COMPARISON OF BOND ENERGIES $M{\cdot}CH_3$ AND MH FOR GROUP IIB METALS (kcal)

Metal	$M{\cdot}CH_3$	MH	Valence state promotion	Bond energy corrected $M{\cdot}CH_3$	Bond energy corrected MH	I.P. (eV)
Zn	35	20	92	127	112	9.4
Cd	21	16	86	107	102	9.0
Hg	7	9	107	114	116	10.4

It is interesting to note that for Hg^+, where no valence state promotion is needed, $D(HgH^+)$ at 53 kcal is much higher than $D(HgH)$ at 8.6 kcal. Indeed, $D(HgH^+)$ is of the same order as $D(MH)$, in which M is a Group IA or IB metal where the bond is also formed by the overlap of two *s* orbitals. An s^1-s^1 bond of this type must also exist in Hg_2^{++}, to be discussed in more detail later.

The heats of formation and bond energies of the covalent compounds

TABLE VII

HEATS OF FORMATION OF HgX_2 AND RHgX AS CONDENSED PHASES AND VAPORS, AND BOND DISSOCIATION ENERGIES[a]

Compound	ΔH_f° (c)	ΔH_f° (gas)	$D_1 + D_2$	D_1	D_2	$\frac{D_1 + D_2}{2}$
$(CH_3)_2Hg$	14.0 ± 1	22.3 ± 1	58.4 ± 2	51.5 ± 2	6.9 ± 3	29
$(C_2H_5)_2Hg$	6.5 ± 1	17.2 ± 1	48.4 ± 4	42.5 ± 2	5.9 ± 4	24
$(n\text{-}C_3H_5)_2Hg$	−6.5 ± 2	6.6 ± 2	49.0 ± 4	—	—	—
$(i\text{-}C_3H_5)_2Hg$	−3.4 ± 1	9.3 ± 1	42.0 ± 4	27.0 ± 5	15 ± 7	21
$(CH_2{:}CH)_2Hg$	—	—	67.4 ± 6	48.3 ± 1	19.1 ± 6	34
$(C_6H_5)_2Hg$	66.8 ± 1.5	93.7 ± 1.6	64.8 ± 4	—	—	32
$HgCl_2$	−55	−33.4	106 ± 2	81 ± 2	24	53
$HgBr_2$	−40.6	(−20)	89 ± 2	72 ± 2	17	45
HgI_2	−25.2	(−5)	69 ± 2	61 ± 1	8	35
CH_3HgCl	−27.8 ± 0.6	−12.3 ± 0.7	68.3 ± 2	64.3 ± 2	24	—
CH_3HgBr	−20.6 ± 0.6	− 4.4 ± 0.7	78.8 ± 2	61.8 ± 2	17	—
CH_3HgI	−10.3 ± 0.6	5.25 ± 0.7	69.0 ± 2	59.0 ± 2	8	—
C_2H_5HgCl	−34.0 ± 0.7	−15.8 ± 1.0	84.3 ± 3	60.3 ± 2	24	—
C_2H_5HgBr	−25.9 ± 0.7	−7.6 ± 1.0	74.6 ± 3	57.6 ± 3	17	—
C_2H_5HgI	−15.9 ± 0.8	3.0	61.7 ± 3	53.7 ± 3	8	—
C_6H_5HgCl	0.0 ± 1.2	24.5 ± 1.5	90.5 ± 3	66.4 ± 3	24	—
C_6H_5HgBr	7.8 ± 1.2	—	80.6 ± 4	63.6 ± 4	17	—
C_6H_5HgI	17.6 ± 1.2	—	69.6 ± 4	61.6 ± 4	8	—
$(CN)_2Hg$	62.5	88.5 ± 2	144 ± 2	123 ± 7	23 ± 6	72

[a] Skinner (*56*).

of divalent mercury of the types R_2Hg, RHgX, and HgX_2 (where R = organic group and X = halogen) are given in Table VII.

The most striking feature of the bond energies of these covalent mercury compounds is the large difference between the bond dissociation energies, $HgR_2 \rightarrow HgR + R$ (D_1) and $HgR \rightarrow Hg + R$ (D_2). The cause of this is the very high valence state promotion energy for mercury. In forming the first bond it is necessary to put in the whole of the promotion energy, but the second bond is formed without much further reorganization of the mercury orbitals. This effect is also observed with zinc and cadmium, but is less marked. Table VIII shows the data for $Zn(CH_3)_2$, $Cd(CH_3)_2$, and $Hg(CH_3)_2$. It can be seen that the energy $M(CH_3)_2 \rightarrow MCH_3 + CH_3$ (D_1) follows closely the I.P. of M without correction for valence state promotion, in contrast to that of $MCH_3 \rightarrow M + CH_3$ (shown in Table VI). It follows that $D_1 + D_2 +$ valence state promotion will also follow the I.P. order. It can be seen, however, that even after correction the Hg—CH_3 bond is weaker than might be expected.

TABLE VIII

BOND DISSOCIATION ENERGIES OF $M(CH_3)_2$ (M = Zn, Cd, AND Hg)

Metal	D_2 (kcal)	D_1 (kcal)	$D_1 + D_2$ (kcal)	Valence state promotion (kcal)	$D_1 + D_2$ corrected (kcal)	I.P. (eV)
Zn	35	47	82	92	174	9.4
Cd	21	46	67	86	153	9.0
Hg	7	52	59	107	166	10.4

There is an interesting consequence of the large difference between D_1 and D_2 for the mercury alkyls and the mercuric halides. Let us consider the reaction of a mercury alkyl with mercury,

$$R_2Hg\,(g) + Hg\,(g) \rightarrow RHgHgR\,(g)$$

using dimethylmercury as an example.

From the data in Table VII, $\Delta H = 52$ kcal for the reaction:

$$(CH_3)_2Hg\,(g) \rightarrow CH_3Hg\,(g) + CH_3\,(g)$$

Since

$$\Delta H_f \quad (CH_3)_2Hg\,(g) = 22 \text{ kcal} \quad \text{and} \quad \Delta H_f \quad CH_3\,(g) = 32 \text{ kcal}$$

it follows that

$$\Delta H_f \quad CH_3Hg\,(g) = 42 \text{ kcal}$$

This means that $\Delta H = 62$ kcal for the reaction,

$$(CH_3)_2Hg\,(g) + Hg\,(g) \rightarrow 2CH_3Hg\,(g)$$

and therefore the heat of dimerization of CH_3Hg would need to be at least 62 kcal if a volatile mercurous dimethyl were to be stable to disproportionation. This explains why no volatile mercurous alkyls are known. If D_1 for dimethylmercury were 29 kcal, the mean bond energy, then ΔH_f of $CH_3Hg(g)$ would be 19 kcal and the heat of reaction of dimethylmercury with a mercury atom would be only 14 kcal, and volatile mercurous alkyls would be stable to disproportionation for even a weak Hg—Hg bond. It is known that compounds corresponding to $(RHg)_n$ are obtained in condensed phases, but nothing is known of their structure. Proceeding in the same way, it can be shown that Hg_2Cl_2 should not exist in the vapor phase or as a covalent liquid:

$$HgCl_2\,(g) + Hg\,(g) \rightarrow 2HgCl\,(g) \qquad \Delta H = 121 \text{ kcal}$$

It is in fact found that the vapor in equilibrium with mercurous chloride, an ionic solid, is a mixture of mercuric chloride and mercury.

IV. Redistribution Equilibria of Mercury(II) Compounds

The experimental data up to 1964 have been reviewed by Lockhart (*43*), and some further reactions have been studied by Reynolds and Daniel (*52*). Much work has been done on the mechanism of these reactions, to be discussed later; attention here will be confined to the equilibria of the types

$$R_2Hg + R_2'Hg \rightleftarrows 2RHgR' \qquad (1)$$

$$HgX_2Y + HgY_2 \rightleftarrows 2HgXY \qquad (2)$$

$$R_2Hg + HgX_2 \rightleftarrows 2RHgX \qquad (3)$$

either in the vapor phase or in nonpolar solvents. For a single reaction of type (1), if the redistribution is statistical then the equilibrium constant $K = 4$. If K is < 4 the grouping on the left is preferred, while $K > 4$ implies a preference for the mixed product. Some experimental values are given in Table IX.

TABLE IX

REDISTRIBUTION OF EQUILIBRIA

$R_2Hg + R_2'Hg \rightleftarrows 2RHgR'$ (at 90°)

R	R′	K
CH_3	C_2H_5	1.8
C_2H_5	n-C_3H_7	4.5
C_2H_5	i-C_3H_7	5.3
C_2H_5	C_6H_5	5.0
C_2H_5	C_2H_3	86
C_2H_5	cyclo-C_3H_5	130
n-C_3H_7	i-C_3F_7	$>2 \times 10^3$
i-C_3H_7	i-C_3F_7	$>2 \times 10^3$
C_2H_3	cyclo-C_3H_5	(did not redistribute)

Data for the systems of type (2) where X = halogen are given in Table X. The data are expressed here as a heat of reaction to form the unsymmetrical products. As these reactions will have only a very small entropy change, these results indicate that all the reactions proceed essentially to completion.

For reactions of types (1) and (2) there are some examples in which it is difficult for kinetic reasons to establish the position of equilibrium. One example is given by Reynolds and Daniel (*52*), who found that

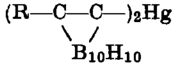
TABLE X

HEATS OF REDISTRIBUTION REACTIONS IN THE GAS PHASE

$R_2Hg + HgX_2 \rightarrow 2RHgX$

R	X	$-\Delta H$ (kcal)
CH_3	Cl	14
CH_3	Br	10
CH_3	I	8
C_2H_5	Cl	15
C_2H_5	Br	12
C_2H_5	I	8
C_6H_5	Cl	11

$(CH_2{=}CH)_2Hg$ and $(\text{cyclo-}C_3H_5)_2Hg$ did not redistribute under their conditions. Similarly, $(C_6F_5)_2Hg$ (*7*), $(C_6Cl_5)_2Hg$ (*47*), and organomercuric derivatives of barenes (*62*),



$(\text{R}-\underbrace{\text{C}-\text{C}}_{\text{B}_{10}\text{H}_{10}}-)_2\text{Hg}$

all react with $HgCl_2$ under only the most vigorous conditions and, similarly, compounds RHgX revert to R_2Hg only slowly if at all under the influence of reagents such as KCN and KI, which promote symmetrization by complex formation with the mercuric halide.

Quantitative studies on the third type of redistribution reaction, that between the individual mercuric halides, have been carried out by Marcus and Eliezer (*44*), and the results for the halides with no excess of halide ion present are shown in Table XI.

TABLE XI

REDISTRIBUTION EQUILIBRIA

$HgX_2 + HgY_2 \rightleftharpoons 2HgXY$

Complex	log K
HgClBr	0.6
HgClI	1.0
HgBrI	0.5

Inspection of the figures in Table XI shows that the redistribution proceeds in favor of the unsymmetrical species whenever the two bonding atoms or groups differ appreciably in electronegativity. Marcus and Eliezer (*44*) attempted to give a quantitative account of this for the mercuric halides in terms of a simple electrostatic model. This correctly predicts the above trend but, as might be expected, such a simple model does not give very good quantitative agreement.

V. Compounds in Which Mercury Is Bonded to Nonmetallic Elements

Mercury reacts with the halogens and the Group VIB elements to form binary compounds, but is inert to the other nonmetallic elements. It is known to form bonds to boron, silicon, germanium, phosphorus, and arsenic in certain compounds only. With carbon, mercury compounds of many different types are known. Because of their relative lack of reactivity toward oxygen and water, these organomercury compounds have been employed by organic chemists in a wide range of synthetic and mechanistic studies.

A. Mercury-Boron Compounds

The only known mercury-boron compound is the salt $(Me_4N)_2$-$[(B_{10}H_{12})_2Hg]$, synthesized from the reaction of decaboranylmagnesium iodide with mercuric chloride (*31*).

B. Mercury-Carbon Compounds

The extent of the research interest in organomercury compounds can be judged by the fact that King and Seyferth (*40*) in their *Annual Surveys of Organometallic Chemistry* list 95 references for the year 1965 alone. In the present article, only certain features of interest to inorganic chemists will be selected for discussion; reference will be made where possible to review articles in which specific information has been collected.

Mercury-carbon compounds can be subdivided into two classes: (a) R_2Hg and R′HgR, and (b) RHgX (where X = halogen, ClO_4^-, etc.). Examples of the former type are given in Table XII, and of the latter in Table XIII. The properties of both these classes are greatly influenced by the nature of R. Three separate types can be identified, although there are of course borderline examples. The first type can be defined as those mercurials where R is an aliphatic or aromatic hydrocarbon residue, the

TABLE XII

COMPOUNDS R_2Hg WHERE R IS MONOFUNCTIONAL

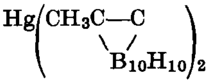
Compound	M.P. (°C)	B.P. (°C)
$Hg(CH_3)_2$	—	92
$Hg(C_2H_5)_2$	—	159
$Hg(CH{=}CH_2)_2$	—	59.5/20 mm
$Hg(C{\equiv}CH)_2$	—	—
$Hg(C_6H_5)_2$	125	204/10.5 mm
	167	—
$Hg(CF_3)_2$	163	—
$Hg(CF_2CF_3)_2$	106–107	—
$Hg(C_6F_5)_2$	142	—
$Hg(CCl_3)_2$	140	—
$Hg(CCl{=}CCl_2)_2$	72–73	—

TABLE XIII

COMPOUNDS RHgX

Compound	M.P.
CH_3HgF	200
CH_3HgCl	167
CH_3HgBr	161
CH_3Hg	152
CH_3HgCN	93
CH_3HgOH	137
CH_3HgOAc	143
CF_3HgCl	76
CF_3HgBr	83
CCl_3HgCl	193
C_6F_5HgBr	155

second type where R is a group of the type $>C{-}C{<}X$ (where X is a reactive group such as OH, Cl, etc.), and the third type where R is a perhalo group, notably CF_3, C_2F_5, or C_6Cl_5.

Although many reactions are known that lead to organomercury compounds (*40*), the principal reactions of preparative importance are given below.

(a) *Grignard reactions* (*6*, *38*, *53*):

$$RMgX + HgX_2 \rightarrow RHgX + MgX_2$$

$$RHgX + RMgX \rightarrow R_2Hg + MgX_2$$

This is a general reaction.

(b) *Amalgam reactions* (*1*, *53*, *57*):

$$2RI + Na/Hg \rightarrow R_2Hg + 2NaX$$

where R = alkyl, vinyl, aryl.

$$2RI + Cd/Hg \rightarrow R_2Hg + CdI_2$$

where R = perfluoroalkyl.

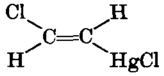
(c) *Mercuration* (*18*, *53*), e.g.:

$$C_6H_5OAc + Hg \rightarrow C_6H_5\cdot HgOAc$$

(d) *Addition reactions* (*1*, *57*), e.g.:

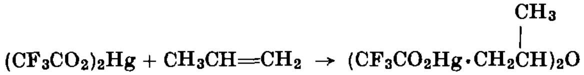
$$HgF_2 + C_2F_4 \rightarrow Hg(C_2F_5)_2$$

$$HgCl_2 + C_2H_2 \rightarrow$$



(e) *Oxymercuration of olefins* (*8*, *24*), e.g.:

$$CH_3OH + C_2H_4 + HgCl_2 \rightarrow CH_3O\cdot CH_2CH_2\cdot HgCl + HCl$$



$$(CF_3CO_2)_2Hg + CH_3CH{=}CH_2 \rightarrow (CF_3CO_2Hg\cdot CH_2\overset{\overset{CH_3}{|}}{C}H)_2O$$

(f) *Acetylide formation* (*19*, *53*):

$$K_2HgI_4 + 2R{-}C{\equiv}CH + 2Et_3N \rightarrow (R{-}C{\equiv}C)_2Hg + 2KI + 2Et_3N\cdot HI$$

The chemical reactions of organomercury compounds other than perfluoro derivatives have been reviewed by Reutov (*51*) and by Dessy and Kitching (*18*). The reactions of perfluoroalkyl and aryl mercurials are broadly similar, and follow the pattern expected for more electronegative groups. These reactions have been extensively studied by the techniques of physical organic chemistry; the classification of reaction types given below is essentially that of Dessy and Kitching.

(a) *Subvalent organomercurials*: It has already been seen that RHgHgR would not be expected to be stable to disproportionation. However, by electrolytic reduction of RHgX in NH_3, $EtOH/H_2O$, and $CH_3OCH_2CH_2OCH_3$, a series of reduced species of empirical formula RHg have been obtained. These materials catalyze a number of reactions of organomercurials. No definite structural assignment has yet been possible.

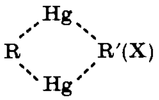
(b) *Symmetrization reactions* $2RHgX \rightarrow R_2Hg + HgX_2$: These reactions are brought about by reagents that remove HgX_2 from the system, and hence displace the equilibrium that normally lies with RHgX. Typical reagents are halide ions, NH_3, and R_3P. Recent work by Coates and Lauder (*12*) has shown by isolating the intermediates that this reaction, at least in some cases, proceeds by the mechanism:

$$RHgX + R_3P \rightarrow (RHgPR_3)^+X^-$$

$$2(RHgPR_3)^+X^- \rightarrow R_2Hg + R_3P_2HgX_2$$

In the case of the perfluoro compounds, derivatives of the type $(C_6F_5)_2Hg(bipy)$ and $[Hg(CF_3)_2I_2]^{2-}$ are sufficiently stable to be isolated (*1, 57*).

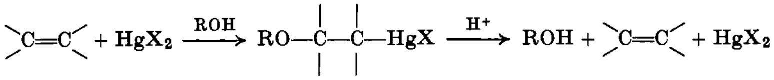
(c) *Exchange reactions*: Equilibrium data for reactions $R_2Hg + R_2'Hg \rightleftharpoons 2RHgR'$ have already been given. It has been shown that both R_2Hg and RHgX undergo rapid isotope exchange with Hg metal, and a transition state of the type



is thought to be important.

(d) *RHg^+ species*: Direct evidence for RHg^+ comes from the Raman studies of Goggin and Woodward on $RHgClO_4$ solutions (*28*). They observe that one species present is $RHgOH_2{}^+$. Stability constant data for the ion RHg^+ in water (where $R = CH_3$ and CF_3) have already been given. This concept has been used to interpret the kinetics of solvolytic reactions of RHgX compounds.

(e) *Oxymercuration-deoxymercuration*:



$$>C=C< + HgX_2 \xrightarrow{ROH} RO-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-HgX \xrightarrow{H^+} ROH + >C=C< + HgX_2$$

Oxymercuration Deoxymercuration

N.m.r. studies have shown that mercury-olefin adducts involve only σ-bonds. The details of the kinetics of both the above steps have received much study (*18*).

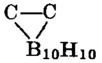
(f) *$>$C—Hg bond cleavage*: The most important examples of this class of reactions are:

$$R_2Hg + HgX_2 \rightarrow 2RHgX$$

$$RR'Hg + HCl \rightarrow RH + R'HgCl$$

$$RR'Hg + Br_2 \rightarrow RHgBr + R'Br \rightarrow R'Br + HgBr_2$$

The first of these reactions proceeds readily where R is alkyl or aryl but, as has been noted, certain groups such as C_6F_5 and



give rise to slow reactions.

The action of hydrogen chloride on RR′Hg has been studied for a range of groups R and R′ and a series established,

$$CF_2{:}CF = C_6H_5 > C_6F_5 > CH{:}CH_2 > CH_3 > C_2F_5$$

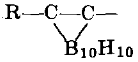
so that the further to the left in the series a group occurs, the greater is its tendency to be cleaved from Hg (*57*), e.g.:

$$C_6F_5{\cdot}Hg{\cdot}CH_3 + HCl \rightarrow C_6F_5H + CH_3HgCl$$

$$CH_3{\cdot}Hg{\cdot}C_2F_5 + HCl \rightarrow CH_4 + C_2F_5HgCl$$

This reaction has also been studied from a mechanistic viewpoint with optically active groups (*18*).

Bromination in general removes from mercury the same groups as HCl. The C_6F_5 and



groups proved to be exceptions to this and it may well be that a different mechanism operates here. Certainly $(C_6F_5)_2Hg$ is unique in its ability to form stable adducts with R_3P, and coordination of a bromine molecule may be an intermediate step (*57*).

(g) *Radical reactions*: The thermal and photochemical decompositions of organomercurials proceed by radical mechanisms. These reactions and the fate of the radicals formed are reviewed by Bass (*2*).

(h) *Carbene formation*: Compounds having groups such as CCl_3, CCl_2Br, etc., bonded to mercury decompose to give carbenes:

$$PhHgCCl_3 \rightarrow PhHgCl + CCl_2$$

In some cases this is reversible:

$$PhHgCl + CH_2N_2 \rightarrow PhHgCH_2Cl + N_2$$

C. Compounds in Which Mercury Is Bonded to Silicon and Germanium

Wiberg and his co-workers (*60*) have isolated and characterized a stable mercury-silicon compound from the reaction:

$$Me_3SiX + (\text{excess})\ Na/Hg \rightarrow (Me_3Si)_2Hg + 2NaX$$

This compound melts at 102°–104°C with decomposition and may be sublimed *in vacuo.* Attempts to extend this reaction to compounds containing Si—H bonds failed to produce compounds of the type $(Me_2SiH)_2Hg$, but a polymeric compound Me_2SiHg was formed. The corresponding $(Ph_3Si)_2Hg$ was obtained but was less stable than the methyl derivative.

Bis(trimethylsilyl)mercury decomposes quantitatively on heating to give hexamethyldisilane and mercury, and with hydrogen chloride gives trimethylsilane, trimethylchlorosilane, and mercury.

The corresponding $(Me_3Ge)_2Hg$ has also been obtained (*27*).

D. Compounds in Which Mercury Is Bonded to Nitrogen, Phosphorus, and Arsenic

A series of compounds containing Hg—N bonds are formed by the reaction of ammonia on mercuric chloride; these have long been known but only since the application of X-ray structure determinations have their chemical natures been understood (*29*):

(a) "Fusible white precipitate" or mercuric ammines:

$$HgCl_2 + 2NH_3 \rightarrow (NH_3)_2HgCl_2$$

(b) "Infusible white precipitate" or mercuric amides and mercury imides:

$$HgCl_2 + NH_3 + NH_4OH \rightarrow HgNH_2Cl$$

$$HgBr_2 + NH_3 + NH_4OH \rightarrow Hg_2NHBr$$

(c) Millon's base:

$$HgCl_2 + (\text{excess})\ NH_4OH \rightarrow (Hg_2N)OH \cdot 2H_2O$$

In the mercuric ammines, the linear group $(H_3N—Hg—NH_3)^{++}$ $[d(Hg—N) = 2.10\ \text{Å}]$ is found in a statistical cubic structure of halide ions such that the mercury atom is the center of a face (i.e., with four nearest-neighbor chlorines), and the NH_3 unit is near the center of the cube. In the less stable py_2HgCl_2, two chlorines lie at 2.34 Å from Hg and two more at 3.25 Å, while the Hg—N distance is 2.60 Å. In both cases the special position of two ligands, which runs through mercury chemistry, is again emphasized. In the mercuric amides, the main structural feature is a polymeric zigzag chain $—NH_2—Hg—NH_2—Hg—$; the imides have a layer structure, while Millon's base has a tetrahedral giant lattice.

The rather unstable compounds $(RHgNH_3)^+X^-$, as was previously mentioned, have been obtained by the action of NH_3 on RHgX, while the more stable $(bipy)Hg(C_6F_5)_2$ has been isolated and characterized (*7*).

If nitrogen is bonded to electronegative groups, compounds of a different type are formed (*58, 61*):

$$HgF_2 + 2CF_3{\cdot}N{=}CF_2 \rightarrow Hg[N(CF_3)_2]_2$$

$$HgF_2 + 2SF_5N{=}CF_2 \rightarrow Hg[NCF_3(SF_5)]_2$$

The group $N(CF_3)_2$ behaves as a pseudohalogen.

Much less is known of compounds containing mercury bonded to phosphorus and arsenic. Mercuric salts react with PH_3 and AsH_3, but nothing is known concerning the structure of the products (*44a*). The action of tertiary phosphines or arsines on mercuric halides or salts of halomercurate ions in ethanol leads to the formation of compounds of the type $(R_3)P_2HgX_2$, corresponding to the mercuric ammines (*17, 23*). In general the reaction does not proceed beyond the stage L_2HgX_2 but, with the bidentate *o*-phenylenebisdimethylamine, $HgL_2{}^{2+}$ is formed (*42*). The compounds $Hg[P(CF_3)_2]_2$ and $Hg[As(CF_3)_2]_2$ do not appear to be formed; when mercury reacts with $(CF_3)_2PCl$ the product formed is $[(CF_3)_2P]_2$.

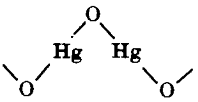
E. Compounds in Which Mercury Is Bonded to Oxygen, Sulfur, and Selenium

Mercury reacts directly with oxygen, sulfur, and selenium to give compounds of the type HgX. The oxide and sulfide exist in two forms differing only slightly in energy:

		O	S	Se
ΔH_fHgX (kcal)	(a)	−21.68	−13.90	−5.1
	(b)	−21.56	−12.90	

These heats of formation follow the expected order. As in the case of the halogens, the order of stability constants in solution follows the inverse order. It is more difficult, however, to give a quantitative description in this case since, with divalent ions, species containing OH^- and O^{2-} are possible and direct comparisons are not always valid.

The simplest mercury-oxygen compound is the solid oxide HgO. This exists in two forms. In one form, the basic unit

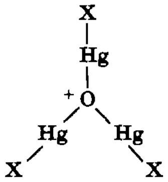


that is similar to that in amidomercuric compounds is planar and, in the other, is spiral in form. If the oxide is heated in a sealed tube with an alkali metal oxide, or better a peroxide, compounds M_2HgO_2 are formed

(*37*). These are colorless solids, which at once revert to mercuric oxide and alkali metal hydroxide with water. They contain the linear structural unit $[O{-}Hg{-}O]^{2-}$.

The tendency of the OH^- ion to form a strong covalent bond to mercury means that salts of oxy acids, except in strongly acidic media, are present as oxy salts, and even mercuric chloride and bromide give rise to a series of oxyhalides. This, like the mercury-halide-ammonia system, has long been known but was systematized only with the determination of structures by X-ray techniques. The main structural features occurring in these systems are as follows (*29*).

(a) Mercurioxonium cations,



where $X = Cl^-$, O^+ to give an extended lattice [e.g., $(ClHgO)_3Cl = 2HgCl_2 \cdot HgO$, and $[Hg_3O_2]^{++}SO_4^{--} = HgSO_4 \cdot 2HgO$], in which the coordination about oxygen is a very flat pyramid. One HgX unit can also be replaced by H.

(b) Distorted tetrahedra: an example here is mercuric sulfite where two mutually normal planes, containing O—Hg—O with bond angles 159° and 144°, are observed.

(c) Ionic lattices; e.g., $K_3Hg(NO_2)_4 \cdot NO_3$.

Combined oxygen is rather a poor ligand for the mercuric ion, as for mercury compounds. Compounds of the type $[HgL_6][ClO_4]$, however, have been observed, where L = pyridine-*N*-oxide, dimethylsulfoxide, tetramethylene-sulfone, and thioxan oxide (*5*). Where the anion tends to form a covalent bond to mercury, the coordination number is reduced; thus $HgCl_2 \cdot 2CH_3SO$ is observed and is finally analogous to the $HgCl_2L_2$ compounds formed by Group VB donors.

Although water is a poor ligand for Hg^{++}, it can be important in determining reactivity. In the mercuration of aromatic rings a marked acceleration is observed by neutral salts such as sodium perchlorate. This has been interpreted as a lowering of the activity of H_2O and hence leaving Hg^{++} relatively free from solvation, in which form it is more reactive.

Although there are many formal similarities, mercury-sulfur compounds differ in many ways from their oxygen counterparts. In oxygen compounds, except where bonding is mainly ionic, the characteristic digonal coordination of mercury is dominant. In the corresponding sulfur compounds, marked distortion occurs and structures that may be thought of as distorted tetrahedra are common. The mercurioxonium structures, found in certain mercury oxyhalides, do have their counterparts in mercurisulfonium compounds, which are rather more stable.

Mercuric sulfide in the stable modification cinnabar has six sulfur atoms closer to mercury than the six of the van der Waals radii. Two of these are much closer (2.36 Å) than the other four, which are in two pairs (3.10 and 3.30 Å). The two nearest sulfur atoms make a bent S-Hg-S system with an angle of 172.4°. The black mercuric sulfide obtained on precipitation from solution has a zinc blende structure (*29*).

Although its solubility product is very low, mercuric sulfide will dissolve in concentrated solutions of sodium sulfide, and alkali metal salts M_2HgS_2, formally analogous to M_2HgO_2, can be obtained. Mercuric sulfide will also dissolve to some extent in concentrated solutions of mercuric salts. On heating these solutions the sulfide ion is oxidized by the mercuric ions. It is possible that the solution contains some type of mercurisulfonium species; Grdenić and Markusić (*30*) obtained and characterized a mercuric sulfonium species by the reaction:

$$3(CH_3Hg)_2S + H_2Cr_2O_7 \rightarrow [(CH_3Hg)_3S]_2Cr_2O_7 + H_2S$$

The alkyl mercaptan derivatives of mercury, $(RS)_2Hg$, have long been known. They are obtained by the vigorous action of mercaptans on mercuric oxide (*30*):

$$2CH_3SH + HgO \rightarrow (CH_3S)_2Hg + H_2O$$

The phenyl and perfluoroalkyl derivatives are obtained by the reaction (*4*):

$$RSSR + Hg \rightarrow (RS)_2Hg$$

Examples are listed in Table XIV.

TABLE XIV

COMPOUNDS OF THE TYPE $(RS)_2Hg$

	M.P.	B.P.
$(CH_3S)_2Hg$	144	—
$(C_2H_5S)_2Hg$	76	(dec.)
$(i\text{-}C_3H_7S)_2Hg$	58	—
$(CF_3S)_2Hg$	39.4	182
$(C_7H_5S)_2Hg$	151.2	—

In their chemical behavior these compounds are very similar to the corresponding R_2Hg compounds. Thus they lead to derivatives RSHgX when X = halogen, and where $R = CF_3$ the species $(CF_3S)_2HgX_2{}^{2-}$ can be obtained (*20*). The corresponding selenium derivatives $(CF_3Se)_2Hg$ have also been studied and are broadly similar (*11*). The equilibria in the reaction

$$(CF_3S)_2Hg + HgX_2 \rightarrow 2(CF_3S)HgX$$

have been studied by Raman spectroscopy in methanol (*11*) and the results are shown in Table XV.

TABLE XV

EQUILIBRIUM CONSTANTS FOR $Hg(SCF_3)_2 + HgX_2 \rightarrow 2CF_3SHgX$ AND THE CORRESPONDING SELENIUM DERIVATIVES

HgX_2	$(CF_3S)_2Hg$	$(CF_3Se)_2Hg$
Cl	20 ± 10	20 ± 2
Br	2.3 ± 0.3	15 ± 10
I	1.67 ± 0.15	2.03 ± 0.02
SCN	1.35 ± 0.06	2.34 ± 0.06

Mercaptans will also react with mercuric halides to give solid complexes of the type $R_2S \cdot 2HgX_2$, $R_2S \cdot HgX_2$, and $(R_2S)_2HgX_2$. The structure of $R_2S \cdot HgX_2$ has been determined in the case of the complexes of diethylmercaptan with mercuric chloride and shown to be $[Et_2SHgCl]^+Cl^-$ (*3*).

F. MERCURY-HALOGEN COMPOUNDS

The bond energies of the mercuric halides have already been discussed, and the complexes formed between the mercuric halides and halide ions in solution will be discussed in more detail below (Section VI). This section will be concerned with the solid halides and halide complexes (*29*).

Mercuric fluoride has an ionic structure with each mercury atom having eight nearest-neighbor fluorines. The other mercury halides all have structures in which covalent bonding is important. In mercuric chloride, the basic unit is the linear Cl-Hg-Cl with no other chlorine atoms closer than the run of the van der Waals radii. Mercuric bromide by contrast has a layer structure with six Hg—Br distances less than the run of the van der Waals radii. Mercuric iodide has a structure based on HgI_4 tetrahedra that are corner-linked.

The mercuric halides other than fluoride are not dissociated in aqueous media. They are soluble in excess of alkali halide to give HgX_3^- and HgX_4^{2-} species. Interestingly, the sparingly soluble iodide is also soluble in excess of mercuric salts. Raman spectroscopic studies (*10*) have shown that the species present are $HgCl^+$, $HgBr^+$, and HgI^+ and also in the case of the iodide $[Hg—I—Hg]^{3+}$

The ions HgX_3^-, HgX_4^{2-}, and more complex systems such as $Hg_2X_7^{3-}$ have been extensively used as precipitants for quaternary ammonium, phosphonium, and sulfonium salts. The chemistry and structural features of these compounds have been comprehensively reviewed by Deacon (*16*).

VI. Bond Energies and Equilibria in Aqueous Media

There is now a considerable body of data available on the equilibria between metals and ligands in aqueous solutions (*56a*). This has led to much discussion of the nature of metal-ligand bonding and a classification of metals into types A and B according to their tendency to form complexes whose stability is such that K (the stability constant) increases in the order $F^- > Cl^- > Br^- > I^-$ for type A, and the reverse order for type B (*9*). Mercury is a type B metal in this classification, while Cd is borderline and Zn, Cu, Sr, and Ba are type A. Mercury alone of the Group II metals can form salts based on the Hg_2^{++} ion in aqueous media, although Cd_2^{++} has been detected in $NaAlCl_4$ solution.

The data for the mercury halides will be discussed in some detail, as these illustrate rather well the unique position of mercury among the Group II elements. In Table XVII are given the thermodynamic data for the successive steps in complex formation between mercuric ions and halide ions (*56a*).

It can be seen that there is a marked break in both the stability constant and the heat of reaction at $n = 2$, corresponding to the formation of a neutral species HgX_2. Thus, for the formation of iodo complexes, K_2 for the reaction

$$HgI^+ + I^- \rightarrow HgI_2$$

is greater by 10^7 than K_3 for the reaction

$$HgI_2 + I^- \rightarrow HgI_3^-$$

Conversely, K_1 and K_2 on the one hand and K_3 and K_4 on the other are of comparable magnitude. This expresses in numerical terms the statement, "Mercury tends to form two bonds at 180° and does not readily increase its coordination number". It will be shown later that this statement is less true for "hard" than for "soft" ligands.

TABLE XVI

Thermodynamic Data for Complex Formation by Hg^{++}[a]

Ligand	log K				ΔH (kcal)				ΔS (e.u.)			
	K_1	K_2	K_3	K_4	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔS_1	ΔS_2	ΔS_3	ΔS_4
OH^-	11.86	10.27										
CN^-	18.00	16.70	3.83	2.98	← 59.5 →				← −10 →			
SCN^-	16.43		2.71	1.98	← 35 →				← −20 →			
$SeCN^-$	← 26.4 →			2.47	← 46.5 →				← −20.8 →			
NH_3	8.8	8.7	1.00	0.78	24.7		3.3	3.6	2.3		−6.4	−8.3
NO_2^-	← 15 →											
NO_3^-	0.11	−0.1										
S^{2-}	50.23	(K_{so})										
$S_2O_3^{2-}$	29.27											
SO_3^{2-}	24.07											
SO_4^{2-}	1.42											
Se^{2-}	−59	(K_{so})										
SeO_3^{2-}	12.48											
F^-	1.03				−0.85				8			
Cl^-	6.74	6.48	0.85	1.00	5.9	6.9	2.2	0.1	11.1	6.3	3.0	5.1
Br^-	9.05	8.28	2.41	1.26	10.1	10.7	3.0	4.1	9	−5	−2	−2
I^-	12.87	10.95	3.67	2.37	17.6	15.0	3.6	4.0	← 13.7 →			
CH_3NH_2	8.6	9.3	0.4									
$NH_2CH_2CH_2NH_2$	14.3		9.0									
$HO \cdot CH_2CH_2NH_2$	8.51		8.81									
$(NH_2)_2CH(CH_3)CH_2$	← 23.5 →											
$CH_3O \cdot CH_2CH_2NH_2$	9.19		8.65									
CH_3COOH	8.43											
$EDTA^{4-}$	← 21.78 →				← 18.9 →				← 35.5 →			

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[a] The measurements (*56a*) are not all made under identical conditions, but the inaccuracies so caused are minor and do not invalidate the conclusions drawn in the text.

TABLE XVII

THERMODYNAMIC DATA FOR SUCCESSIVE STEPS IN COORDINATION OF Hg^{++} BY HALIDE IONS

	$\log K_n$				$-\Delta H_n$				ΔS_n			
n:	1	2	3	4	1	2	3	4	1	2	3	4
Cl^-	6.74	6.48	0.85	1.00	5.9	6.9	2.2	0.1	11.1	6.3	3.0	5.1
Br^-	9.05	8.28	2.41	1.26	10.1	10.7	3.0	4.1	9	−5	−2	−2
I^-	12.87	10.95	3.67	2.37	17.6	15	3.6	4.0	← 13.7 →			

It is possible by e.m.f. and other measurements to relate the heat and free energy of formation of an aqueous ion to that of a solvated proton. If a value of the heat of hydration of a proton can be deduced, then it is possible to determine the absolute heat of formation of a metal ion, and hence the heat of solvation if the heat of formation of the gaseous ion is known. This has been done by Yatsimirskii (*59*), and enables all the heat terms in the diagram below to be evaluated:

$$\begin{tikzcd}
& \mathrm{Hg^{++}(gas)} + 2\mathrm{Cl^{-}(gas)} \arrow[r, "\Delta H \text{ solvation}"] & \mathrm{Hg^{++}(aq)} + 2\mathrm{Cl^{-}(aq)} \quad \text{(A)} \\
\text{Hg metal} + \mathrm{Cl_2(gas)} \arrow[ur] \arrow[dr, "\Delta H_f"] & & \text{(at infinite dilution)} \\
& \mathrm{HgCl_2(c)} \arrow[r, "\Delta H \text{ solution}"] & \mathrm{HgCl_2(aq)} \quad \text{(B)}
\end{tikzcd}$$

Similar cycles for other metals and other halogens can obviously be written. Table XVIII shows the heat of formation of halides of Ca, Cd, and Hg as ionic solutions at infinite dilution, using the terms in (A), while Table XIX shows the calculation using the terms in (B). It can be seen that for both Ca and Cd the result obtained is the same in each case, showing, as is well known, that the halides of these elements dissolve to give ionic solutions at infinite dilution. By contrast, the values of $-\Delta H$ calculated by route (A) for HgX_2 are smaller than those calculated by route (B). This means that the actual heat of formation of $HgX_2(aq)$ at infinite dilution (B) is greater than that calculated for an assembly of ions (A). The magnitude of this disparity increases from −17 kcal for $HgCl_2$ through −25 kcal for $HgBr_2$ to −37 kcal for HgI_2, that is, in the order expected for increasing covalency. An interesting check on these calculations is that these difference figures should equal the observed

TABLE XVIII

HEATS OF FORMATION OF ION PAIRS AT INFINITE DILUTION FOR CaX_2, CdX_2, AND HgX_2 (kcal)

Ion	ΔH_f $M^{++}(g)$	$\Delta H_{solvation}$	$\therefore \Delta H_f$ $M^{++}(aq)$	ΔH_f $(M^{++} + 2Cl^-)(aq)$	ΔH_f $(M^{++} + 2Br^-)(aq)$	ΔH_f $(M^{++} + 2I^-)(aq)$
Ca^{++}	464	−386	78	−206	−184	−156
Cd^{++}	627	−439	188	−96	−74	−46
Hg^{++}	690	−443	247	−35	−13	+15
	$\Delta H'$ X^-	$\Delta H_{solvation}$	$\therefore \Delta H_f$ $X^-(aq)$			
Cl	−58	−84	−142			
Br^-	−55	−76	−131			
I^-	−50	−67	−117			

TABLE XIX

HEATS OF FORMATION OF SOLUTIONS OF CaX_2, CdX_2, AND HgX_2 (kcal)

	$\Delta H_f(c)$			$\Delta H_{solution}$			$\therefore \Delta H$ $MX_2(aq)$		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
Ca	−190	−161	−182	−18	−26	−28	−208	−187	−156
Cd	−93	−76	−48	−4	−1	+4	−97	−76	−44
Hg	−55.0	−40.5	−25.2	+3	+2	(est. +3)	−52	−38	(−22)

heat of formation of HgX_2 from $Hg^{++} + 2X^-$, that is, $\Delta H_1 + \Delta H_2$ in Table XVI. These figures in fact are −13 kcal for $HgCl_2$, −21 kcal for $HgBr_2$, and −33 kcal for HgI_2.

The "class B" character of the mercuric ion in aqueous media must not be taken to imply that the order of the bond energies is HgI > HgBr > HgCl. Indeed, reference to Table VII shows that the reverse is true. From the data in Table XVIII it can be shown that

$$HgCl_2\,(g) + 2I^-\,(g) \rightarrow HgI_2\,(g) + 2Cl^-\,(g) \qquad \Delta H = +7 \text{ kcal}$$

while from Table XVIII,

$$HgCl_2\,(aq) + 2I^-\,(aq) \rightarrow HgI_2\,(aq) + 2Cl^-\,(aq) \qquad \Delta H = -23 \text{ kcal}$$

and

$$2(\Delta H_{solvation}Cl^- - \Delta H_{solvation}I^-) = -34 \text{ kcal}$$

It is reasonable to assume that the difference in solvation energy between the two un-ionized species $HgCl_2$ and HgI_2 will be small. It can be seen that the difference in reaction heat between gas phase and solution can be accounted for by the difference in solvation energy of the halide ions. A more elaborate but essentially similar treatment is given by Pöe and Vaidya (*48*). Similar calculations can be carried out for the hydrogen halides:

$$HCl\,(g) + 2I^-\,(g) \rightarrow HI\,(g) + Cl^-\,(g) \qquad \Delta H = +15$$

$$HCl\,(aq) + 2I^-\,(aq) \rightarrow HCl\,(aq) + I^-\,(aq) \qquad \Delta H = +2$$

Once again the difference is close to the difference of the solvation of the halides, but there is no change of sign so that the stability order HCl > HBr > HI is the same both in water and in the gas; this is "class A" pattern.

The "class B" behavior of mercury with halide ions is also shown in its behavior toward ligands of Group VI. For ligands such as NO_3^- and SO_4^{2-}, where binding is through oxygen, log K is small. Where binding is

TABLE XX

STABILITY CONSTANTS AND REACTION HEATS[a] FOR

$R \cdot Hg^+ + L^{A-} \rightarrow RHgL^{(A-1)-}$

Ligand	R = CH_3			R = CF_3
	log K	$-\Delta H$	ΔS	log K
F^-	1.50	—	—	—
Cl^-	5.25	6.0	+3.6	5.78
Br^-	6.62	9.9	−3.6	7.24
I^-	8.60	—	—	9.63
OH^-	9.37	8.5	+13.7	10.76
S^{2-}	21.2	—	—	—
CN^-	14.1	22.1	−11.4	—
SCN^-	6.05	11.2	−10.6	—
CH_3HgSCN	1.65	—	—	—
NH_3	7.60	—	—	—
$S_2O_3^{2-}$	10.90	11.7	+9.9	—

[a] Schwarzenbach and Schellenberg (*54*).

to sulfur as in $S_2O_3^{2-}$, SO_3^{2-}, and SCN^-,log K is much larger and is even higher in $SeCN^-$ than in SCN^-.

The stability constants of a series of nitrogen bases have been determined by Davidson (*15*), who found that they could be expressed by the relation:

$$\log K_{Hg} = 0.93 \log K_H + 1.15$$

In this case, the reversal of the order of stability constants between mercury and hydrogen is not observed; the solvation energy of the neutral free base will be relatively small and does not have a major effect.

The ion CH_3Hg^+ (Table XX) is very similar to Hg^{++}. As might be expected, the values of log K_1 for this ligand are similar to but smaller than log K_2 for Hg^{++} with the same ligand. When CH_3 is replaced by the more electron-attracting CF_3, intermediate values are obtained. The ion CH_3Hg^+ behaves essentially as acceptor for one ion only. This is illustrated by the two steps,

$$CH_3Hg^+ + SCN^- \rightarrow CH_3HgSCN \qquad \log K = 6.05$$

$$CH_3HgSCN + SCN^- \rightarrow CH_3HgSCN^- \qquad \log K = 1.65$$

corresponding to a change between K_2 and K_3 for Hg^{++} with SCN^- of ~8 to 2.7.

It is interesting in this context to consider the stability of the aqueous mercurous ion. This can be regarded either as a complex of a Hg atom with Hg^{++} or as a compound of two Hg^{+} ions, both of which can be regarded as $d^{10}s^{1}$ species. If it is assumed that the heat of hydration of Hg^{+} is similar to that of Ag^{+} at 117 kcal (Cu^{++} is very similar to Zn^{++}; therefore we may assume that Ag^{+} is similar to Cd^{+}, and Cd^{++} very close to Hg^{++}; this can also be deduced from theoretical calculations on heats of hydration), it is then possible to calculate ΔH_f Hg^{+}(aq) from the first I.P. of mercury. The heat of reaction

$$Hg^{++}(aq) + Hg\ metal \rightarrow 2Hg^{+}(aq)$$

is then

$$2(\Delta H_f\quad Hg^{+}) - \Delta H_f\quad Hg^{++}(aq) = 2(257 - 117) - 247\ kcal$$
$$= 33\ kcal$$

The observed heat of the reaction

$$Hg^{++}(aq) + Hg\ metal \rightarrow Hg_2^{++}(aq)$$

is −0.82 kcal. This would imply an $^{+}Hg—Hg^{+}$ bond energy of 34 kcal if it is assumed that ΔH_{hyd} $Hg^{++} = 2\Delta H_{hyd}$ Hg^{+}. In view of the value $D(Hg^{+}—H) = 53$ kcal, this is not unreasonable. Proceeding in a similar way for cadmium, the heat of disproportionation of Cd^{+} is −54 kcal, which is substantially higher than for Hg^{+}. Further, the lower I.P. for Cd and Cd^{+} than for Hg and Hg^{+} indicates, as is observed in other cases, that bonds to cadmium will be less strong than to mercury. Quite small changes in solvation energies will, however, serve to alter greatly the stability of both Hg^{+} and Cd^{+}, and indeed Cd_2^{++} has been shown to exist in the compound $Cd_2(AlCl_4)_2$ in $NaAlCl_4$ solution (*13*).

A further limitation on the stability of mercurous compounds is provided by the value of the equilibrium constant

$$K = \frac{[Hg^{++}(aq)]}{[Hg\ mole][Hg^{++}\ (aq)]} \qquad \log K = 1.92 \text{ at } 25°$$

in relation to the stability constants of mercuric complexes. Any ligand for which log K is significantly greater than 1.92 will lead to disproportionation. Table XVI shows that stable soluble mercurous salts can be expected only for oxygen donors and for F^{-} in aqueous media. This is known to be the case. The well-known mercurous halides are all insoluble and their solubility products decrease in the order $Hg_2Cl_2 > Hg_2Br_2 > Hg_2I_2$, as they must if disproportionation is to be avoided.

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