

THE DIAMAGNETIC SUSCEPTIBILITIES OF MERCURY IN VARIOUS STATES OF COMBINATION

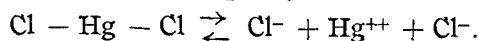
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IN three previous papers published from this laboratory the susceptibility constants for rubidium,¹ bismuth² and tin³ have been calculated from their compounds. Further, in a note published in *Current Science*, the specific and atomic diamagnetic susceptibilities of mercury obtained from Kahlbaum's extra pure mercuric compounds are given. It has been shown that the values obtained from these compounds are almost the same as those obtained by E. Vogt,⁴ Bates and Tai⁵ and are slightly lower than those of Honda,⁶ Owen,⁷ and Davis and Keeping.⁸ The higher atomic susceptibility obtained by Shur⁹ in the vapour state and its close resemblance with the theoretically calculated value by Slater's method has been explained on the existence of mercury in the monoatomic state in vapour. The lower diamagnetic values of mercury in the liquid state have been attributed to the poly-atomic molecule of mercury on the assumption that the free electrons in the outer orbit of mercury may be interchanging between the component atoms to form an aggregate of poly-atomic molecule. In the present communication the diamagnetic susceptibilities of mercury in various states of linkages have been critically examined.

The small size of the ions and their double charge impart to the element the facility to pass into the covalent state and to form the covalent compounds with a variety of elements such as halogens, oxygen, nitrogen, and carbon. Mercury halides unlike the salts of alkaline earths are more volatile and more soluble in organic solvents. Their conductivities in the fused state are very small. No sharp distinction can be drawn between covalence and electro-valence as a substance like hydrochloric acid behaves as a covalent compound as a pure liquid and as an electrovalent one in solution. It is however definitely understood that the two types of valency do exist and can be distinguished from each other. There are also various intermediate types of linkages between strongly electrovalent rock salt and strongly covalent methane as follows :

(1) KCl, (2) HCl, (3) HgCl₂, (4) HgC₂N₂, (5) H₂O, (6) CH₄. Thus mercuric chloride is partly electrovalent and partly covalent as follows :



The diamagnetic constants for divalent mercury obtained by various workers are not the same. Meyer,¹⁰ Pascal,¹¹ Wilsdon¹² and Kido¹³ are notable amongst them. Their values vary from 31.2 to 46 while Pauling,¹⁴ Slater¹⁵ and Angus¹⁶ get the theoretical values 55, 47.77 and 47.57 respectively.

(The values refer to $-\chi \cdot 10^6$).

Besides this, mercury forms double salts. It cannot always be assumed that a double salt really contains a complex molecule. There is a possibility of a crystalline aggregate formation of simple salt molecules. Mercury has a valency group of four electrons or a pair of covalent links. In presence of other salts, it can co-ordinate with one or two negative atoms such as chlorine, bromine and iodine. Thus the double salts can be represented as KIHgI_2 or $\text{K}(\text{HgI}_3)$ and $2\text{KI} \cdot \text{HgI}_2$ or $\text{K}_2(\text{HgI}_4)$. It has been referred to by Bhatnagar and Mathur in their book¹⁷ that mercury, its halides, cyanide, and the double chlorides with potassium are all diamagnetic, but potassium iodomercurate on the other hand is paramagnetic. The question arises as to why it should be so. To understand more fully this behaviour, the magnetic properties of some double salts are also examined.

Further, mercury forms complex salts of uncertain structure particularly when these salts are dissolved in some organic solvents and the inferences drawn in literature from this behaviour are both ambiguous and vague. Considering the uncertainties of the work so far accomplished and the fact that many important conclusions may be derived from it, it was felt desirable to investigate mercury in various states of combination with the help of more sensitive and accurate instruments paying due regard to the purity of the materials employed.

Experimental

The apparatus employed for the determination of magnetic susceptibilities of solids was the magnetic interference balance devised by Bhatnagar and Mathur,¹⁸ and manufactured by Messrs. Adam Hilger, Ltd., London. The sensitivity of this apparatus can be judged from the fact that a deflection of the tube of the order of $1/500$ cm. corresponds to 600 divisions on the drum of the interferometer, and the accuracy of observation can easily be said to be one in one thousand. The values of χ_M given in the following tables have been calculated according to the formula :

$$\chi_M = \chi_a M_a + (\chi_w m_w - \chi_a m_a) \frac{r - r_1}{r_2 - r_1}$$

where

- χ = the magnetic susceptibility of the unknown substance ;
- M = the mass of the substance taken ;

- χ_a = magnetic susceptibility of air ;
 M_a = mass of the air which fills the same volume as the substance ;
 χ_w = magnetic susceptibility of water ;
 m_w = mass of water ;
 m_a = mass of air which fills the same volume as occupied by water ;
 r = deflection with the unknown substance ;
 r_1 = deflection due to the tube and air ;
 r_2 = deflection with water and tube.

The values of susceptibilities have been checked up in a suitably modified form of Gouy's balance.¹⁹ According to this method the susceptibilities can be calculated by the equation :

$$\chi_{d_2} = \frac{1}{m_{d_2}} \left[(\chi_{d_1} m_{d_1} - \chi_a \cdot m_{ad_1}) \frac{W_{d_2}}{W_{d_1}} + \chi_a \cdot m_{ad_2} \right]$$

where the letters have the usual significance.

The specific susceptibilities in the dissolved state have been determined by the aid of a modified form of Decker's balance.²⁰ The susceptibilities can be calculated according to the equation :

$$\chi_L = \frac{\phi_L \left[\frac{\chi_w - \chi_a}{\phi_w - \phi_a} \right] + \left[\frac{\chi_a \phi_w - \phi_w \phi_a}{\phi_w - \phi_a} \right]}{d}$$

where

- χ_L = mass susceptibility of the solution ;
 χ_a = mass susceptibility of the air ;
 χ_w = mass susceptibility of the water ;
 ϕ_L = angle of torsion due to the solution ;
 ϕ_a = angle of torsion due to the air.
 ϕ_w = angle of torsion due to the water ;
 d = density of the solution.

In the case of solution, susceptibility of the salt has been calculated with the help of the relation :

$$\chi_L = \chi_{\text{salt}} \cdot C_{\text{salt}} + \chi_{\text{solvent}} (1 - C_{\text{salt}})$$

where C_{salt} denotes the concentration of the salts in solution.

The purity of the substances employed was of a very high standard and no substance was used unless its purity was established. Kahlbaum and Merck's extra pure specimens were re-purified, and their physical constants determined. The exhaustive qualitative and quantitative analyses were undertaken in order to test their purity.

The results obtained are tabulated below :

TABLE I

Specific Susceptibilities of Inorganic Mercury Compounds and the Susceptibility Constants of Mercury derived from them

Substance	Sp. Sus. Gouy's Balance $-\chi \cdot 10^6$	Sp. Sus. Inter- ference Balance $-\chi \cdot 10^6$	Sus. Constants $-\chi \cdot 10^6$		
			Mol. Sus. $-\chi \cdot 10^6$	Sus. for -ve radi- cals $-\chi \cdot 10^6$	Sus. Con- stants $-\chi \cdot 10^6$
HgCl ₂	0.313	0.3177	86.3	40.2	46.1
HgBr ₂	0.305	0.3032	109.2	61.2	48.0
HgO	0.243	0.2432	52.7	4.6	48.1

Theoretical Susceptibility Constants

$$-\chi \cdot 10^6$$

55.0 (Pauling)

47.78 (Slater)

47.57 (Angus)

Specific Susceptibilities by other Authors

HgCl ₂	0.301 (Vardhachari)
	0.298 (Kido)
	0.19 (Meyer)
	0.24 (Wilsdon)
HgBr ₂	0.3 (Meyer)
HgO	0.24 (Meyer)
	0.243 (Mathur and Nevgi)

TABLE II
*Specific Susceptibilities of Organic Mercuric Compounds and the
 Susceptibility Constants of Mercury in them*

Substance	Sp. Sus. Gouy's Balance $-\chi \cdot 10^6$	Sp. Sus. Inter- ference Balance $-\chi \cdot 10^6$	Sus. Constants $-\chi \cdot 10^6$		
			Mol. Sus. $-\chi \cdot 10^6$	Sus. for -ve radi- cals $-\chi \cdot 10^6$	Sus. Con- stants $-\chi \cdot 10^6$
Mercury-di-phenyl $\text{Hg}(\text{C}_6\text{H}_5)_2$	0.3984	141.3	104.5	36.8
Mercury-di-benzyl $\text{Hg}(\text{C}_6\text{H}_5\text{CH}_2)_2$	0.4270	163.4	128.3	35.1
N-propyl mercuric iodide $\text{C}_3\text{H}_7\text{-Hg-I}$	0.342	0.3408	126.3	83.25	43.05
N-butyl mercuric iodide $\text{C}_4\text{H}_9\text{-Hg-I}$	0.36	0.3588	138.0	95.15	42.85

Susceptibility Constants Obtained by Pascal

Substance	Susceptibility Constants $-\chi \cdot 10^6$
$\text{Hg}(\text{CH}_3)_2$	46.0
$\text{Hg}(\text{C}_2\text{H}_5)_2$	40.8
$\text{Hg}(\text{C}_5\text{H}_{11})_2$	35.4
Limiting value	33.1

TABLE III
*Specific Susceptibilities of Inorganic Mercurous Compounds and the
 Susceptibility Constants of Mercury from them*

Substance	Sp. Sus. Gouy's Balance $-\chi \cdot 10^6$	Sp. Sus. Inter- ference Balance $-\chi \cdot 10^6$	Sus. Constants		
			Mol. Sus. $-\chi \cdot 10^6$	Sus. for -ve radi- cals $-\chi \cdot 10^6$	Sus. Con- stants $-\chi \cdot 10^6$
Hg_2Cl_2	0.305	0.3039	$(71.73)_2$	$(20.1)_2$	$(51.6)_2$
Hg_2Br_2	0.297	0.2970	$(83.33)_2$	$(30.6)_2$	$(52.7)_2$
Hg_2I_2	0.299	0.2995	$(98.09)_2$	$(44.6)_2$	$(53.5)_2$

By Kido (40)₂

TABLE IV
Specific Susceptibilities of Mercury Double Salts

Substance	Sp. Sus. Gouy's Balance $-\chi \cdot 10^6$	Sp. Sus. Inter- ference Balance $-\chi \cdot 10^6$	Mol. Susceptibility $-\chi M \cdot 10^6$	
			Observed	Calculated
HgI ₂ ·KI	0.355	0.3542	219.8	67.2 (KI) 143.0 (HgI ₂) 210.2
NH ₄ I·HgI ₂ ·H ₂ O ..	0.373	0.3722	229.8	66 (NH ₄ I) 13 (H ₂ O) 143 (HgI ₂) 222

TABLE V
Specific Susceptibilities of Mercury Salts in the Pyridine Solution on
Decker's Modified Balance

Substance	Sp. Sus. in solution $-\chi \cdot 10^6$	Sp. Sus. in the solid state $-\chi \cdot 10^6$
HgCl ₂	0.2337	0.313
HgBr ₂	0.1674	0.305

Discussion of Results

Several interesting points emerge from a closer examination of the results tabulated above. The results can be tested in the following five groups:

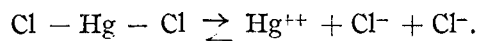
1. Mercury in the inorganic mercuric compounds.
2. Mercury in the organic mercuric compounds.
3. Mercury in the inorganic mercurous compounds.
4. Mercury double salts.
5. Mercury salts in the dissolved state.

1. *Mercury inorganic compounds in the bivalent state.*—The specific susceptibilities for the mercuric compounds are slightly higher than those recorded by previous authors (see Table I). Naturally, the molecular susceptibilities calculated from them came out to be higher. While finding out the

susceptibility constants for mercury in the bivalent state, the question arises as to what values should be taken for the negative radicals. In order to bring this point into prominence, an attempt has been made to calculate the susceptibility constants from one of the compounds, namely mercuric bromide by subtracting the different values of bromine obtained by various authors as follows :

HgBr ₂ :—	Mol. Sus. — $\chi \cdot 10^6$	Sus. Constants — $\chi \cdot 10^6$	Values of —ve radicals — $\chi \cdot 10^6$
	109.2	44.2	32.5 (Br) Reichendar
		46.4	31.4 (Br) Farquharson
		39.8	34.7 (Br) Kido
		48.0	30.6 (Br) Pascal

It is obvious that the constants are not the same. It has therefore been found desirable to calculate them by substituting the atomic values of Pascal for the negative radicals as the compounds exist mostly in the covalent state. No better values other than those of Pascal are at present available for the compounds in the covalent state. Accordingly the susceptibility constant comes out to be 46 to 48. The values cannot be compared with those obtained by other authors for the simple reason that they have made no distinction between the two kinds of linkages. It is rather curious to note that the susceptibility constants from the inorganic compounds are different from those derived from organic compounds. It has already been shown in the introduction that the compounds such as mercuric chloride are partly covalent and partly electrovalent.



It is well known that in going from the strongly electrovalent compounds, such as rock salt, to the strongly covalent compounds, such as methane, the sizes of ions are deformed. The sizes of covalent compounds are generally small. Thus the difference in the susceptibility constants mentioned above can very well be explained on the above assumption. The theoretical susceptibility constants obtained by Pauling, Slater and Angus are 55, 47.78 and 47.57 respectively. The present values closely correspond with the values calculated according to Slater and Angus.

2. *Organic mercuric compounds* (Table II).—It has already been pointed out that the susceptibility constants of mercury in organic compounds are lower than those which are obtained from the inorganic ones. Further, the

susceptibility constants from mercury-di-phenyl and di-benzyl are different from those which are derived from N-butyl and N-propyl-mercuric iodides. The former compounds are really the true organic ones while the latter are partly organic and partly inorganic. The susceptibility constants therefore should be midway between the constants from inorganic and organic compounds. The present results are therefore in agreement with this assumption. Further, Pascal has shown that the atomic coefficient of magnetization is not a constant quantity but it decreases with the increase of the molecular weight of organic radicals with which mercury is combined, approaching a limit 33.1. Perhaps, this may be the cause of the different values observed. It is rather interesting to note that the susceptibility constants from true organic compounds closely correspond with those which are obtained for liquid mercury.

3. *Mercurous compounds* (Table III).—The mercurous compounds are all diamagnetic. From this and a number of other facts it follows that these compounds exist in polymerised form. The susceptibility constants are between $(51.6)_2$ and $(53.6)_2$ while Kido has found it to be $(40)_2$. As has been pointed out, one is not completely justified in comparing the present values with those of Kido due to the different values for negative radicals substituted by him. However, the difference between the susceptibility constants of mercury in the ic and ous state is in the same direction and remains nearly the same.

4. *Double salts of mercury* (Table IV).—Mercury in the mercuric state contains a pair of normal covalent links. In presence of other salts such as potassium iodide, it can co-ordinate with one or two negative atoms. The number of linkages is thus increased by one or two. These are called co-ordinate linkages. The formation of the double salts may well be represented by saying that mercury acquires the necessary electrons from the combining salts. The constitutive atoms of the combining salts supply the necessary number of electrons to mercury. The exchange takes place as a donor and an acceptor. If a double salt is considered to be an aggregate of simple salts and is without any complex formation, the susceptibility of the salt should be additive. But the values obtained presently for these double salts are rather higher than those calculated from the additivity law. According to Bhatnagar, Verma and Kapur,²¹ the co-ordinate formation causes an increment in the diamagnetism of some molecular compounds. The present results are therefore in line with them. The anomalous behaviour of potassium-iodo-mercurate could not be traced.

5. *Mercury compounds in the dissolved state* (Table V).—All the mercury salts being covalent are soluble in organic solvents in which they form

complex compounds. One is therefore, not completely justified in calculating the susceptibility constants from them. The specific susceptibilities in pyridine are rather low when compared with those in solid state.

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