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MOOL CHAND MEHRA, M.Sc.,
(UNIVERSITY OF RAJASTHAN)

STUDIES ON THE STABILITIES OF SOME METAL SELENITE, SULPHIDE, AND SELENIDE COMPLEXES IN SOLUTION

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To
The Memory of My
Mother

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Studies on the Stabilities of Some Metal Selenite, Sulphide, and Selenide Complexes in Solution

Introduction:

A coordination or complex compound contains usually a central metal ion or an atom surrounded by a number of oppositely charged ions or neutral molecules known as ligands. The maximum number of ligands attached to the metal ion is its coordination number. When the group, bearing the metal ion and the ligands, is positively or negatively charged, it is termed as a complex ion. A complex is therefore a species formed by the association of two or more species, each of them capable of independent existence. The complex may exist in solid, liquid, or gas phase. This study shall, however, be concerned only with the complex formation in an aqueous medium.

The electronic concept of the coordination compounds (1) indicates that these are formed as a result of Lewis acid-base reactions, where the metal ion is the acid (or acceptor) and the ligand is the base (or donor). It therefore follows that the tendency, in general, in metals to form complexes increases with their increasing electron affinity. It is also true that almost all the molecules and ions with at least a free pair of electrons will tend to form complexes with metal ions; this tendency usually increases with the increasing proton affinity (base strength) of the ligand.

Schematically, the coordination reaction may be written as:

$$(1.1) \qquad (M) + 2\ (A) \rightleftharpoons (A \rightarrow M \leftarrow A)$$

where (M) is the metal ion, and (A) is the ligand molecule.

The free metal ion in an aqueous medium is surrounded by a sheath of the aqueous ions, such that the coordination requirements of the metal ion are saturated by water molecules (91). The complex formation reaction of the metal ion in an aqueous medium,therefore, involves the replacement of the water molecules from its hydration shell by the complex-forming ligand molecules. If the ligand occupies one or several positions or the coordination sites on the same cation, the resulting complex remains soluble in the homogeneous medium. If the ligand molecule links two or more cations together (bridging ligands such as OH^- or CO_3^{-2}) precipitation sets in immediately so that an infinite network of a coagulate or an ordered crystal lattice results. Thus both the reactions, complex formation in homogeneous medium and also the formation of the precipitates, can be taken into consideration in judging the tendency towards coordination.

Schwarzenbach (2) has expressed the opinion that the transition of a simple metal ion in solution to precipitation proceeds through complex formation reaction and the mononuclear complexes are almost, always, present in the homogeneous solution above the precipitate. It, therefore, follows that when the metal compound has low solubility, the tendency to form complexes in solution between the metal ion and the precipitating ligand will also be strong, i.e. smaller the solubility product of the insoluble compound, the more stable are the bonds between the cation and the anion. When employed to the heterogeneous inorganic systems in general, one may assume that aqueous complexes will appear in contact with the precipitate of the system. This view is supported to a large degree by the studies on some sulphide (72)(66) and halide (89)(90) equilibria, where mononuclear aqueous complexes have been found in contact with the precipitate of the compound.

It is therefore possible that some other inorganic systems similar to metal sulphides, e.g. metal selenides, could also give rise to aqueous complexes. Very meagre information concerning such systems is available and even a qualitative data is lacking on such equilibria.

The definition of the Complex Stability Constant:

The most important way to characterize complex formation in solution is to determine the equilibrium constant of the complex formed. This constant has also been termed as the formation constant or stability constant and can be derived by the application of the law of mass action, e.g. for the species defined in eq. (1.1), the over-all stability constant β may be written as:

$$(1.2) \qquad \beta = \frac{(MA_2)}{(M).(A)^2}$$

It depends upon the equilibrium concentrations of the interacting species or the activities of the substances involved in the complex formation. The nature of the complex species formed in a particular system depends on the nature of the metal ion that constitutes the central ion, and the properties of the ligand atom involved in the complex formation reaction (5).

There has been a resurgence of interest in the study of equilibria of the inorganic complexes in aqueous solution during the past few years (3)(92)(93). This has helped in the better understanding of the chemistry of the aqueous solutions. As more accurate values of the stability constants become available through the study of complex equilibria, interactions between metal ions, ligand, and solvent can be put on a quantitative basis. However, according to Sillen (4), the agreement of different authors on the values of the stability constants is such as to leave a doubt about the reliability of much of the available data. Sillen has therefore proposed three basic requirements to study the existence of different postulated species in solution.

(i) Constant ionic medium.
(ii) As broad range of concentration as possible.
(iii) As high experimental accuracy as possible.

The use of constant ionic medium makes it possible to use the equilibrium concentrations of the species taking part in the reaction, thereby avoiding the difficult task of determining the activities of the species.

The formation of the mononuclear complexes with ligand (A) and the metal ion (M) in solution may be written as:

(1.3) $(M) + (A) \rightleftharpoons (MA)$

(1.4) $(MA) + (A) \rightleftharpoons (MA_2)$

(1.5) $(MA_2) + (A) \rightleftharpoons (MA_3)$

.....

(1.6) $(MA_{N-1}) + (A) \rightleftharpoons (MA_N)$

where N is the maximum coordination number of the metal.
(It is customary to omit in such representations the charges on the complexes and the attachment of the solvent molecules to the metal ion).

The equilibrium or the stability constant for the individual reaction may be expressed as:

(1.7) $$K_1 = \frac{(MA)}{(M).(A)}$$

(1.8) $$K_2 = \frac{(MA_2)}{(MA).(A)}$$

(1.9) $$K_3 = \frac{(MA_3)}{(MA_2).(A)}$$

.....

(1.10) $$K_N = \frac{(MA_N)}{(MA_{N-1}).(A)}$$

The constants $K_1,K_2,K_3,\ldots..K_N$ are termed as the stepwise stability constants and are related to the over-all stability constant β through a simple relationship:

(1.11) $$\beta_N = K_1.K_2.K_3\ldots\ldots K_N$$

(1.12) $$\beta_N = \frac{(MA_N)}{(M).(A)^N}$$

The β and the K values are constant at a specified ionic strength because these are related to the concentrations of the reacting species. True thermodynamic constants defined in terms of the activities of the species do not vary with the ionic strength but are related to the concentration stability constants through the following expression.

(1.13) $$^{T}K_1 = \frac{\{MA\}}{\{M\}.\{A\}} = \frac{(MA)}{(M).(A)} \cdot \frac{\gamma\ MA}{\gamma\ M.\gamma\ A}$$

(1.14) $$^{T}K_1 = K_1 \cdot \frac{\gamma\ MA}{\gamma\ M\ .\gamma\ A}$$

$^{T}K_1$ = Thermodynamic constant.

γ = Activity coefficients of the species involved.

If in the eq. (1.14) the activity coefficients are known, the true thermodynamic constant can be easily evaluated by the substitution of the concentration stability constant K_1. Unfortunately the activity coefficients are not readily available. The stepwise stability constants are therefore determined at several known ionic strengths and the results are extrapolated to infinite dilutions (5) to yield the constant at zero ionic strength, i.e. thermodynamic constant. Alternatively, one may work near infinite dilution so that the activity coefficients may be regarded as unity and hence the thermodynamic constant is evaluated directly.

It is also possible to calculate the activity coefficients of the species by using the Debye-Hückel equation (94), or its modified form as suggested by Guggenheim (95) and Davies (96); these calculations have been discussed fully by Prue (6). Such calculations are possible only when the ionic strength of the medium is not too high. The last two methods, however, impose serious limitations if one wishes to study the ionic equilibrium and the complex formation at a broad concentration range. A higher ligand concentration is essential in some cases, particularly, when the aqueous complexes are weak in character or the system is complicated by the simultaneous existence of several complex species. It has, therefore, been suggested (7) to abandon the calculations of the equilibrium constants at infinite dilution. This is especially true for the complicated systems, where the presence of several species at the same time makes it exceedingly difficult to calculate the thermodynamic formation constant for each complex. In such systems it has been found essential to use a salt medium and compute the stability constants valid in that particular medium (4)(97). If the ionic strength is kept high by the addition of a supporting electrolyte and the concentrations of the species taking part in the reaction are low in comparison with the ionic strength, it can be assumed that the activity coefficients are very nearly constant (98). The law of mass action can therefore be applied directly using concentrations for the activities to obtain the formation constants.

The ionic strength is usually controlled with an inert electrolyte having high solubility and known to contribute very little towards complex formation with the central metal ion. The alkali metal perchlorates meet these requirements fully and sodium perchlorate has therefore been generally employed in such experiments. The perchlorate anion has very little tendency to form soluble complexes with the central metal ions. The use of inert electrolyte has some inherent disadvantages also. The controlled ionic medium method makes such properties (e.g. the conductivity), which are influenced very much by the presence of the supporting electrolyte, inapplicable to close studies of stepwise formation of the complexes. However, the advantage of having a constant ionic medium outweighs its disadvantages (4).

Historical:

Most of the present day methods for the study of ionic equilibria in aqueous medium were introduced in the beginning of the century. The developments in the chemistry of complex ion equilibria have been reviewed from time to time in the publications of Sillen (4), Rossotti and Rossotti (8), Biedermann and Sillen (9), and Bjerrum (37).

The stepwise complex formation was first shown in the study of Hg - Cl system, when aqueous complexes $HgCl^+$, $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{-2}$ were detected by Morse (10) and Sherrill (11). These authors also introduced the use of Hg electrode and applied the e.m.f. measurements to determine the central ion concentrations in Mercury (II)complexes. Euler (12) also employed the e.m.f. method to study the complexes of NH_3 and CN^- ligands with Ag^+, Zn^{+2}, and Cd^{+2} as the central ions, and used the respective metals as electrodes for the measurement of the concentrations of their free ions. Bodländer and his collaborators (13)(14)(15)(16) were the first to introduce the use of constant ionic medium and studied the complex formation of Cu^+, Ag^+, and Hg^{+2} in halide and pseudohalide systems. Classical studies of Bjerrum (17) later proved the existence of six successive aqueous complexes in the Cr-SCN system, thus putting the idea of the stepwise complex formation on a solid footing.

The important concept of ionic strength and activity was introduced by Lewis and Randall (99) in the early 1920's and later given a theoretical foundation by the Debye-Hückel theory (94). In the following years most of the research work dealing with equilibria in electrolyte solutions was directed towards the determination of the thermodynamic equilibrium constants for simple systems in which only one step was to be considered at a time, e.g. as was done in the work of Owen (100), and Popoff and Newman (101) on the silver chloride system. In complicated systems, where several complexes were found to co-exist, the thermodynamic constants could not be calculated in a straight forward manner. Guntelberg (88) attempted to evaluate the thermodynamic constants for the Pb-Cl system, and found the experimental results could not be interpreted distinctly. This work illustrated clearly that there would be little point in studying the complicated equilibria in dilute solutions, with an aim to establish the thermodynamic constants.

Revival of interest in the complicated systems followed soon after the development of the constant ionic medium approach by Bjerrum (18) and Leden (19). These authors developed accurate methods for the stepwise complex formation in a system at high ionic strength and over a wide range of the ligand concentration. Leden used as high as 3M, $NaClO_4$ in his studies on the halide complexes of Cd and Ag. Although the constants measured remain valid for the particular medium, yet one can reasonably be certain that the same species exist in another similar medium. Since then the use of constant ionic medium with an inert electrolyte has been consistently made a part of the study of the complicated system involving aqueous complex formation.

Derivation of the Stability Constants:

The calculations of a series of stepwise stability constants involve considerable mathematical manipulations. In an aqueous system, when the metal ion and the ligand are present in appropriate concentrations, an equilibria involving the intermediate complexes, $MA, MA_2, MA_3, \ldots MA_N$ is soon established. In order to find out the stepwise stability constants or the over-all stability constants, it is more convenient to employ a number of functions of the system. These functions can be readily evaluated from the experimental data and also hold a fairly simple relationship with the formation constants of the complexes. Some of these functions defining stepwise complex formation have been extensively utilized, in recent years, in the calculation of the formation constants of the complexes in aqueous medium (8)(21)(97). A brief description of the two well-known methods of Bjerrum (18) and Leden (19) is given below.

Bjerrum's Method:

Bjerrum has defined the "Formation Function", $\bar{n}$, the average number of ligands attached to the central ion M, as

$$(1.15) \qquad \bar{n} = \frac{C_a - (A)}{C_m}$$

where C_a is the total ligand concentration. (A) is the unbound ligand concentration. C_m is the total metal concentration.

$$(1.16) \qquad \bar{n} = \frac{MA + 2MA_2 + 3MA_3 + \ldots . + NMA_N}{M + MA + MA_2 + \ldots . + MA_N}$$

$$(1.17) \qquad \bar{n} = \frac{\beta_1(A) + 2\beta_2(A)^2 + \ldots . + N\beta_N(A)^N}{1 + \beta_1(A) + \beta_2(A)^2 + \ldots + \beta_N(A)^N}$$

A simple rearrangement of the above eq. (1.17) gives,

$$(1.18) \quad \bar{n} + (\bar{n} - 1)\beta_1(A) + (\bar{n}-2)\beta_2(A)^2 + \ldots \quad (\bar{n}-N)\beta_N(A)^N = 0$$

The physical significance of the formation function, $\bar{n}$, is that it represents the characteristic average coordination number. It may vary from zero, when no complex formation takes place in solution, i.e. $C_a = (A)$, to the limiting maximum value of the coordination number. In the absence of the stepwise complex formation and with a sufficient excess of the ligand, $\bar{n}$ is equal to the coordination number. In abbreviated form,

$$(1.19) \qquad \bar{n} = \frac{\sum_{i=1}^{i=N} i \, \beta_i \, (A)^i}{1 + \sum_{i=1}^{i=N} \beta_i (A)^i}$$

thus showing that in a mononuclear complex system, $\bar{n}$ is a function of the free ligand concentration (A) only. Knowing $\bar{n}$ as a function of the free ligand concentration, it is possible to determine the concentration constants of the system; $\bar{n}$ is calculated from the knowledge of the experimentally observed quantities C_m, C_a, and (A). Once $\bar{n}$ is known the eq. (1.18) can be employed to set up N linearly independent equations, where N experiments have been performed. Bjerrum (18) has described the methods of calculating the over-all stability constants, β_i from the solution of sets of equations mentioned above.

Leden's method:

Leden (19) and Fronaeus (20) have introduced another function, Φ, "Degree of Complex Formation". It involves the ratio of the metal total, C_m, to the free metal ion concentration (M), in the equilibrium.

$$(1.20) \qquad \Phi = \frac{C_m}{(M)}$$

The function, Φ, may vary from one (when no complexing occurs, i.e. $C_m = M$) to a very large value depending upon the stability constants of the complexes and the ligand concentration.

$$(1.21) \qquad \Phi = \frac{(M) + (MA) + (MA_2) + \ldots\ (MA_N)}{(M)}$$

$$(1.22) \qquad \Phi = 1 + \beta_1(A) + \beta_2(A)^2 + \ldots\ \beta_N(A)^N$$

$$(1.23) \qquad \Phi = 1 + \sum_{i=1}^{i=N} \beta_i(A)^i$$

To calculate the β_i values, Leden has proposed the method of extrapolation of these functions such that eq. (1.22) above can be transformed as,

$$(1.24) \qquad F_1 = \frac{\Phi - 1}{(A)} = \beta_1 + \beta_2(A) + \ldots\ \beta_N(A)^{N-1}$$

$$\left.\begin{matrix}\text{Limit } F_1 \\ A \rightarrow 0\end{matrix}\right] F_1 = \beta_1$$

The graphical treatment of F_1 as a function of (A) should yield a plot with an intercept β_1. Similarly the successive formation constants may be obtained by the graphical treatment of the successive functions such that

$$(1.25) \qquad F_2 = \frac{F_1 - \beta_1}{(A)} = \beta_2 + \beta_3\ (A) + \ldots\ \beta_N(A)^{N-2}$$

$$\left.\begin{matrix}\text{Limit } F_2 \\ A \rightarrow 0\end{matrix}\right] F_2 = \beta_2$$

The evaluation of the system functions F_1, F_2, etc., requires the knowledge of the free metal ion concentration (M) and (A), the free ligand concentration at equilibrium. The quantity (M) is conveniently estimated by the potentiometric or polarographic methods. When the central ion is in small concentration, i.e. $C_m << C_a$, the quantity C_m is a small fraction of the ligand total C_a; in such cases, the relationship $(A) \simeq C_a$ holds true. The evaluation of (A) where the approximation $A \simeq C_a$ is not valid can be made by the methods described by Sullivan and Hindman (22). This method of calculation is generally referred to as the "Leden Plot".

It has been shown by Sullivan and Hindman (22) that the "Formation Function", $\bar{n}$, and the "Degree of Complex Formation", Φ, for a given system are related mathematically to one another and that the two general methods give the unique values for the formation constants of the complexes. Any discrepancies in calculations for a system must be merely a reflection of the inherent uncertainties involved in the manipulations of the experimental data.

Leden's method has the draw-back that it is applicable to those systems where the concentration of (M), i.e. the concentration of the free central ion can be estimated experimentally. There are relatively few systems that can be handled potentiometrically or polarographically for the free metal ion concentration. Furthermore the physical significance of the calculations is not readily apparent. However, it has the great advantage that graphical manipulation of the data can be avoided for the condition $A \simeq C_a$ holds true when $C_m << C_a$. This method, in principle, is always applicable.

In Bjerrum's method, if the complexes formed are weak or if the central ion is added as a trace concentration of a radioisotope, the term $(C_a - A)$ does not differ appreciably from zero. The eq. (1.15) therefore can not be used directly to calculate $\bar{n}$. The advantages of this method are that it is applicable in all the cases whether the measured quantity be the concentration (M), (A) or a complex (MA_i). Also the plot of $\bar{n}$ as a function of (A) indicates the number of complexes one has to deal with in a particular system.

In the equilibrium studies one generally knows the number of complexes present in the system. There are, however, many unexplored systems where the nature of the equilibria are not too well established. In such cases one is confronted with the problem of establishing the nature of complexes in solution before attempts can be made to evaluate their formation constants. There are still many inorganic systems that have not received a thorough attention so far; for example the aqueous heterogeneous equilibria of the metal chalcogenides with the heavier elements selenium and tellurium. In the present studies an attempt has been made to explore the aqueous equilibria of some metal sulphur and metal selenium systems.

The Scope and the Object of the Thesis:

The atoms that are bound directly to metal ions in complexes are generally from the more electronegative groups, VB, VIB, and VIIB, in the periodic system. In the exhaustive compilation of Sillen and Martell, reference (24), are cited the stability constants of the aqueous complexes and the solubility products of a large number of inorganic systems. There is, however, little information available on the metal selenium or tellurium interactions. It appears certain that even the simple solubility products of such insoluble compounds have not been established experimentally.

Earlier it has been pointed out that the formation of the precipitate constitutes a heterogeneous equilibria where aqueous complexes may be formed in the homogeneous solution above the precipitate. The complexes formed by the metal sulphides, e.g. HgS (72) in contact with solid precipitate have been known for some time. By analogy one may expect the heavier elements of the same group (VIB), to undergo similar aqueous complex formation reactions with metals. The solubility equilibria of some new systems involving metal sulphur and metal selenium interactions have therefore been studied with an aim to establish the nature of their aqueous complexes formed in contact with the respective precipitates. Metal sulphur equilibria in some cases have been re-investigated to clear up some discrepancies noticed in the published literature. Metal selenium and metal selenite equilibria have been studied with an aim to compare them with their corresponding sulphur systems under the similar experimental conditions.

The elements that constituted the central ion were chosen from the transition metals (Mn,Fe,Co) and also the B character elements (Ag,Hg), which have complete d^{10} electrons in their structure (2), and are the well known chalcophil elements. The thesis consists of seven chapters. The general mathematical treatment of the heterogeneous equilibria of these systems is outlined in chapter II, which also describes the general method for the identification of the aqueous complex species in such systems from the solubility equilibrium data.

The experimental procedures are given in chapter III both for the potentiometric and the radiometric methods adopted in this study.

Chapter IV illustrates the electrochemical procedure for the evaluation of the K_{sp} of the Ag and Hg compounds that form the reversible electrode systems. Further it is shown that the electrochemical data can be utilized successfully in the calculation of the ionization constants of the weak dibasic acids H_2Se and H_2SeO_3; these acids constitute the precipitating as well as the complexing ligands in these systems.

Chapter V, VI, VII, describe the individual studies on the metal selenite, sulphide, and selenide systems respectively. In each chapter is included a brief review of the pertinent literature followed by the discussion and the comparison based on the experimental observations of this work.

CHAPTER II

The Theoretical Aspects of the Present Study

The increase in the solubility of a sparingly soluble compound in contact with an excess of the precipitating ligand is an indication that the complex formation takes place. This is true provided the activity coefficients of the species involved can be assumed to remain constant in the medium. Several reports are found in the literature, (25)(26)(27)(28)(29), where such solubility measurements have been utilized in the determination of the formation constants of the complex species in solution. The solubility approach is thus a fairly well established technique to study the heterogeneous equilibria of the inorganic systems.

Some earlier workers have presented the methods for the calculation of the formation constants which either give the results of the predominent species (28) or identify the complex having the lowest coordination (30). The methods of Leden and Bjerrum described earlier (chapter-I) have, however, proved extremely useful in the determination of a large number of stepwise stability constants of the soluble complexes (24). In many complicated systems, particularly when the system has weak complexes or there is the possibility for the formation of mixed complexes, direct application of these methods is often insufficient to obtain significant information on the complex formation. The problem is further complicated in the equilibria of the weak inorganic acids, where the nature of the ligand also changes and depends upon the ionization constants of the acid involved. In such heterogeneous systems the mathematical treatment of the equilibrium data must take into account the solubility product principle, the nature of the ligand species, and the possibilities of the mixed complex formation.

In this study the formation of the normal complexes and other mixed complexes with OH^- as a ligand in alkaline medium have been considered.

Ionization Equilibria of the Ligand Acids:

The systems involved in the present study are all weak dibasic inorganic acids, H_2S, H_2Se, and H_2SeO_3. Their ionization equilibria may be grouped as follows:

(2.1) $$(H_2A) \rightleftharpoons (H^+) + (HA^-)$$

(2.2) $$k_1 = \frac{(H^+)(HA^-)}{(H_2A)}$$

(2.3) $$(HA^-) \rightleftharpoons (H^+) + (A^{-2})$$

(2.4) $$k_2 = \frac{(H^+)(A^{-2})}{(HA^-)}$$

where k_1 and k_2 are the ionization constants and (A^{-2}) is the ligand ion S^{-2}, Se^{-2}, or SeO_3^{-2}.

It is evident from eq (2.1) and (2.3) that the concentration of (HA^-) and (A^{-2}) is a function of pH. Therefore the concentration of each of them at any pH can be calculated from the knowledge of A_{tot}, the analytical concentration of the particular acid.

(2.5) $$A_{tot} = (H_2A) + (HA^-) + (A^{-2})$$

from eq (2.2),(2.4), and (2.5)

(2.6) $$A_{tot} = (A^{-2})\left[\frac{(H^+)^2}{k_1 . k_2} + \frac{(H^+)}{k_2} + 1\right]$$

(2.7) $$A_{tot} = (HA^-)\left[\frac{(H^+)}{k_1} + 1 + \frac{k_2}{(H^+)}\right]$$

Solubility Product Equilibrium:

An insoluble precipitate of sulphide, selenide, or selenite in equilibrium with an excess of the precipitating ligand in solution gives the solubility product relationship as,

(2.8) $$(M^{+2}) + (A^{-2}) = (MA)_{solid}$$

(2.9) $$K_{sp} = (M^{+2}) \cdot (A^{-2}) \quad \text{(in solution)}$$

where (A^{-2}), as before, is the ion S^{-2}, Se^{-2} or SeO_3^{-2}; M is a divalent metal ion, and K_{sp} the solubility product of the compound.

Eq (2.9) shows that the free metal ion concentration and the ligand concentration are interdependent. The concentration of the free metal ions can also be expressed as a function of pH and the total ligand concentration.

From eq (2.6) and eq (2.9) we have

(2.10) $$K_{sp} = (M^{+2}) \left[\frac{A_{tot} \cdot k_1 \cdot k_2}{(H^+)^2 + k_1 (H^+) + k_1 k_2} \right]$$

Complex Formation Equilibria:

The free metal ions in solution in contact with the precipitated metal compound with an excess of the ligand can give rise to the complexes in solution. The complex formation can be expressed in three different phases as follows.

Type I.

(2.11) $$(M^{+2}) + (HA^-) \rightleftharpoons (M(HA)^+)$$

$$(2.12) \qquad (M(HA)^{+}) + (HA^{-}) \rightleftharpoons (M(HA)_2)$$

Type II.

$$(2.13) \qquad (M^{+2}) + (A^{-2}) \rightleftharpoons (MA)$$

$$(2.14) \qquad (MA) + (A^{-2}) \rightleftharpoons (MA_2)^{-2}$$

Type III.

$$(2.15) \qquad (M(HA)^{+}) + (OH^{-}) \rightleftharpoons (M(HA)(OH))$$

$$(2.16) \qquad (MA) + (OH^{-}) \rightleftharpoons (M(A)(OH)^{-})$$

where (M) is a divalent metal ion.

The metal total in solution, (M_{tot}), is thus the sum of all the species in the equilibria.

$$(2.17) \qquad (M_{tot}) = (M^{+2}) + (M_{complex})$$

With the knowledge of the ligand ionization constants and the solubility product equilibrium, it is possible to express the metal total concentration in solution as a function of pH and A_{tot} in the same solution.

The general reaction involving all the possibilities mentioned above for the complex formation may now be written as,

$$(2.18) \qquad (M^{+2}) + x(H^{+}) + x(A^{-2}) + y(OH^{-}) \rightleftharpoons (M(HA)_x(OH)_y)^{2-(x+y)}.$$

The reaction constant for the eq (2.18) is expressed as,

$$(2.19) \qquad \phi_{xy} = \frac{(M(HA)_x(OH)_y)^{2-(x+y)}}{(M^{+2}).(H^{+})^x.(A^{-2})^x.(OH^{-})^y}$$

where the symbol ϕ, signifies the reaction constants, and is unique for such heterogeneous equilibria, involving weak acid interactions.

If both x and y are zero in eq (2.18) we have only the presence of free metal ions, i.e. no complex formation occurs. In other cases depending upon the value of x and y, several types of complexes are possible. To predict the formation of an aqueous complex the basic requirement is therefore the evaluation of the x and y values. By definition even when x and y are zero the value of ϕ_{oo} remains one, since,

$$(2.20) \qquad \phi_{oo} = \frac{(M^{+2})}{(M^{+2})} = 1$$

Using eq (2.17), (2.18), and (2.19) it is possible to write that in an aqueous solution,

$$(2.21) \qquad M_{tot} = \sum_{x=o}^{N-y} \sum_{y=o}^{N-x} \phi_{xy} \cdot (M^{+2}) \cdot (H^{+})^{x} \cdot (A^{-2})^{x} \cdot (OH^{-})^{y}$$

where N is the coordination number of M.

We may now introduce the aqueous equilibrium for the ion product of water,

$$(2.22) \qquad (H^{+}) \cdot (OH^{-}) = K_{w}$$

combining eq (2.10), (2.21), and (2.22) it is possible to transform eq (2.21) into a general equation as a function of pH and A_{tot} only.

$$(2.23) \qquad M_{tot} = \sum_{x=o}^{N-y} \sum_{y=o}^{N-x} \phi_{xy} \cdot K_{sp} \cdot K_{w}^{y} \cdot (A_{tot})^{x-1} \cdot (F_{s}H^{+})^{x-1} \cdot (H^{+})^{x-y}$$

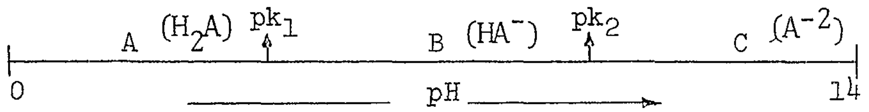
$$\text{where } F_{s}H^{+} = \left[\frac{k_1 \cdot k_2}{(H^{+})^{2} + k_1 (H^{+}) + k_1 \cdot k_2} \right]$$

In principle the solution of eq (2.23) as a function of pH and A_{tot} will establish the nature of the complexes in solution. With the knowledge of their respective ϕ values, one can determine the respective formation constants of the species thus identified.

Theoretical Developments of the Complex Formation Equilibria:

The considerations cited earlier make it apparent now that the general reaction equation (2.23), must be solved in such a manner that the maximum possible information is derived for the complex species. The possible complex forming ligands in this study are HA^-, A^{-2}, and OH^-. The first two are the derivatives of the parent acid H_2A, while the third is the constituent of the medium and becomes important in alkaline regions. The concentrations of these ligand species in turn are governed by their ionization constants, k_1, k_2, and K_w.

Since the ligand acids are all dibasic in character, three pH zones may be expected, where an individual ligand species will exhibit its maximum concentration. We have defined these pH zones as regions A, B, and C of pH and are illustrated below. Based on these distinctions, the complexing characteristics of the ligands may be evaluated theoretically, which are discussed subsequently.



Discussion on Complex Formation Equilibria:

A:- Equilibrium Involving HA^- as Ligand:

The general eq (2.23) found earlier can be simplified if we consider the equilibrium conditions in a dibasic acid as a function of pH. We know that:

$$(2.24) \qquad F_sH^+ = \frac{k_1.k_2}{(H^+)^2 + k_1.(H^+) + k_1.k_2}$$

If $(H^+) >> k_1 >> k_2$ (region A of pH)

$$(2.25) \qquad F_sH^+ = \frac{k_1.k_2}{(H^+)^2}$$

other terms are negligible.

If $k_1 >> (H^+) >> k_2$ (region B of pH)

$$(2.26) \qquad F_sH^+ = \frac{k_2}{(H^+)}$$

other terms become negligible.

If $k_2 >> k_1 >> (H^+)$ (region C of pH)

$$(2.27) \qquad F_sH^+ = 1$$

other terms are negligible.

Introducing eq (2.25),(2.26), and (2.27) into eq (2.23) we have

$$(2.28) \qquad M_{tot} = \sum_{x=o}^{N-y} \sum_{y=o}^{N-x} \phi_{xy}.K_{sp}.K_w^y.(A_{tot})^{x-1}.(H^+)^{2-(x+y)}.(k_1.k_2)^{x-1}$$

$$(2.29) \qquad M_{tot} = \sum_{x=o}^{N-y} \sum_{y=o}^{N-x} \phi_{xy}.K_{sp}.K_w^y.(A_{tot})^{x-1}.(H^+)^{1-y}.(k_2)^{x-1}$$

$$(2.30) \qquad M_{tot} = \sum_{x=o}^{N-y} \sum_{y=o}^{N-x} \phi_{xy}.K_{sp}.K_w^y.(A_{tot})^{x-1}.(H^+)^{x-y}$$

This signifies that the simplification can be made to the extent that in a particular region of pH it is easier to derive information pertaining to a complex species from the simplified equations applicable in the region of interest.

B:- Equilibrium Involving A^{-2} as Ligand:

From the general equilibrium eq (2.23) the role of complexing by the ligand (A^{-2}) is not very apparent. It may now be shown that complexing of this type is a particular case when $pH > pk_2$ in the equilibrium.

From eq (2.6) and eq (2.27) we have,

$$(2.31) \qquad (A_{tot}) = (A^{-2}) \qquad \text{when } pk_2 < pH.$$
$$F_s(H^+) \rightarrow 1$$

Putting this in the general equation (2.23) we get the following equation for the condition $pH > pk_2$ of the ligand acid.

$$(2.32) \qquad M_{tot} = \sum_{x=o}^{N-y} \sum_{y=o}^{N-x} \phi_{xy}.K_{sp}.K_w^y.\ (A_{tot})^{x-1}(H^+)^{-y}$$

$$(2.33) \qquad M_{tot} = \sum_{x=o}^{N-y} \sum_{y=o}^{N-x} \phi_{xy}.K_{sp}.K_w^y.\ (A^{-2})^{x-1}(H^+)^{-y}$$

It may therefore be concluded that should complexing occur with (A^{-2}) as the ligand, it will only be apparent in the regions of pH where $pk_2 < pH$. Any variations in the M_{tot} in this region will indicate complexing of this sort. As seen above in eq (2.33), M_{tot} will be independent of pH unless the OH^- as a ligand participates in the complex formation.

C:- Equilibrium Concentration of Ligand Acid:

In solution the analytical concentration of the ligand acid is given by the sum of all the species present.

$$(2.34) \qquad A_{tot} = (H_2A) + (HA^-) + (A^{-2}) + (A_{complex})$$

Experimentally A_{tot} is always maintained far greater than the metal total concentration, M_{tot}, so that $A_{complex}$ is negligibly small in comparison with other species. Therefore A_{tot} is considered to be the same as given in eq (2.5), even when the complex species are definitely known to be present in the system.

Applications of the General Equation in the Identification of the Complex Species.

In a heterogeneous system normally two or three complexes are present in some appreciable concentrations. If the experimental data are fitted into the general equation assuming all sorts of complexes, sometimes a negative ϕ value is obtained as was observed in an earlier work from this laboratory (31). By definition ϕ must remain positive even when the simple ions are present in contact with the precipitated compound. It is, therefore, essential that the complex species must be identified initially. This can be achieved easily by studying the characteristics of the M_{tot} as a function of pH and A_{tot} in the three different regions of pH discussed earlier. In other words the solubility curves of the system as a function of these two experimental variables will identify a complex species formed in some appreciable concentrations in any particular region of pH.

The concentration of metal total, (M_{tot}), for all practical purposes is the sum of the limited number of the complexes in equilibrium. It is possible to calculate by the law of mass action the variation in the concentration of a given complex as a function of the two experimental variables pH and A_{tot}. The characteristics of an individual complex will be apparent from such a study. If in a given pH region and in a concentration interval of the ligand total, (A_{tot}), the experimentally observed

M_{tot} varies in conformity with a postulated species, we can conclude that the M_{tot} thereby corresponds to the concentration of that particular species. The complex is thus identified and its ϕ value can be calculated from the experimentally determined quantities M_{tot}, pH, and A_{tot}. In this manner if we scan the entire regions of pH and at broad intervals of A_{tot} concentrations, all the complexes formed in some appreciable concentrations in solution can thus be identified. We can say that the experimentally observed quantity M_{tot} represents a general complex $(M(HA)_X(OH)_Y)^{2-(X+Y)}$ in any region of pH. The values of both X and Y are therefore of paramount interest to establish the formula of the complex.

In practice, first the theoretical values of both X and Y are determined for the possible complexes in solution. The experimental data are then compared with these possibilities and the predominence of a complex is ascertained before calculating its formation constant. The theoretical approach to determine X and Y simply involves the solution of the three general equations (2.28), (2.29), and (2.30) or the special eq (2.33) found earlier for the three different regions of pH. These equations for the general complex mentioned above can be written as:

$$(2.35) \quad M_{tot} = \phi_{XY}\cdot K_{sp}\cdot K_w^Y\cdot (k_1\cdot k_2)^{X-1}\cdot (A_{tot})^{X-1}\cdot (H^+)^{2-(X+Y)}$$

$$(2.36) \quad M_{tot} = \phi_{XY}\cdot K_{sp}\cdot K_w^Y\cdot k_2^{X-1}\cdot (A_{tot})^{X-1}\cdot (H^+)^{1-Y}$$

$$(2.37) \quad M_{tot} = \phi_{XY}\cdot K_{sp}\cdot K_w^Y\cdot (A_{tot})^{X-1}\cdot (H^+)^{X-Y}$$

The logarithmic form of the eq (2.35) gives,

$$(2.38) \quad \log M_{tot} = \log \phi_{XY} + \log K_{sp} + Y \log K_w + (X-1) \log A_{tot} + (X-1) \log (k_1\cdot k_2) + 2-(X+Y) \log H^+.$$

From eq (2.38) we obtain on partial differentiation, with respect to pH (at constant A_{tot}),

$$(2.39) \quad \frac{\partial \log M_{tot}}{\partial pH} = (X+Y) - 2$$

(In region A of pH).

Similarly the logarithmic transformation and differentiation of eq (2.36) and eq (2.37) leads to two more functions as

From eq (2.36) we get,

$$(2.40) \quad \frac{\partial \log M_{tot}}{\partial pH} = (Y-1)$$

(In region B of pH).

From eq (2.37) we get,

$$(2.41) \quad \frac{\partial \log M_{tot}}{\partial pH} = (Y-X)$$

(In region C of pH).

The partial differentiation as a function of A_{tot} (at constant pH) gives for all the three equations above,

$$(2.42) \quad \frac{\partial \log M_{tot}}{\partial pA_{tot}} = (1-X)$$

(In all pH regions).

In theory the logarithmic slopes of the variations of M_{tot} as a function of pH and pA_{tot} are therefore clear indications of the existence of a particular complex in some predominent concentration. One can construct now a table showing the theoretical slopes of the possible complexes as a function of pH and pA_{tot}; Table 2.1 and 2.2 provide the data on complexes for the monovalent and divalent metals with their theoretical slopes in the three regions of pH.

In a particular case when pH > pk_2, A_{tot} becomes equal to A^{-2} (cf. eq (2.27) and (2.31)), the general complex assumes the formula $(M(A)_X(OH)_Y)^{2-(X+Y)}$ and the characteristic logarithmic slopes in this case will be as follows;

$$(2.43) \quad \frac{\partial \log M_{tot}}{\partial pH} = Y$$

(in the region C of pH).
(at constant A_{tot}).

$$(2.44) \quad \frac{\partial \log M_{tot}}{\partial pA_{tot}} = (1-X)$$

(at constant pH).

It is now apparent from eq (2.43) that in case of (A^{-2}) complexing the pH effect is negligible unless (OH^-) also participates in the complex formation, i.e. a mixed complex formation. The theoretical slopes calculated in table 2.1 and 2.2, include the possibilities of complexing of this nature as well.

TABLE NO. 2.1

Theoretical Slopes of Postulated Complex Species.
Monovalent metal ion, Coordination Number-4.

Species		$\frac{\partial \log M_{tot}}{\partial pH}$		$\frac{\partial \log M_{tot}}{\partial pA_{tot}}$
	$pH < pk_1$	$pk_1 < pH < pk_2$	$pk_2 < pH$	
(M^+)	-1	-0.5	0	+0.5
$(M(HA))$	0	-0.5	-1	-0.5
$(M(HA)_2^-)$	+1	-0.5	-2	-1.5
$(M(HA)_3^{-2})$	+2	-0.5	-3	-2.5
$(M(HA)_4^{-3})$	+3	-0.5	-4	-3.5
$(M(HA)(OH)^-)$	+1	+0.5	0	-0.5
$(M(HA)(OH)_2^{-2})$	+2	+1.5	+1	-0.5
$(M(HA)_2(OH)^{-2})$	+2	+0.5	-1	-1.5
$(M(HA)_2(OH)_2^{-3})$	+3	+1.5	0	-1.5
$(M_2(HA)(OH))$	0	0	0	0
$(M(A)^-)$	-	-	0	-0.5
$(M(A)_2^{-3})$	-	-	0	-1.5
$(M(A)(OH)^{-2})$	-	-	+1	-0.5
$(M(A)(OH)_2^{-3})$	-	-	+2	-0.5
$(M(A)_2(OH)^{-4})$	-	-	+1	-1.5
$(M(A)_2(OH)_2^{-5})$	-	-	+2	-1.5
$(M(OH))$	0	+0.5	+1	+0.5
$(M(OH)_2^-)$	+1	+1.5	+2	+0.5

TABLE NO. 2.2

Theoretical Slopes of the Postulated Complex Species.
Divalent Metal ion, Coordination Number-4.

Species	$\frac{\partial \log M_{tot}}{\partial pH}$			$\frac{\partial \log M_{tot}}{\partial pA_{tot}}$
	$pH < pk_1$	$pk_1 < pH < pk_2$	$pk_2 < pH$	
(M^{+2})	-2	-1	0	+1
$(M(HA)^{+})$	-1	-1	-1	0
$(M(HA)_2)$	0	-1	-2	-1
$(M(HA)_3^{-})$	+1	-1	-3	-2
$(M(HA)_4^{-2})$	+2	-1	-4	-3
$(M(HA)(OH))$	0	0	0	0
$(M(HA)_2(OH)^{-})$	+1	0	-1	-1
$(M(HA)_2(OH)_2^{-2})$	+2	+1	0	-1
$(M(HA)_3(OH)^{-2})$	+2	0	-2	-2
$(M(HA)(OH)_3^{-2})$	+2	+2	+2	0
$(M(A))$	-	-	0	0
$(M(A)_2^{-2})$	-	-	0	-1
$(M(A)(OH)^{-})$	-	-	+1	0
$(M(A)(OH)_2^{-2})$	-	-	+2	0
$(M(OH)^{+})$	-1	0	+1	+1
$(M(OH)_2)$	0	+1	+2	+1

The general inferences that may be drawn from the considerations cited above in the general theory and the theoretical slopes shown in table 2.1 and 2.2 are as follows.

1. When only one complex species is in equilibrium with the precipitate, characteristic slopes of this complex are exhibited in the three different regions of pH. Fig. 2.1 demonstrates the shapes of the solubility curves based on these theoretical slopes.

2. The solubility curves change slopes gradually in the bordering regions AB or BC of the pH. A solubility maxima or minima may be expected depending upon the nature of the complex involved. Furthermore, it is not possible to have such variations in the solubility anywhere except when pH is very near to the pk's of the ligand acid.

3. Each complex has a characteristic slope in each of the three pH regions. The distinction of a particular complex can not be made unless the solubility (M_{tot}) is traced over the entire pH range, e.g. three complexes $M(HA)_2$, $M(HA)(OH)$, and $M(OH)_2$ have a slope of zero in the region A of pH, thus in this region no distinction is possible; however, for these complexes the slopes change respectively to -1,0,+1 and -2,0,+2 in the regions B and C of pH. Identification of the complex thereby becomes possible from the shapes of the solubility curves in other regions of pH. It is therefore essential that the solubility must be carefully scanned over the entire pH range.

4. The confirmation of the presence of a complex can further be obtained by observing the variations of M_{tot} as a function of A_{tot} at any desired constant pH. Considering, once again, the same complexes mentioned in # 3, we may visualize the respective characteristic slopes of (-1,0,+1) as a

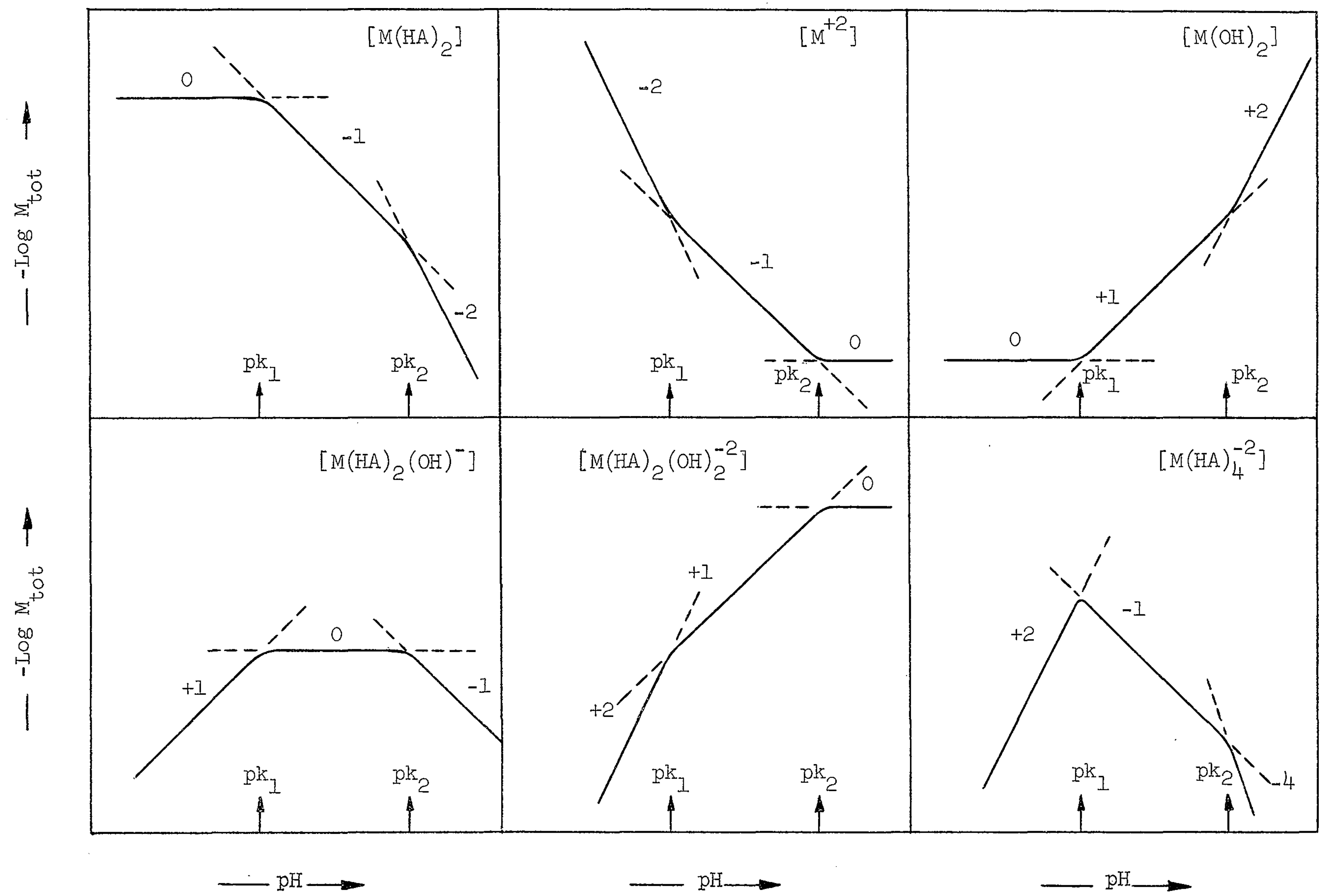


FIGURE 2.1 : Theoretical Slopes of Some Complex Species.

function of A_{tot} at a constant pH, thus indicating all the complexes have distinct solubility slopes that can be utilized in their identification.

5. If several complexes are present simultaneously, the shapes of the solubility curves still indicate their existence as well as their zone of predominence. For example if a system has (M^{+2}), $(M(HA)^{+})$, $(M(HA)_4^{-2})$, and $(M(HA)_2(OH)_2^{-2})$ as the species in the equilibria, the shapes of the theoretical solubility curves for the system will be as shown in fig. 2.2. The confirmation of the individual complex is made possible by studying the solubility variations at a constant pH as a function of A_{tot} in their respective regions of predominence. A glance at fig. 2.2 shows that on increase in A_{tot}, the region of (M^{+2}) is suppressed and of $M(HA)^{+}$ remains constant, but the solubility hump shifts upward by three logarithmic units for $M(HA)_4^{-2}$, while the solubility slopes of the complex $M(HA)_2(OH)_2^{-2}$ too move upward by one logarithmic unit. By selection, a proper zone of pH can be segregated, where M_{tot} evidently corresponds to a particular complex.

6. In case of complexing with the ligand (A^{-2}), the pH effect is negligible when pH > pk_2; nevertheless, the variations of M_{tot} as a function of A_{tot} identify a family of complexes formed by this ligand. As an example the complexes MA, MA_2^{-2}, and MA_3^{-4} can be identified from the slopes of the solubility curve as a function of A_{tot}. Fig. 2.3 explains a curve constructed from the theoretical slopes for such a system.

It may now be concluded that a careful study of the solubility equilibria of an inorganic system with the ligands derived from the weak acids, both as a function of pH and A_{tot}, is essential to establish the nature of the complex species that exist in contact with the solid precipi-

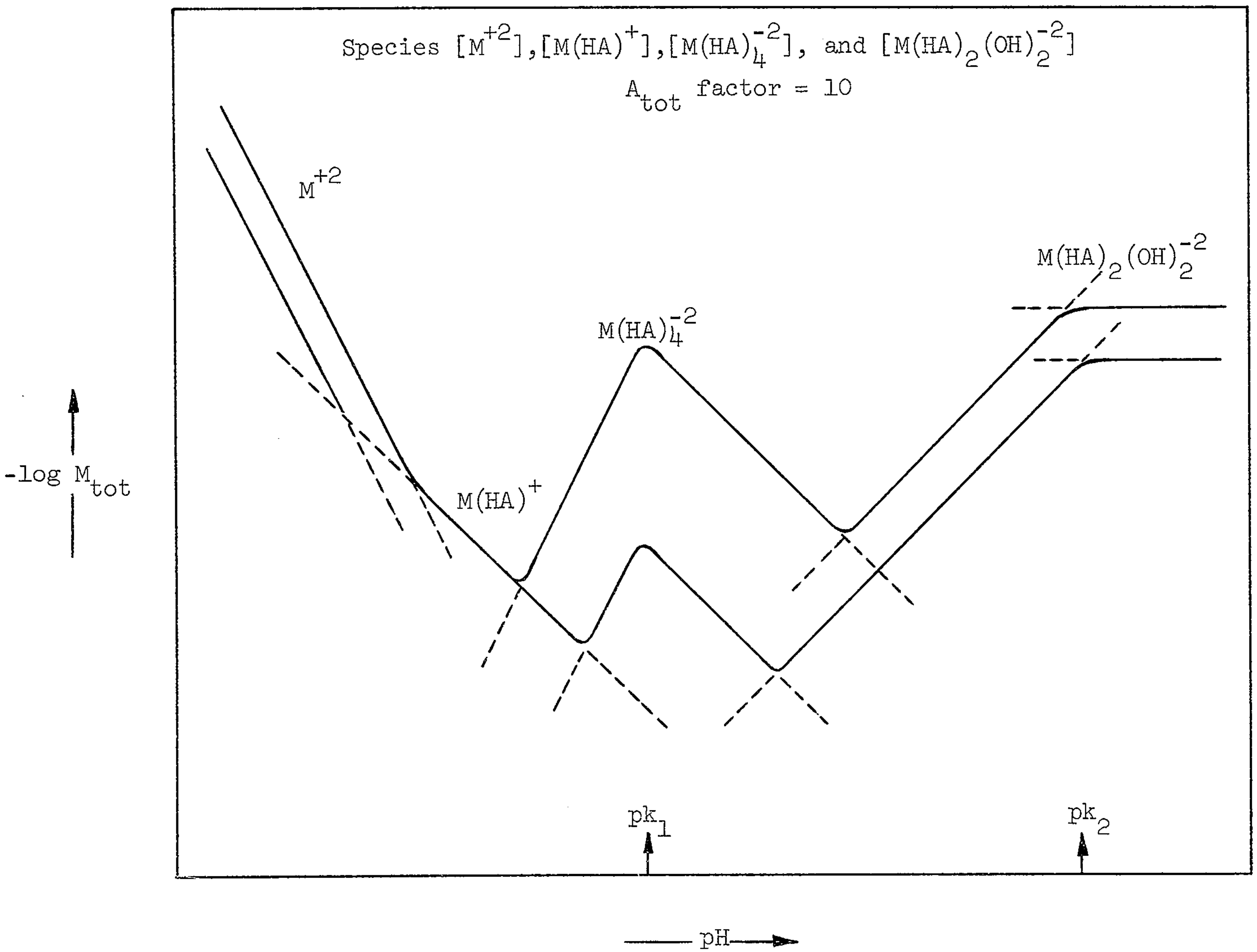


FIGURE 2.2 : Theoretical Solubility Curves of a System.

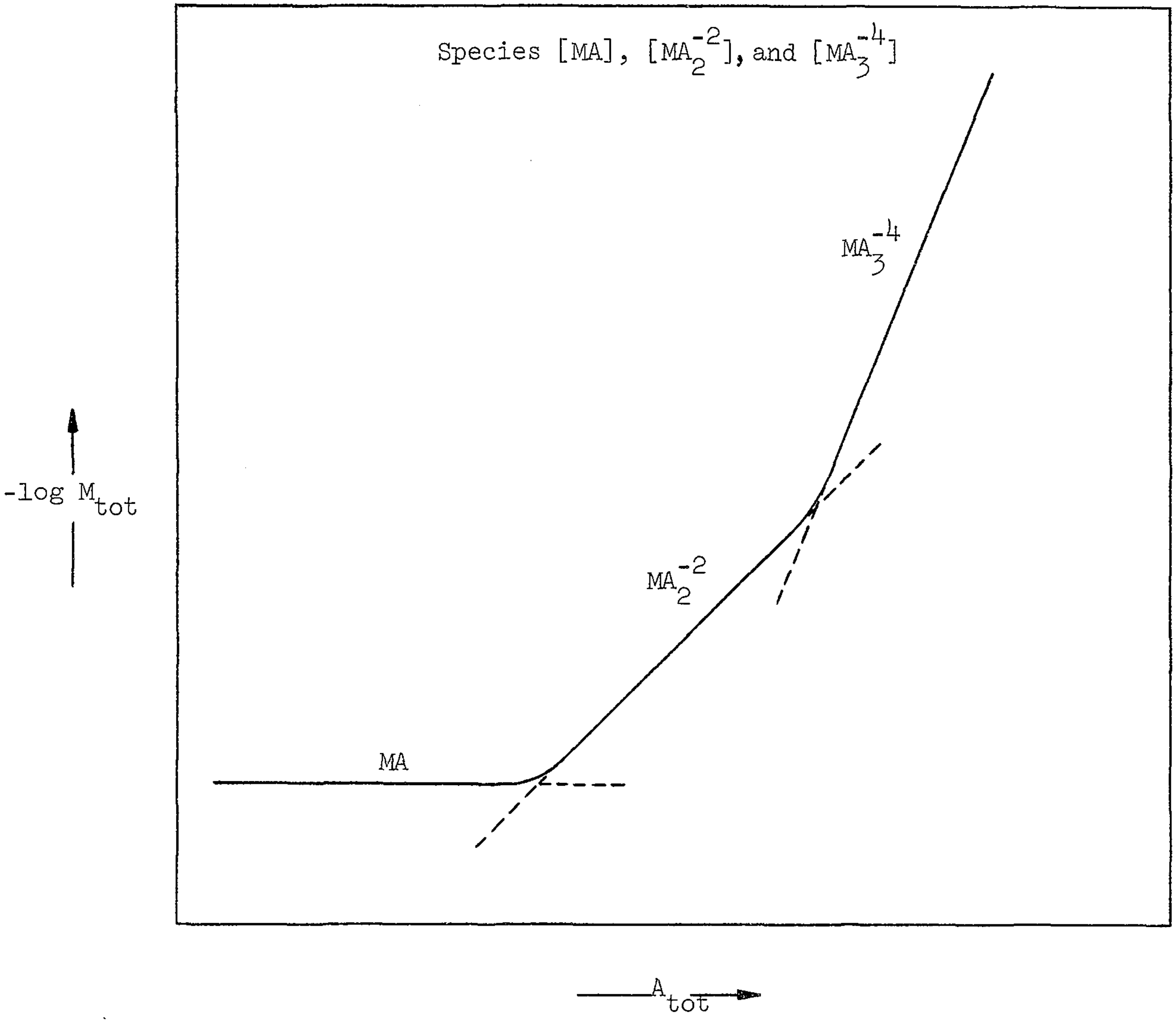


FIGURE 2.3 : Theoretical Variation of M_{tot} as a function of A_{tot} (pH > pk_2).

tate of the system.

Calculation of the Formation Constant:

Once the complex has been identified as discussed previously, M_{tot} in its region of predominence corresponds totally to this species. If more than one species are identified in the same region of pH; M_{tot} is regarded as the sum of the concentration of each of these complexes. In a majority of cases it is possible to select a region of pH where only one complex is present in appreciable concentration, and its reaction constant, ϕ is determined directly by the application of the general complex formation equation appropriate for that region; eq (2.35)(2.36) (2.37) or (2.33).

$$(2.45) \qquad \phi_{XY} = \frac{(M_{tot}) \cdot (A_{tot})^{1-X} \cdot (H^{+})^{Y-X} \cdot (F_{s}H^{+})^{1-X}}{K_{sp} \cdot K_{w}^{Y}}$$

Even for a system in which n complexes are formed simultaneously one can establish a set of n equations involving n values of ϕ_{XY} from the n experimentally determined points. Evaluation of the individual ϕ value for each complex is thereby possible from the mathematical solution of these simultaneous equations. This treatment evidently takes into account only the positive complex formation and definitely eliminates the possibilities of negative ϕ values.

The overall formation constant β of each complex is easily determined from the knowledge of the ϕ value of the same complex. For example, the formation constant of the general complex $(M(HA)_{X}(OH)_{Y})^{2-(X+Y)}$ is given by eq (2.46) below.

$$(2.46) \qquad \beta_{XY} = \frac{(M(HA)_{X}(OH)_{Y}\ )^{2-(X+Y)}}{(M^{+2}) \cdot (HA^{-})^{X} \cdot (OH^{-})^{Y}}$$

Combining eq (2.10), eq (2.45), and eq (2.46) we get the final expression as,

(2.47) $$\beta_{XY} = k_2^X . \phi_{XY}$$

where k_2 is the second ionization constant of the ligand acid, given in eq (2.4).

In the case when complexing occurs after pk_2 of the acid ligand the ϕ_{XY} is same as its normal formation constant β_{XY}.

(2.48) $$\phi_{XY} = \beta_{XY} \quad \text{when } pH > pk_2.$$

CHAPTER III

Experimental Procedures

The solubility procedures were all adopted at 25°C throughout this study at an ionic strength of 1.0 M adjusted with $NaClO_4$, $HClO_4$ and NaOH only.

Preparation of Reagents:

All reagent solutions were prepared in deionized, deoxygenated water always stored under the nitrogen atmosphere.

Standard solutions of NaOH and $HClO_4$ were prepared by dilution and standardized by the usual analytical techniques (33).

The A.R. grade $NaClO_4$ was used to control the ionic strength. However, the perchlorate solutions necessary for the silver experiments were prepared in the laboratory by neutralizing 8.0 M $HClO_4$ ice cold solutions with concentrated NaOH solutions. The resulting 8.0 M $NaClO_4$ was diluted to proper concentrations.

The source of pure Nitrogen was the cylinder supplied by the Matheson Co. The gas was saturated with water by bubbling through 0.5 M $NaClO_4$ solution then passed through a vessel packed with glass wool to remove any droplets of the solution.

Metal solutions were prepared from the A.R. grade chemicals without further purification. The perchlorate form was obtained in all cases. The oxide or the carbonate was decomposed with $HClO_4$ if the perchlorate was not readily available. All stock solutions were standardized by the gravimetric methods (33).

The reagents NaHS and NaHSe for the metal sulphide and selenide studies were synthesized in the laboratory. The preparation is described below. The reagent grade selenous acid was used in the Ag_2SeO_3 studies. When necessary the stock solution of the selenous acid was preneutralized with NaOH to obtain higher concentration of selenite ions at any desired pH value.

Preparation of NaHS and NaHSe:

These salts may be obtained by the general reaction of the interaction of sodium alcoholate with the corresponding acid, H_2S or H_2Se.

$$C_2H_5ONa + H_2S = C_2H_5OH + NaHS$$

$$C_2H_5ONa + H_2Se = C_2H_5OH + NaHSe$$

The alcoholate of sodium is easily prepared by the direct action of metal Na with dehydrated ethyl alcohol. The resulting salt in the final reaction is precipitated in a medium of anhydrous ether. It is filtered under the nitrogen pressure and washed several times with anhydrous ether. The apparatus is described in Fig. (3.1).

The H_2S was obtained from the cylinder supplied by the Matheson Co. The gas was washed with water before bubbling through the alcoholate solution.

The gas H_2Se was generated by the action of dilute HCl on Al_2Se_3 in the absence of any oxygen and directly passed into the alcoholate solution. The selenide was precipitated as before with anhydrous ether. However, even with the best precautions the solutions of reagents were

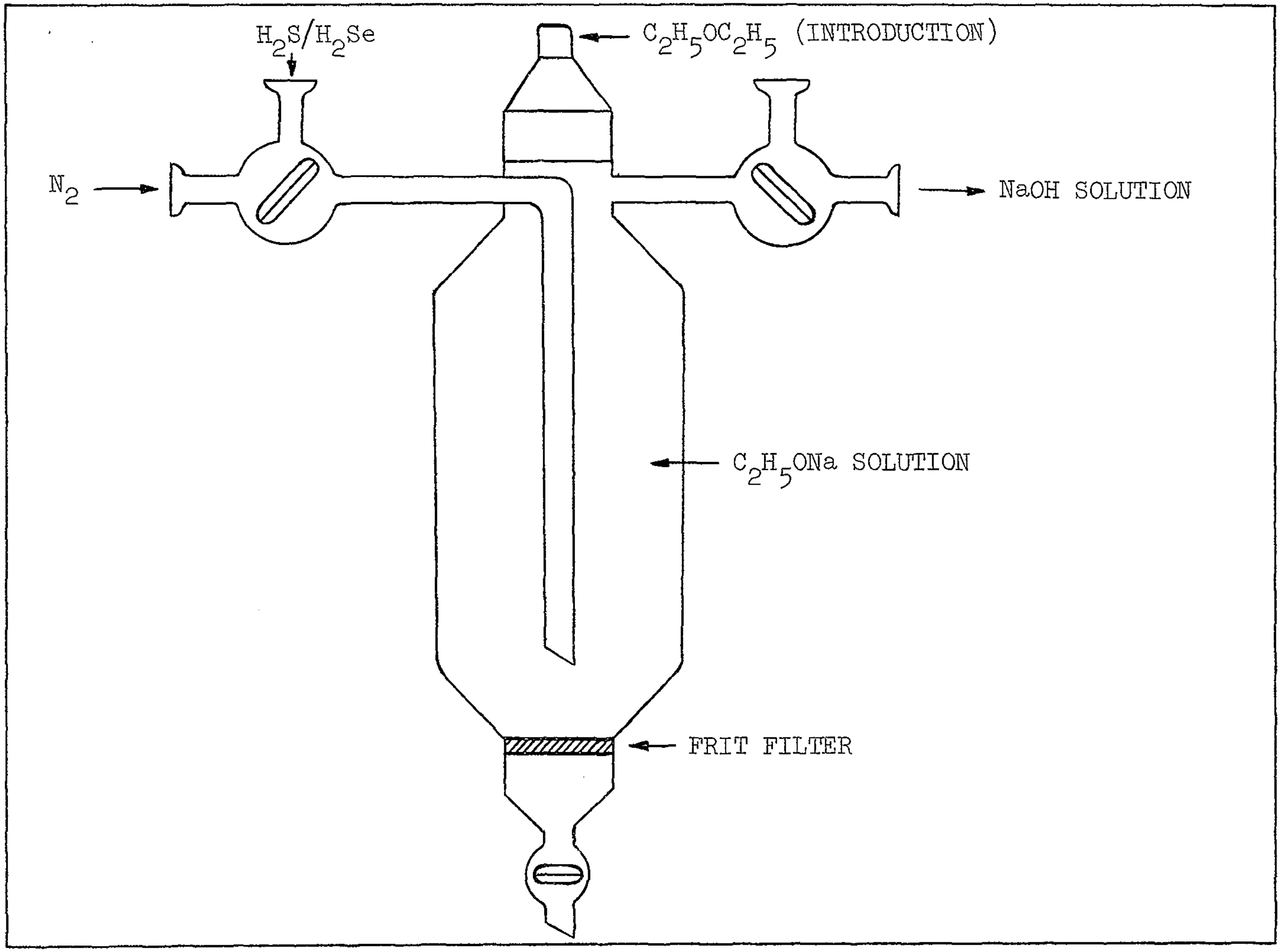


FIGURE 3.1 : Apparatus for Synthesis of NaHS and NaHSe.

faintly coloured. In both the cases the stock solutions of the reagents were therefore prepared fresh when necessary and standardized iodimetrically. The method for the estimation of the sulphide is known (33), while that of selenide has been described by Wood (34).

Potentiometric Determination of pH:

The chemical cell of a glass electrode and a normal calomel electrode was employed to measure the pH of the sample solution.

glass electrode/ test solution// agar, 1.0 M$NaClO_4$ // normal calomel electrode

The salt bridge of agar in 1.0 M $NaClO_4$ was used to prevent the direct contact with the solution of the reference cell. The glass electrode, when not in use, was kept in a buffer solution of pH 4.

The Polymetron, type-42, pH meter was used for the potential measurements. The instrument was initially calibrated with the NBS certified buffers. However, at low pH's HCl and at high pH's NaOH solutions were used to calibrate the pH meter. Table (3.1) and Fig. (3.2) below show a typical calibration curve between the potential of the cell and the pH. It is apparent that the linearity at low and high pH values deviates considerably; so it was made a routine practice to measure the potential of the cell and convert it into pH from the calibration curve. The calibration curve was established fresh whenever a new set of measurements were made.

TABLE NO. 3.1

Calibration of pH Meter with known Buffers and Standards.

Solution	1.0 M HCl	0.1 M HCl	Buff. NBS	Buff. NBS	Buff. NBS	Buff. NBS	0.1 M NaOH	1.0 M NaOH
pH	0.08	1.10	4.00	6.00	7.00	10.0	12.88	13.88
E_{mv}	+301	+286	+117	0.0	-61	-240	-383	-411

Potentiometric Determination of pAg^+ :

The knowledge of free (Ag^+) ions concentration was essential to calculate the solubility products of the silver systems; Ag_2SeO_3, Ag_2S and Ag_2Se. A silver metal electrode in conjunction with a normal calomel electrode was used to determine (pAg^+) potentiometrically. The electrochemical cell was essentially the same as used in the pH determinations except that the glass electrode was replaced by the silver electrode. The pH meter was again employed as the potentiometer to measure the cell potential in each case. In fact both pH and pAg^+ were determined at the same time by the interchange of the electrodes in the cell assembly. The experimental cell may be described as

$$Ag/\ Ag^+\text{-}\ \underset{}{\overset{\text{(solid)}}{\text{compound}}}\ //\ \overset{\text{agar,}}{1.0\ M NaClO_4}\ //\ \begin{matrix}\text{normal}\\ \text{calomel}\\ \text{electrode}\end{matrix}$$

The Nernst equation for the cell reaction may be written as

$$(3.1)\quad E = E^o_{Ag} - 0.05916\ pAg^+$$

where E = cell potential, E^o_{Ag} = standard cell potential in 1.0 M $NaClO_4$

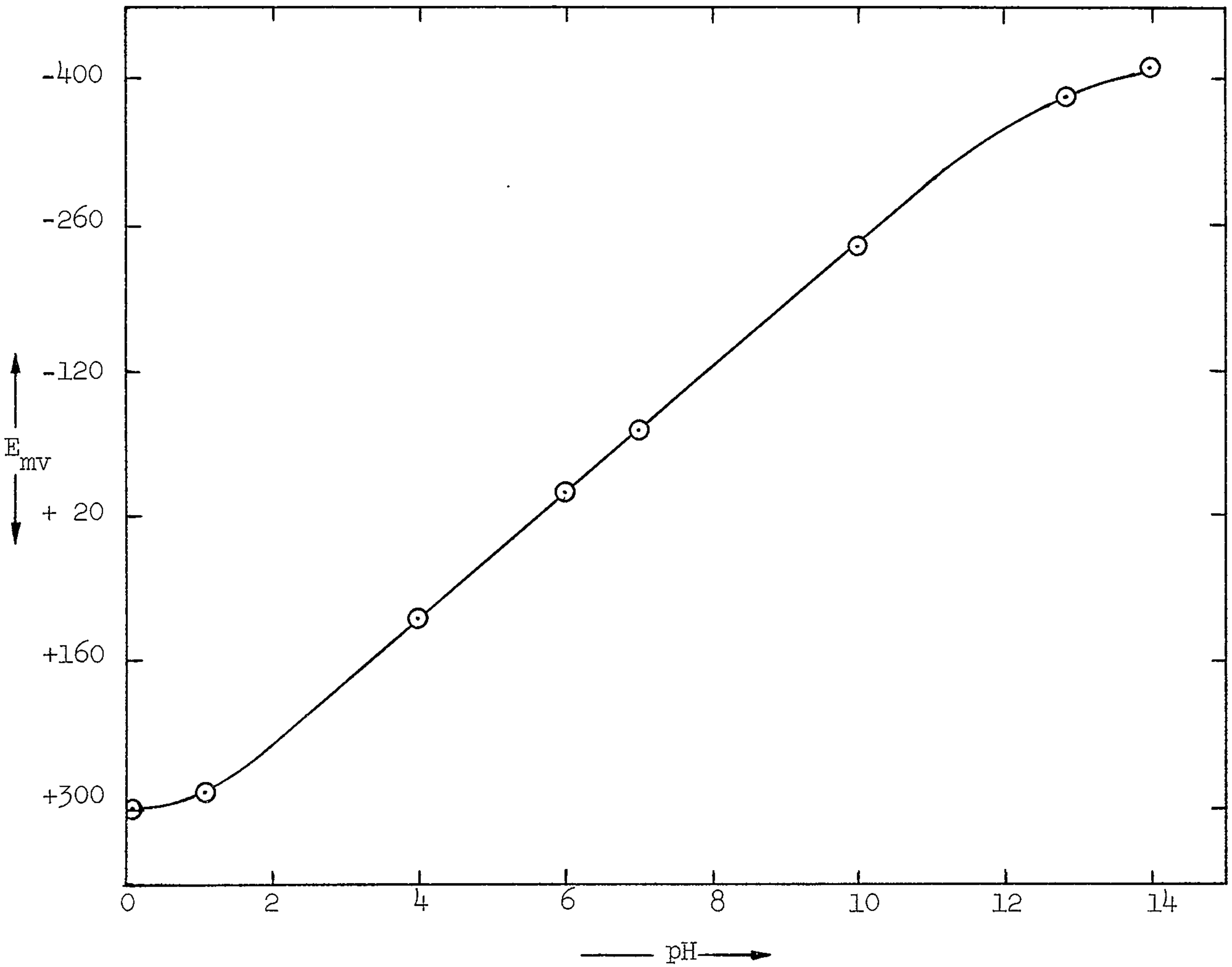


FIGURE 3.2 : Calibration Curve of pH.

medium. E^{o}_{Ag} was determined experimentally with the help of a few silver solutions of known concentrations in 1.0 M $NaClO_4$. Table 3.2 below gives the measured potentials of the cells using known silver concentrations.

TABLE NO. 3.2

Measured Potentials of pAg^{+} in 1.0 M $NaClO_4$

pAg^{+}	3.15	3.45	3.75	4.25	4.55	4.85
E_{mv}	+329	+312	+294	+264	+246	+229

Putting these results in the eq (3.1) above gives an average value of E^{o}_{Ag} as 515.7 mv. This value was, therefore, used in all calculations involving pAg^{+} concentrations.

$$(3.2) \qquad pAg^{+} = \frac{515.7 - E_{cell}}{59.16}$$

The values of pAg^{+} given in chapter IV are calculated from the expression mentioned in eq (3.2).

Potentiometric Determination of pHg^{+2}:

The electrochemical cell employed for the determination of pHg^{+2} was similar to the silver studies except that the indicator electrode was of the metal mercury. The electrode was obtained from the Metrohm assembly No. 354, for the inverse polarography equipment and was the hanging drop type. This offered the advantage that the mercury surface could be precisely reproduced thus permitting a cross check on the measured cell potentials. The cell, as before, was used in conjunction with a normal calomel electrode and the same pH meter was used as the potentiometer. The pH and pHg^{+2} were measured at the same time in the same cell by the interchange of the electrodes. The cell in this case is

$$Hg/\ Hg^{+2} = \begin{matrix}\text{(solid)}\\ \text{compound}\end{matrix} \; // \; \begin{matrix}\text{agar,}\\ 1.0\text{ M NaClO}_4\end{matrix} \; // \; \begin{matrix}\text{normal}\\ \text{calomel}\\ \text{electrode}\end{matrix}$$

The Nernst equation for the cell reaction is given as

$$(3.3) \qquad E = E^{o}_{Hg} - 0.02958\ pHg^{+2}$$

where E^{o}_{Hg} = standard cell potential in 1.0 M $NaClO_4$ medium. E^{o}_{Hg} was determined from the potentials of the known samples of the complexes of mercury (II) with ligands derived from halogens and pseudohalogens. Table 3.3 gives the concentrations pHg^{+2} and their potentials, which when inserted in eq (3.3) above directly give the E^{o}_{Hg} for mercury (II) in 1.0 M $NaClO_4$. The average value of 570.7 mv was observed against normal calomel. With the knowledge of E^{o}_{Hg}, the term pHg^{+2} in an unknown sample could then be calculated from the expression,

$$(3.4) \qquad pHg^{+2} = \frac{570.7 - E_{cell}}{29.58}$$

The values of pHg^{+2} reported in chapter IV for the sulphide and the selenide systems are derived on the basis of the expression (3.4).

TABLE NO. 3.3

Measured Potentials of pHg^{+2} in 1.0 M $NaClO_4$

Ligand	Br^-	I^-	CNS^-	CN^-
$p\beta_4$	21.00	29.83	21.99	41.40
pHg^{+2}	20.00	28.83	20.99	40.40
E_{mv} (measured)	-55	-279	-40	-604
Reference	(Bethge) (47)	(Qvarfort) (48)	(Sherrill) (49)	(Sherrill) (49)

The pHg^{+2} (orig) in these measurements was 10^{-3}M and the ligand concentration was 0.1 M, with the ionic strength adjusted to 1.0 M with $NaClO_4$.

The discussions on the electrochemical measurements have been postponed till the end of chapter IV.

Radiometric Estimation of M_{tot}:

The metal total concentration in an equilibrated sample throughout this study has been determined radiometrically. The physical characteristics of the radioisotopes used in the present study are summarized in table 3.4.

TABLE NO. 3.4

Physical Characteristics of Radioisotopes

Radio-Isotope	$T_{\frac{1}{2}}$	E_{β} MeV	E_{γ} MeV	Daughter Product (Inactive)
Hg - 203	47 d	0.21	0.28	Tl-203
Co - 60	5.2 y	0.31	1.33 1.17	Ni-60
Mn - 54	314 d	-	0.84	Fe-54
Fe - 59	45 d	1.56	1.10 1.29	Co-59
Ag - 110	249 d	0.54	0.66 0.88	Cd-110

In each case the radioactivity was determined by scintillation spectrometry. The instrument used was Phillips single channel gamma ray spectrometer coupled with a well type Tl activated NaI crystal that could accommodate five milliliters of the sample solution in the plastic counting capsule. The radioactivity was counted directly under the photopeak of the respective radioisotope. The radioisotopes were obtained either in the carrier free form or their inactive contents were known.

The standard inactive stock solution of the metal perchlorate was mixed with sufficient concentration of its radiotracer to give a measurable count rate even at a thousand-fold dilution. In general a count rate of 20 c. p. m / ml at a calculated dilution of 10^{-8}M was always maintained. In the final sample at least 1000 counts were obtained to maintain a consistency in the statistical fluctuations.

A calibration curve was drawn between the radioactivity and the concentration by successive dilutions of the prepared radioactive stock solution, maintaining always the same ionic strength of 1.0 M in $NaClO_4$. The concentration of the metal total in an unknown sample was read from the calibration curve with the knowledge of its radioactivity. The calibration curve was drawn fresh whenever new sets of experiments were made. This treatment eliminates the correction of errors due to the decay of the radioactivity, change in the counter efficiency and the instrument background.

Analytical Procedures:

Preparation of Samples:

The solubilities of the precipitates of selenite, sulphides and selenides of Ag and Hg have been determined in two batches. The first batch consisted of inactive precipitation at desired pH intervals at a known excess of the ligand concentration. The second batch was repeated similarly but with the radioactive solutions.

The radioactive work was further repeated at several excess of the ligand concentrations. The pH's were adjusted with the sufficient quantities of $HClO_4$ and NaOH only, while the ionic strength of unity was completed with the solutions of $NaClO_4$.

The studies on the solubility equilibria of Mn, Fe, Co, systems were carried out with the radioactive solutions at different excess of the ligand concentrations. The pH's were similarly adjusted with $HClO_4$ and NaOH only with the ionic strength made up to 1.0 M with $NaClO_4$.

The precipitations were made in 100 ml standard flasks immersed in a water bath at 25°C. The reagents were so mixed that the ligand was always the last constituent. The flasks were sealed immediately following precipitation and the system was allowed to equilibrate for 6 days at the constant temperature (25°C).

Measurement of pH, pAg^+, and pHg^{+2}:

On attainment of the equilibrium, the aqueous samples from the inactive work were transferred under nitrogen pressure to a 5-necked flask fitted with the glass electrode, metal indicator electrode, and the normal calomel electrode. The flask was dried and flushed thoroughly for several minutes with nitrogen before each transfer. The pH and the free metal ion concentration in each case were then determined potentiometrically. A glass fritted filter was used in each case to prevent any carry over of the particulate matter from the equilibrated flask. The apparatus used in these measurements is described in figure (3.3).

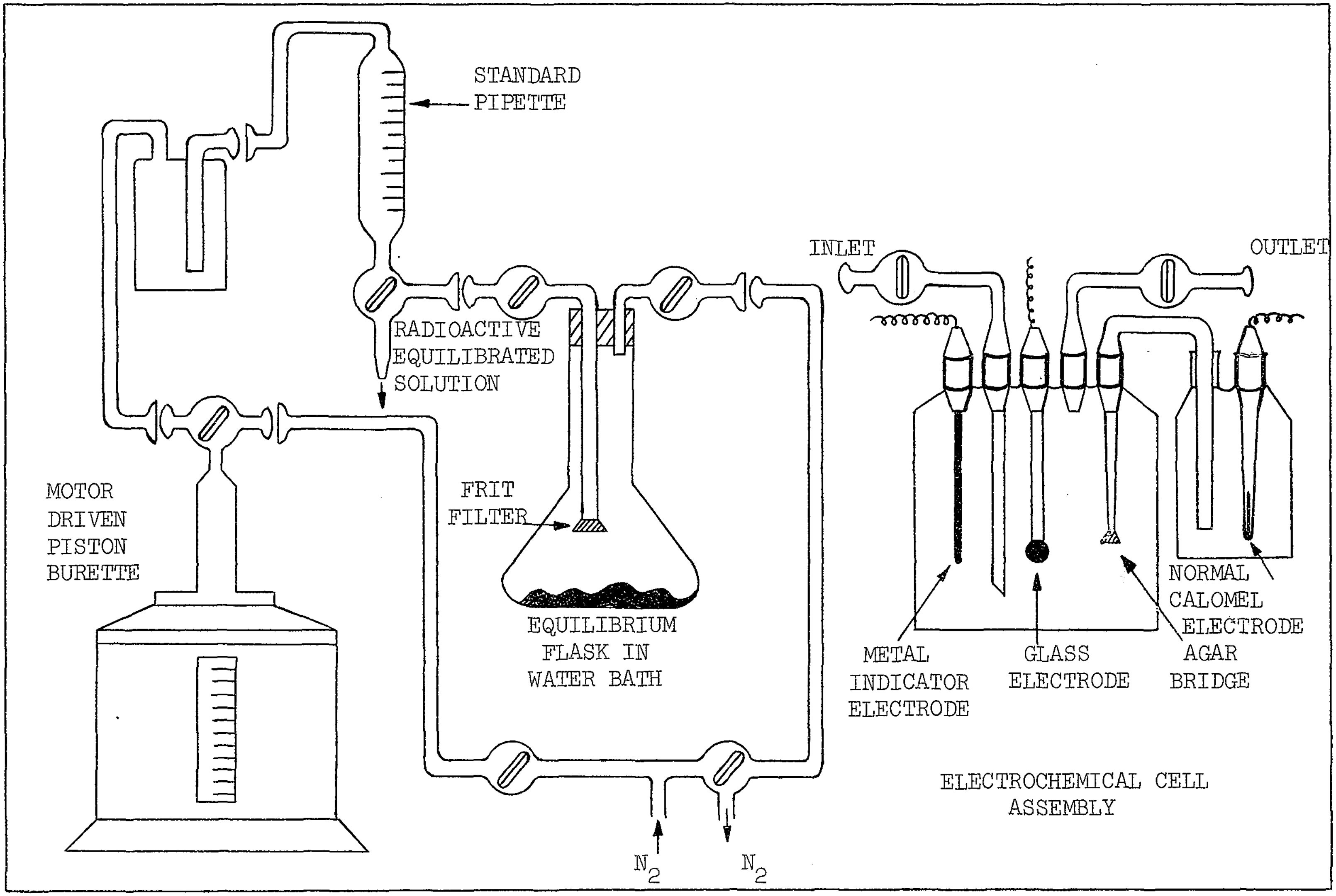


FIGURE 3.3 : Apparatus for Measuring pH, M^{+n}, M_{tot}, S_{tot}, and Se_{tot}.

Radiometric Measurement of M_{tot}:

The equilibrated solutions in the radioactive work were similarly transferred under nitrogen pressure to the graduated pipette (fig. 3.3) and a 5 ml aliquot was directly withdrawn in the counting capsule. In each case the samples were withdrawn in triplicate and their count rates were observed under the photopeak of the radioisotope. If the radioactivity in the three samples was not within the statistical fluctuations, the sample as a whole was discarded and repeated for the same pH and A_{tot}. The metal concentration of the sample was obtained by comparing its radioactivity with the concentration-activity calibration curve drawn under the similar experimental conditions.

Measurement of S_{tot} and Se_{tot}:

The concentration of the excess of the ligand in each sample was determined iodimetrically. A 5 ml aliquot of the equilibrated sample was transferred from the pipette (fig. 3.3) to an iodine solution of higher known concentration. The unreacted iodine was back titrated with a standard $Na_2S_2O_3$ solution. The difference then gave the ligand concentration in each case.

CHAPTER IV

Ionization Constants of Acids, H_2S, H_2Se, H_2SeO_3 and Solubility Products of their Silver and Mercury Compounds

The ionization constants of the ligand acids, H_2A, and the K_{sp} of their insoluble compounds, at a specified ionic strength must be known precisely, for the calculation of the formation constants of their aqueous complexes. A method is discussed here that permits simultaneous evaluation of the pk values and the K_{sp} in the same system at any desired ionic strength. Essentially the method is applicable to those cations that form a reversible electrode system, whereby their ionic concentrations could be traced potentiometrically. Also the ionization constants must be within the limits of pH range. The method, thus, provides direct information on the concentration constants at a desired ionic strength.

Theoretical Treatment:

In eq (2.2), (2.4), (2.6), and (2.10) a relationship has been established between the ionization constants of the ligand acid and the K_{sp} of its sparingly soluble compound in a particular medium. From eq (2.6) and (2.10), we get,

$$(4.1) \qquad A_{tot} = \frac{K_{sp}}{(M^{+n})}\left[\frac{(H^+)^2}{k_1 . k_2} + \frac{(H^+)}{k_2} + 1\right]$$

where (M^{+n}) is the cation that forms the reversible electrode system. The cations in this study will be Ag^+ and Hg^{+2}.

For the monovalent ion silver eq (4.1) may be written as,

$$(4.2) \qquad A_{tot} = \frac{K_{sp}}{(Ag^+)^2} \cdot \left[\frac{(H^+)^2}{k_1 . k_2} + \frac{(H^+)}{k_2} + 1 \right]$$

Simplification of eq (4.2)

If $H^+ >> k_1 >> k_2$

$$(4.3) \qquad \frac{(Ag^+)^2 . (A_{tot})}{K_{sp}} = \frac{(H^+)^2}{k_1 . k_2}$$

(region A of pH)

$$(4.4) \qquad \frac{(Ag^+)^2 . (A_{tot})}{(H^+)^2} = \frac{K_{sp}}{k_1 . k_2} = A_z \quad \text{(a constant).}$$

If $k_1 >> H^+ >> k_2$

$$(4.5) \qquad \frac{(Ag^+)^2 . (A_{tot})}{K_{sp}} = \frac{(H^+)}{k_2}$$

(region B of pH)

$$(4.6) \qquad \frac{(Ag^+)^2 . (A_{tot})}{(H^+)} = \frac{K_{sp}}{k_2} = B_z \quad \text{(a constant).}$$

If $k_2 >> k_1 >> H^+$

$$(4.7) \qquad \frac{(Ag^+)^2 . (A_{tot})}{K_{sp}} = 1$$

(region C of pH)

$$(4.8) \qquad (Ag^+)^2 . (A_{tot}) = K_{sp} = C_z \quad \text{(a constant).}$$

The constants A_z, B_z, and C_z, can be evaluated in their respective pH regions, since all the terms in eq (4.4),(4.6), and (4.8), on the left hand side are experimentally observable quantities. Transformation of these equations into logarithmic form gives, (4.9) $$2 \log(Ag^+) - 2 \log(H^+) + \log (A_{tot}) = \log A_z$$

(4.10) $$2 \log(Ag^+) - \log (H^+) + \log (A_{tot}) = \log B_z$$

(4.11) $$2 \log(Ag^+) + \log (A_{tot}) = \log C_z$$

Partial differentiation of eq (4.9), (4.10), and (4.11), as a function of pH gives the following values of the theoretical slopes in their respective pH regions (at a constant A_{tot}).

(4.12) $$\frac{\partial \log (Ag^+)}{\partial pH} = -1 \qquad \text{(region A of pH)}$$

(4.13) $$\frac{\partial \log (Ag^+)}{\partial pH} = -0.5 \qquad \text{(region B of pH)}$$

(4.14) $$\frac{\partial \log (Ag^+)}{\partial pH} = 0 \qquad \text{(region C of pH).}$$

Simple transformation of eq (4.1) in a similar manner for the divalent ion (Hg^{+2}) will show the theoretical slopes as follows.

(4.15) $$\frac{\partial \log (Hg^{+2})}{\partial pH} = -2 \qquad \text{(region A of pH)}$$

(4.16) $$\frac{\partial \log (Hg^{+2})}{\partial pH} = -1 \qquad \text{(region B of pH)}$$

(4.17) $$\frac{\partial \log (Hg^{+2})}{\partial pH} = 0 \qquad \text{(region C of pH).}$$

Figure (4.1) gives the theoretical slopes in both the cases that correspond to the functions considered above.

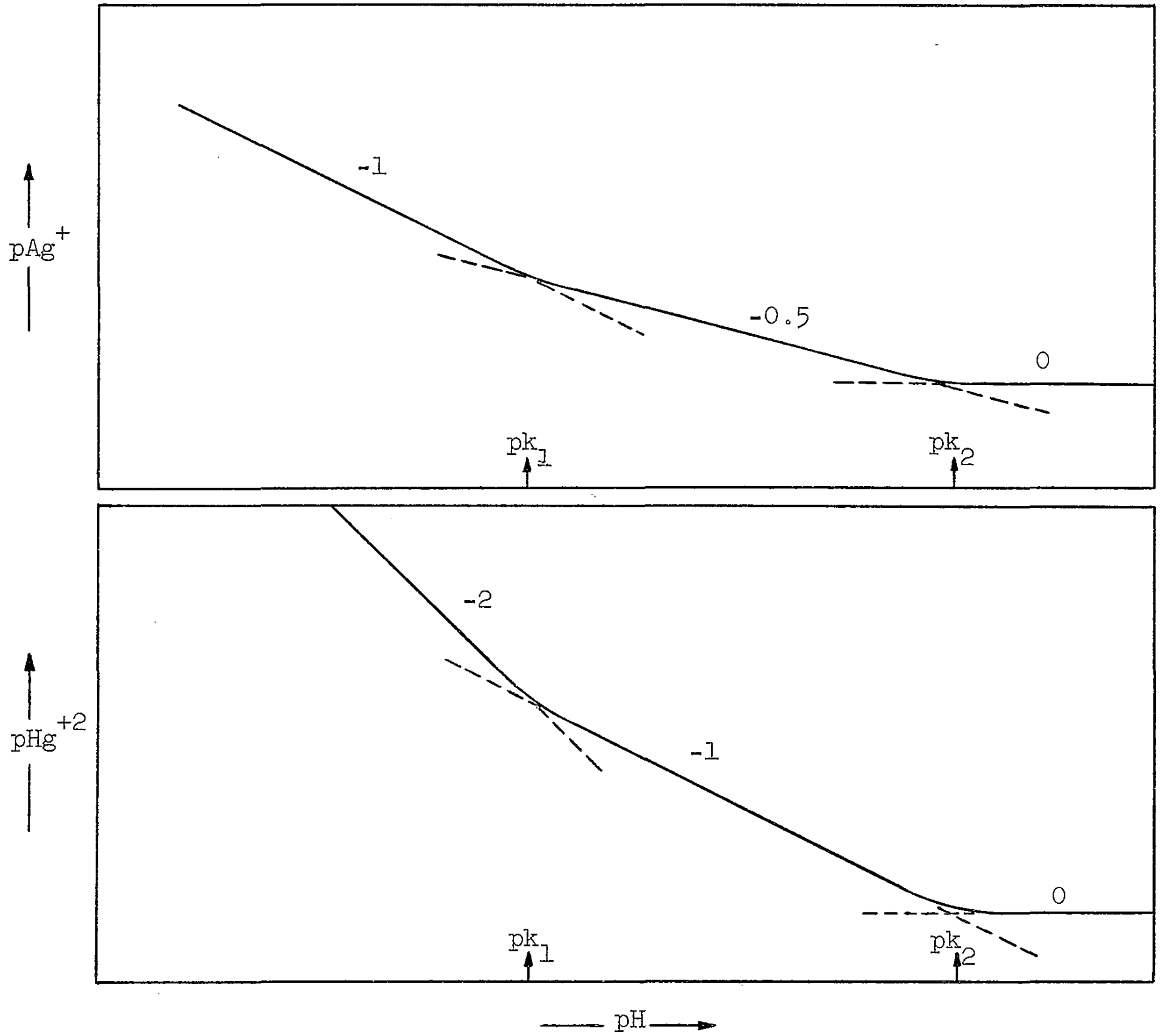


FIGURE 4.1 : Theoretical Slopes of pAg$^+$ and pHg^{+2} as a Function of pH.

The potentiometric solubility of an inorganic sparingly soluble silver or mercury compound should therefore correspond to these theoretical slopes if the system is in equilibrium. In other words the concentration of free Ag^+ ions or free Hg^{+2} ions will vary at a constant A_{tot}, as a function of pH with the slopes of -1,-0.5,0 and -2,-1,0 respectively in the pH regions defined earlier.

Calculation of Solubility Products and Dissociation Constants:

The experimental determination of (Ag^+), (H^+), and (A_{tot}) directly gives the constants A_z, B_z, and C_z from the eq (4.4), (4.6), and (4.8).

$$(4.18) \quad A_z = \frac{K_{sp}}{k_1 . k_2} \quad , \quad B_z = \frac{K_{sp}}{k_2} \quad , \quad C_z = K_{sp}$$

Utilizing eq (4.18) we get,

$$(4.19) \quad \frac{B_z}{A_z} = \frac{K_{sp}}{k_2} \cdot \frac{k_1 . k_2}{K_{sp}} = k_1$$

$$pk_1 = pB_z - pA_z$$

$$(4.20) \quad \frac{C_z}{B_z} = \frac{K_{sp}}{K_{sp}} \cdot k_2 = k_2$$

$$pk_2 = pC_z - pB_z$$

The solubility product for the silver system is directly obtained with the evaluation of the constant C_z, when the experimental slope of $\log(Ag^+)$ as a function of pH assumes a slope of zero (eq (4.8) and (4.11)). The constants B_z and A_z are evaluated further from the experimental data.

The two ionization constants of the ligand acid, k_1 and k_2 are then calculated with the help of eq (4.19) and (4.20) given above.

With the evaluation of the k_1 and k_2 from the silver system, the solubility products in the divalent mercury systems are calculated from the region A of pH, where the solubility curves exhibit a slope of -2 as a function of Hg^{+2} and pH (cf. eq 4.15, fig. 4.1). In this pH region the A_{tot} is given by the simplified equation similar to eq (4.3). The calculation of the solubility product constant is shown in eq (4.21) and (4.22).

From eq (4.1) in its simplified form in region A of pH, we obtain,

$$(Hg^{+2}) \cdot (A_{tot}) = \frac{K_{sp} \cdot (H^+)^2}{(k_1 . k_2)} \tag{4.21}$$

(region A of pH)

$$K_{sp} = \frac{(Hg^{+2}) \cdot (A_{tot}) \cdot (k_1 . k_2)}{(H^+)^2} \tag{4.22}$$

The Concentration Constants of the Sulphide Systems:

The Ionization Constants of H_2S:

The ionization constants of H_2S at one molar ionic strength have been recently determined in this laboratory (31)(32), by the glass electrode measurements. These values appear to be the best available in the literature and have been employed in the present calculations as well.

H_2S : $pk_1 = 6.90 \pm 0.03$

$pk_2 = 13.48 \pm 0.18$

Solubility Product of Ag_2S:

The potentiometric solubility measurements of the Ag_2S system are given in table 4.1. The graphical representation of the experimental data in fig. 4.2, show two distinct slopes of -1 and -0.5 in the pH regions A and B, discussed earlier. This is in complete agreement with the theoretical slopes in fig. 4.1 . The solubility product of Ag_2S is calculated from the data along the slope -1.

$$K_{sp}\ (Ag_2S) = \frac{(Ag^+)^2 . (S_{tot}) . (k_1 . k_2)}{(H^+)^2}$$

$$= (Ag^+)^2 . (S^{-2})$$

$$pK_{sp} = 2pAg^+ + pS^{-2}$$

$$= 49.03 \quad \sigma = \pm 0.20$$

Solubility Product of HgS:

The potentiometric data in this case are given in table 4.2 and shown in fig. 4.3. The solubility is in agreement with the slopes of -2 and -1 in the region A and B of pH. Utilizing the data along the slope of -2, one gets the solubility product of HgS.

$$K_{sp}\ (HgS) = \frac{(Hg^{+2}) . (S_{tot}) . (k_1 . k_2)}{(H^+)^2}$$

$$= (Hg^{+2}) . (S^{-2})$$

$$pK_{sp} = pHg^{+2} + pS^{-2}$$

$$= 51.94 \quad \sigma = \pm 0.31$$

TABLE NO. 4.1

Potentiometric Solubility of Ag_2S at Different pH, and pK_{sp} of Ag_2S at $\mu = 1.0$ $NaClO_4$: pAg^+(orig)= 3.35 M

S.No.	pH	$-mv_{Ag^+}$	pAg^+	pS_{tot}	$p\ S^{-2}$	pK_{sp}
1	0.80	353	14.68	1.21	19.99	49.35
2	0.90	362	14.84	1.22	19.80	49.48
3	0.90	350	14.63	1.37	19.95	49.21
4	1.05	354	14.70	1.37	19.65	49.05
5	1.10	357	14.75	1.37	19.55	49.05
6	1.17	358	14.77	1.38	19.42	48.96
7	1.25	362	14.84	1.37	19.25	48.93
8	1.27	365	14.89	1.36	19.20	48.98
9	1.40	367	14.92	1.37	18.95	48.79
10	1.47	376	15.07	1.37	18.81	48.95
11	1.47	375	15.05	1.38	18.82	48.92
12	1.67	388	15.27	1.35	18.39	48.93
13	1.85	403	15.53	1.36	18.04	49.10
14	2.35	423	15.87	1.36	17.04	48.78
15	5.90	635	19.45			
16	6.15	646	19.64			
17	6.40	663	19.92			
18	6.70	674	20.11			
19	6.80	687	20.33			
20	7.20	697	20.50			
21	8.00	723	20.94			
22	8.30	732	21.09			
23	8.70	754	21.46			
24	9.37	765	21.65			
25	11.70	844	22.98			
26	12.00	853	23.13			
27	12.25	859	23.24			
28	12.60	861	23.27			
29	12.75	866	23.35			
30	13.15	869	23.41			

$$pS^{-2} = pk_1 + pk_2 + pS_{tot} - 2\ pH$$

$$pK_{sp} = 2\ pAg^+ + pS^{-2}$$

$$= 49.03 \quad \sigma = \pm\ 0.20.$$

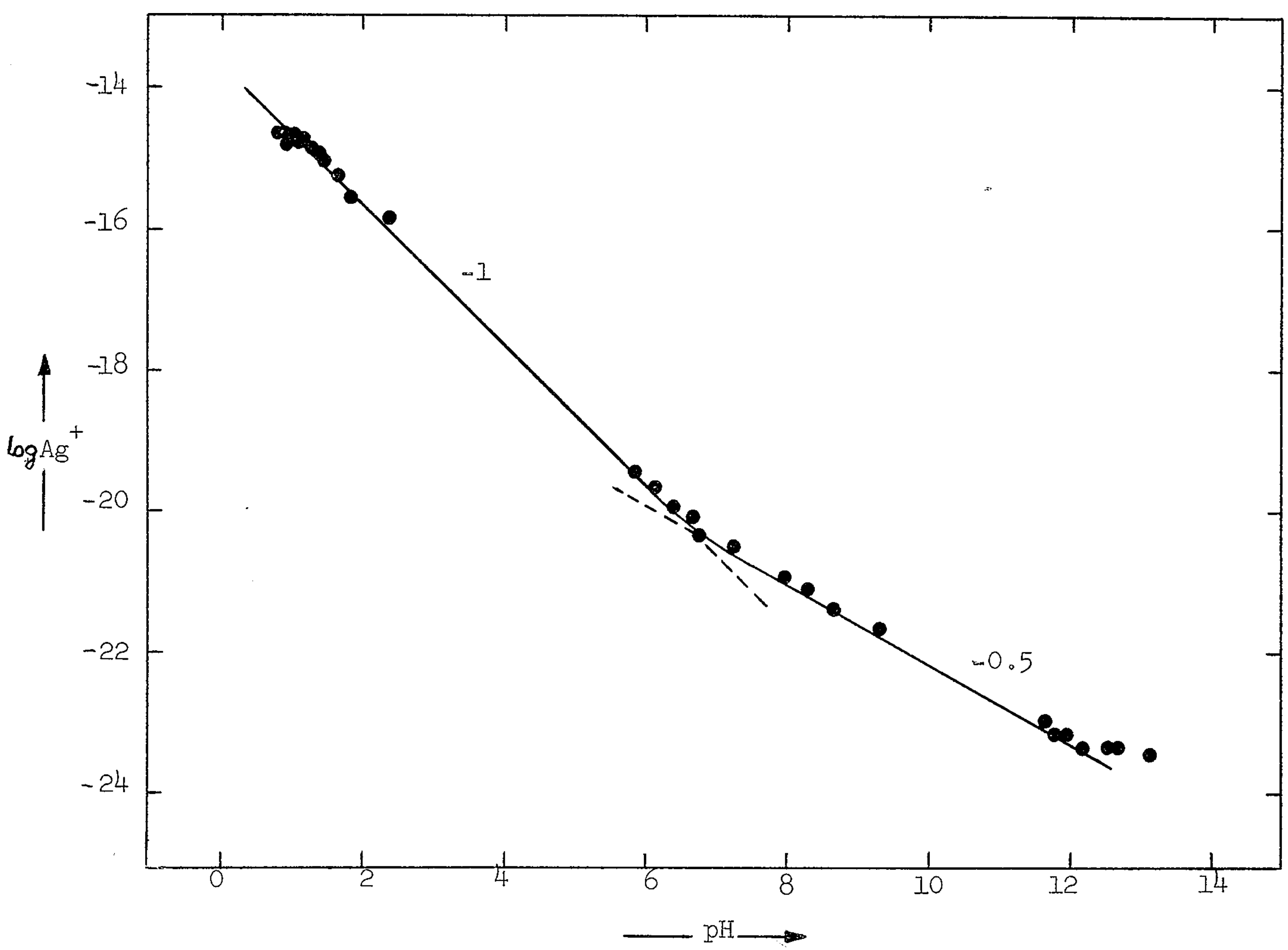


FIGURE 4.2 : Potentiometric Solubility of Ag_2S as a function of pH.

The Concentration Constants of the Selenide Systems:

Potentiometric Solubility Data of Ag_2Se:

The potentiometric solubility data for the system Ag_2Se are shown in table 4.3 and fig. 4.4. The characteristic slopes of -1, -0.5, and 0 are apparent around pH 3.5 and 11.5, respectively.

Solubility Product of Ag_2Se:

The K_{sp} in this case is directly obtained from the knowledge of the constant C_z.

$$C_z = K_{sp} = (Ag^+)^2.(Se_{tot}) = (Ag^+)^2.(Se^{-2})$$

When $pH > pk_2$, $Se_{tot} = Se^{-2}$.

$$pK_{sp} = 2pAg^+ + pSe^{-2}$$

$$= 53.79 \quad \sigma = \pm 0.08$$

The calculations are given in table 4.3.1 .

Ionization Constants of H_2Se:

The constants A_z and B_z in the respective pH regions are evaluated from the experimental data in table 4.3. The calculations for the two constants pk_1 and pk_2 are given in tables 4.3.2 and 4.3.3 .

$$pk_1 = pB_z - pA_z$$

$$pk_1 = 3.48 \quad \sigma = \pm 0.22$$

$$pk_2 = pC_z - pB_z$$

$$pk_2 = 11.60 \quad \sigma = \pm 0.18$$

TABLE NO. 4.2

Potentiometric Solubility of HgS at Different pH,
and pK_{sp} of HgS at $\mu = 1.0$ $NaClO_4$
pHg^{+2} (orig) = 3.30 M.

S.No.	pH	$-mv_{Hg^{+2}}$	pHg^{+2}	pS_{tot}	pS^{-2}	pK_{sp}
1	0.85	377	32.04	1.70	20.38	52.42
2	0.98	373	31.90	1.73	20.13	52.03
3	1.02	375	31.97	1.62	19.96	51.93
4	1.15	384	32.27	1.70	19.78	52.05
5	1.20	380	32.14	1.70	19.68	51.82
6	1.22	386	32.34	1.78	19.72	52.06
7	1.40	397	32.71	1.65	19.23	51.94
8	1.40	383	32.24	1.70	19.28	51.52
9	1.50	404	32.95	1.85	19.23	52.18
10	1.75	411	33.19	1.92	18.80	51.99
11	1.75	402	32.88	1.69	18.57	51.45
12	1.80	420	33.49	1.85	18.63	52.12
13	2.00	435	34.00	1.70	18.08	52.08
14	2.00	429	33.80	1.85	18.23	52.03
15	2.15	429	33.80	1.85	17.93	51.73
16	2.60	444	34.30	1.75	16.93	51.23
17	5.30	640	40.93	1.69	11.47	52.40

TABLE NO. 4.2 (Contd.)

S.No.	pH	$-mv_{Hg^{+2}}$	pHg^{+2}	pS_{tot}
18	6.45	674	42.08	1.68
19	6.55	681	42.31	1.64
20	6.77	694	42.75	1.64
21	7.02	702	43.02	1.65
22	7.25	712	43.36	1.64
23	7.45	717	43.53	1.64
24	7.47	719	43.60	1.64
25	7.50	719	43.60	1.66
26	7.52	721	43.67	1.64
27	7.55	717	43.53	1.64
28	7.85	736	44.17	1.67
29	8.82	765	45.15	1.67
30	9.57	794	46.13	1.67
31	10.90	838	47.62	1.68
32	11.30	848	47.96	1.65
33	11.60	859	48.33	1.67
34	11.95	863	48.47	1.67

$pS^{-2} = pk_1 + pk_2 + pS_{tot} - 2\ pH$

$pK_{sp} = pHg^{+2} + pS^{-2}$

$= 51.94 \quad \sigma = \pm\ 0.31$

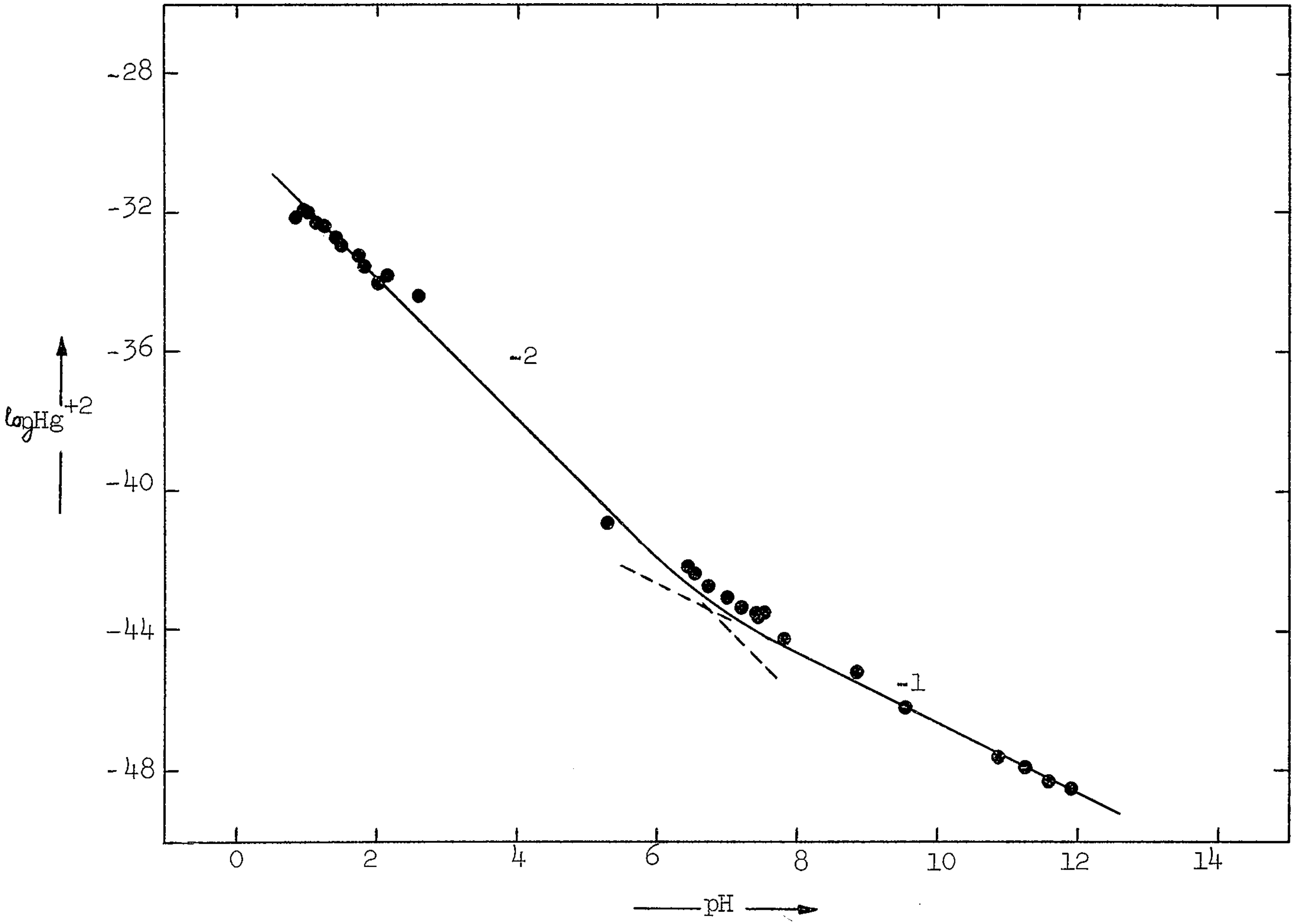


FIGURE 4.3 : Potentiometric Solubility of HgS as a function of pH.

TABLE NO. 4.3

Potentiometric Solubility of Ag_2Se at Different pH and at μ = 1.0 $NaClO_4$: pAg (orig) = 3.35 M.

S.No.	pH	$-mv_{Ag^+}$	pAg^+	pSe_{tot}
1	1.27	668	20.00	1.43
2	1.37	668	20.00	1.53
3	1.72	692	20.41	1.56
4	1.92	698	20.51	1.59
5	2.15	706	20.65	1.39
6	2.45	723	20.93	1.49
7	3.80	798	22.20	1.56
8	4.10	822	22.61	1.23
9	4.17	810	22.41	1.54
10	4.40	836	22.85	1.26
11	4.50	827	22.69	1.25
12	4.72	832	22.78	1.27
13	4.75	826	22.68	1.61
14	5.22	839	22.90	1.38
15	5.35	853	23.13	1.24
16	5.47	860	23.25	1.24
17	9.77	989	25.43	1.23
18	10.00	976	25.21	1.57
19	10.90	1006	25.72	1.24
20	11.80	1016	25.89	1.32
21	12.30	1030	26.16	1.38
22	12.65	1034	26.19	1.33
23	12.77	1034	26.19	1.39
24	12.95	1038	26.26	1.28
25	13.10	1035	26.21	1.37
26	13.20	1037	26.24	1.22
27	13.30	1040	26.29	1.24
28	13.55	1041	26.31	1.32
29	13.60	1039	26.38	1.28

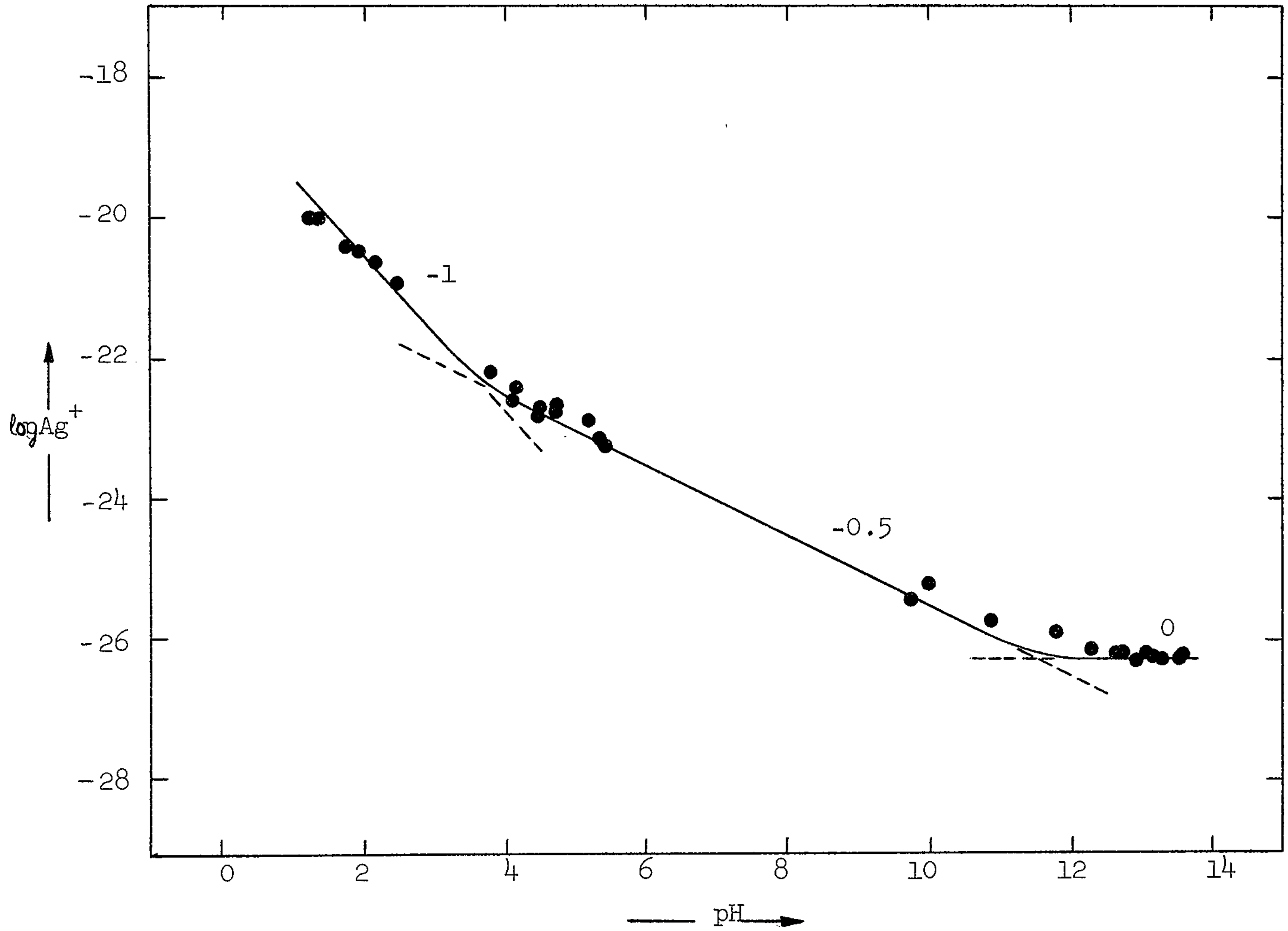


FIGURE 4.4 : Potentiometric Solubility of Ag_2Se as a function of pH.

Solubility Product of HgSe:

Table 4.4 and fig. 4.5 represent the potentiometric solubility data for HgSe. The data from characteristic slope of -2 in region A of pH, along with the two ionization constants of H_2Se found above, have been utilized to calculate the solubility product of this compound.

$$
\begin{aligned}
K_{sp}\ (HgSe) &= \frac{(Hg^{+2}).(Se_{tot}).(k_1.k_2)}{(H^+)^2} \\
&= (Hg^{+2}).(Se^{-2}) \\
pK_{sp} &= pHg^{+2} + pSe^{-2} \\
&= 56.61 \qquad \sigma = \pm 0.22
\end{aligned}
$$

The Concentration Constants of the Selenite System:

Potentiometric Solubility of Ag_2SeO_3:

The experimental solubility results for the silver compound in this case are furnished in table 4.5 and represented graphically in fig. 4.6. The pAg^+ concentration shows two changes in the solubility slopes around pH 2.2 and 8.0, thus indicating again that the system behaves in accordance with the theory.

Solubility Product of Ag_2SeO_3:

The K_{sp} in this case too is calculated from the constant C_z.

$$C_z = K_{sp}\ (Ag_2SeO_3) = (Ag^+)^2.(SeO_{3\ tot})$$

When pH > pk_2 $SeO_{3\ tot} = SeO_3^{-2}$

$$= (Ag^+)^2.(SeO_3^{-2})$$

TABLE NO. 4.3.1

Calculation of Solubility Product of Ag_2Se.

(Experimental Data from table 4.3).

E.No.	pAg^+	$2\ pAg^+$	pSe_{tot}	pK_{sp}
22	26.19	52.38	1.33	53.71
23	26.19	52.38	1.39	53.77
24	26.26	52.52	1.28	53.80
25	26.21	52.42	1.37	53.79
26	26.24	52.48	1.22	53.70
27	26.29	52.58	1.24	53.82
28	26.31	52.62	1.32	53.94
29	26.28	52.56	1.28	53.84

$$pC_z = pK_{sp} = 2\ pAg^+ + pSe_{tot}$$

$$= 53.79 \quad \sigma = \pm 0.08.$$

TABLE NO. 4.3.2

Calculation of k_2 of H_2Se.

E.No.	$2\ pAg^+$	pSe_{tot}	pB_z	pk_2
10	45.70	1.26	42.56	11.23
11	45.38	1.25	42.13	11.66
12	45.56	1.27	42.11	11.68
13	45.36	1.61	42.22	11.57
14	45.80	1.38	41.96	11.83
15	46.26	1.24	42.15	11.64
16	46.50	1.24	42.29	11.50
17	50.86	1.23	42.32	11.47
18	50.42	1.57	41.99	11.80

$$pk_2 = pC_z - pB_z = 11.60 \quad \sigma = \pm 0.18.$$

$$pB_z = 2\ pAg^+ + pSe_{tot} - pH$$

TABLE NO. 4.3.3

Calculation of k_1 of H_2Se.

E.No.	2 pAg^+	pSe_{tot}	pA_z	pk_1
1	40.00	1.43	38.89	3.30
2	40.00	1.53	38.79	3.40
3	40.82	1.56	38.94	3.25
4	41.02	1.59	38.77	3.42
5	41.30	1.39	38.39	3.80
6	41.88	1.49	38.47	3.72

$pk_1 = pB_z - pA_z = 3.48 \quad \sigma = \pm 0.22.$

$pA_z = 2\ pAg^+ + pSe_{tot} - 2\ pH.$

TABLE NO. 4.4

Potentiometric Solubility of HgSe at Different pH, and pK_{sp} of HgSe at $\mu = 1.0$ $NaClO_4$: pHg^{+2} (orig) = 3.23 M.

S.No.	pH	$-mv_{Hg^{+2}}$	pHg^{+2}	pSe_{tot}	pSe^{-2}	pK_{sp}
1	0.55	644	41.06	1.94	15.92	56.98
2	0.80	666	41.81	1.83	15.31	57.12
3	1.07	673	42.04	1.59	14.53	56.57
4	1.10	666	41.81	1.58	14.46	56.27
5	1.15	679	42.25	1.59	14.37	56.62
6	1.17	676	42.15	1.76	14.50	56.65
7	1.20	679	42.25	1.52	14.20	56.45
8	1.25	687	42.52	1.58	14.16	56.68
9	1.27	685	42.45	1.61	14.15	56.60
10	1.37	694	42.75	1.57	13.91	56.66
11	1.45	695	42.79	1.61	13.79	56.58
12	1.62	701	42.99	1.59	13.43	56.42
13	1.77	715	43.46	1.59	13.13	56.59
14	2.20	737	44.21	1.54	12.22	56.43
15	2.55	760	44.99	1.54	11.52	56.51
16	3.22	782	45.73	1.52		
17	3.50	802	46.41	1.55		
18	3.90	813	46.78	1.60		
19	4.97	852	48.10	1.57		
20	7.57	916	50.30	1.65		
21	8.15	975	52.25	1.59		
22	9.95	968	52.01	1.57		
23	11.15	1026	53.98	1.47		

$$pSe^{-2} = pk_1 + pk_2 + pSe_{tot} - 2\ pH.$$

$$pK_{sp} = pHg^{+2} + pSe^{-2} = 56.61 \quad \sigma = \pm 0.22.$$

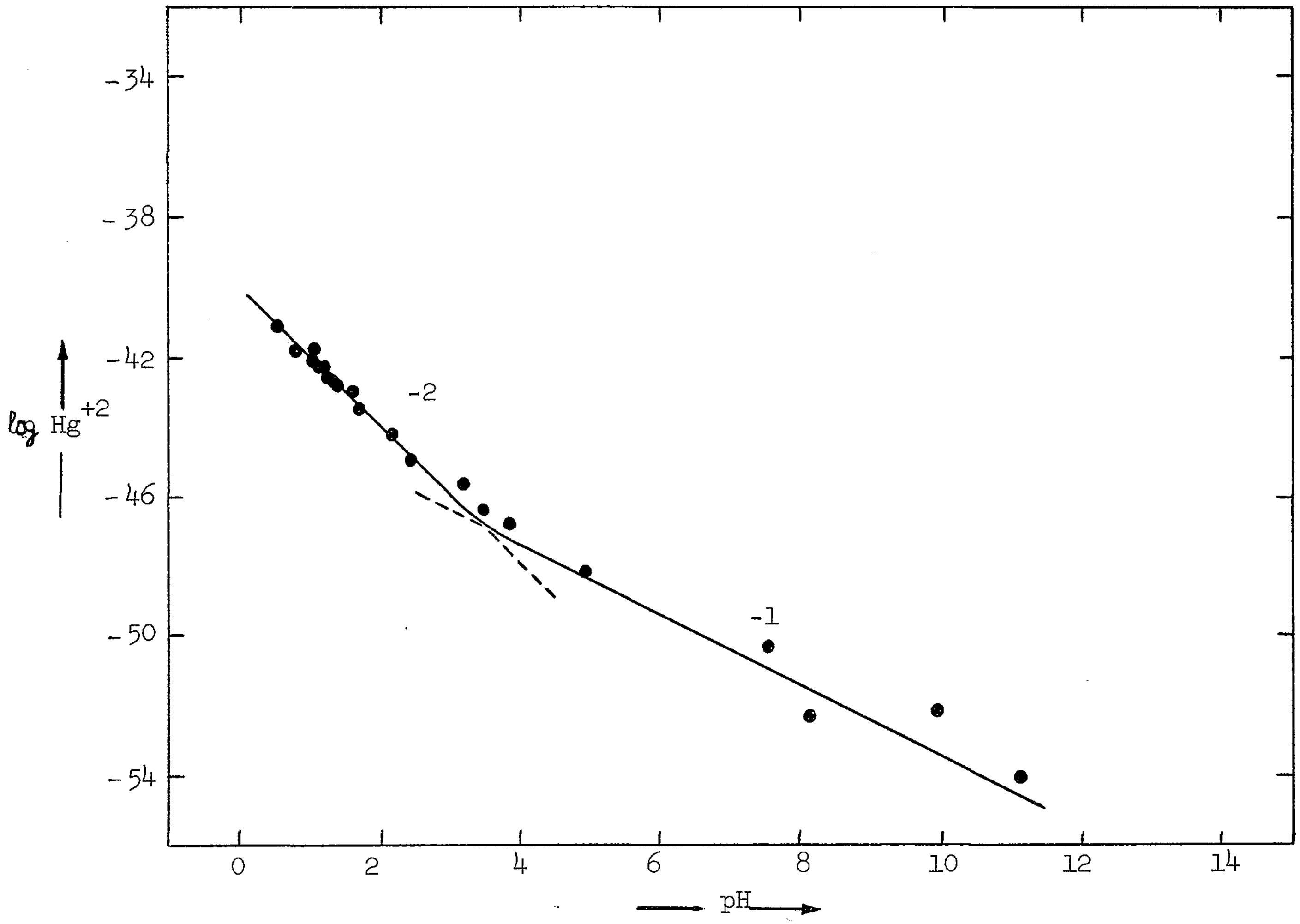


FIGURE 4.5 : Potentiometric Solubility of HgSe as a function of pH.

TABLE NO. 4.5

Potentiometric Solubility of Ag_2SeO_3 at Different pH.

pAg^+ (orig) = 2.30 M $pH_2SeO_{3\ tot}$ = 1.32 M.

μ = 1.0 $NaClO_4$.

S.No.	pH	+mv/$_{Ag^+}$	pAg^+	S.No.	pH	+mv/$_{Ag^+}$	pAg^+
1	1.20	325	3.22	28	3.70	221	4.98
2	1.25	324	3.24	29	4.00	207	5.22
3	1.28	323	3.26	30	4.30	207	5.22
4	1.30	320	3.31	31	5.12	174	5.77
5	1.35	318	3.34	32	5.82	153	6.13
6	1.37	318	3.34	33	6.05	169	5.86
7	1.45	316	3.37	34	6.30	155	6.10
8	1.47	313	3.43	35	6.85	133	6.47
9	1.50	313	3.43	36	7.65	115	6.77
10	1.55	310	3.48	37	7.65	115	6.77
11	1.57	309	3.49	38	8.20	105	6.94
12	1.60	308	3.51	39	8.80	100	7.03
13	1.67	305	3.56	40	9.17	97	7.08
14	1.70	300	3.64	41	10.30	92	7.16
15	1.75	297	3.70	42	11.50	87	7.25
16	1.85	295	3.73	43	11.65	90	7.20
17	1.95	290	3.81	44	11.95	90	7.20
18	2.00	284	3.91	45	12.55	93	7.14
19	2.25	275	4.07	46	12.75	95	7.11
20	2.35	268	4.18	47	12.77	96	7.09
21	2.40	263	4.27	48	12.80	92	7.16
22	2.48	260	4.32	49	13.00	97	7.08
23	2.57	261	4.30	50	13.00	98	7.06
24	2.75	251	4.47	51	13.00	94	7.12
25	2.78	251	4.47	52	13.05	95	7.11
26	3.05	241	4.64	53	13.07	99	7.04
27	3.45	229	4.84	—	—	—	—

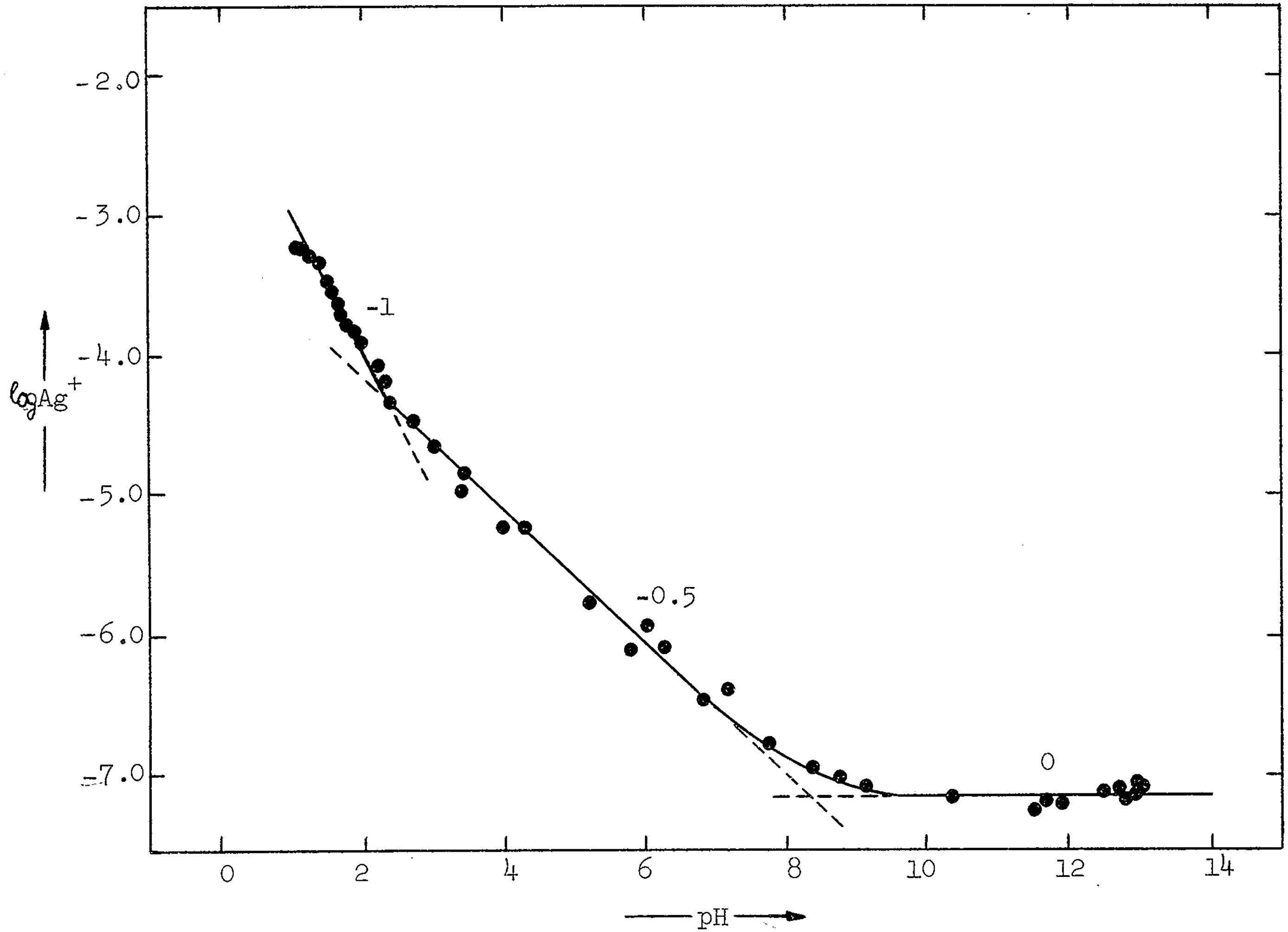


FIGURE 4.6 : Potentiometric Solubility of Ag_2SeO_3 as a function of pH.

$$pC_z = pK_{sp} = 2pAg^+ + pSeO_3^{-2}$$

$$pK_{sp} = 15.58 \quad \sigma = \pm 0.12$$

Calculations are given in table 4.5.1 .

Ionization Constants of H_2SeO_3 :

The two ionization constants k_1 and k_2 of the acid H_2SeO_3 are determined from the knowledge of the two experimental constants A_z and B_z, as was done earlier in case of H_2Se. The calculations are tabulated in 4.5.2 and 4.5.3 .

$$pk_2 = pC_z - pB_z$$

$$= 8.12 \quad \sigma = \pm 0.28$$

$$pk_1 = pB_z - pA_z$$

$$= 2.26 \quad \sigma = \pm 0.09$$

Discussion of Results:

Ionization constants of H_2S have been determined in the earlier studies by the conductometric and the colorimetric methods or calculated from the thermodynamic functions (24). In a medium of high ionic strength, as in this study, the thermodynamic constants are of little practical use. Hence the concentration constants appropriate for the medium must be known. These constants have been recently calculated at higher ionic strengths by the use of glass electrode (table 4.6), the results are, however, inconsistent. We, therefore, preferred to use the values of Torma (32) obtained at one molar medium ($NaClO_4$), which was also maintained throughout this study.

TABLE NO. 4.5.1

Solubility Product of Ag_2SeO_3.

(Experimental Data from table 4.5)

E.No.	2 pAg^+	pK_{sp}
41	14.32	15.64
42	14.50	15.82
43	14.40	15.72
44	14.40	15.72
45	14.28	15.60
46	14.22	15.54
47	14.18	15.50
48	14.32	15.64
49	14.16	15.48
50	14.12	15.44
51	14.24	15.56
52	14.22	15.54
53	14.08	15.40

$$pSeO_3^{-2} = pH_2SeO_{3\ tot}$$

$$pC_z = pK_{sp} = 2\ pAg^+ + pSeO_3^{-2} = 15.58;\ \sigma = \pm\ 0.12.$$

TABLE NO. 4.5.2

Calculation of k_2 of H_2SeO_3.

E.No.	2 pAg^+	pB_z	pk_2
29	10.44	7.76	7.82
30	10.44	7.46	8.12
31	11.54	7.74	7.84
32	12.26	7.76	7.82
33	11.72	6.99	8.59
34	12.20	7.34	8.24
35	12.94	7.41	8.17
36	13.54	7.21	8.37

$$pB_z = 2\ pAg^+ + pSeO_{3\ tot} - pH.$$

$$pk_2 = pC_z - pB_z.$$

$$= 8.12 \quad \sigma = \pm 0.28$$

TABLE NO. 4.5.3

Calculation of k_1 of H_2SeO_3

E.No.	$2\ pAg^+$	pA_z	pk_1
1	6.44	5.36	2.10
2	6.48	5.30	2.16
3	6.52	5.28	2.18
4	6.62	5.34	2.12
5	6.68	5.30	2.16
6	6.68	5.26	2.20
7	6.74	5.16	2.30
8	6.86	5.24	2.22
9	6.86	5.18	2.28
10	6.96	5.18	2.28
11	6.98	5.16	2.30
12	7.02	5.14	2.32
13	7.12	5.10	2.36
14	7.28	5.20	2.26
15	7.40	5.22	2.24
16	7.46	5.08	2.28
17	7.62	5.04	2.42
18	7.82	5.14	2.32

$$pA_z = 2\ pAg^+ + pSeO_{3\ tot} - 2\ pH$$

$$pk_1 = pB_z - pA_z = 2.26 \quad \sigma = \pm 0.09.$$

TABLE NO. 4.6

Ionization Constants of H_2S in Aqueous Medium
(Glass Electrode Measurements)

Author	T^oC	μ	pk_1	pk_2	Reference
Epprecht	-	0.0	6.48	-	(24)
Kubli	20	0.0	7.06	12.44	(24)
Yui	25	0.0	6.91	-	(24)
Zust	25	0.1	6.83	12.92	(41)
Widmer	20	1.0	6.67	14.01	(42)
Torma	25	1.0	6.90	13.48	(32)

The literature available on the ionization constants of H_2Se and H_2SeO_3 is even meagre and insufficient. Table 4.7 and 4.8, show that there is a considerable amount of uncertainty in the reported values of the ionization constants of these acids e.g., the pk_2 values of both the acids differ by several logarithmic units from one author to another.

Therefore, it became essential to determine our own constants, in a medium of 1.0 M $NaClO_4$, which could be employed further in the calculations involving complex formation with these two acids as the ligands.

TABLE NO. 4.7

Ionization Constants of H_2Se in Aqueous Medium

Author	T°C	μ	pk_1	pk_2	Reference
Bruner	25	dil.	3.77	-	(24)
de Hlasko	25	dil.	3.73	-	(24)
Hagisawa	25	0.0	3.89	11.00	(24)
Lingane	25	Var.	-	14.00	(24)
Wood	22	0.0	-	15.00	(34)

TABLE NO. 4.8

Ionization Constants of H_2SeO_3 in Aqueous Medium

Author	T°C	μ	pk_1	pk_2	Reference
Blanc	25	dil.	2.57	7.29	(24)
Rosenheim	r.t.	Var.	2.31	-	(24)
Willcox	r.t.	Var.	2.40	8.06	(24)
Hagisawa	25	0.0	2.62	8.32	(24)
Latimer	25	0.0	2.57	6.60	(24)

Our results for H_2Se show that the first ionization constant, pk_1, is lowered in one molar ionic strength while the second constant, pk_2, remains close to the value of Hagisawa (cf. table 4.7). The potentiometric method for the determination of the ionization constants with silver electrode appears equally reliable in this case. It has been shown before, in H_2S studies, that the ionization constants do not change appreciably with increasing ionic strength of the medium. However, the present values appear very different from the data of Lingane or Wood (table 4.7), who have reported the values for pk_2, at least three logarithmic units different from our results. There certainly seems to be something wrong with their data. Fig. (4.4), shows that the potentiometric solubility of Ag_2Se becomes constant as a function of pH, beyond pH 12. Theoretical derivation of the solubility pattern also indicates that this behaviour is possible only, when $Se_{tot} = Se^{-2}$, i.e., $pH > pk_2$ of H_2Se (cf. eq 4.8 and 4.14). This observation, therefore, confirms that the constant, pk_2, must fall below the value of pH 12, as has been found by calculations. Furthermore the results agree well with the determination of Hagisawa based on the potentiometric titration with glass electrode. Evidently the present results are the best available for the medium of one molar ionic strength.

Similarly in case of H_2SeO_3, the first constant, pk_1, is lowered somewhat, while the second constant, pk_2, is in agreement with the published literature (table 4.8). Our measurements adequately prove that the value of 6.60 for the pk_2, mentioned by Latimer (52) is positively an error by more than a logarithmic unit (fig. 4.6).

The afore-mentioned procedure thus affords another method for the calculation of the ionization constants of the weak polybasic acids at any desired ionic strength. In principle this method is always applicable when the system forms a sparingly soluble compound and its cation constitutes a thermodynamic reversible electrode system.

The potentiometric method employed in this study is based on reliable determinations of the potentials of the electrochemical cells with Ag and Hg electrodes in a medium of S^{-2}, Se^{-2} and SeO_3^{-2}. It is, however, known since several years that definite potentials are developed in Ag_2S -NaHS medium (35)(36), and in HgS system with an excess of sulphide (38)(65)(72). The uncertainties on what happens, especially when very small concentrations of Ag^+ and Hg^{+2} are involved (10^{-20}- 10^{-40}M), cast some doubt for the potential measurements. The solubility products of these systems have, therefore, been calculated from the thermodynamic data (39)(40). The recent determinations of Schwarzenbach and Widmer (74), (76), for the potentials of mercury and silver sulphides in 1.0 M $NaClO_4$ demonstrate that the metal indicator electrodes in both the cases respond to correct potentials for Ag^+ and Hg^{+2} ions.

The electrochemical measurements on the sulphides of silver and mercury in this study fully support the above mentioned views. The dependency of pAg^+ and pHg^{+2} on pH, whereby satisfying the solubility product relationship (cf. fig. 4.2, 4.3, 4.4, and 4.5) in the respective cases, illustrates unambiguously the reliability of such potential measurements. The solubility product constants calculated directly by the potentiometric method are in good agreement with the published literature (table 4.9). The small difference in our data compared with the data of Schwarzenbach and Widmer may be attributed to the difference in the values of the ionization constants for H_2S in the two studies. The correct potential response for the very small concentrations of Ag^+ and Hg^{+2} ions may be regarded as due to the presence of the large concentrations of the soluble thiocomplexes of the order of 10^{-5}-10^{-8}M/liter. The stability of the electrode potential even in acidic medium further confirms the presence of big quantities of the aqueous complexes. Furthermore, the small value of pAg^+ or pHg^{+2} does not effect the results, since it is only the calculated results which measure the free energy of the transfer of metal to ionic form in the aqueous complexes.

Discussion of the Electrochemical Procedures:

The electrode reaction in case of silver proceeds with an electron transfer as,

$$(4.23) \quad Ag^{+} + e^{-} \rightleftharpoons Ag^{o}$$

The Nernst equation for the cell reaction with silver electrode in conjunction with a normal calomel electrode, may be written as,

$$(4.24) \quad E_{Ag} = {}^{T}E^{o}_{Ag} + 0.05916 \log a_{Ag^{+}}$$

where ${}^{T}E^{o}_{Ag}$ = Thermodynamic standard potential of cell

$a_{Ag^{+}}$ = Activity of Ag^{+}

The thermodynamic standard potentials of all the known metal electrodes and the standard reference electrodes have been tabulated by Latimer (52). In a medium of 1.0 M ionic strength the eq (4.24) above changes to,

$$(4.25) \quad E_{Ag} = E^{o}_{Ag} + 0.05916 \log (Ag^{+})$$

where $E^{o}_{Ag} = {}^{T}E^{o}_{Ag} + 0.05916 \log \gamma_{Ag^{+}}$

$\gamma_{Ag^{+}}$ = Activity Coefficient of (Ag^{+}) in 1.0 M $NaClO_4$ medium.

Since the ionic strength in such a medium is constant, it is, therefore, assumed that the activity coefficients also remain constant. The knowledge of E^{o}_{Ag} thus directly relates the cell potential to the concentration of the ion Ag^+ (eq 4.25). Experimentally it has been proved (cf. table 3.2) that analytically known concentrations of Ag^+ in 1.0 M $NaClO_4$ obey the Nernst equation; E^o_{Ag} could thus be established from the known silver concentrations. The concentrations of free ions Ag^+ in a medium of S^{-2}, Se^{-2}, SeO_3^{-2} could further be estimated from the knowledge of the potentials of the cells and the E^o_{Ag} established above. The values of the solubility products of Ag_2S and Ag_2SeO_3 calculated in this study are in good agreement with the literature values, thus proving the utility of the electrochemical approach.

There is, however, no literature available on the selenides of metals. Nevertheless, we can conclude confidently that for this unexplored Ag_2Se system, the calculated value of its solubility product in 1.0 M medium is also correct.

For the similar studies in case of Hg system, E^o_{Hg}, the standard cell potential in conjunction with normal calomel electrode must be known for 1.0 M medium. Hence Nernst equation could be utilized for the evaluation of free Hg^{+2} concentrations in the heterogeneous mediums of S^{-2}, Se^{-2}. The Nernst equation for the cell reaction can be written as,

$$(4.26) \quad E_{Hg} = {}^{T}E^o_{Hg} + 0.02958 \log a_{Hg^{+2}}$$

where ${}^{T}E^o_{Hg}$ = Thermodynamic standard potential of the cell.

$a_{Hg^{+2}}$ = Activity of Hg^{+2}

In a medium of one molar ionic strength this changes to

$$(4.27) \quad E_{Hg} = E^o_{Hg} + 0.02958 \log (Hg^{+2})$$

where $E^o_{Hg} = {}^{T}E^o_{Hg} + 0.02958 \log \gamma_{Hg^{+2}}$

$\gamma_{Hg^{+2}}$ = Activity Coefficient of Hg^{+2}.

TABLE NO. 4.9

Published Data on the Solubility Products of Ag_2S, HgS, and Ag_2SeO_3.

Reference (24), (74), (76)

S.No.	Author	T^oC μ	Ag_2S pK_{sp}	Author	T^oC μ	HgS pK_{sp}	Author	T^oC μ	Ag_2SeO_3 pK_{sp}
1	Bernfeld	Rt. 0.1 NaHS	47.75	Knox	25.0 var.	53.50	Chukhlantsev	20.0 var.	15.01
2	Jellinek and Czerwinski	10 NaHS var.	49.50	Goates *et al.*	25.0 0.0	51.05	Lin and Pan	25.0 0.0	14.74
3	Rivitz	25.0 0.0	51.48	Latimer	25.0 0.0	53.80	Selivanova *et al.*	25.0 0.0	15.55
4	Goates *et al.*	25.0 0.0	49.15	Ringbom	25.0 0.0	51.80			
5	Latimer	25.0 0.0	50.26	Czemanske	25.0 0.0	52.73			
6	Ringbom	25.0 0.0	49.20	Immerwahr	var.	47.17			
7	Czamanske	25.0 0.0	49.20	Schwarzenback and Widmer	20.0 1.0 $NaClO_4$	50.96			
8	Schwarzenbach *et al.*	25.0 0.1 $NaClO_4$	50.00						
9	Schwarzenbach and Widmer	20.00 1.0 $NaClO_4$	49.70						

However, E^o_{Hg} in this case could not be established easily, since in close proximity to the metal electrode the reaction

$$(4.28) \quad Hg^o + Hg^{+2} \rightleftharpoons Hg_2^{++} \qquad K = \sim 100$$

complicates the electrochemical measurements (43)(44)(45). Fortunately the compounds of monovalent mercury such as Hg_2S do not exist and disproportionate into HgS and Hg^o. The HgS and its thiocomplexes are not reduced further by Hg^o (46). Consequently equilibration of HgS with Hg^o does not influence the aqueous complexes in solution. In such cases the amount of Hg_2^{++} formed is so small that stoichiometrically it may be neglected.

Nevertheless, E^o_{Hg} in this case is calculated in an indirect method. Bethge (47), Qvarfort (48), and Sherrill (49) have shown that Hg^{+2} forms stable aqueous complexes with halogens and pseudohalogens whereas the monovalent mercury only precipitates in presence of these ligands. Utilizing their experimental data one can calculate the concentration of the free Hg^{+2} ions present in a complexed system, and from the measured cell potential of such a system, E^o_{Hg} can be determined. These calculations have been shown in chapter III (cf. table (3.3)). The concentration of free Hg^{+2} calculated in the complexed system is so small that the monovalent mercury, even if formed at the electrode, does not precipitate at such small dilutions. Furthermore, the instability of the monovalent mercury complexes with these ligands does not influence the equilibrium between Hg^{+2} and its complexes appreciably. The measured cell potential is therefore directly related to the concentration of Hg^{+2} ions.

The value of K_{sp} for HgS found using the experimentally measured standard potential, E^o_{Hg}, is in close agreement with the previously reported literature (cf. table 4.9). It is, therefore, certain that for the new HgSe system also this method gives the correct constant for its solubility product. This work could therefore be regarded as the first report on the experimental determination of the solubility product constants of the metal selenides.

The electrochemical determination of pH, one may recall, signifies the $\log a_{H^+}$, the activity of the hydrogen ions in solution. The computation of the stoichiometric stability constants requires the knowledge of the H^+ ion concentration rather than its activity. Our experience has shown that the linearity at low and high pH values is not maintained (cf. fig 3.2) between the cell potential and the pH. The convertion of the cell potential to the hydrogen ion concentration is therefore rather involved. Consequently the measured pH values have been employed as if these signify the H^+ ion concentrations. Calculations in this manner have been made before (50)(51) but the constants measured in reality remain mixed activity concentration constants, often called as "Brönsted Constants" (8).

CHAPTER V

The Aqueous Selenite-Complexes of Metals.

Silver

The interactions of selenous acid with cation Ag^+ have been studied by Chukhlantsev (53), Lin and Pan (54), and Selivanova et al. (55). These authors have only reported the simple solubility product of the compound Ag_2SeO_3 under acidic and neutral conditions in HCl, HNO_3, and H_2SO_4 media. Deshmukh and Sankaranaryana (56) have observed the quantitative precipitation of normal silver selenite in the pH range 4 - 8 and even suggested this as an analytical method for the determination of silver. Apparently no evidence is yet available on any complex formation in this system. We have reexamined the silver selenite reactions over the entire pH range and at different increments of the selenite concentrations. Surprisingly the solubility of the precipitated silver compound has been found to increase in alkaline conditions as a function of the selenite concentration. In a medium of controlled ionic strength this behaviour clearly indicates the complex formation. The nature of these complexes has been established and their formation constants have been evaluated.

Experimental Observations:

Tables 5.1, 5.2, and 5.3 and fig. 5.1, give the results of the solubility of the precipitated Ag_2SeO_3 as a function of pH at three different selenite total concentrations . It is apparent from the solubility data that around pH 8.0 the silver concentration in the solution increases and quickly attains a limiting slope of zero as a function of pH. Further experiments in alkaline conditions (cf. fig. 5.2, table 5.4) indicate a regular increase in the silver selenite solubility as a function of selenite concentration. The solubility slopes in this case change from −0.5 to −1.5, thus showing the presence of at least two complexes.

Identification of the Complex Species:

The solubility curves (fig. 5.1) show a slope of -1.0 and -0.5 in acidic and nearly neutral solutions. The two ionization constants k_1 and k_2 of the acid H_2SeO_3 found earlier (chapter IV) are also in the same pH regions. Apparently the acid (H_2SeO_3) and its first deprotonated product ($HSeO_3^-$), do not influence the solubility of the precipitate; since the solubility curves only conform to the presence of free Ag^+ ions in the medium. It is further confirmed when Ag_{tot} in these pH regions decreases with an increase in the selenite concentration, indicating that the simple solubility product relationship is obeyed without reservations. The reversal of this trend in alkaline region, when pH > pk_2 of H_2SeO_3, is evidently due to complex formation. Furthermore, it is only the SeO_3^{-2} ion that enhances the solubility of the precipitated Ag_2SeO_3. The experimental evidence strongly points to at least two complexes because of the two distinct slopes that are exhibited as a function of SeO_3^{-2} (cf. fig. 5.2). These slopes of −0.5 and −1.5 are also in agreement with the two theoretical possibilities for the complexes ($AgSeO_3^{-1}$) and ($Ag(SeO_3)_2^{-3}$) in contact with the solid Ag_2SeO_3 (cf. table (2.1)).

The Formation Constants of the Complex Species:

The complex ($Ag(SeO_3)_2^{-3}$) is formed when Ag_{tot} and the selenite total concentration correspond to the solubility slope of −1.5 at a constant pH. The Ag_{tot} may now be regarded as totally due to this species.

$$Ag_{tot} = (Ag(SeO_3)_2^{-3})$$

when pH > pk_2 $(SeO_3^{-2}) = (SeO_{3\ tot})$

$$\phi_{12} = \frac{(Ag_{tot})}{(Ag^+).(SeO_{3\ tot})^2}$$

$$-p\phi_{12} = pAg^+ + 2pSeO_{3\ tot} - pAg_{tot}$$

$$-p\beta_{12} = -p\phi_{12} = 3.76 \quad \sigma = \pm 0.05$$

The calculations of $-p\phi_{12}$ from the experimental data are given in table 5.5; pAg^+ is calculated from the K_{sp} found in chapter IV.

The complex $Ag(SeO_3)^{-1}$ is formed at lower selenite concentrations when the solubility exhibits a slope of -0.5 as a function of the selenite total concentration. It is probable that at lower selenite concentrations both the species are present in the equilibria. The pAg_{tot} in such an event will be sum of the two complexes.

$$Ag_{tot} = (Ag(SeO_3)^{-1}) + (Ag(SeO_3)_2^{-3})$$

$$Ag_{tot} = \phi_{11}\ (Ag^+).(SeO_{3\ tot}) + \phi_{12}\ (Ag^+).(SeO_{3\ tot})^2$$

$$\phi_{11} = \frac{(Ag_{tot}) - \phi_{12}(Ag^+).(SeO_{3\ tot})^2}{(Ag^+).(SeO_{3\ tot})}$$

$$-p\beta_{11} = -p\phi_{11} = 2.42 \quad \sigma = \pm 0.12$$

Calculations of this complex from the experimental data are given in table 5.6.

TABLE NO. 5.1

Aqueous Solubility of Ag_2SeO_3 at Different pH.

pAg_{tot} (orig) = 2.44 M $pH_2SeO_{3\ tot}$ = 2.19 M.

μ = 1.0 $NaClO_4$.

S.No.	pH	pAg_{tot}	S.No.	pH	pAg_{tot}
1	1.27	2.52	24	3.35	4.10
2	1.29	2.55	25	3.42	4.12
3	1.35	2.59	26	3.52	4.20
4	1.40	2.56	27	4.17	4.49
5	1.45	2.74	28	6.00	5.32
6	1.50	2.80	29	6.45	5.48
7	1.60	2.86	30	6.50	5.52
8	1.67	2.87	31	6.85	5.50
9	1.72	2.95	32	7.10	5.60
10	1.80	2.98	33	7.30	5.70
11	1.95	3.00	34	7.42	5.67
12	2.07	3.21	35	7.45	5.67
13	2.17	3.31	36	7.80	5.60
14	2.42	3.55	37	8.10	5.70
15	2.50	3.49	38	8.17	5.64
16	2.60	3.67	39	10.00	5.47
17	2.67	3.75	40	10.85	5.62
18	2.75	3.77	41	11.00	5.65
19	2.79	3.80	42	11.35	5.65
20	2.85	3.84	43	11.60	5.65
21	2.90	3.87	44	12.05	5.65
22	2.97	3.93	45	12.25	5.60
23	3.08	4.02	46	12.60	5.50

TABLE NO. 5.2

Aqueous Solubility of Ag_2SeO_3 at Different pH.

pAg (orig) = 2.44 M $pH_2SeO_{3\ tot}$ = 1.00 M.

μ = 1.0 $NaClO_4$.

S.No.	pH	pAg_{tot}	S.No.	pH	pAg_{tot}
1	1.55	3.20	29	6.37	5.57
2	1.65	3.30	30	6.52	5.70
3	1.75	3.45	31	6.95	5.60
4	1.80	3.51	32	7.30	5.65
5	1.95	3.62	33	7.45	5.50
6	2.00	3.66	34	7.72	5.57
7	2.05	3.70	35	7.80	5.47
8	2.10	3.77	36	7.95	5.51
9	2.15	3.82	37	8.05	5.42
10	2.25	3.90	38	8.15	5.36
11	2.35	3.95	39	8.25	5.42
12	2.37	4.00	40	8.45	5.29
13	2.45	4.05	41	8.55	5.25
14	2.52	4.10	42	8.72	5.12
15	2.65	4.20	43	8.85	5.20
16	2.75	4.31	44	9.07	5.10
17	2.97	4.41	45	9.67	5.15
18	3.17	4.47	46	9.90	5.20
19	3.25	4.55	47	10.10	5.29
20	3.35	4.63	48	11.12	5.20
21	3.40	4.62	49	11.37	5.25
22	3.55	4.72	50	11.62	5.20
23	3.75	4.80	51	11.82	5.22
24	4.12	4.95	52	12.00	5.12
25	4.53	5.17	53	12.05	5.26
26	5.32	5.30	54	12.10	5.17
27	5.70	5.47	55	12.30	5.10
28	5.77	5.50			

TABLE NO. 5.3

Aqueous Solubility of Ag_2SeO_3 at Different pH.

pAg (orig) = 3.40 $pH_2SeO_{3\ tot}$ = 0.70 M.

μ = 1.0 $NaClO_4$.

S.No.	pH	pAg_{tot}
1	2.60	4.44
2	3.00	4.62
3	3.60	4.83
4	5.95	5.75
5	6.75	5.75
6	7.10	5.55
7	7.15	5.77
8	7.25	5.67
9	7.35	5.55
10	7.55	5.47
11	7.57	5.45
12	7.75	5.32
13	7.77	5.37
14	7.90	5.25
15	8.02	5.20
16	8.05	5.23
17	8.20	5.12
18	8.30	5.07
19	8.45	5.10
20	8.50	5.04
21	8.60	5.05
22	8.75	5.00
23	8.85	4.96
24	8.95	5.00
25	10.80	5.00
26	12.27	4.96

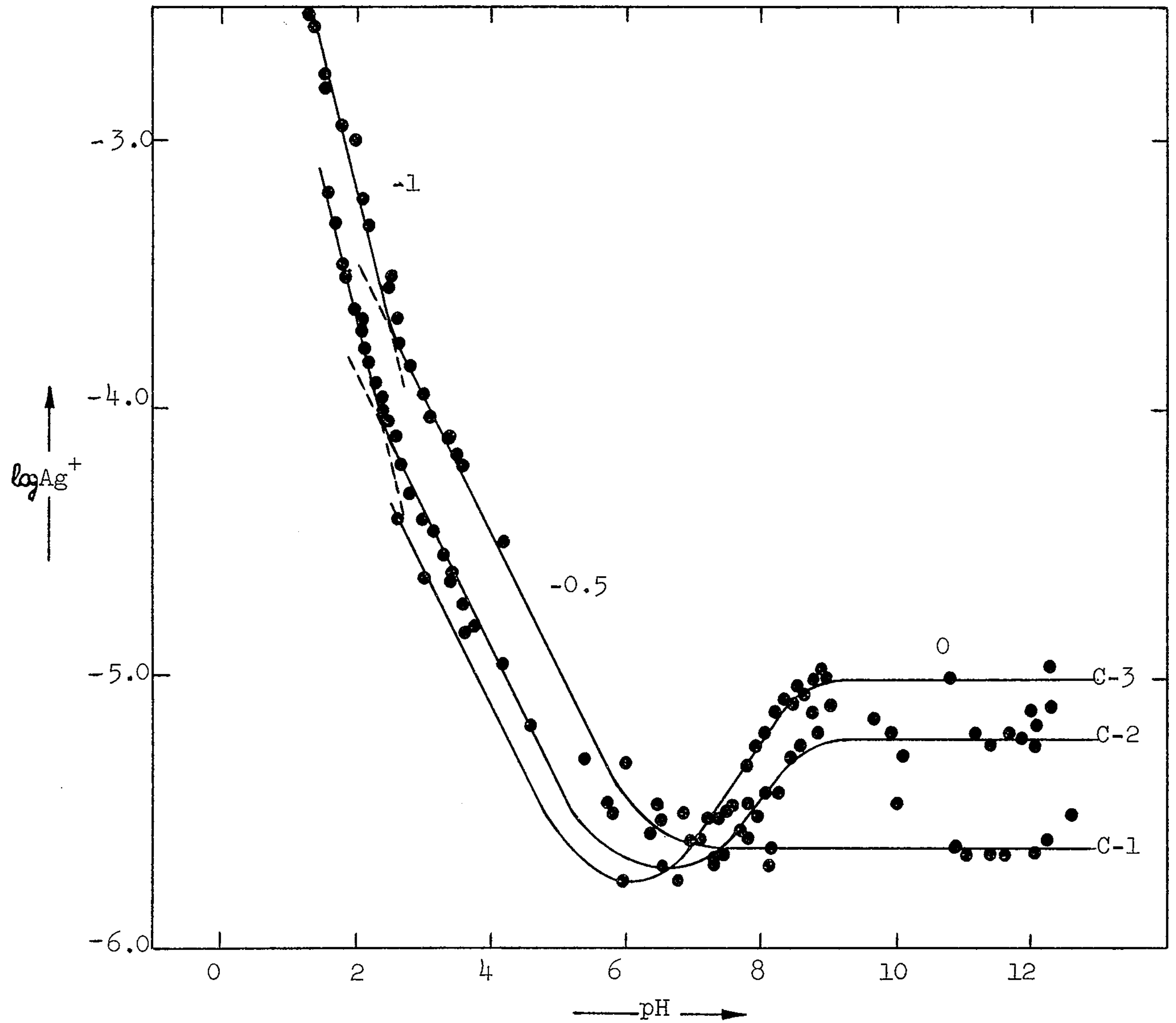


FIGURE 5.1 : Radiometric Solubility of Ag_2SeO_3 at Different Excess of $SeO_{3\ tot}$.

TABLE NO. 5.4

Aqueous Solubility of Ag_2SeO_3 With Increasing Selenite.
pAg (orig) = 3.40 M μ = 1.0 $NaClO_4$.

S.No.	pH	$SeO_{3\ tot}$ M	$pSeO_{3\ tot}$	pAg_{tot}
1	9.60	0.001	3.00	6.00
2	9.67	0.003	2.52	6.22
3	9.60	0.005	2.30	6.15
4	9.65	0.008	2.10	6.15
5	9.47	0.010	2.00	6.17
6	9.45	0.020	1.70	5.97
7	9.40	0.030	1.52	5.92
8	9.40	0.050	1.30	5.72
9	9.40	0.070	1.16	5.62
10	9.40	0.090	1.05	5.42
11	9.45	0.100	1.00	5.36
12	9.55	0.200	0.70	4.97
13	9.75	0.300	0.52	4.75
14	9.73	0.400	0.40	4.55
15	9.72	0.500	0.30	4.42
16	9.70	0.600	0.22	4.32
17	9.70	0.700	0.16	4.25
18	9.70	0.800	0.10	4.19
19	9.70	0.900	0.05	4.18

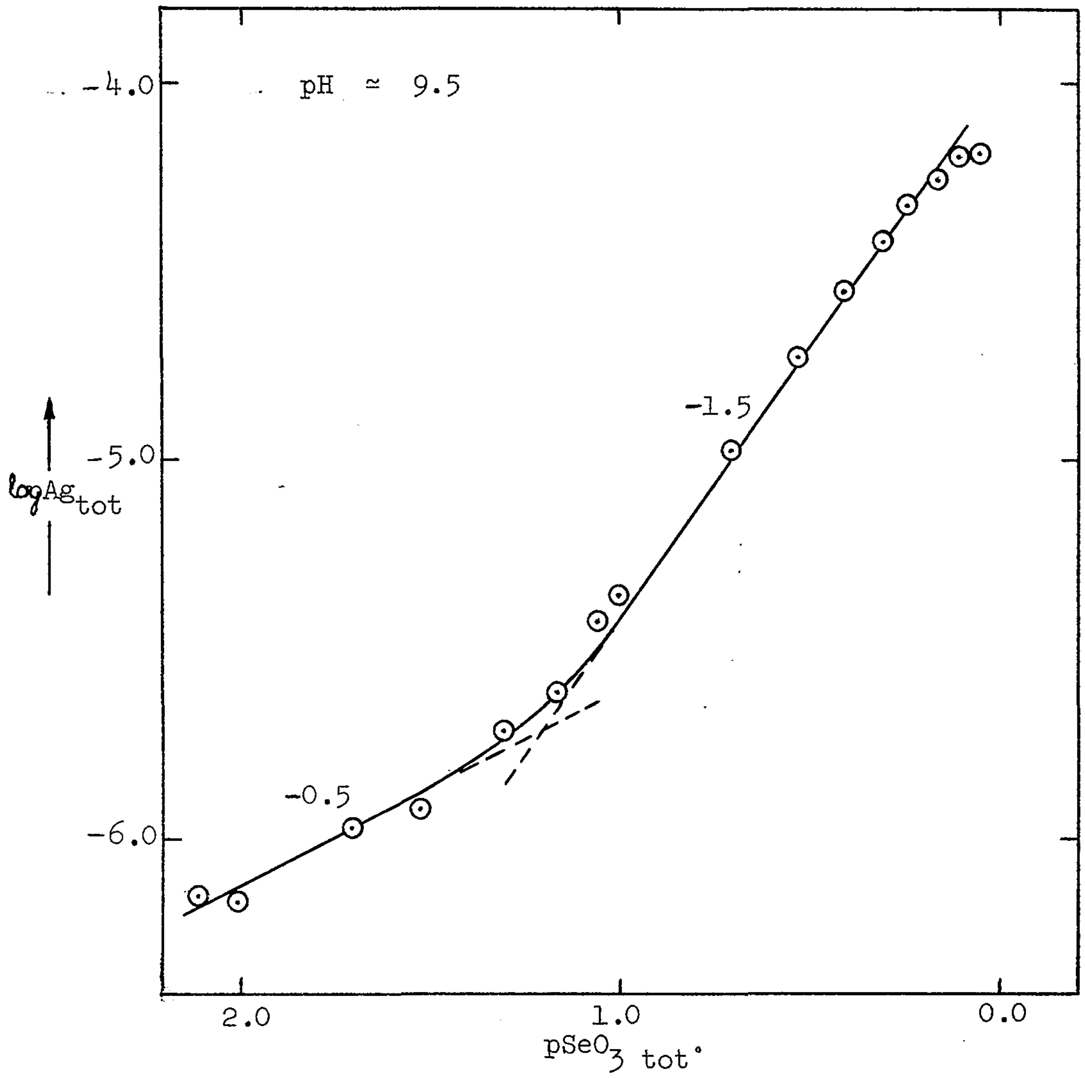


FIGURE 5.2 : Radiometric Solubility of Ag_2SeO_3 as a Function of Increasing $SeO_{3\,tot}$.

TABLE NO. 5.5

Calculation of the Formation Constant of Complex

$[Ag(SeO_3)_2]^{-3}$

(Experimental Data from table 5.4)

E.No.	pAg_{tot}	$pSeO_{3\ tot}$	$2\ pSeO_{3\ tot}$	pAg^+	$-p\phi_{12}$
19	4.18	0.05	0.10	7.76	3.68
18	4.19	0.10	0.20	7.74	3.75
17	4.25	0.16	0.32	7.71	3.78
16	4.32	0.22	0.44	7.68	3.80
15	4.42	0.30	0.60	7.64	3.82
14	4.55	0.40	0.80	7.59	3.74

$$SeO_{3\ tot} = SeO_3^{-2}$$

$$-p\phi_{12} = -pAg_{tot} + pAg^+ + 2\ pSeO_{3\ tot}$$

$$-p\beta_{12} = -p\phi_{12} = 3.76 \quad \sigma = \pm 0.05.$$

TABLE NO. 5.6

Calculation of the Formation Constant of Complex

$[Ag(SeO_3)]^{-1}$

E.No.	pAg_{tot}	pAg_c	$pSeO_{3\ tot}$	pAg^+	$-p\phi_{11}$
5	6.17	6.23	2.00	6.79	2.56
6	5.97	6.09	1.70	6.94	2.55
7	5.92	6.16	1.52	7.03	2.40
8	5.72	6.07	1.30	7.14	2.37
9	5.62	6.15	1.16	7.21	2.22
10	5.42	5.88	1.05	7.26	2.43

$$Ag_{tot} = [Ag(SeO_3)]^{-1} + [Ag(SeO_3)_2]^{-3}$$

$$pAg_c = p[Ag\ SeO_3]^{-1}$$

$$-p\beta_{11} = -p\phi_{11} = 2.42 \quad \sigma = \pm 0.12.$$

Discussion of the Results:

The solubility curves of the precipitated Ag_2SeO_3 (fig. 5.1) show two important results. Firstly there is no influence of H_2SeO_3 or $HSeO_3^-$ on the solubility of silver selenite, i.e., these species are too weak to form coordination complexes. If any of these two species were capable of acting as the complexing ligands, the solubility of the precipitated selenite would have increased in the regions of predominence of H_2SeO_3 or $HSeO_3^-$, i.e., before or around pk_1 of the acid H_2SeO_3. The solubility curves in these cases conform to the presence of the free Ag^+ ions in the medium (cf. table 2.1). Apparently Ag_2SeO_3 has a simple solubility till pk_2 of the acid H_2SeO_3. This observation is in agreement with the results of the earlier studies on this system (56).

Secondly, the experimental solubility of Ag_2SeO_3 increases in the pH regions, when $pH > pk_2$ of H_2SeO_3. This could have arisen due to the formation of aqueous silver hydroxy complexes because of the increased alkalinity of the medium. Under similar experimental conditions such silver hydroxy complexes have been observed by Gubeli and Ste-Marie (59) in this laboratory. The other possible reason for the increase in the solubility could be the formation of some unknown selenite complexes. The fact remains that the Ag_2SeO_3 solubility increases around the pk_2 of H_2SeO_3, yet it behaves independent of pH; this observation rules out any hydroxy-complex formation in any form. It is thus certain that some unreported selenite complexes are present in the alkaline pH regions in the silver selenite system.

The species (SeO_3^{-2}) predominates the H_2SeO_3 equilibria in the pH region of interest; obviously this must be the complexing ligand as well.

This illustrates that in selenous acid, SeO_3^{-2} is by far the strongest complexing ligand.

The nature of the aqueous complexes is further ascertained from the solubility slopes exhibited by silver selenite as a function of selenite concentration at a constant pH. The formation of two distinct slopes is a clear indication of the presence of two complexes as well. The constitution of the complexes as 1:1 and 1:2 ratio of silver and selenite is in complete agreement with the theoretical possibilities (table 2.1). This observation lends full support to the theory developed for such heterogeneous equilibria and the aqueous complex formation (chapter II). It has neatly resolved the formation of two weak complexes and demonstrated the usefulness of the experimental and the mathematical treatment of the equilibrium data.

Earlier studies (53), (55), and (56) on silver selenite had been focused mainly in acidic and near alkaline conditions, perhaps with an aim to establish the aqueous solubility product of this compound; our result is also close to the reported value for this constant which, thus, confirms the earlier findings. The experience in this study now indicates further that in pH regions before pk_2 of H_2SeO_3, Ag_2SeO_3 has the simple solubility with hardly any tendency towards complex formation. It is not surprising that the earlier workers failed to observe any conspicuous solubility characteristics in these pH regions to suspect a complex formation. Evidently studies must be performed over the entire pH range and at broad concentration intervals of the selenite total to obtain a correct information on the silver selenite interactions.

Complex formation in the parallel system Ag_2SO_3 has been reported by Chateau et al., (57)(58), who have vouched for the species $AgSO_3^-$, $Ag(SO_3)_2^{-3}$, $Ag(SO_3)_3^{-5}$ in the aqueous equilibrium at higher sulphite concentrations. It is reasonable to expect that the silver selenite complexing should also occur in an analogous manner. It is even possible that such aqueous complexes may also be formed in the analogous Ag_2TeO_3 system, where hardly any quantitative information is available as yet.

CHAPTER VI

The Aqueous Thio-Complexes of Metals

Silver, Mercury, Manganese, Iron, and Cobalt.

Metal sulphides as a rule, apart from those of alkalies and alkaline earths, are characterized by great and often extreme, insolubility. Therefore we find a vast majority of metals occur in nature as sulphide ores. The heavy metal sulphides are so insoluble that many of them do not decompose by dilute acids. Their aqueous solubility products (24)(60) are so small that even after repressing the sulphide ion concentration in solution by hydrogen ion, only a very small concentration of metal ion can be present in solution in equilibrium with the solid sulphide. Based on these reactions, analytical methods have been developed for the estimation of metals as sulphides (61)(62).

The theoretical solubilities of approximately 10^{-15}M and 10^{-20}M are obtained on the basis of the solubility product principle for the sulphides of silver and mercury respectively. These are of course too low to be detected by analytical means. However, the experimental studies of Weigel (63) and Biltz (64) have shown their aqueous solubilities to be of the order of 10^{-7} - 10^{-8}M by conductivity and ultramicroscopic methods. Some authors have questioned the reliability of these results (65), yet the redeterminations of Treadwell _et al._ (66)(67), in the later years, have shown the aqueous solubility results to be of the same order of magnitude in a H_2S saturated medium. Evidently the real solubilities of the metal sulphides are much higher (several orders of ten) than that could be predicted by the solubility product principle. Some other natural processes also indicate that perhaps the sulphide solubilities are higher than those obtained by the theoretical calculations. Recent geochemical determinations of Hemley (68), Barnes (69) and others (70)(71) on the aqueous chemistry of the metal sulphides have shown that the deposits of the sulphide ores cannot be explained by the extremely small solubilities given by their solubility products. These authors have therefore concluded that aqueous complex formation is responsible for their increased solubilities and their subsequent transport and ore formation.

From the foregoing considerations it is apparent that, when employed to sulphide chemistry, one may reasonably assume that several thio-complexes are possible in solution in equilibrium with the precipitated sulphide.

Survey of the Researches on Thio-Complexes of Metals:

Mercury sulphide complexes are probably the earliest known, when Knox (72) showed the increase in HgS solubility in alkaline medium, as a function of sulphide concentration, to be due to the complex HgS_2^{-2}. More recently Treadwell and Schaufelberger (67) have observed that in H_2S saturated solutions the increased HgS solubility in acidic regions can be explained by assuming the formation of complex $Hg(HS)_2$. Dubey and Ghosh (73) have determined the effect of alkali sulphides and hydroxides on HgS and reached the same conclusion of Knox, that the complex HgS_2^{-2} is formed in alkaline conditions, at higher sulphide concentrations. Schwarzenbach and Widmer (74) have reported the formation of the complexes $Hg(HS)_2$, $Hg(HS)(S)^-$, and HgS_2^{-2} in different pH regions in HgS - sulphide equilibria. In a recent determination Barnes <u>et al</u>. (69) have found some unusual mercury thio-complexes in a medium of high sulphur content with liquid H_2S. The constitutions of these complexes have been described as $HgS(H_2S)_2$, $Hg(HS)_3^-$,

$HgS(HS)_2^{-2}$, and HgS_2^{-2} in the different pH regions.

Treadwell and Hepenstrick (66) have also found evidence for the silver thio-complex Ag(HS) in the Ag_2S system. Schwarzenbach, Gubeli, and Zust (75) and Schwarzenbach and Widmer (76) have observed additional evidence for the complex species $Ag(HS)_2^-$, AgS_2^{-3} , and $Ag_2S_3H_2^{-2}$ in the different pH regions of the Ag_2S equilibria. Ol'Shanskii et al. (77) have also determined the solubility of silver sulphide in hydrogen sulphide medium and have correlated the increased solubility to the thio-complexes Ag(HS) and AgS^-.

Several other sulphide systems have been investigated more recently. Hemley (68) and Anderson (78) have studied the PbS equilibria and found some definite solubility characteristics which could be attributed to the complex formation. However, these authors have failed to agree on the mechanism of the complex formation. Hemley (68) has postulated the complex species to be $Pb(HS)_2$ and $Pb(HS)_3^-$ whereas the latter argued in favour of the formation of a general complex $PbS.nH_2S$. Dubey and Ghosh (79) have also shown the formation of antimony sulphide complex, $Sb_2S_4^{-2}$, in Sb_2S_3 - sulphide interactions. Barnes (80) has argued for the formation of the thio-complex, $ZnS.HS^-$, in ZnS-sulphide system, while Gubeli and Ste-Marie (81) have shown the constitution of this complex to be Zn(HS)(OH). Ste-Marie, Torma, and Gubeli (31) have also demonstrated the formation of the thio-complexes $Cd(HS)^+$, $Cd(HS)_2$, $Cd(HS)_3^-$, and $Cd(HS)_3^{-2}$ in the aqueous equilibria of the CdS system.

Conclusions concerning thio-complexes of metal sulphides which can be drawn from the previous studies are as follows:

1. The data on thio-complexes of metal sulphides are meagre and many

systems have remained unexplored so far.

2. Thio-complexes of metals in known cases exist in weakly acidic to alkaline conditions but their stoichiometries are uncertain.

The systems Ag_2S and HgS have been, therefore, reexamined in order to establish the nature of their complexes unambiguously. Investigations have also been undertaken on the sulphides of the first transition group metals. The systems MnS, FeS, and CoS have been studied under the similar experimental conditions.

Experimental Results:

The System Ag_2S:

The solubility data of Ag_2S at four different sulphide concentrations are given in table 6.1 and presented graphically in fig. 6.1. The solubility of Ag_2S precipitated in H_2S medium at the same ionic strength is given in table 6.2. The solubility curves show that silver concentration in solution under neutral conditions increases appreciably. Exclusive experiments were therefore conducted in a neutral medium at considerably higher sulphide concentrations to study the sulphur effect. The results are tabulated in 6.3, and shown graphically in fig. 6.2. The solubility of Ag_2S was similarly determined in alkaline conditions and the results are given in table 6.4 and fig. 6.3.

Interpretation of Results:

The solubility data indicate that the Ag_2S solubility initially remains constant (pH 1-4), then it increases in the close vicinity of pk_1 of H_2S, and finally in alkaline medium (pH 10-13) it attains the same value as in the acidic region. The system has therefore two distinct features: (a) when the solubility is independent of the experimental variables pH and S_{tot}, and (b) when the solubility exhibits characteristic slopes both as a function of pH and S_{tot} in the neutral medium.

In the first case, comparison of the experimental data with the theoretical possibility (table 2.1) at once confirms the formation of the thio-complex $Ag_2(HS)(OH)$, since this is the only species that remains unaffected with change in pH or S_{tot}.

In the second case the solubility slopes measured from the curve of the highest S_{tot} (fig. 6.1) give a value of +1 and -0.5 before and after pk_1 of H_2S. The slope as a function of S_{tot} at constant pH (fig. 6.2) remains consistently at -1.5. The only complex that corresponds to these characteristic slopes is the species $Ag(HS)_2^-$ (cf. table 2.1), which is thus identified.

Calculation of the Formation Constants:

$(Ag_2(HS)(OH))$:

The formation constant of this complex is calculated from the data in table 6.4, which includes the experimental data of table 6.1 for the same pH range. It is possible to do so since it has been shown that the complex is the same in acidic or in alkaline conditions.

$$\phi_{11} = \frac{(Ag_2(HS)(OH))}{(Ag^+)^2.(S^{-2}).(H^+).(OH^-)}$$

$$= \frac{Ag_{tot}}{K_{sp}.K_w}$$

$-p\phi_{11} = 55.37 \quad \sigma = \pm 0.16$

$$\beta_{11} = \frac{(Ag_2(HS)(OH))}{(Ag^+)^2 . (HS^-) . (OH^-)}$$

$-p\beta_{11} = -(pk_2 + p\phi_{11}) = 41.89$

$(Ag(HS)_2^-)$:

The data from table 6.3, which includes the experimental data of the curves of the highest solubility fig. 6.1 in table 6.1, are employed to evaluate the constant of formation of this species.

$$\phi_{20} = \frac{(Ag(HS)_2^-)}{(Ag^+) . (S^{-2})^2 . (H^+)^2}$$

$-p\phi_{20} = -p(Ag(HS)_2^-) + pAg^+ + 2pS^{-2} + 2pH.$

$Ag_{tot} = (Ag(HS)_2^-) + (Ag_2(HS)(OH))$

$-p\phi_{20} = 43.93 \quad \sigma = \pm 0.06.$

$$\beta_{20} = \frac{(Ag(HS)_2^-)}{(Ag^+) . (HS^-)^2}$$

$-p\beta_{20} = -(2pk_2 + p\phi_{20}) = 16.97.$

TABLE NO. 6.1

Solubility of Ag_2S at Different pH and pS_{tot}

pAg (orig) = 3.50 M, μ = 1.0 $NaClO_4$

S.No.	pH	C-1		pH	C-2		pH	C-3		pH	C-4	
		pAg_{tot}	pS_{tot}		pAg_{tot}	pS_{tot}		pAg_{tot}	pS_{tot}		pAg_{tot}	pS_{tot}
1	0.35	7.91	2.40	0.90	7.89	2.02	0.85	7.64	1.62	0.05	7.60	1.41
2	0.55	8.02	2.33	1.00	7.67	1.98	1.00	7.58	1.59	0.10	7.53	1.41
3	0.80	7.74	2.55	1.05	7.62	1.98	1.40	7.59	1.59	0.55	7.93	1.43
4	1.15	7.62	2.26	1.35	7.56	1.89	1.65	7.77	1.60	0.75	7.65	1.44
5	1.50	7.83	2.55	1.55	7.54	1.94	1.90	7.56	1.61	1.70	7.58	1.42
6	1.85	7.93	2.16	2.25	7.74	2.01	2.05	7.61	1.58	3.95	7.79	1.43
7	2.15	7.58	2.36	3.95	7.85	2.00	2.20	7.54	1.61	5.95	6.96	1.39
8	2.55	7.76	2.55	5.40	7.96	1.94	5.00	7.77	1.60	6.30	6.58	1.39
9	3.95	7.83	2.40	5.60	8.03	1.88	6.05	7.32	1.57	6.50	6.39	1.39
10	5.70	7.50	2.32	5.90	7.48	1.98	6.50	6.81	1.60	6.65	6.27	1.40
11	5.95	7.74	2.16	5.95	7.55	1.92	6.70	6.82	1.59	6.85	6.22	1.39
12	6.90	7.58	2.33	6.10	7.54	1.88	6.90	6.82	1.59	7.00	6.15	1.37
13	7.60	7.44	2.16	6.20	7.54	1.89	6.95	6.83	1.54	7.20	6.28	1.37
14	8.05	7.72	2.40	6.30	7.43	1.97	7.25	6.88	1.55	7.50	6.54	1.35
15	9.55	7.55	2.40	6.80	7.33	1.92	7.50	7.00	1.55	8.20	6.85	1.34
16	10.30	7.67	2.34	7.40	7.27	1.87	8.90	7.23	1.53	10.50	7.35	1.34

TABLE NO. 6.1 (Contd)

S.No.		C-1			C-2			C-3			C-4	
	pH	pAg_{tot}	pS_{tot}	pH	pAg_{tot}	pS_{tot}	pH	pAg_{tot}	pS_{tot}	pH	pAg_{tot}	pS_{tot}
17	10.80	7.60	2.39	8.95	7.74	1.94	10.80	7.61	1.55	11.05	7.62	1.36
18	11.20	7.80	2.19	10.70	7.48	2.04	11.10	7.80	1.51	11.40	7.58	1.35
19	11.50	7.81	2.21	10.95	7.75	1.93	11.40	7.68	1.54	11.65	7.78	1.36
20	12.30	7.87	2.40	11.35	7.50	1.88	11.45	7.42	1.55	11.70	7.72	1.35
21	12.95	7.88	2.28	11.65	7.73	1.87	11.50	7.60	1.55	11.70	7.69	1.37
22	–	–	–	12.00	7.54	1.96	11.95	7.58	1.55	11.80	7.70	1.34
23	–	–	–	12.15	7.67	1.96	12.05	7.56	1.54	11.90	7.88	1.34
24	–	–	–	12.30	7.73	1.93	12.20	7.52	1.53	11.95	7.82	1.36
25	–	–	–	–	–	–	12.30	7.60	1.54	12.00	7.80	1.34
26	–	–	–	–	–	–	13.15	7.50	1.54	12.05	7.49	1.35
27	–	–	–	–	–	–	–	–	–	12.30	7.70	1.36
28	–	–	–	–	–	–	–	–	–	13.20	7.98	1.36

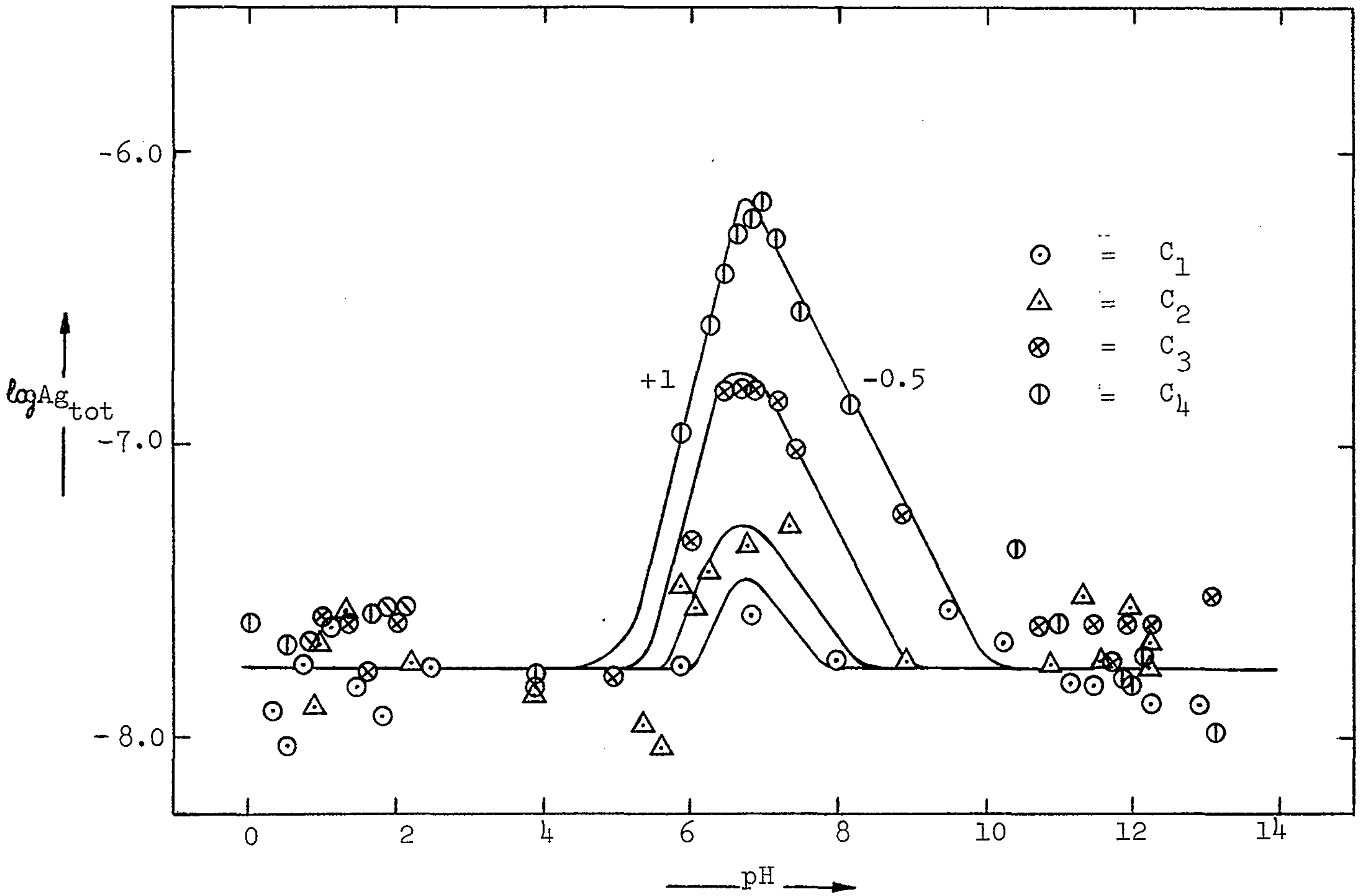


FIGURE 6.1 : Solubility of Ag_2S at Different Excess of S_{tot}, as a Function of pH.

TABLE NO. 6.2

Solubility of Ag_2S in H_2S Medium.

pAg (orig) = 3.27 M μ = 1.0 $NaClO_4$.

S.No	pH	pAg_{tot}	pS_{tot}
1	1.50	7.55	1.08
2	1.60	7.71	1.08
3	1.70	8.05	1.08
4	1.80	7.58	1.05
5	2.10	8.07	1.14
6	2.60	7.96	1.09
7	4.75	7.90	1.08
8	5.10	7.96	1.08
9	5.25	7.82	1.09
10	5.45	8.05	1.10
11	5.50	7.71	1.08
12	5.60	7.41	1.08

TABLE NO. 6.3

Solubility of Ag_2S in Neutral Medium.
Calculation of $p\phi_{20}$ and $p\beta_{20}$ for
Complex $[Ag(HS)_2]^-$

S.No.	pH	pAg_{tot}	pS_{tot}	pAg_c	pS^{-2}	pAg^+	$-p\phi_{20}$	$-p\beta_{20}$
1	7.40	6.66	1.30	6.71	7.50	20.76	43.85	16.89
2	7.43	6.02	0.88	6.03	7.04	20.99	43.90	16.94
3	7.47	5.87	0.77	5.88	6.88	21.07	43.89	16.93
4	7.38	5.66	0.71	5.67	6.93	21.05	44.00	17.04
5	7.40	5.59	0.62	5.59	6.82	21.10	43.95	16.99
6	7.40	5.54	0.55	5.54	6.75	21.14	43.90	16.94
7	7.43	5.39	0.52	5.39	6.68	21.17	44.00	17.04
8 *	7.50	6.54	1.34	6.58	7.42	20.80	44.06	17.10
9 *	7.50	7.00	1.56	7.11	7.64	20.69	43.86	16.90

$$pAg_c = pAg_{tot} - pAg_2\,(HS)(OH)$$

$$-p\phi_{20} = pAg^+ + 2pS^{-2} + 2\,pH - pAg_c = 43.93;\ \sigma = \pm 0.06.$$

$$-p\beta_{20} = -(2\,pk_2 + p\phi_{20}) = 16.97$$

(* Data from C-4 and C-3 Table 6.1.)

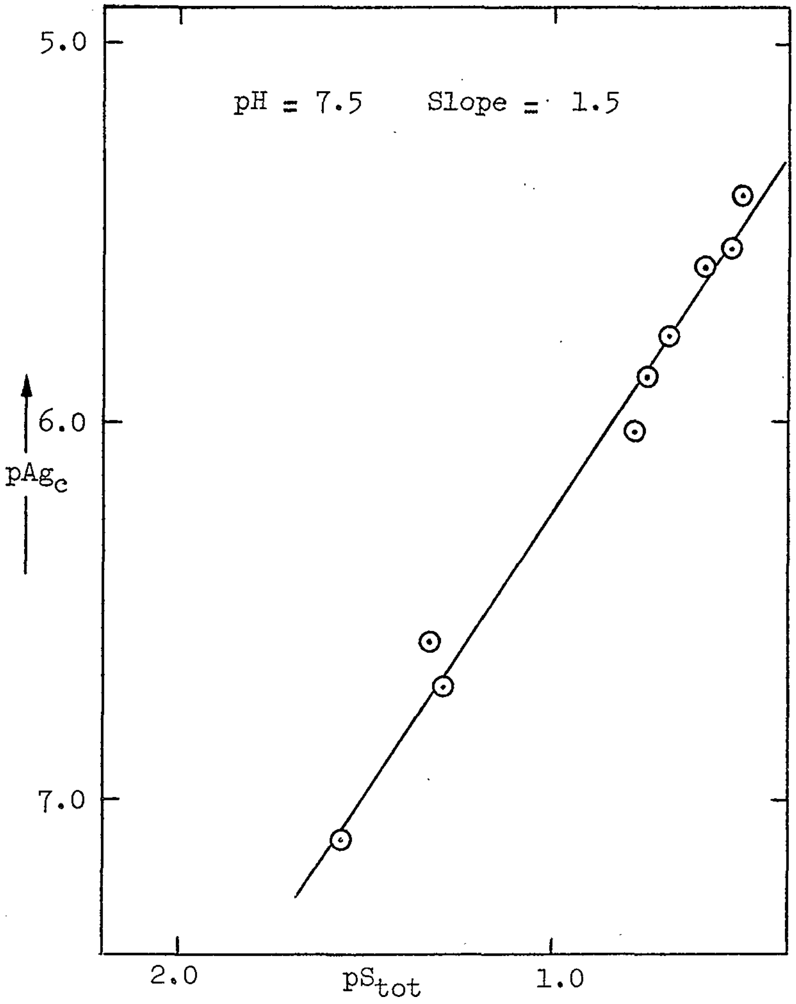


FIGURE 6.2 : Solubility of Ag_2S as a Function of S_{tot} in Neutral Medium.

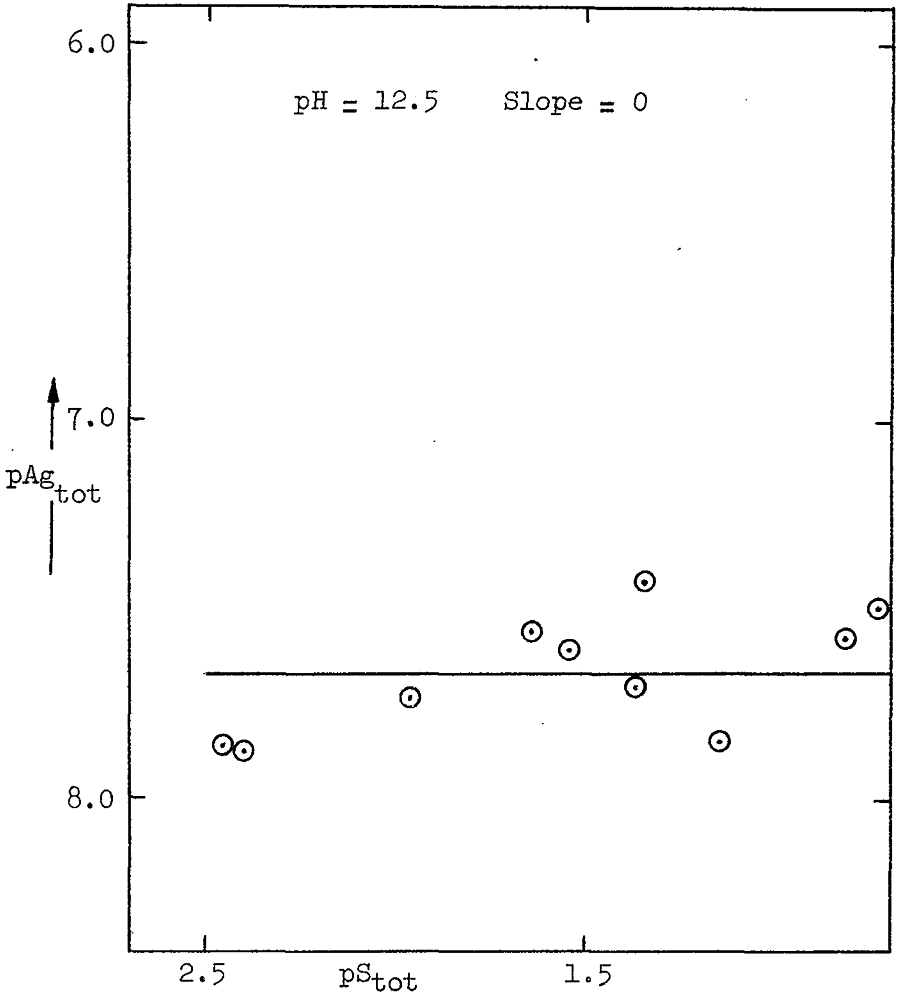


FIGURE 6.3 : Solubility of Ag_2S as a Function of S_{tot} in Alkaline Medium.

TABLE NO. 6.4

Solubility of Ag_2S in Alkaline Medium

Calculation of $p\phi_{11}$ and $p\beta_{11}$ for

Complex $[Ag_2(HS)(OH)]$

S.No	pH	pAg_{tot}	pS_{tot}	$-p\phi_{11}$	$-p\beta_{11}$
1	11.52	7.85	2.46	55.18	41.70
2	12.05	7.55	1.64	55.48	42.00
3	12.40	7.42	1.34	55.61	42.13
4	12.57	7.85	1.14	55.18	41.70
5	13.00	7.57	0.81	55.46	41.98
6	13.10	7.49	0.72	55.54	42.06
7 *	12.30	7.87	2.40	55.16	41.68
8 *	12.30	7.73	1.96	55.30	41.82
9 *	12.30	7.60	1.54	55.43	41.95
10 *	12.30	7.70	1.36	55.33	41.85

$$-p\phi_{11} = -pAg_{tot} + pK_{sp} + pK_w^{**}$$

$$-p\phi_{11} = 55.37 \qquad \sigma = \pm 0.16$$

$$-p\beta_{11} = -(pk_2 + p\phi_{11})$$

$$= 41.89$$

(* Data from C_1, C_2, C_3 and C_4 Table 6.1)

(** pK_w = 14.0, utilized here and in the subsequent calculations)

Discussion of the Results:

There are available now three sets of data on the solubility of silver sulphide under conditions somewhat similar to this study. Treadwell and Hepenstrick (66) have determined the solubility in a H_2S saturated medium (i.e., 0.1 M H_2S) from pH 1 to 7. Schwarzenbach, Gubeli, and Zust (75) have measured it in 0.1 M $NaClO_4$ and at 0.01 M S_{tot} concentration, while Schwarzenbach and Widmer (76) have studied the same at still higher S_{tot} and ionic strength, (1.0 M $NaClO_4$ and 0.02 M S_{tot}) . From the available data the average Ag_{tot} in pH region 1 - 4, are tabulated below.

	Author	Ag_{tot} (average) pH (1-4)	$\frac{\Delta \log Ag_{tot}}{\Delta \log S_{tot}}$	
1.	Treadwell and Hepenstrick	1.4×10^{-6}M	2.68	(1,2)
2.	Schwarzenbach, Gubeli, and Zust	3.0×10^{-9}M	4.00	(1,3)
3.	Schwarzenbach and Widmer	1.84×10^{-9}M		

In this pH region S_{tot} is essentially in the form of H_2S, so these authors have assumed that the complex formation proceeds as

$$(Ag_2S) + (H_2S) \rightleftharpoons 2\,(Ag(HS))$$

Since in their determinations H_2S is the only difference, one may expect that this postulated complex will show a slope of 0.5 as a function of S_{tot}, in accordance with the theoretical possibility. However, the variations of Ag_{tot} with S_{tot} calculated from their data hardly agree with the postulated species. Another striking observation is that in the two determinations of Schwarzenbach et al., the Ag_{tot} is lowered when S_{tot} is increased in the medium and this is contrary to the principle of complex formation.

We, therefore, concluded that the data from Schwarzenbach et al. (75), (76) have the same solubility with the minor difference being due to the experimental fluctuations, and the data from Treadwell and Hepenstrick (66) are unusually high, possibly due to some experimental error. This was soon proved to be the case when on redetermination in H_2S medium by the radiometric method, the solubility of Ag_2S was found to be of the same order as in normal NaHS precipitations (cf. table 6.2). It is reasonable to conclude now that the complex that predominates the solubility equilibria in acidic pH regions is independent of both the pH and S_{tot}. Of course the same argument stands for the alkaline pH regions as well, where the Ag_2S solubility attains the same value as in the acidic medium. The complex that satisfies these conditions is the species $Ag_2(HS)(OH)$, which may be formed by the reaction,

$$(Ag_2S) + (H_2O) \rightleftharpoons (Ag_2(HS)(OH))$$

The fact that the Ag_2S solubility in acidic medium remains constant even at considerably increased S_{tot} concentration (figure 6.1) clearly proves that H_2S is too weak a ligand to form coordination complexes. In fact aqueous molecular complexes of this sort have so far not been proved unambiguously. The solubilities found in this study are slightly higher than the results of Schwarzenbach et al. but are in good agreement with the data of Ol'Shanskii et al. (77), who have also made radiometric investigations on the Ag_2S solubilities at 25°C in a H_2S saturated medium.

The species HS^-, becomes the predominent constituent in H_2S equilibria after pH 6, i.e. near the pk_1 of the acid. If the solubility of a sparingly soluble sulphide increases in neutral conditions, it is possible to correlate this characteristic property to thio-complexing with HS^- as the coordinating ligand. The solubility of the system Ag_2S, in fact, increases in neutral pH regions, thereby confirming the formation of a thio-complex of this sort. The experimental slopes of the solubility fully conform to the theoretical species, $Ag(HS)_2^-$, without reservation. Schwarzenbach and Widmer (76) have also identified the same complex as the principal species in their study on silver sulphide and even the values of the formation constant for this complex in the two studies are in close agreement.

In alkaline medium even with an increase in the concentration of S_{tot} several times higher than the concentrations employed by Schwarzenbach et al., our observation is very much in disagreement with their findings. We have not found any increase in the Ag_2S solubility to predict the formation of some other higher thio-complexes of silver with HS^- or S^{-2} as the ligands. On the other hand they have not only observed an increase in the solubility but have defined the constitutions of the complexes as well, such as AgS^-, $Ag_2S_3H_2^{-2}$, and AgS_2^{-3}. If these were true, the formation of any one of these complexes would have exhibited the characteristic solubility slopes. The fact remains that the earlier authors have studied this system only at one excess of S_{tot} and predicted the formation of thio-complexes in solution. We have scrupulously investigated at several higher increments of the S_{tot} and still nothing conspicuous has been noticed which may indicate the formation of higher complexes in alkaline medium. The only difference in the experimental technique in both the studies has been the use of ammine buffers. Schwarzenbach et al. have employed buffers to control the pH of the medium, while in this study the medium was kept free of buffers and the pH's were controlled with $HClO_4$, NaOH solutions. It is therefore possible that the presence of ammine buffers leads to somewhat increased Ag_2S solubility thereby permitting erroneous conclusions for the higher thio-complexes. In conclusion it is worth pointing out that in an unbuffered medium of controlled ionic strength only two aqueous complexes $Ag_2(HS)(OH)$ and $Ag(HS)_2^{-2}$ predominate the silver sulphide system. Nevertheless the basic idea stands well proved that in spite of its low aqueous solubility, Ag_2S does form soluble coordination complexes.

The System HgS:

The solubility results of HgS over the entire pH range at three different S_{tot} in excess are given in table 6.5 and shown in fig. 6.4. The solubility curves exhibit two distinct changes in neutral and alkaline conditions. The slopes in these pH regions of interest, as a function of S_{tot}, are plotted in fig. 6.5 and 6.6 respectively.

Interpretation of the Solubility Results:

The solubility curves in this case can be divided into three pH zones; pH (1 - 5), pH (5 - 7.5), and pH (8 - 10.5), where the Hg_{tot} progressively changes in the solution. In the first zone of pH, the solubility remains unaffected even with an increase of S_{tot}. Thus we have once again a complex that is independent of the experimental variables. In the second zone of pH, the Hg_{tot} increases initially and soon attains a slope of zero around pK_1 of H_2S; also it has a slope of one as a function of S_{tot}. In other words the new complex has one sulphide ion more than the previous species. In the third pH zone the solubility still increases further with a slope of one both as a function of pH and S_{tot}, which indicates that although the

TABLE NO. 6.5

Solubility of HgS at Different pH and pS_{tot}.

pHg_{tot} (orig) = 3.30 M μ = 1.0 $NaClO_4$.

S.No.	pH	C-1 pHg_{tot}	pS_{tot}	pH	C-2 pHg_{tot}	pS_{tot}	pH	C-3 pHg_{tot}	pS_{tot}
1	0.25	8.05	2.13	0.20	7.92	1.38	0.30	7.52	1.18
2	0.45	7.45	2.01	0.40	7.93	1.37	0.40	7.76	1.09
3	1.00	7.70	2.11	0.85	7.97	1.69	0.70	7.60	1.09
4	1.60	7.45	2.04	0.90	7.59	1.43	0.95	7.66	1.15
5	2.20	8.10	2.06	1.10	7.70	1.54	1.15	8.00	1.28
6	2.50	7.44	2.09	1.35	7.97	1.40	1.55	8.02	1.32
7	2.62	7.55	2.23	1.60	7.98	1.67	1.80	7.89	1.27
8	2.75	7.64	2.05	2.30	7.68	1.42	1.87	7.97	1.37
9	3.00	7.72	2.31	3.20	8.00	1.65	2.07	8.16	1.29
10	3.05	8.19	2.07	3.27	8.00	1.65	3.15	8.12	1.35
11	3.22	8.02	2.33	5.55	7.42	1.56	5.22	7.44	1.13
12	3.47	8.08	2.33	5.87	7.22	1.66	5.80	6.97	1.09
13	5.25	7.80	2.24	5.97	7.14	1.43	5.85	7.12	1.08
14	5.67	7.60	2.37	6.05	6.95	1.35	5.90	6.74	1.12

TABLE NO. 6.5 (Contd)

		C-1			C-2			C-3	
S.No.	pH	pHg_{tot}	pS_{tot}	pH	pHg_{tot}	pS_{tot}	pH	pHg_{tot}	pS_{tot}
15	5.80	7.61	2.23	6.20	6.84	1.36	6.00	6.76	1.09
16	5.85	7.81	2.31	6.25	7.04	1.44	6.09	6.67	1.09
17	5.95	8.13	2.07	6.35	6.90	1.39	6.25	6.57	1.25
18	6.05	7.97	2.00	6.45	6.82	1.53	6.30	6.42	1.08
19	6.40	7.97	2.13	6.60	6.87	1.40	6.40	6.42	1.16
20	6.75	7.86	2.11	6.70	6.70	1.49	6.45	6.52	1.06
21	6.95	7.76	2.00	6.75	6.76	1.36	6.50	6.50	1.02
22	7.20	7.53	2.00	6.80	6.88	1.42	6.60	6.52	1.05
23	7.30	7.80	2.02	6.85	6.95	1.35	6.65	6.52	1.07
24	7.80	7.48	2.02	6.87	6.92	1.45	6.72	6.52	1.02
25	8.15	7.17	1.96	6.90	6.85	1.40	6.80	6.56	1.05
26	9.40	5.67	1.98	6.95	6.80	1.33	6.82	6.62	1.02
27	9.70	5.35	2.00	6.97	6.86	1.34	6.97	6.61	1.03
28	10.10	4.93	2.02	7.00	6.97	1.35	7.10	6.67	1.02
29	10.15	4.89	2.01	7.02	6.89	1.33	7.45	6.63	1.02
30	10.45	4.61	1.96	7.05	6.82	1.34	7.67	6.56	1.02

TABLE NO. 6.5 (Contd)

S.No.	C-1			C-2			C-3		
	pH	pHg_{tot}	pS_{tot}	pH	pHg_{tot}	pS_{tot}	pH	pHg_{tot}	pS_{tot}
31	10.60	4.50	2.10	7.10	6.81	1.33	7.72	6.45	1.02
32	10.75	4.32	2.01	7.15	6.89	1.35	7.95	6.05	1.01
33	10.80	4.26	2.02	7.35	6.74	1.34	8.27	5.91	1.02
34	11.00	4.14	1.98	7.47	6.64	1.33	8.70	5.47	1.02
35	11.05	4.01	2.01	7.60	6.65	1.33	9.27	4.90	1.02
36	11.10	4.07	1.93	7.75	6.42	1.30	9.40	4.77	1.00
37	11.15	4.00	1.98	7.85	6.34	1.32	9.65	4.46	1.02
38	11.20	3.95	1.94	8.20	6.09	1.32	9.72	4.36	1.01
39	11.30	3.87	1.95	8.30	6.00	1.32	10.20	3.87	1.02
40	11.45	3.76	1.96	8.80	5.39	1.33	10.30	3.75	1.00
41	11.53	3.70	1.96	9.80	4.64	1.33	10.40	3.68	1.00
42	11.55	3.67	1.97	9.85	4.57	1.32	10.55	3.52	1.00
43	11.60	3.62	2.09	10.32	4.00	1.30	10.70	3.40	1.02
44	11.75	3.52	2.02	10.67	3.69	1.32	10.75	Soluble	—
45	—	—	—	10.92	3.50	1.30	10.95	Soluble	—
46	—	—	—	10.99	Soluble	—		—	—

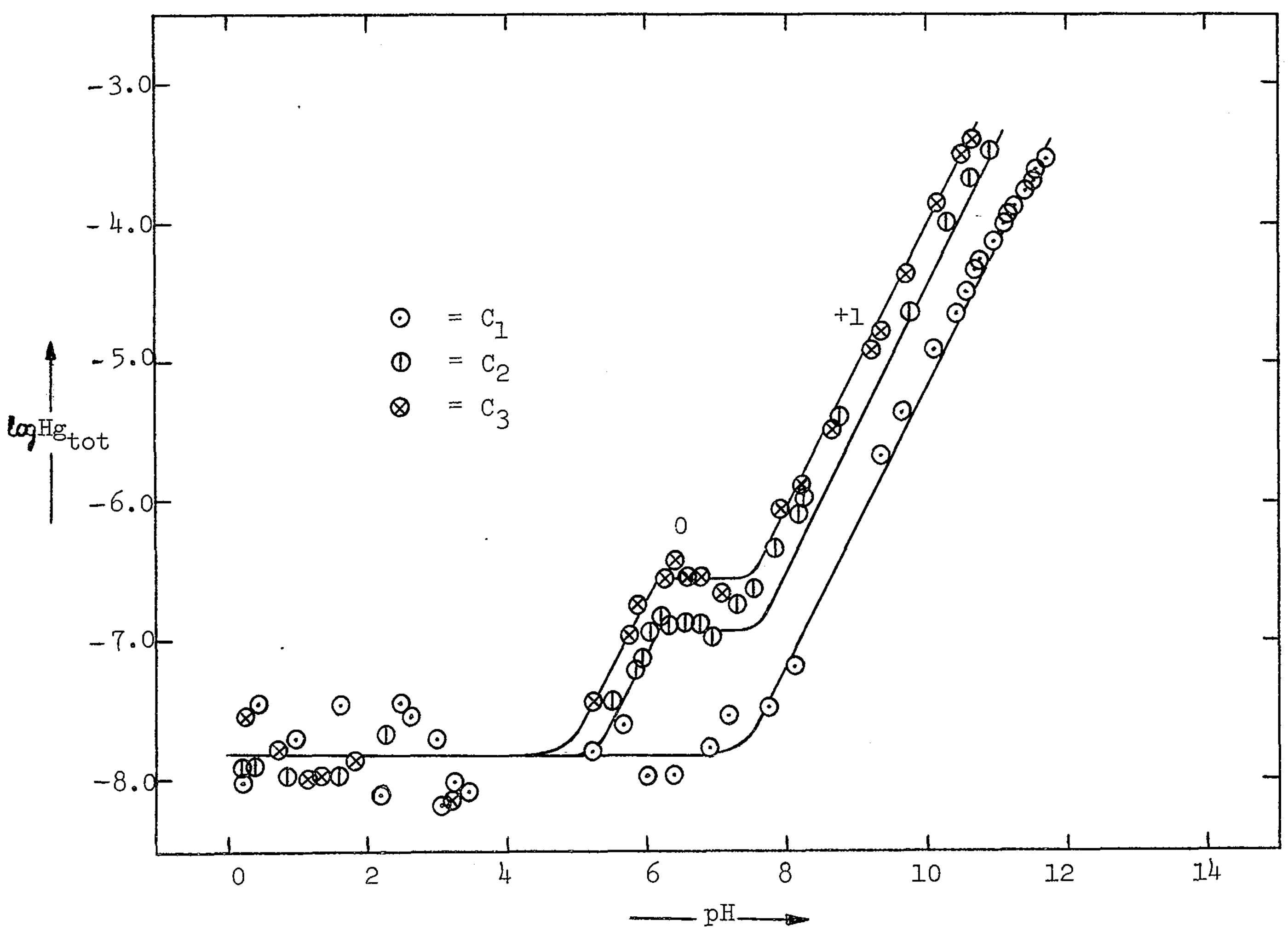


FIGURE 6.4 : Solubility of HgS at Different pH and S_{tot}.

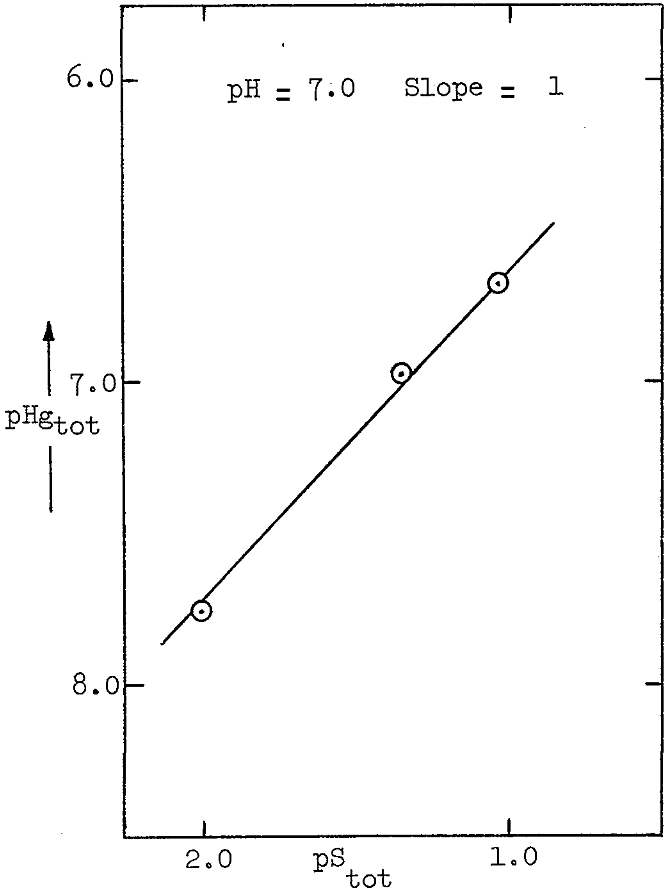


FIGURE 6.5 : Hg$_{tot}$ as a Function of S$_{tot}$.

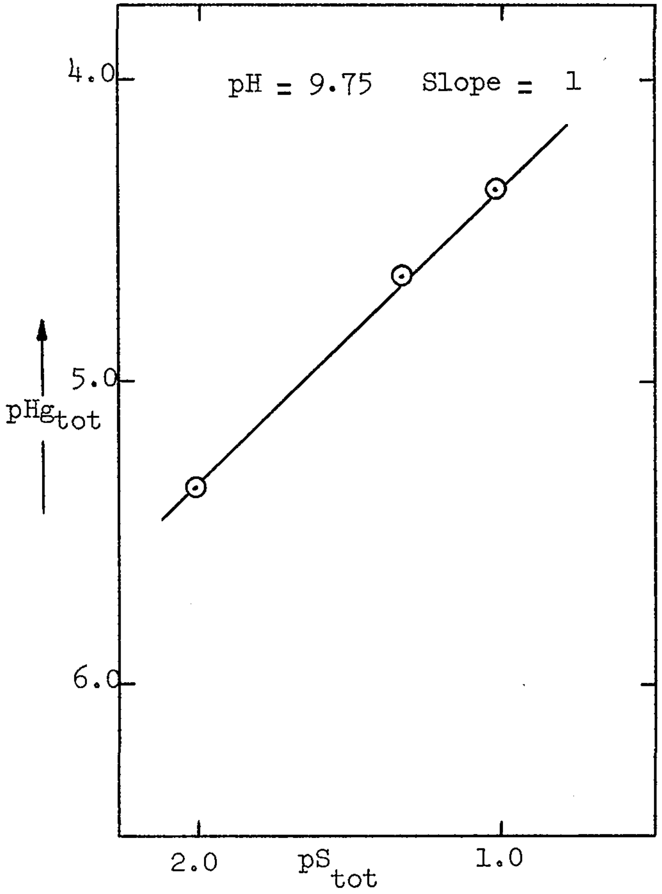


FIGURE 6.6 : Hg$_{tot}$ as a Function of S$_{tot}$.

sulphur association remains the same, there is an increase of one OH^- ion in the complex now formed. Comparison of this data with the theoretical possibilities (table(2.2))at once identifies the following species.

$(Hg(HS)(OH))$ stable, pH 1 - 5.
$(Hg(HS)_2(OH))^-$ stable, pH 5 - 7.5.
$(Hg(HS)_2(OH)_2)^{-2}$ stable, pH 8 - 10.5

Calculation of the Formation Constants:

$(Hg(HS)(OH))$:

The calculations for the formation constant of this complex are tabulated in 6.6 .

$$\phi_{11} = \frac{(Hg(HS)(OH))}{(Hg^{+2}).(H^+).(S^{-2}).(OH^-)}$$

$$= \frac{Hg_{tot}}{K_{sp}.K_w}$$

$$-p\phi_{11} = 58.10 \qquad \sigma = \pm 0.23$$

$$\beta_{11} = \frac{(Hg(HS)(OH))}{(Hg^{+2}).(HS^-).(OH^-)}$$

$$-p\beta_{11} = -(pk_2 + p\phi_{11}) = 44.62.$$

$(Hg(HS)_2(OH)_2)^{-2}$:

Selecting the experimental points from the solubility slope at pH when the contribution of other complexes is negligible, gives the concentration of this complex. The data from the solubility curves where the

TABLE NO. 6.6

Calculation of $p\phi_{11}$ and $p\beta_{11}$ for
Complex [Hg(HS)(OH)]: (Experimental Data pH 0-4)
(Curves C_1, C_2 and C_3 Table 6.5).

pH	C-1 pHg_{tot}	$-p\phi_{11}$	pH	C-2 pHg_{tot}	$-p\phi_{11}$	pH	C-3 pHg_{tot}	$-p\phi_{11}$
0.25	8.05	57.89	0.20	7.92	58.02	0.30	7.52	58.42
0.45	7.45	58.49	0.40	7.93	58.01	0.40	7.76	58.18
1.00	7.70	58.24	0.85	7.97	57.97	0.70	7.60	58.34
1.60	7.45	58.49	0.90	7.59	58.35	0.95	7.66	58.28
2.20	8.10	57.84	1.10	7.70	58.24	1.15	8.00	57.94
2.50	7.44	58.50	1.35	7.97	57.97	1.55	8.02	57.92
2.62	7.55	58.39	1.60	7.98	57.96	1.80	7.89	58.05
2.75	7.64	58.30	2.30	7.68	58.26	1.87	7.97	57.97
3.00	7.72	58.22	3.20	8.00	57.94	2.07	8.16	57.78
3.05	8.19	57.75	3.27	8.00	57.94	3.15	8.12	57.82
3.22	8.02	57.92	—	—	—	—	—	—
3.47	8.08	57.86	—	—	—	—	—	—

$-p\phi_{11} = -pHg_{tot} + pK_{sp} + pK_w = 58.10 \quad \sigma = \pm 0.23.$

$-p\beta_{11} = -(pk_2 + p\phi_{11}) = 44.62.$

slope of one as a function of pH and S_{tot} is well formed, can be attributed to this complex. Table 6.7 gives the calculations of this species from the three solubility curves (table 6.5).

$$\phi_{22} = \frac{(Hg(HS)_2\ (OH)_2)^{-2}}{(Hg^{+2}).(S^{-2})^2.(H^+)^2.(OH^-)^2}$$

$$= \frac{(Hg_{tot})}{K_{sp}.\ K_w^2.\ \ (S^{-2})}$$

$$-p\phi_{22} = -pHg_{tot} + pK_{sp} + pS^{-2} + 2\ pK_w$$

$$-p\phi_{22} = 80.33 \qquad \sigma = \pm 0.06.$$

$$\beta_{22} = \frac{(Hg(HS)_2(OH)_2)^{-2}}{(Hg^{+2}).(HS^-)^2.(OH^-)^2}$$

$$-p\beta_{22} = -(2pk_2 + p\phi_{22})$$

$$= 53.37.$$

$(Hg(HS)_2(OH)^-)$:

This complex is formed in near neutral conditions when the solubility slope after an initial increase attains a limiting slope of zero around pk_1. The data for this complex are selected from curves 2 and 3 (fig. 6.4), since it is not formed appreciably at S_{tot} concentration in curve 1. As Hg_{tot} is the sum of all the complexes in this pH region, the concentration of this species is therefore found by the algebric difference of the concentrations of other two complexes from the Hg_{tot}. The concentration of the other two species is found from the knowledge of their formation constants calculated above.

TABLE NO. 6.7

Complex $[Hg(HS)_2(OH)_2]^{-2}$, $p\phi_{22}$ and $p\beta_{22}$.

(Experimental Data from all the Curves table 6.5).

S.No.	pH	pHg_{tot}	pS_{tot}	pS^{-2}	$-p\phi_{22}$
C-1					
27	9.70	5.35	2.00	5.78	80.37
28	10.10	4.93	2.02	5.40	80.41
29	10.15	4.89	2.01	5.34	80.39
30	10.45	4.61	1.96	4.99	80.32
31	10.60	4.50	2.10	4.98	80.42
32	10.75	4.32	2.01	4.74	80.36
33	10.80	4.26	2.02	4.70	80.38
34	11.00	4.14	1.98	4.46	80.26
35	11.05	4.01	2.01	4.44	80.37
36	11.10	4.07	1.98	4.31	80.18
37	11.20	3.95	1.94	4.22	80.21
38	11.30	3.87	1.95	4.13	80.20
C-2					
41	9.80	4.64	1.33	5.01	80.31
42	9.85	4.57	1.32	4.95	80.32
43	10.32	4.00	1.30	4.46	80.40
44	10.67	3.69	1.32	4.13	80.38
45	10.92	3.50	1.30	3.86	80.30
C-3					
37	9.65	4.46	1.02	4.85	80.33
38	9.72	4.36	1.01	4.77	80.35
39	10.20	3.87	1.02	4.30	80.37
40	10.30	3.75	1.00	4.18	80.37
41	10.40	3.68	1.00	4.08	80.34
42	10.55	3.52	1.00	3.93	80.35
43	10.70	3.40	1.02	3.79	80.33

$$- p\phi_{22} = - pHg_{tot} + pK_{sp} + pS^{-2} + 2\ pK_{w} = 80.33; \sigma = \pm 0.06.$$

$$- p\beta_{22} = -(2\ pk_{2} + p\phi_{22}) = 53.37.$$

$$Hg_{tot} = (Hg(HS)(OH)) + (Hg(HS)_2(OH)^-) + (Hg(HS)_2(OH)_2^{-2})$$

$$(Hg(HS)_2(OH)^-) = Hg_{tot} - \phi_{11}.K_{sp}.K_w - \phi_{22}.K_{sp}.K_w^2.(S^{-2})$$

$$\phi_{21} = \frac{(Hg(HS)_2(OH)^-)}{(Hg^+)^2.(H^+)^2.(S^{-2})^2.(OH^-)}$$

$$= \frac{Hg_{tot} - \phi_{11}.K_{sp}.K_w - \phi_{22}.K_{sp}.K_w^2.(S^{-2})}{K_{sp}.K_w.(H^+).(S^{-2})}$$

$$-p\phi_{21} = 74.11 \quad \sigma = \pm 0.17$$

$$\beta_{21} = \frac{(Hg(HS)_2(OH)^-)}{(Hg^{+2}).(HS^-)^2.(OH^-)}$$

$$-p\beta_{21} = -(2pk_2 + p\phi_{21})$$

$$= 47.15.$$

Calculated results are tabulated in 6.8.

Discussion of the Results:

The equilibrium solubilities given in table 6.5 are much higher than those could be due to the ionic species in solution, and these suggest that aqueous complexes are also present in the HgS system.

In the first zone of pH discussed earlier, the complex formation reaction may be written as

$$(HgS) + H_2O \rightleftharpoons (Hg(HS)(OH))$$

$$(Hg(HS)(OH)) = Hg_{tot}$$

This observation is parallel to the solubility trend found in case of Ag_2S, which means that the first step in complex formation in sparingly

TABLE NO. 6.8

The Complex $[Hg(HS)_2(OH)^-]$, $p\phi_{21}$ and $p\beta_{21}$

(Experimental Data from Curve 2 and 3, table 6.5)

C.No.	pH	pHg_{tot}	pS_{tot}	pS^{-2}	pHg_c	$-p\phi_{21}$
<u>C-2</u>						
21	6.75	6.76	1.36	8.47	6.82	74.34
22	6.80	6.88	1.42	8.45	6.96	74.23
23	6.85	6.95	1.35	8.31	7.07	74.03
24	6.87	6.92	1.45	8.38	7.02	74.17
25	6.90	6.85	1.40	8.28	6.94	74.18
26	6.95	6.80	1.33	8.15	6.90	74.14
27	6.97	6.86	1.34	8.12	6.98	74.05
28	7.00	6.97	1.35	8.08	7.12	73.90
29	7.02	6.89	1.33	8.03	7.04	73.95
30	7.05	6.82	1.34	8.00	6.95	74.04
31	7.10	6.81	1.33	7.92	6.95	74.01
32	7.15	6.89	1.35	7.87	7.09	73.87
<u>C-3</u>						
22	6.60	6.52	1.05	8.41	6.56	74.39
23	6.65	6.52	1.07	8.34	6.56	74.37
24	6.72	6.52	1.02	8.18	6.57	74.27
25	6.80	6.56	1.05	8.09	6.62	74.21
26	6.82	6.62	1.02	8.02	6.69	74.09
27	6.97	6.61	1.03	7.81	6.71	74.01
28	7.10	6.67	1.02	7.61	6.86	73.79

$$- p\phi_{21} = -pHg_c + pK_{sp} + pK_w + pH + pS^{-2}$$

$$= 74.11 \quad \sigma = \pm 0.17$$

$$- p\beta_{21} = - (2pk_2 + p\phi_{21})$$

$$= 47.15.$$

soluble sulphides is the formation of a mixed hydroxy species in the system as a whole.

In concomitance with the increasing HgS solubility in pH regions close to pk_1, we may predict the formation of a new complex that becomes predominent over the previous one. Since HS^- is the complex forming ligand in this pH region, the new complex, evidently, incorporates additional HS^- ions. The reaction may be written as,

$$(Hg(HS)(OH)) + x(HS^-) \rightleftharpoons (Hg(HS)_x(OH))^{-x}$$

Fig. 6.5 shows that the solubility slope in this pH region as a function of S_{tot} is one, i.e. only one HS^- enters the complex; hence in equation above the value of x is also one. The constitution of the complex may therefore be expressed as, $Hg(HS)_2(OH)^-$. This complex is justified both theoretically and experimentally. The formation of this mixed hydroxy species is certain, otherwise the presence of the solubility plateau in neutral pH region is difficult to explain fully. It is interesting to compare this observation with that of Schwarzenbach and Widmer (74), who have postulated the constitution of the complex in this region as Hg(HS)S. The complex proposed here may also be written as $Hg(HS)S.H_2O$ i.e. a hydrated form. If the form Hg(HS)S is considered the solubility of the system after pk_1 should decrease with a slope of one till pk_2 of H_2S. On the contrary our three observations have shown that the horizontal slope persists in this region, which strongly confirms the formation of complex $Hg(HS)_2(OH)^-$. Evidently the experimental results are best explained by assuming the formation of a mixed hydroxy species.

Further, a third complex must also be presumed in a more alkaline medium beyond pH 8, to account for the continuous increase in the HgS solubility.

Since HS^- is still the principal complex forming ligand, it is unlikely that the new complex incorporates any additional HS^- ions and furthermore the solubility slope as a function of S_{tot} still remains one (fig. 6.6). However, the charge of the complex is definitely raised by one unit since the solubility increases with a slope of one as a function of pH. The only change in the medium that can be perceived is the presence of free OH^- ions because of the increased alkalinity. It is therefore reasonable to infer that the free OH^- ions participate further in the complex formation. The reaction for the formation of the new species can be represented as,

$$(Hg(HS)_2(OH)^-) \;+\; (OH^-) \;\rightleftharpoons\; (Hg(HS)_2(OH)_2^{-2})$$

From these observations it appears that in the HgS system a stepwise complex formation occurs depending upon the pH of the medium.

$$(Hg(HS)(OH)) \;+\; (HS^-) \;\underset{\sim 5}{\overset{pH}{\rightleftharpoons}}\; (Hg(HS)_2(OH)^-) \;+\; (OH^-) \;\underset{\sim 8}{\overset{pH}{\rightleftharpoons}}\; (Hg(HS)_2(OH)_2^{-2})$$

Our interpretation of the last mentioned complex also differs with the assumptions of the other authors. The form HgS_2^{-2} has been proposed for this complex (72)(73); we can represent the complex as $HgS_2^{-2}.2H_2O$, i.e. a dihydrated species. Earlier in the silver selenite studies it has been proved (chapter V) that when pure SeO_3^{-2} complexing occurs the pH effect becomes negligible and the solubility slopes assume a slope of zero as a function of pH as pH > pk_2. On this reasoning one may conclude that perhaps the complex HgS_2^{-2} may be possible at higher sulphide concentrations when pH > pk_2 of H_2S. But in the limited sulphide concentration range, as in this study, where the pH effect is still very pronounced, the experimental data is fully explained by assuming a mixed hydroxy complexing with the ligand HS^-.

Our solubility data on HgS are in close agreement with those of Schwarzenbach and Widmer (74) but are lower than those of Treadwell and

Schaufelberger (67) at about the same S_{tot} employed by these authors. It is possible the experimental technique adopted by the latter authors leads to somewhat higher solubilities as was shown in Ag_2S studies. It is abundantly clear now that both in Hg and in Ag sulphides, the formation of a thio-hydroxy complex, in the initial phase of precipitation, remains a definite step in their solubility equilibria. This observation contradicts some of the earlier results, e.g. the formation of complex $Hg(HS)_2$ in acidic medium (74). It has been shown theoretically (chapter - II) that such a complex shall be independent of pH in regions before the pk_1 of H_2S but a characteristic slope of one as a function of S_{tot} at constant pH, will confirm its formation. The necessity of investigations at different excess of S_{tot} can well be appreciated now; otherwise, a wrong set of assumption completely invalidates the best experimental effort. It may be argued further that mixed hydroxy complex formation is a characteristic property of the HgS system as a whole. Pure thio-complexing does occur in Ag_2S system inspite of the initial mixed hydroxy complex formation. However, the HgS system has a different behaviour and the experimental data can best be explained only by assuming a series of mixed hydroxy complexes in the equilibrium.

Recently Barnes et al. (69) have reported the formation of mercury thio-complexes involving molecular H_2S. This is definitely the first study of this kind in liquid H_2S medium and the results certainly are interesting. However, a comparison of this study with their results is not possible because of the different experimental conditions in both the cases. Their measurements have been carried out essentially at zero ionic strength, whereas it is one molar in the present case. Nevertheless, it may be pointed out that these authors have studied the HgS equilibria only at one excess of S_{tot} and based their conclusions on complex formation in combination with other published data (74). This introduces a certain amount of ambiguity since it has been shown above that some of the conclusions in the earlier work are open to question.

The Transition Metal Sulphides:

MnS, FeS, and CoS:

The solubility data of the individual sulphides at different S_{tot} in excess and over the entire pH range are given in table 6.9, 6.12, and 6.15, respectively. The data are also shown graphically in fig. 6.7, 6.8, and 6.9 respectively. The solubility behaviour is very similar in all the three cases. The solubility curves show a slope of -2 in the initial phase of precipitation, followed by a horizontal slope of zero over the rest of the pH scale, except for the CoS. The cobalt sulphide system has somewhat increased solubility in the neutral pH regions.

Interpretation of the solubility curves is simple in this case. The slope of -2 indicates the presence of free metal ions in the medium in contact with the solid sulphide. The slope of zero signifies, as before, a complex independent of the experimental variables, pH and S_{tot}. The formula may be written as M(HS)(OH), where M is Mn^{+2}, Fe^{+2}, or Co^{+2}.

The CoS has higher solubility in the pH regions where HS^- becomes the predominent species in the aqueous equilibria of H_2S. Apparently the HS^- complexing leads to increased Co_{tot} in the solutions. The nature of this complex was ascertained by studying the CoS solubility at still higher increments of S_{tot} in the neutral pH regions. The experimental data shown in

TABLE NO. 6.9

Solubility of MnS at Different pH and pS$_{tot}$

pMn$_{tot}$ (orig) = 3.07 M μ = 1.0 NaClO$_4$.

S.No.	pH	C-1	pS$_{tot}$	pH	C-2	pS$_{tot}$	pH	C-3	pS$_{tot}$
		pMn$_{tot}$			pMn$_{tot}$			pMn$_{tot}$	
1	4.40	3.08	1.74	5.70	3.07	1.50	5.24	3.07	1.48
2	5.78	3.09	1.76	6.16	3.40	1.52	5.78	3.08	1.32
3	6.22	3.35	1.73	6.24	3.54	1.49	6.12	3.69	1.32
4	6.24	3.44	1.74	6.25	3.60	1.50	6.26	3.91	1.32
5	6.28	3.52	1.75	6.38	3.88	1.52	6.34	4.03	1.37
6	6.32	3.61	1.71	6.50	4.04	1.50	6.46	4.09	1.34
7	6.36	3.66	1.71	6.56	4.03	1.48	6.52	4.27	1.34
8	6.38	3.71	1.74	6.57	4.19	1.50	6.72	4.50	1.34
9	6.42	3.68	1.75	6.68	4.36	1.49	6.82	4.67	1.35
10	6.46	3.74	1.72	6.76	4.48	1.50	6.96	4.86	1.34
11	6.50	3.83	1.71	6.80	4.67	1.49	7.10	5.07	1.32
12	6.52	3.90	1.72	6.90	4.68	1.46	7.28	5.31	1.31
13	6.54	3.99	1.74	6.90	4.74	1.49	7.32	5.39	1.32
14	6.62	4.06	1.74	6.96	4.81	1.50	7.54	5.53	1.33

TABLE NO. 6.9 (Contd)

S.No.	pH	C-1	pS$_{tot}$	pH	C-2	pS$_{tot}$	pH	C-3	pS$_{tot}$
		pMn$_{tot}$			pMn$_{tot}$			pMn$_{tot}$	
15	6.66	4.12	1.72	7.06	4.90	1.47	7.64	5.66	1.31
16	6.72	4.26	1.74	7.08	4.96	1.46	7.96	5.83	1.32
17	6.76	4.42	1.71	7.16	4.98	1.51	8.22	6.09	1.31
18	6.86	4.48	1.72	7.28	5.12	1.48	9.86	6.23	1.32
19	6.98	4.66	1.72	7.44	5.40	1.47	11.52	6.44	1.32
20	7.58	5.47	1.68	8.16	5.75	1.45	11.72	6.43	1.31
21	9.06	5.85	1.71	9.50	5.96	1.47	12.72	6.38	1.32
22	9.30	6.34	1.81	10.86	6.40	1.48	13.30	6.50	1.31
23	10.84	6.17	1.74	11.58	6.10	1.50	13.62	6.43	1.30
24	11.38	6.43	1.76	12.66	6.17	1.47	13.76	6.27	1.25
25	12.54	6.02	1.72	13.16	6.04	1.47	13.95	5.99	1.30
26	13.10	6.06	1.69	13.90	6.02	1.50	—	—	—
27	13.10	5.93	1.64	13.95	6.01	1.48			
28	13.84	6.01	1.72	—	—	—			
29	13.96	5.85	1.68						
30	13.98	5.94	1.71						

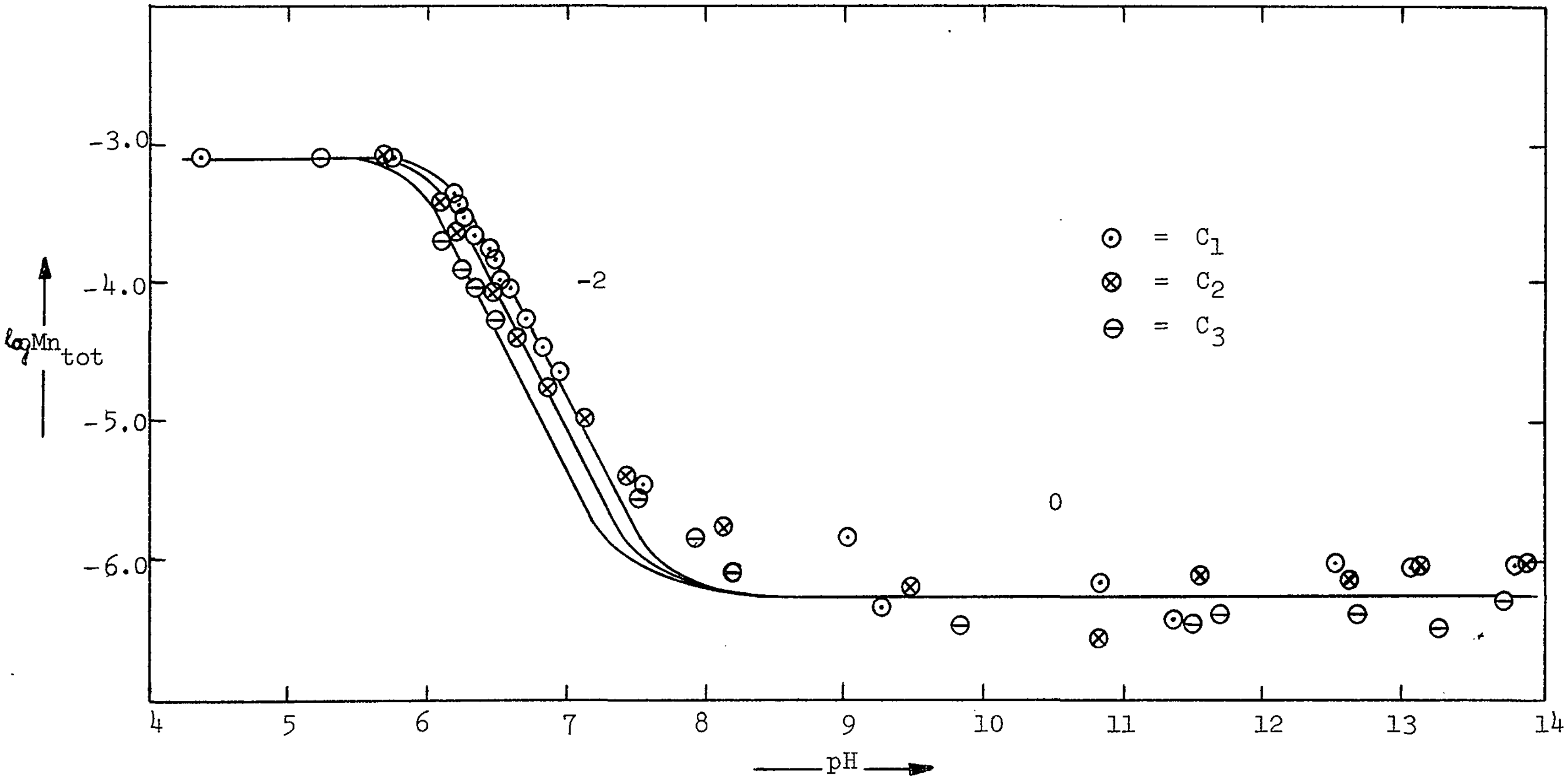


FIGURE 6.7 : Solubility of MnS at Different pH and S_{tot}.

fig. 6.10, indicate that the CoS solubility increases as a function of S_{tot} with a slope of −3. The curve of highest solubility for CoS as a function of pH (cf. fig. 6.9) shows a slope of +2 and -1 before and after pk_1 of H_2S. Comparison of these data with the theoretical possibility (table 2.2) confirms the formation of complex $Co(HS)_4^{-2}$ in this system.

Calculation of the Formation Constants:

The Solubility Product Constants:

The experimental data where the sulphide solubility curves show a slope of -2 with respect to pH give the concentration of the free metal ions in equilibrium. From the knowledge of S_{tot}, the concentration of the free S^{-2} ions can be calculated with the help of the two ionization constants of the H_2S discussed earlier (chapter IV). The solubility product constant is then evaluated by the simple product of these two factors.

$$(M^{+2}) \cdot (S^{-2}) = K_{sp}$$

when pH < 5.

$$(M^{+2}) = M_{tot}$$

$$(S^{-2}) = \frac{S_{tot} \cdot k_1 . k_2}{(H^+)^2}$$

when pH > 5.

$$(S^{-2}) = \frac{S_{tot} \cdot k_1 . k_2}{(H^+)^2 + k_1 (H^+)}$$

For FeS and CoS

$$K_{sp} = \frac{Fe_{tot} . S_{tot} . k_1 . k_2}{(H^+)^2}$$

$$K_{sp} = \frac{Co_{tot} . S_{tot} . k_1 . k_2}{(H^+)^2}$$

For MnS

$$K_{sp} = \frac{Mn_{tot} \cdot S_{tot} \cdot k_1 \cdot k_2}{(H^+)^2 + k_1 (H^+)}$$

The calculated results are presented in tables 6.10, 6.13, and 6.17, respectively.

pK_{sp} MnS = 13.11 $\sigma = \pm 0.07$

pK_{sp} FeS = 17.80 $\sigma = \pm 0.18$

pK_{sp} CoS = 21.50 $\sigma = \pm 0.27$

Complex M(HS)(OH):

The calculated results for each complex are tabulated in 6.11, 6.14, and 6.18, respectively.

$$\phi_{11} = \frac{(M(HS)(OH))}{(M^{+2}).(H^+).(S^{-2}).(OH^-)}$$

where M^{+2} = Mn, Fe, or Co.

$$= \frac{(M_{tot})}{k_{sp} \cdot K_w}$$

$$-p\phi_{11} = -pM_{tot} + pK_{sp} + pK_w$$

$$\beta_{11} = \frac{(M(HS)(OH))}{(M^{+2}).(HS^-).(OH^-)}$$

$$-p\beta_{11} = -(pk_2 + p\phi_{11})$$

$-p\phi_{11}$ MnS = 20.94 $\sigma = \pm 0.20$

$-p\phi_{11}$ FeS = 27.26 $\sigma = \pm 0.13$

$-p\phi_{11}$ CoS = 28.81 $\sigma = \pm 0.10$

TABLE NO. 6.10

Calculations of Solubility Product of MnS.

(Experimental Data from Curves C_1, C_2, and C_3; table 6.9)

pMn^{+2}	pS^{-2}	pK_{sp}	pMn^{+2}	pS^{-2}	pK_{sp}
C-1					
3.35	9.75	13.10	3.88	9.23	13.11
3.44	9.75	13.19	4.04	9.01	13.05
3.52	9.65	13.17	4.03	8.94	12.97
3.61	9.55	13.16	4.19	8.90	13.09
3.66	9.48	13.14	4.36	8.72	13.08
3.71	9.48	13.19	4.48	8.60	13.08
3.68	9.41	13.09	4.67	8.52	13.19
3.74	9.31	13.05	4.68	8.34	13.02
3.83	9.23	13.16	4.74	8.37	13.11
3.90	9.21	13.11	4.81	8.29	13.10
3.99	9.26	13.25	C-3		
4.06	9.06	13.12	3.69	9.53	13.22
4.12	8.98	13.10	3.91	9.28	13.19
4.24	8.93	13.17	4.03	9.18	13.21
4.26	8.89	13.15	4.09	8.93	13.02
4.42	8.81	13.23	4.27	8.82	13.09
4.48	8.66	13.14	4.50	8.50	13.00
4.66	8.46	13.12	4.67	8.35	13.02
			4.86	8.13	12.99
C-2					
3.40	9.65	13.05			
3.54	9.47	13.01			
3.60	9.46	13.06			

$$pK_{sp} = pMn^{+2} + pS^{-2} = 13.11 \qquad \sigma = \pm 0.07$$

$$S^{-2} = \frac{k_1 \cdot k_2 \cdot S_{tot}}{[H^+]^2 + k_1 [H^+]}.$$

TABLE NO. 6.11

Complex [Mn(HS)(OH)], $p\phi_{11}$ and $p\beta_{11}$

(Experimental Data Curve C-1, C-2, and C-3; table 6.9)

S.No.	pH	pMn_{tot}	$-p\phi_{11}$
C-1			
23	10.84	6.17	20.94
24	11.38	6.43	20.68
25	12.54	6.02	21.09
26	13.10	6.06	21.05
27	13.10	5.93	21.18
28	13.84	6.01	21.10
29	13.96	5.85	21.26
30	13.94	5.94	21.17
C-2			
22	10.86	6.40	20.71
23	11.58	6.10	21.01
24	12.66	6.17	20.94
25	13.16	6.04	21.07
26	13.90	6.02	21.09
27	13.95	6.01	21.10
C-3			
20	11.52	6.44	20.68
21	11.72	6.43	20.67
22	12.72	6.38	20.73
23	13.30	6.50	20.61
24	13.62	6.43	20.68
25	13.76	6.27	20.84
26	13.95	5.99	21.12

$-p\phi_{11} = 20.94 \qquad \sigma = \pm 0.20.$

$-p\beta_{11} = -(pk_2 + p\phi_{11}) = 7.46$

TABLE NO. 6.12

Solubility of FeS at Different pH and pS_{tot}

pFe_{tot} (orig) = 2.26 M μ = 1.0 $NaClO_4$.

S.No.	pH	C-1	pS_{tot}	pH	C-2	pS_{tot}	pH	C-3	pS_{tot}
		pFe_{tot}			pFe_{tot}			pFe_{tot}	
1	2.85	2.26	1.45	4.97	4.76	1.18	6.10	4.80	1.76
2	2.97	2.26	1.48	5.42	4.51	1.15	6.50	4.99	1.69
3	3.16	2.29	1.45	6.28	4.28	1.16	6.80	4.80	1.73
4	3.20	2.30	1.47	6.60	4.25	1.15	7.00	4.89	1.72
5	3.22	2.49	1.61	7.48	4.40	1.15	9.50	4.57	1.72
6	3.27	2.69	1.60	7.75	4.44	1.14	10.40	4.43	1.64
7	3.32	2.51	1.39	13.35	4.48	1.03	11.05	4.81	1.64
8	3.35	2.48	1.50	13.65	4.44	1.04	11.50	4.86	1.66
9	3.40	2.58	1.48	13.85	4.44	1.03	11.75	4.67	1.65
10	3.47	2.86	1.45	13.90	4.44	1.05	12.30	4.64	1.68
11	4.75	4.51	1.39	—	—	—	13.00	4.56	1.62
12	5.55	4.50	1.37				13.15	4.56	1.63
13	6.00	4.99	1.49				13.35	4.54	1.62

TABLE NO. 6.12 (Contd)

		C-1			C-2			C-3	
S.No.	pH	pFe_{tot}	pS_{tot}	pH	pFe_{tot}	pS_{tot}	pH	pFe_{tot}	pS_{tot}
14	6.82	4.93	1.46						
15	7.06	4.41	1.35						
16	11.30	4.74	1.34						
17	11.80	4.64	1.38						
18	12.10	4.56	1.51						
19	12.45	4.52	1.34						
20	12.78	4.56	1.49						
21	13.14	4.49	1.49						
22	13.25	4.47	1.34						
23	13.32	4.44	1.52						
24	13.50	4.48	1.31						
25	13.65	4.40	1.32						
26	13.92	4.45	1.47						

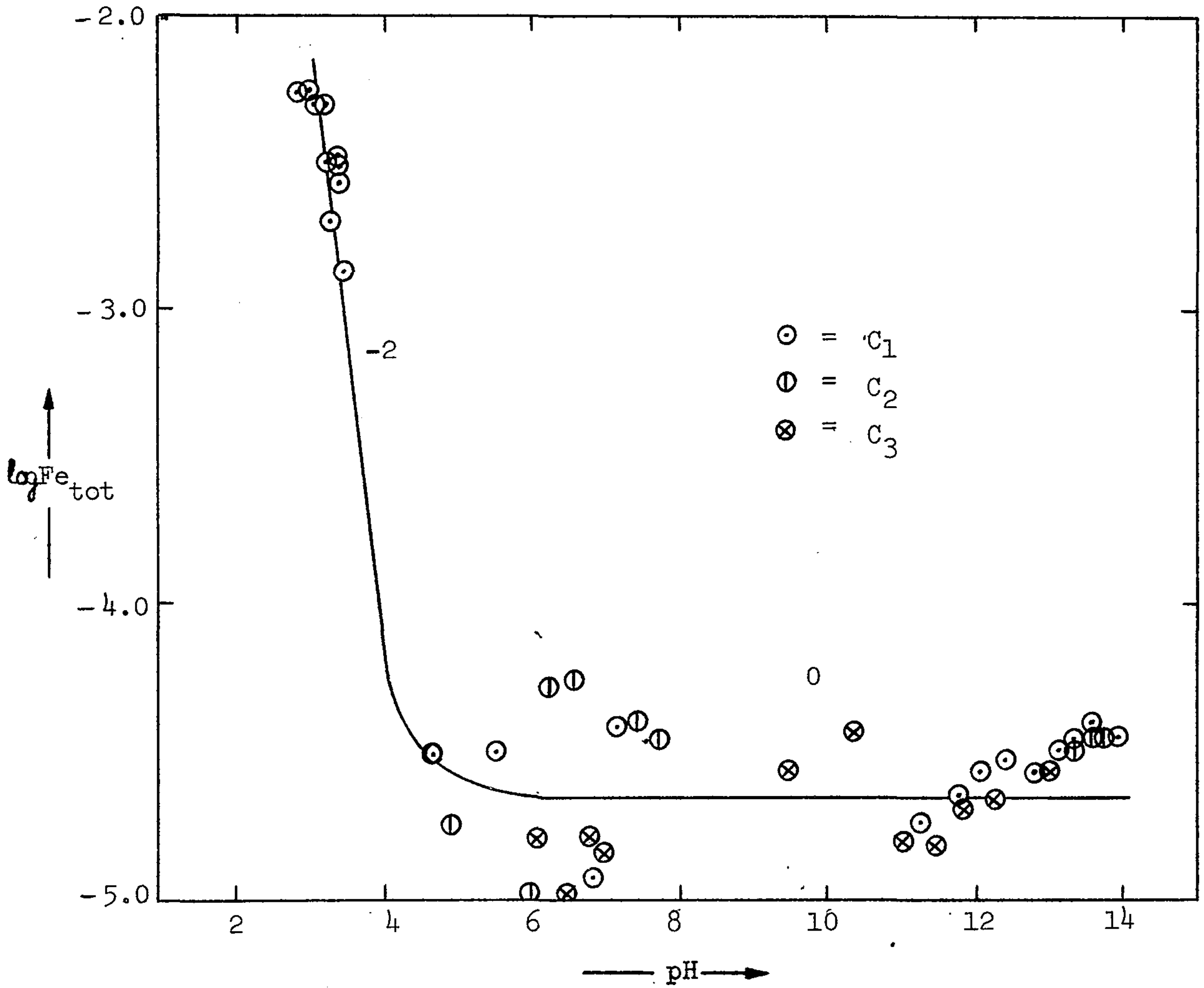


FIGURE 6.8 : Solubility of FeS at Different pH and S_{tot}.

TABLE NO. 6.13

Solubility Product of FeS.

(Experimental Data Curve C-1; table 6.12).

E.No.	pFe^{+2}	pS_{tot}	pS^{-2}	pK_{sp}
3	2.29	1.45	15.51	17.80
4	2.30	1.47	15.45	17.75
5	2.49	1.61	15.55	18.04
6	2.69	1.60	15.44	18.13
7	2.51	1.39	15.13	17.64
8	2.48	1.50	15.18	17.66
9	2.58	1.48	15.06	17.64
10	2.86	1.45	14.89	17.75

$$pS^{-2} = pS_{tot} + pk_1 + pk_2 - 2\ pH.$$

$$pK_{sp} = pFe^{+2} + pS^{-2}$$

$$= 17.80 \quad \sigma = \pm 0.18$$

TABLE NO. 6.14

Complex [Fe(HS)(OH)], $p\phi_{11}$ and $p\beta_{11}$

(Experimental Data from all the Curves)

(C_1, C_2 and C_3; table 6.12)

pH	pFe_{tot}	$-p\phi_{11}$	pH	pFe_{tot}	$-p\phi_{11}$
C-1					
7.06	4.41	27.39	13.65	4.44	27.36
11.30	4.74	27.06	13.85	4.44	27.36
11.80	4.64	27.16	13.90	4.44	27.36
12.10	4.56	27.24	C-3		
12.45	4.52	27.28	7.00	4.89	26.91
12.78	4.56	27.24	9.50	4.57	27.23
13.14	4.49	27.31	10.40	4.43	27.37
13.25	4.47	27.33	11.05	4.81	26.99
13.50	4.48	27.32	11.50	4.86	26.94
13.65	4.40	27.40	11.75	4.67	27.13
13.92	4.45	27.35	12.30	4.64	27.16
C-2			13.10	4.56	27.24
7.48	4.40	27.40	13.15	4.56	27.24
7.75	4.44	27.36	13.35	4.54	27.26
13.35	4.48	27.32			

$$-p\phi_{11} = -pFe_{tot} + pK_{sp} + pK_w.$$

$$-p\phi_{11} = 27.26 \qquad \sigma = \pm 0.13.$$

$$-p\beta_{11} = -(pk_2 + p\phi_{11})$$

$$= 13.78$$

TABLE NO. 6.15

Solubility of CoS at Different pH and pS_{tot}

pCo_{tot} (orig) = 3.30 M μ = 1.0 $NaClO_4$.

S.No.	pH	C-1 pCo_{tot}	pS_{tot}	pH	C-2 pCo_{tot}	pS_{tot}	pH	C-3 pCo_{tot}	pS_{tot}
1	1.60	3.45	2.40	1.80	3.68	1.65	1.50	3.68	1.45
2	1.75	3.49	2.38	1.95	3.72	1.68	1.96	3.96	1.52
3	1.96	3.51	2.38	2.40	4.03	1.79	2.30	4.23	1.48
4	2.15	3.57	2.32	2.50	4.23	1.90	2.70	4.77	1.50
5	2.22	3.66	2.28	3.20	5.53	1.98	2.85	5.00	1.50
6	2.26	3.60	2.32	3.40	5.60	1.72	3.25	5.91	1.51
7	2.35	3.65	2.32	3.55	6.37	1.73	4.00	6.40	1.49
8	2.40	3.69	2.38	5.50	6.73	1.86	5.70	6.43	1.49
9	2.50	3.81	2.30	6.65	6.07	1.79	6.00	5.94	1.50
10	2.60	3.96	2.36	6.95	5.94	1.98	6.25	5.58	1.43
11	2.60	3.89	2.22	7.35	5.94	1.80	6.35	5.63	1.44
12	2.87	4.03	2.30	7.60	6.13	1.78	6.55	5.68	1.43
13	3.47	5.76	2.51	7.75	5.96	1.77	6.65	5.43	1.42
14	3.75	5.95	2.56	8.65	6.46	1.80	6.85	5.40	1.42
15	6.10	6.73	2.37	8.70	6.68	1.81	7.00	5.28	1.44

TABLE NO. 6.15 (Contd)

S.No.		C-1			C-2			C-3	
	pH	pCo_{tot}	pS_{tot}	pH	pCo_{tot}	pS_{tot}	pH	pCo_{tot}	pS_{tot}
16	7.00	6.40	2.25	10.30	6.68	1.77	7.20	5.10	1.38
17	7.10	6.56	2.32	10.50	6.92	1.74	7.30	5.18	1.38
18	7.40	6.86	2.34	10.90	6.62	1.75	7.45	5.33	1.37
19	7.50	6.68	2.24	11.05	6.94	1.77	7.60	5.36	1.41
20	9.65	6.60	2.25	11.75	6.65	1.76	7.84	5.66	1.38
21	10.00	6.61	2.24	12.60	6.82	1.76	8.15	5.97	1.36
22	10.65	6.73	2.22	13.10	6.53	1.75	8.25	5.90	1.39
23	10.85	6.60	2.24	13.50	6.85	1.75	8.80	6.23	1.34
24	11.00	6.73	2.24	—	—	—	10.55	6.53	1.34
25	11.20	6.86	2.29	—	—	—	10.70	6.45	1.35
26	11.25	6.71	2.20	—	—	—	11.65	6.50	1.36
27	13.15	6.68	2.06	—	—	—	13.30	6.68	1.33
28		—	—	—	—	—	13.45	6.70	1.33
29	—	—	—	—	—	—	13.50	6.60	1.34

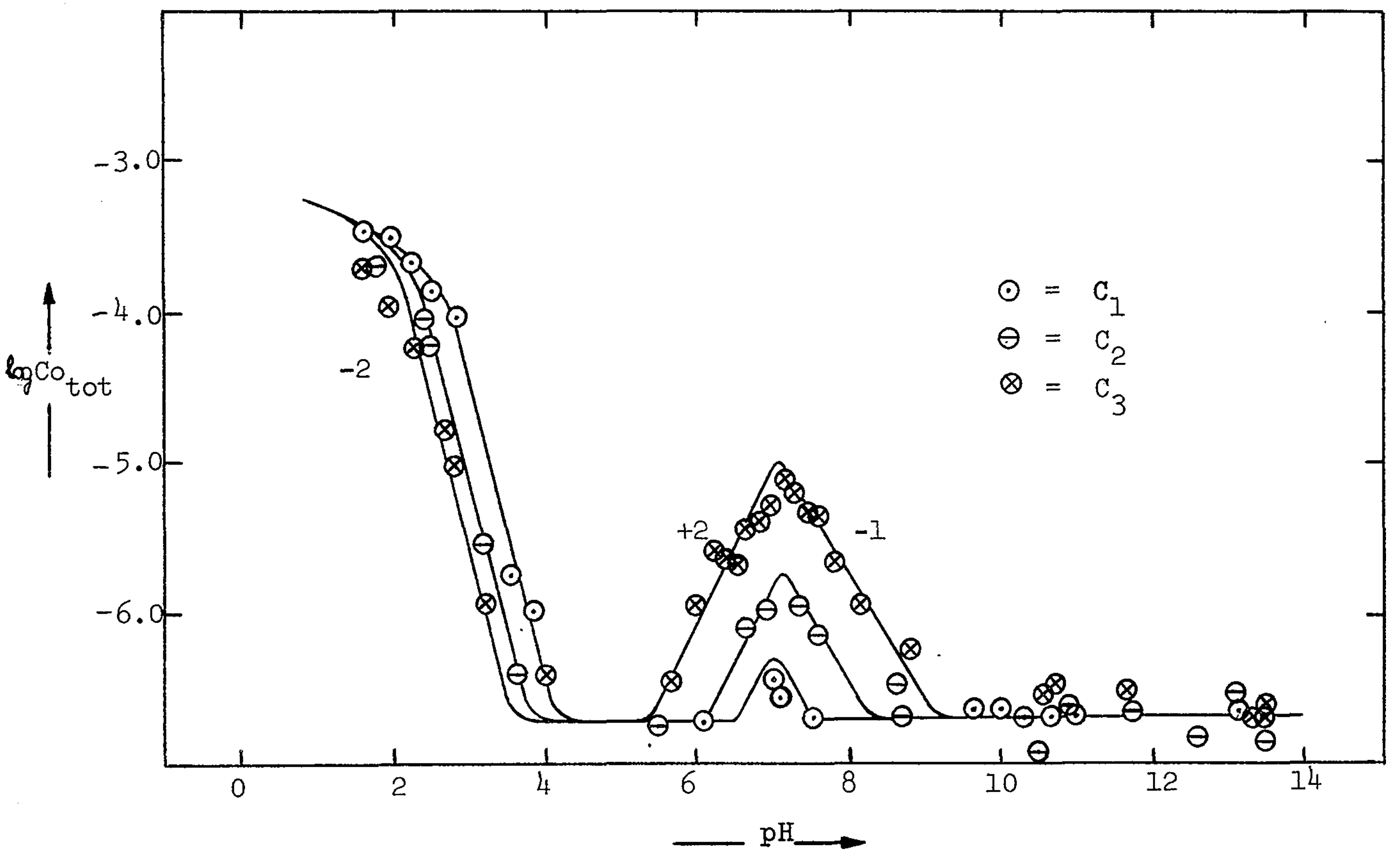


FIGURE 6.9 : Solubility of CoS at Different pH and S_{tot}.

The β values calculated from the ϕ values for these systems are,

$$-p\beta_{11}\ \text{MnS} = 7.46$$

$$-p\beta_{11}\ \text{FeS} = 13.78$$

$$-p\beta_{11}\ \text{CoS} = 15.33$$

The Complex $Co(HS)_4^{-2}$:

The calculations for the formation constant of this complex from the experimental solubility data are given in table 6.19.

$$\phi_{40} = \frac{(Co(HS)_4^{-2})}{(Co^{+2}).(H^+)^4.(S^{-2})^4}$$

$$= \frac{(Co_{tot})}{K_{sp}.\ (H^+)^4.(S^{-2})^3}$$

$$-p\phi_{40} = -pCo_{tot} + pK_{sp} + 4pH + 3pS^{-2}$$

$$-p\phi_{40} = 68.80 \qquad \sigma = \pm 0.22$$

$$\beta_{40} = \frac{(Co(HS)_4^{-2})}{(Co^{+2})(HS^-)^4}$$

$$-p\beta_{40} = -(4pk_2 + p\phi_{40})$$

$$= 14.88.$$

Discussion of the Results:

Earlier studies on the transition metal sulphides have been done with an interest to establish their simple solubility products. The constants available (24), (60), have either been obtained from the thermodynamic data or calculated at some variable ionic strengths of the medium. To make calculations meaningful and for the correct interpretations of the

TABLE NO. 6.16

Solubility of CoS in Neutral Conditions

at Higher Excess of S_{tot}

pCo_{tot} = 3.29 M, μ = 1.0 $NaClO_4$.

E.No.	pH	pCo_{tot}	pS_{tot}
1	6.70	4.55	1.29
2	6.80	4.50	1.29
3	7.05	4.65	1.28
4	7.15	4.45	1.29
5	7.37	4.57	1.29
6	7.50	4.62	1.30
7	7.87	4.65	1.29
8	6.60	4.10	1.09
9	6.72	4.26	1.09
10	6.80	4.31	1.10
11	6.90	4.25	1.08
12	7.00	4.08	1.07
13	7.50	4.14	1.09
14	7.72	4.30	1.08
15	7.87	4.35	1.08

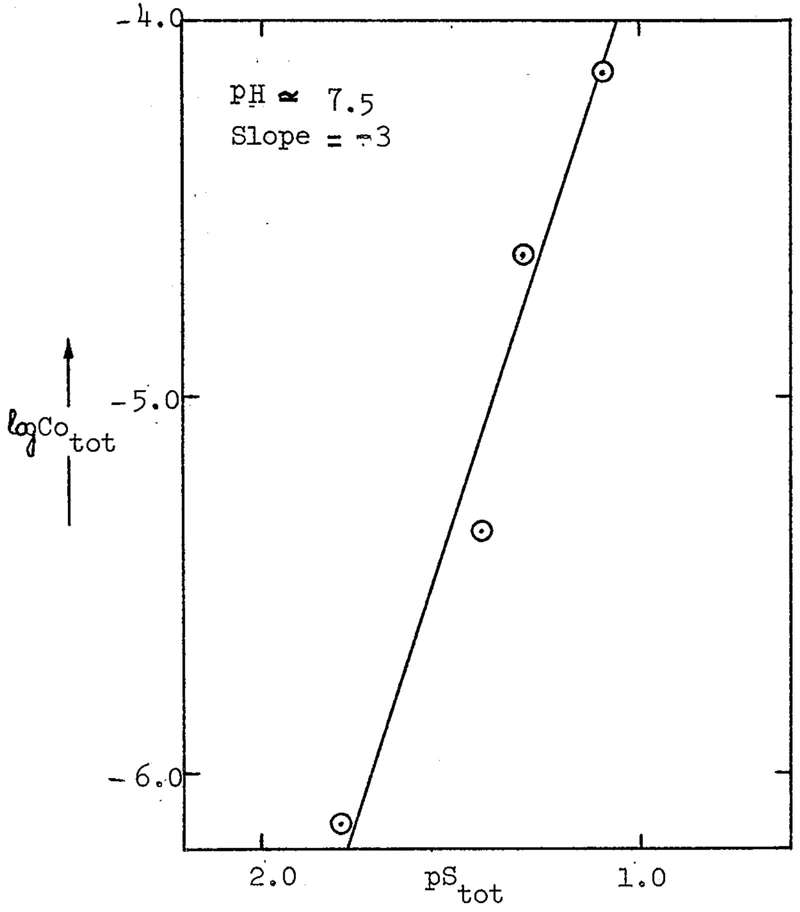


FIGURE 6.10 : Solubility of CoS as a Function of S_{tot}.

TABLE NO. 6.17

Calculation of Solubility Product of CoS.

(Experimental Data from table 6.15).

pH	pCo^{+2}	pS^{-2}	pK_{sp}
C-1			
2.15	3.57	18.40	21.97
2.22	3.66	18.22	21.88
2.26	3.60	18.18	21.78
2.35	3.65	18.00	21.65
2.40	3.69	17.96	21.65
2.50	3.81	17.68	21.49
2.60	3.96	17.54	21.50
2.60	3.89	17.40	21.29
2.87	4.03	16.94	20.97
3.47	5.81	15.95	21.76
3.75	6.02	15.45	21.47
C-2			
2.40	4.03	17.38	21.41
2.50	4.23	17.27	21.50
3.20	5.53	15.94	21.47
3.40	5.63	15.29	20.97
C-3			
2.30	4.23	17.26	21.49
2.70	4.77	16.48	21.25
2.85	5.00	16.17	21.17
3.25	5.98	15.39	21.37

$$pCo^{+2} = pCo_{tot} - pCo(HS)(OH)$$

$$pS^{-2} = pS_{tot} + pk_1 + pk_2 - 2\ pH$$

$$pK_{sp} = pCo^{+2} + pS^{-2} = 21.50 \quad \sigma = \pm 0.27.$$

TABLE NO. 6.18

The Complex Co(HS)(OH) , $p\phi_{11}$ and $p\beta_{11}$
(Experimental Data in Alkaline pH)
(table 6.15 pH = 10 - 13)

pH	pCo_{tot}	pS_{tot}	$-p\phi_{11}$
C-1			
11.00	6.73	2.24	28.77
11.20	6.86	2.24	28.64
11.25	6.71	2.20	28.79
13.15	6.68	2.06	28.82
C-2			
11.75	6.65	1.76	28.85
12.60	6.82	1.76	28.68
13.10	6.53	1.63	28.97
13.50	6.85	1.63	28.65
C-3			
11.65	6.50	1.36	29.00
13.30	6.68	1.33	28.82
13.45	6.70	1.32	28.80
13.50	6.60	1.34	28.90

$$-p\phi_{11} = -pCo_{tot} + pK_{sp} + pK_{w}$$

$$-p\phi_{11} = 28.81 \qquad \sigma = \pm 0.10.$$

$$-p\beta_{11} = -(pk_2 + p\phi_{11})$$

$$= 15.33$$

TABLE NO. 6.19

The Complex $[Co(HS)_4]^{-2}$, $p\phi_{40}$ and $p\beta_{40}$

(Experimental Data T. 6.15 (C_3) and T. 6.16).

pH	pCo_{tot} Complex	4 pH	3 pS^{-2}	$-p\phi_{40}$
C-3				
6.55	5.73	26.20	26.82	68.79
6.65	5.46	26.60	26.07	68.71
6.85	5.43	27.40	25.20	68.67
7.00	5.30	28.00	24.39	68.59
7.20	5.11	28.80	23.52	68.71
7.30	5.19	29.20	23.10	68.61
7.45	5.35	29.80	22.53	68.48
7.60	5.38	30.40	22.05	68.57
7.84	5.70	31.36	21.21	68.37
T (6.16)				
6.70	4.55	26.80	25.37	69.12
6.80	4.50	27.20	24.96	69.16
7.05	4.65	28.20	23.82	68.87
7.15	4.45	28.60	23.43	69.08
7.37	4.57	29.48	22.59	69.00
7.50	4.62	30.00	22.14	69.02
7.87	4.65	31.48	20.82	69.15
6.60	4.10	26.40	25.05	68.85
6.72	4.26	26.88	24.45	68.57
6.80	4.31	27.20	24.39	68.78
6.90	4.25	27.60	23.88	68.73
7.00	4.08	28.00	23.40	68.82
7.52	4.14	30.00	21.51	68.87
7.72	4.30	30.88	20.70	68.78
7.87	4.35	31.48	20.19	68.82

$- p\phi_{40} = 68.80 \quad \sigma = \pm 0.22.$

$- p\beta_{40} = -(4\ pk_2 + p\phi_{40}) = 14.88.$

solubility data, precise knowledge of the solubility products of Mn, Fe, and Co sulphides at a unit ionic strength was essential. The first attempt was therefore to obtain these constants from the solubility data at the requisite ionic strength. Theoretically it has been shown (chapter II) that when pH < pk_1 the relationship between M_{tot} and pH is governed by eq (2.35) and the logarithmic solubility slope at a constant A_{tot} is given by eq (2.39).

$$\frac{\partial \log M_{tot}}{\partial pH} = (x + y) - 2$$

When both x and y are zero, i.e. the complex formation is negligible, and the system has only free (M^{+2}) ions in equilibrium,

$$\frac{\partial \log M_{tot}}{\partial pH} = -2$$

This indicates that under these conditions, $(M^{+2}) = M_{tot}$, and the M_{tot} concentration will decrease with a slope of -2, with an increase in pH of the medium. All the three systems studied here show this characteristic slope of -2, thus the presence of free metal ions in respective pH regions is ascertained without doubt. With the knowledge of S_{tot} the calculation of the K_{sp} becomes straight forward. These observations prove that in such systems the solubility product constants can be evaluated at any desired ionic strength irrespective of the formation of thio-complexes in solution.

The quantity (M^{+2}) remains far below the concentration of M_{tot} found experimentally in alkaline medium. This behaviour is evidently due to aqueous complex formation. Khodakovskii (82) has also expressed a similar opinion on the basis of his recent studies on the solubilities of the metal sulphides. In the present study this complex has been identified as

M (HS)(OH) and found in all the sulphide systems investigated. In reality it may not even be considered a true complex in the sense that other thio-complexes have been encountered, e.g. in Ag_2S and HgS systems. This does not, however, mean that thio-complexes with transition metals are non-existent. Perhaps it is the limitation in the theoretical approach which fails to identify another complex if its concentration happens to fall below than that of the simple hydrated species, M (HS)(OH). Nevertheless, should a thio-complex be formed in some appreciable concentration in the system, the M_{tot} will exhibit variations around the pk's of H_2S. The well defined solubility slopes originating from these variations will identify the complex thus formed. The CoS studies lend full support to this argument, where the identification of the species, $Co(HS)_4^{-2}$, formed in the neutral pH regions, has been rendered possible from the solubility slopes of the system. Probably in their sulphides too the transition elements follow the Irving William order (83), i.e. the metal tendency to coordinate increases with an increase in the At.No. of the element. This seems to be preserved in the solubility product constants of the elements investigated here.

Jörgensen (87) has mentioned that in strong (and hence alkaline) solutions of HS^-, CoS and NiS are soluble, although no details have been cited on the nature of the aqueous solutions. Mickwitz (84) has reported the formation of the complex species Co(HS)(OH), and $Co(HS)_2$ in the CoS-sulphide system. The detailed investigations have now shown that the principal complex in the CoS equilibria is the tetra-coordinated species, $Co(HS)_4^{-2}$, while the other species Co(HS)(OH) is only the hydrated form of the undissociated aqueous CoS. In the light of these observations it appears probable that the next higher systems, NiS and CuS would also form such thio-complexes before the group tendency diminishes at Zn. The information available on the solution chemistry of Ni and Cu sulphides is very meagre and hence a comparison of their complexing characteristics at this stage is not possible. However, Gubeli and Ste-Marie (81) have already shown that little thio-complexing occurs in the ZnS system.

CHAPTER VII

The Aqueous Seleno-Complexes of Metals
Silver, Mercury, and Manganese

A large number of complexes with O and S donor ligands are known (87) and the stability constants of a majority of these are available in aqueous and non-aqueous media (24). Earlier in this study (chapter VI) the natures of the thio-complexes formed with the ligands of H_2S have been elucidated unambiguously. Conspicuously lacking from such studies on complexes are significant investigations on Se and Te donor properties in contrast to O and S donor ligands. It is surprising that even the simple aqueous solubilities of the metal selenides and tellurides have not been measured experimentally. The apparent lack of interest in the solution chemistry of the heavy metal chalcogenides may be partly attributed to the abnoxious character of the many compounds formed with the elements, selenium and tellurium. Nevertheless, comparative studies of the donor properties of the analogous systems containing S, Se, and Te are desirable. The results of the investigations initiated on the complexing characteristics of the selenium ligands derived from H_2Se, under similar experimental conditions,are reported in this chapter.

Three systems, Ag_2Se, HgSe, and MnSe have been studied. The first two were selected primarily on the grounds that their corresponding sulphides form exceptionally stable thio-complexes in their heterogeneous equilibria. Furthermore, the two elements Ag and Hg constitute stable and thermodynamically reversible electrode systems that permit the potentiometric determinations for the free metal ion concentrations in solution (chapter IV). MnSe was chosen since it offers the best example in the transition metal selenides.

Its calculated solubility product has been reported to be the highest in the series (85) of the first transition elements group. Consequently the radioanalytical technique can be usefully applied to get direct experimental evidence on the aqueous solubility and the seleno-complex formation in MnSe.

Experimental Results:

The System Ag_2Se:

The solubility curves of Ag_2Se are shown in fig. 7.1 and the experimental data are tabulated at different increments of total selenium in table 7.1. The solubility curves on inspection show that the Ag_2Se solubility remains constant and unaffected with an increase in selenium concentration till the pH attains a value of approximately 10. The solubility increases thereafter with a slope of one as a function of pH. Maintaining pH constant, the solubility increases with a slope of +1.5 as a function of Se_{tot}, (fig. 7.2); the experimental data are tabulated in 7.2. The interpretation is simple in this case, since the solubility slopes suggest only two complex species in the system. The first complex is independent of pH and Se_{tot} and exists in all the solubility curves as long as these maintain a slope of zero as a function of pH and Se_{tot}, the two experimental variables. Similar species have been encountered earlier in the sulphur systems and the formula of the complex can now be directly written as $Ag_2(HSe)(OH)$. The other complex is unique since it is formed in regions when pH > pk_2, i.e. where the selenium complexing ligand (Se^{-2}) becomes the predominating species in H_2Se equilibria. Comparison of the experimental slopes with the theoretical possibility readily identifies the complex as $(Ag(Se)_2(OH)^{-4})$ (cf. table 2.1).

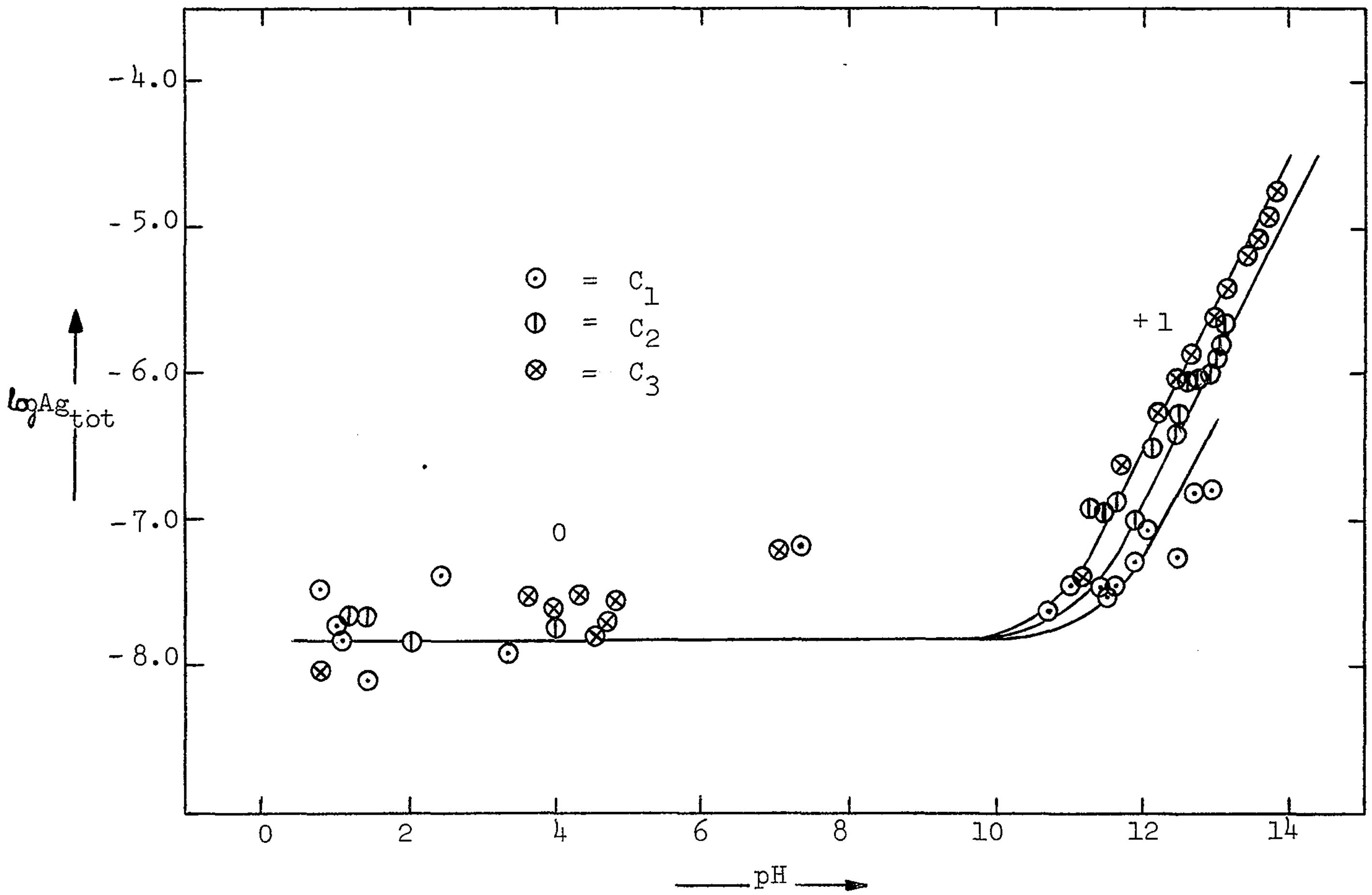


FIGURE 7.1 : Solubility of Ag_2Se as a Function of pH and Se_{tot}.

TABLE NO. 7.1

Solubility of Ag_2Se at Different pH and Se_{tot}

pAg (orig) = 3.40 M $\mu = 1.0$ $NaClO_4$.

S.No.	pH	C-1 pAg_{tot}	pSe_{tot}	pH	C-2 pAg_{tot}	pSe_{tot}	pH	C-3 pAg_{tot}	pSe_{tot}
1	0.80	7.47	1.93	1.20	7.64	1.66	0.85	8.03	1.25
2	0.92	7.75	2.08	1.25	7.57	1.72	0.90	8.12	1.19
3	1.07	7.72	2.15	1.42	7.66	1.71	1.00	7.77	1.45
4	1.10	7.85	2.08	1.55	7.87	1.72	3.35	7.64	1.18
5	1.45	8.10	2.18	2.10	7.82	1.75	3.40	7.64	1.26
6	2.45	7.37	1.98	4.05	7.72	1.71	3.65	7.52	1.18
7	3.40	7.90	1.92	11.35	6.92	1.62	4.00	7.62	1.19
8	7.35	7.17	1.97	11.50	6.95	1.64	4.37	7.51	1.22
9	10.75	7.62	1.84	11.70	6.87	1.64	4.55	7.80	1.42
10	11.07	7.44	1.84	12.05	6.40	1.62	4.75	7.48	1.16
11	11.45	7.45	1.93	12.20	6.50	1.64	4.75	7.69	1.12
12	11.50	7.50	2.02	12.50	6.28	1.60	4.85	7.56	1.33
13	11.65	7.55	1.94	12.62	6.06	1.60	4.90	7.37	1.45
14	11.70	7.44	1.81	12.82	6.03	1.62	7.10	7.20	1.79

TABLE NO. 7.1 (Contd)

S.No.	pH	C-1 pAg_{tot}	pSe_{tot}	pH	C-2 pAg_{tot}	pSe_{tot}	pH	C-3 pAg_{tot}	pSe_{tot}
15	11.95	7.28	1.76	13.00	6.00	1.59	11.20	7.32	1.24
16	11.97	6.97	1.85	13.00	5.97	1.59	11.75	6.62	1.18
17	12.10	7.07	1.81	13.05	5.90	1.67	12.25	6.27	1.23
18	12.50	7.25	1.85	13.07	5.85	1.58	12.50	6.02	1.19
19	12.75	6,80	1.83	13.10	5.80	1.58	12.70	5.85	1.18
20	13.00	6.78	1.89	13.12	5.74	1.58	12.80	5.72	1.20
21	–	–	–	13.15	5.65	1.58	12.90	5.79	1.18
22	–	–	–	–	–	–	13.05	5.62	1.21
23	–	–	–	–	–	–	13.17	5.47	1.23
24	–	–	–	–	–	–	13.20	5.40	1.19
25	–	–	–	–	–	–	13.30	5.34	1.14
26	–	–	–	–	–	–	13.45	5.17	1.20
27	–	–	–	–	–	–	13.60	5.07	1.20
28	–	–	–	–	–	–	13.70	5.02	1.12
29	–	–	–	–	–	–	13.75	4.95	1.10
30	–	–	–	–	–	–	13.82	4.87	1.14
31	–	–	–	–	–	–	13.85	4.72	1.10

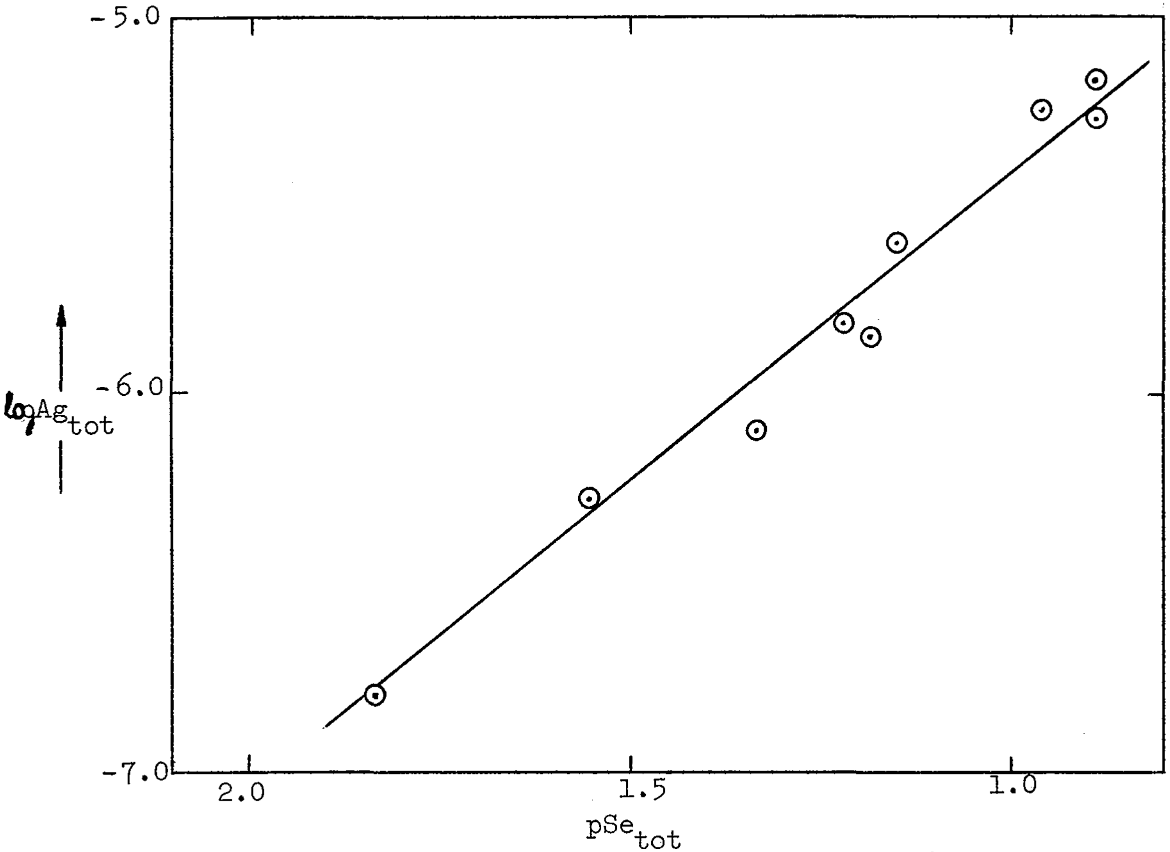


FIGURE 7.2 : Solubility of Ag_2Se as a Function of Se_{tot}

pH ≃ 12.5 Slope = −1.5

TABLE NO. 7.2

Solubility of Ag_2Se as a Function Se_{tot}
pAg (orig) = 3.40 M μ = 1.0 $NaClO_4$.

S.No.	pH	pAg_{tot}	pSe_{tot}
1	12.75	6.80	1.83 *
2	12.50	6.28	1.60 *
3	12.40	6.10	1.33
4	12.40	5.81	1.22
5	12.70	5.85	1.18 *
6	12.50	5.60	1.15
7	12.65	5.25	0.96
8	12.70	5.17	0.88
9	12.95	5.21	0.86

(* Data from Curve C_1, C_2 and C_3 table 7.1).

TABLE NO. 7.3

Complex $[Ag_2(HSe)(OH)]$, $p\phi_{11}$ and $p\beta_{11}$.
[Experimental Data pH (1-4)].

C.No.	Average pAg_{tot}	$-p\phi_{11}$	$-p\beta_{11}$
C-1	7.74	60.05	48.45
C-2	7.71	60.08	48.48
C-3	7.67	60.12	48.52

$$-p\phi_{11} = -pAg_{tot} + pK_{sp} + pK_w = 60.09 \quad \sigma = \pm 0.10$$

$$-p\beta_{11} = -(pk_2 + p\phi_{11}) = 48.49.$$

The System HgSe:

The experimental solubility data of this system are shown in fig. 7.3 and table 7.4. A good deal of similarity may be observed in this system with the corresponding HgS system. The solubility initially remains constant and unaffected with changes in the pH or Se_{tot}, thus maintaining the familiar slope of zero as a function of these two variables. Further the solubility curves around pk_1 of H_2Se indicate an increase in the Hg_{tot} of the medium and quickly these attain a limiting slope of zero as a function of pH. However, a slope of one is observed in the same pH region as a function of Se_{tot}. But after pH 6, the solubility of HgSe continuously increases further with a slope of one (fig. 7.3) as a function of pH, while solubility slope as a function of Se_{tot} still remains one (cf. fig. 7.4) thereby indicating the formation of still another complex. Interpretation of the data with the help of the theoretical slopes (table 2.2) identifies the following species in solution.

$(Hg(HSe)(OH))$.	stable in pH	0 - 3.0
$(Hg(HSe)_2(OH))^-$	stable in pH	4.0 - 5.5
$(Hg(HSe)_2(OH)_2^{-2})$	stable in pH	7.0 - 10.0.

Similar complexes have been observed in the HgS equilibria, but their regions of existence are different from this system.

The System MnSe:

The system MnSe has a slope of -2 in acidic regions followed by a constant slope of zero in all other pH regions. The experimental data are presented in table 7.5 and fig. 7.5. The slope of -2 is an indication that only free Mn^{+2} ions predominate the system in the initial phase of precipitation, i.e. like its sulphide, the MnSe has also little tendency to form coordination complexes, with the ligand species of H_2Se system in the acidic medium. The slope of zero in alkaline regions is evidently free of the influence of the experimental variables pH and Se_{tot}; hence the complex in this pH zone is the familiar species Mn(HSe)(OH).

Calculation of the Formation Constants:

$(Ag_2(HSe)(OH))$:

Table 7.3 gives the calculations for the formation constant of this complex. The Ag_{tot} are averaged out for all the three excess of Se_{tot} between pH 1 and 4, i.e. along the curves where the solubility is constant as a function of pH and Se_{tot}.

$$\phi_{11} = \frac{(Ag_2(HSe)(OH))}{(Ag^+)^2.(H^+).(Se^{-2}).(OH^-)}$$

$$= \frac{(Ag_{tot})}{K_{sp}.K_w}$$

$$-p\phi_{11} = 60.09 \qquad \sigma = \pm 0.10$$

$$\beta_{11} = \frac{(Ag_2(HSe)(OH))}{(Ag^+)^2.(HSe^-).(OH^-)}$$

$$-p\beta_{11} = -(pk_2 + p\phi_{11})$$

$$= 48.49.$$

$(Ag(Se)_2(OH)]^{-4}$:

Table 7.6 gives the processed data for stability constant of this complex. Experimental solubility data from all the three solubility curves (table 7.1) are included from the pH zone, where the slope of one is well

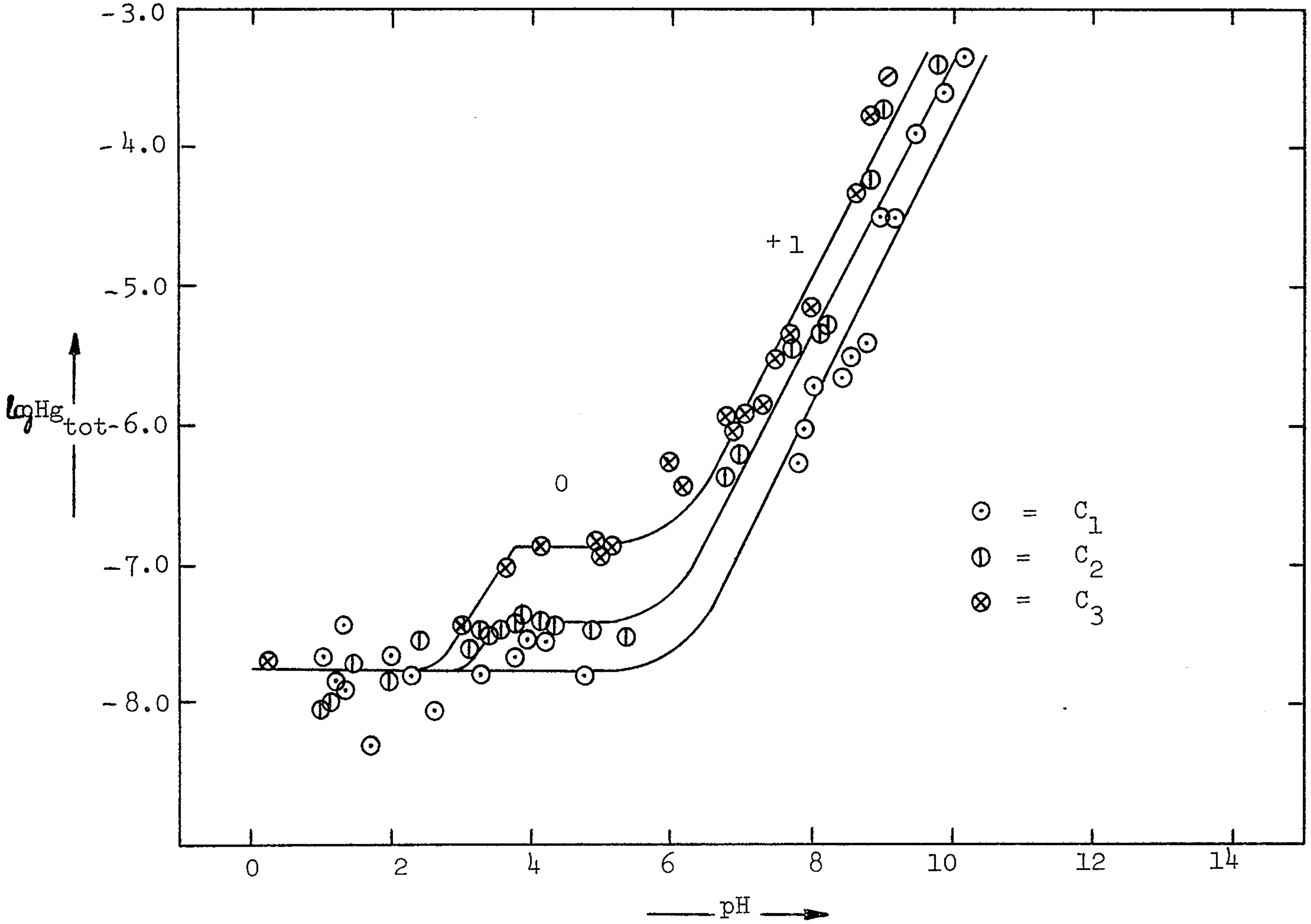


FIGURE 7.3 : Solubility of HgSe as a Function of pH and Se$_{tot}$.

TABLE NO. 7.4

Solubility of HgSe at Different pH and pSe_{tot}

pHg (orig) = 3.30 M μ = 1.0 $NaClO_4$.

S.No.	pH	C-1		pH	C-2		pH	C-3	
		pHg_{tot}	pSe_{tot}		pHg_{tot}	pSe_{tot}		pHg_{tot}	pSe_{tot}
1	1.08	7.65	1.74	1.05	8.02	1.31	0.30	7.67	1.37
2	1.10	7.82	1.90	1.10	8.10	1.23	3.00	7.37	1.20
3	1.25	7.52	1.84	1.15	7.99	1.27	3.70	7.00	1.18
4	1.28	7.82	1.83	1.50	7.72	1.32	4.15	6.85	1.21
5	1.35	7.42	1.77	2.00	7.82	1.30	4.92	6.82	1.18
6	1.37	7.82	1.84	2.45	7.55	1.29	4.95	6.98	1.18
7	1.39	7.90	1.80	3.15	7.59	1.28	5.20	6.92	1.18
8	1.75	8.30	1.85	3.30	7.47	1.34	6.00	6.25	1.07
9	2.00	7.65	1.87	3.40	7.50	1.27	6.20	6.42	1.14
10	2.30	7.80	1.92	3.45	7.35	1.31	6.80	5.93	1.10
11	2.65	8.03	1.86	3.60	7.45	1.30	6.97	6.05	1.16
12	3.15	7.62	1.76	3.65	7.40	1.31	7.10	5.90	1.06
13	3.30	7.77	1.81	3.80	7.40	1.31	7.35	5.81	1.11

TABLE NO. 7.4 (Contd)

S.No.		C-1			C-2			C-3	
	pH	pHg_{tot}	pSe_{tot}	pH	pHg_{tot}	pSe_{tot}	pH	pHg_{tot}	pSe_{tot}
14	3.37	7.50	1.74	3.85	7.35	1.31	7.50	5.52	1.09
15	3.50	7.87	1.80	3.87	7.39	1.29	7.65	5.60	1.08
16	3.80	7.65	1.76	3.90	7.32	1.32	7.68	5.44	1.13
17	4.00	7.52	1.83	3.95	7.35	1.31	7.70	5.40	1.07
18	4.25	7.55	1.72	4.15	7.39	1.30	8.00	5.15	1.12
19	4.45	8.01	1.80	4.22	7.45	1.28	8.65	4.30	1.08
20	4.80	7.80	1.80	4.55	7.35	1.25	8.82	3.75	1.08
21	4.90	7.48	1.73	4.60	7.45	1.27	9.05	3.48	1.08
22	7.85	6.25	1.70	4.65	7.35	1.27	—	—	—
23	7.90	6.02	1.64	4.67	7.44	1.37			
24	7.95	5.62	1.76	4.70	7.54	1.31			
25	8.05	5.70	1.65	4.85	7.55	1.23			
26	8.45	5.65	1.81	4.90	7.47	1.32			
27	8.55	5.50	1.68	5.40	7.52	1.29			

TABLE NO. 7.4 (Contd)

S.No.	pH	C-1 pHg_{tot}	pSe_{tot}	pH	C-2 pHg_{tot}	pSe_{tot}	pH	C-3 pHg_{tot}	pSe_{tot}
28	8.70	5.41	1.64	6.80	6.37	1.22			
29	9.00	4.50	1.81	7.00	6.20	1.26			
30	9.20	4.52	1.77	7.75	5.44	1.29			
31	9.50	3.89	1.68	8.15	5.32	1.28			
32	9.85	3.67	1,78	8.20	5.30	1.26			
33	9.90	3.59	1.73	8.25	5.16	1.28			
34	10.15	3.37	1.81	8.85	4.22	1.27			
35	10.20	3.35	1.77	9.05	3.72	1.27			
36	–	–	–	9.80	3.40	1.27			

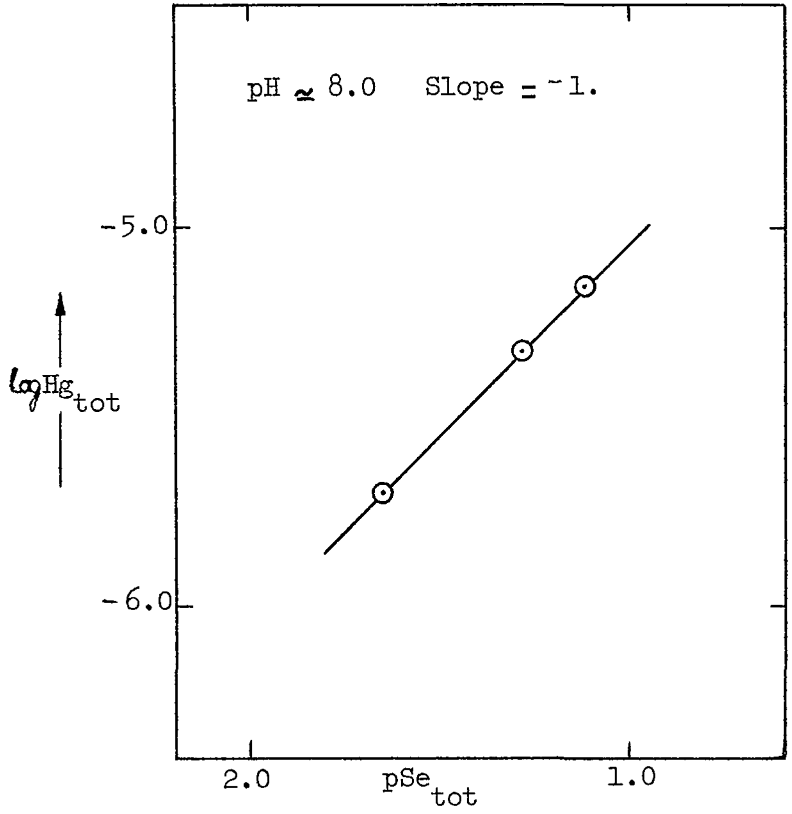


FIGURE 7.4 : Hg_{tot} as a Function of Se_{tot}.

TABLE NO. 7.5

Solubility of MnSe at Different pH and pSe_{tot}

pMn (orig) = 3.12 M μ = 1.0 $NaClO_4$

S.No.	pH	C-1	pSe_{tot}	pH	C-2	pSe_{tot}	pH	C-3	pSe_{tot}
		pMn_{tot}			pMn_{tot}			pMn_{tot}	
1	3.37	3.12	—	4.37	3.40	1.91	4.57	3.35	1.46
2	3.65	3.12	—	5.40	3.82	1.98	7.75	6.65	1.47
3	3.90	3.12	—	8.15	6.45	1.84	10.10	6.52	1.45
4	4.22	3.13	1.19	9.20	6.42	2.01	11.10	6.65	1.45
5	4.32	3.31	1.23	10.50	6.45	1.88	11.70	6.40	1.63
6	4.42	3.32	1.21	10.75	6.45	1.93	13.60	6.00	1.42
7	4.55	3.85	1.20	11.35	6.75	1.93	—	—	—
8	4.77	4.40	1.13	13.15	6.50	1.87			
9	4.80	4.60	1.23	13.50	6.75	1.90			
10	5.30	5.10	1.18	—	—	—			
11	5.40	4.65	1.18	—	—	—			
12	5.70	5.87	1.08						
13	6.30	5.75	1.14						
14	7.70	6.30	1.16						
15	9.05	6.07	1.21						
16	10.75	6.40	1.15						
17	11.55	6.50	1.17						
18	12.00	6.61	1.17						

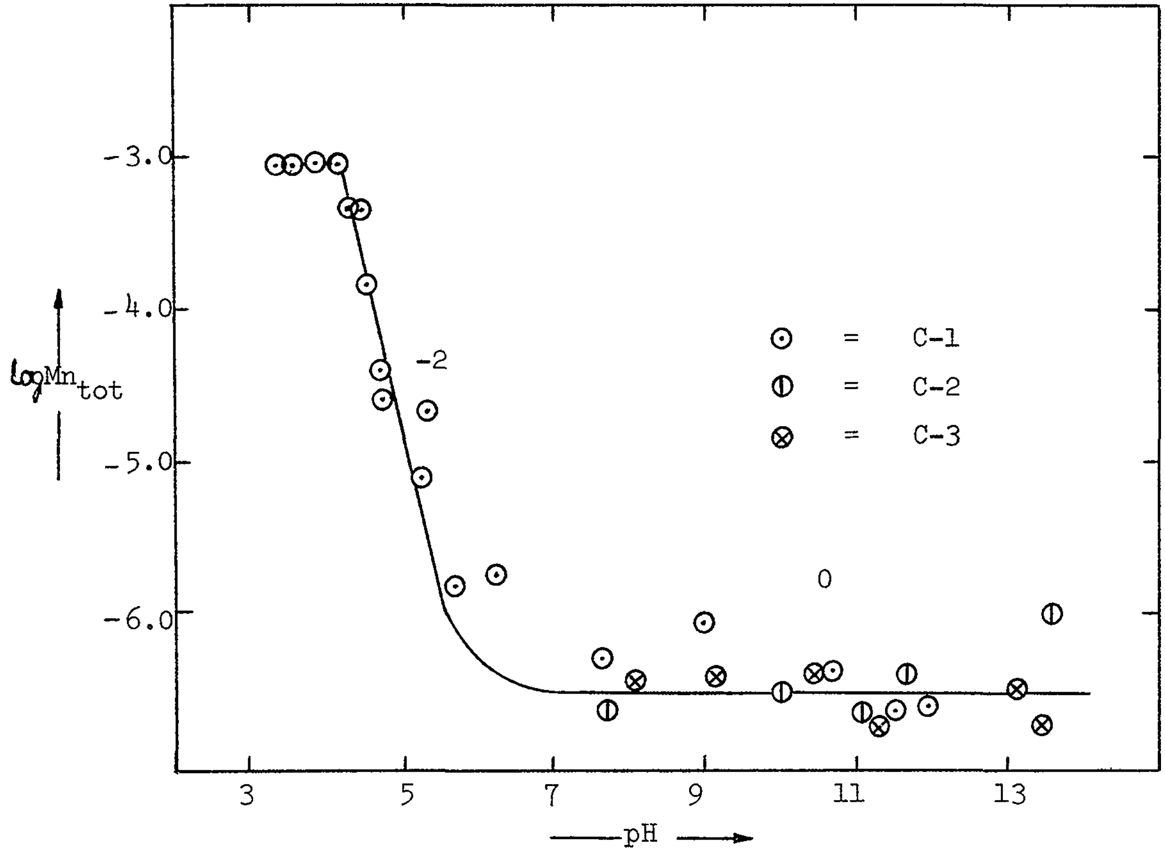


FIGURE 7.5 : Solubility of MnSe as a Function of pH and Se$_{tot}$.

formed and at the same time is appreciably removed from the pk_2 of H_2Se.

$$\phi_{21} = \frac{(Ag(Se)_2(OH))^{-4}}{(Ag^+).(Se^{-2})^2.(OH^-)}$$

$$(Ag_{tot}) = (Ag_2(HSe)(OH)) + (Ag(Se)_2(OH))^{-4}$$

$$(Ag(Se)_2(OH))^{-4} = (Ag_{tot})-(Ag_2(HSe)(OH)) = (Ag_c)$$

$$-p\phi_{21} = -pAg_c + pAg^+ + 2pSe^{-2} + pOH^-$$

$$= 24.07 \quad \sigma = \pm 0.19$$

$$-p\beta_{21} = -p\phi_{21} = 24.07.$$

Hg(HSe)(OH):

Table 7.7 gives the calculations for this complex. The concentration of this complex is obtained from the experimental data before pk_1 of H_2Se.

$$\phi_{11} = \frac{(Hg(HSe)(OH))}{(Hg^{+2}).(H^+).(Se^{-2}).(OH^-)}$$

$$= \frac{(Hg_{tot})}{K_{sp}.K_w}$$

$$-p\phi_{11} = 62.78 \quad \sigma = \pm 0.22$$

$$\beta_{11} = \frac{(Hg(HSe)(OH))}{(Hg^{+2}).(HSe^-).(OH^-)}$$

$$-p\beta_{11} = -(pk_2 + p\phi_{11})$$

$$= 51.18.$$

$(Hg(HSe)_2(OH)_2)^{-2}$:

The experimental data for this complex from all the three solubility curves (fig. 7.1) are tabulated in 7.8. The experimental points are

TABLE NO. 7.6

Complex $[Ag(Se)_2(OH)]^{-4}$, $p\phi_{21}$, $p\beta_{21}$.

(Experimental Data from the Solubility Curves, table 7.1)

C.No.	pH	pAg_{tot}	pSe_{tot}	pAg^+	pOH^-	pAg_c	$-p\phi_{21}$
C-1	12.50	7.25	1.87	25.97	1.50	7.44	23.77
	12.75	6.80	1.83	25.98	1.25	6.86	24.03
	13.00	6.78	1.89	25.95	1.00	6.83	23.90
C-2	13.00	6.00	1.59	26.10	1.00	6.01	24.27
	13.05	5.90	1.61	26.09	0.95	5.90	24.36
	13.07	5.85	1.58	26.10	0.93	5.85	24.34
	13.10	5.80	1.58	26.10	0.90	5.80	24.42
	13.12	5.74	1.58	26.10	0.88	5.74	24.40
C-3	12.70	5.87	1.18	26.30	1.30	5.88	24.08
	12.80	5.72	1.20	26.29	1.20	5.72	24.17
	12.90	5.79	1.18	26.30	1.10	5.79	23.97
	13.05	5.62	1.20	26.29	0.95	5.62	24.02
	13.17	5.47	1.23	26.28	0.83	5.47	24.10
	13.20	5.40	1.19	26.30	0.80	5.40	24.08
	13.30	5.34	1.14	26.32	0.70	5.34	23.96
	13.45	5.17	1.20	26.29	0.55	5.17	24.07
	13.60	5.07	1.20	26.29	0.40	5.07	24.02
	13.70	5.02	1.11	26.34	0.30	5.02	23.84
	13.75	4.95	1.10	26.34	0.25	4.95	23.84
	13.82	4.87	1.14	26.32	0.18	4.87	23.91
	13.85	4.72	1.10	26.34	0.15	4.72	23.97

$pAg_c = pAg_{tot} - pAg_2\,(HSe)(OH).$

$-p\phi_{21} = -p\beta_{21} = 24.07 \quad \sigma = \pm 0.19.$

selected from the pH regions where the solubility slope is well defined for this complex.

$$
\begin{aligned}
\phi_{22} &= \frac{(Hg(HSe)_2(OH)_2)^{-2}}{(Hg^{+2})\cdot(H^+)^2\cdot(Se^{-2})^2\cdot(OH^-)^2} \\
&= \frac{(Hg_{tot})}{K_{sp}\cdot K_w^2\cdot(Se^{-2})} \\
-p\phi_{22} &= 84.24 \quad \sigma = \pm 0.32 \\
\beta_{22} &= \frac{(Hg(HSe)_2(OH)_2)^{-2}}{(Hg^{+2})\cdot(HSe^-)^2\cdot(OH^-)^2} \\
-p\beta_{22} &= -(2pk_2 + p\phi_{22}) \\
&= 61.04.
\end{aligned}
$$

$Hg(HSe)_2(OH)^-$:

The increasing solubility of HgSe in pH regions in the immediate vicinity of pk_1 of H_2Se gives the concentration of this complex. The calculated data are given in table 7.9.

$$
\begin{aligned}
(Hg_{tot}) &= (Hg(HSe)(OH)) + (Hg(HSe)_2(OH)^-) + (Hg(HSe)_2(OH)_2^{-2}) \\
(Hg\ (HSe)_2(OH))^- &= (Hg_{tot}) - (Hg(HSe)(OH)) - (Hg(HSe)_2(OH)_2^{-2}) \\
&= (Hg_c) \\
\phi_{21} &= \frac{(Hg_c)}{(Hg^{+2})\cdot(H^+)^2\cdot(Se^{-2})^2\cdot(OH^-)} \\
&= \frac{(Hg_c)}{K_{sp}\cdot K_w\cdot(Se^{-2})(H^+)} \\
-p\phi_{21} &= -pHg_c + pK_{sp} + pSe^{-2} + pK_w + pH \\
&= 75.96 \qquad \sigma = \pm 0.31 \\
-p\beta_{21} &= -(2pk_2 + p\phi_{21}) \\
&= 52.76
\end{aligned}
$$

TABLE NO. 7.7

Complex $[Hg(HSe)(OH)]$, $p\phi_{11}$, $p\beta_{11}$
(Experimental Data before pk_1 of H_2Se).

C.No.	pH	pHg_{tot}	$-p\phi_{11}$
C-1	1.08	7.65	62.96
	1.10	7.82	62.79
	1.25	7.52	63.09
	1.28	7.82	62.79
	1.35	7.42	63.19
	1.37	7.82	62.79
	1.39	7.90	62.71
	1.75	8.30	62.31
	2.00	7.65	62.96
	2.30	7.80	62.81
	2.65	8.03	62.58
C-2	1.05	8.02	62.59
	1.10	8.10	62.51
	1.15	7.99	62.62
	1.50	7.72	62.89
	2.00	7.82	62.79

$-p\phi_{11} = -pHg_{tot} + pK_{sp} + pK_w = 62.78 \quad \sigma = \pm 0.22.$

$-p\beta_{11} = -(pk_2 + p\phi_{11}) = 51.18$

TABLE NO. 7.8

Complex $[Hg(HSe)_2(OH)_2]^{-2}$, $p\phi_{22}$, $p\beta_{22}$
(Experimental Data Alkaline Medium from Table 7.4)

C.No.	pH	pHg_{tot}	pSe_{tot}	pSe^{-2}	$-p\phi_{22}$
C-1	8.05	5.70	1.65	5.20	84.11
	8.45	5.65	1.81	4.96	83.92
	8.55	5.50	1.67	4.72	83.83
	8.70	5.41	1.66	4.56	83.76
	9.00	4.50	1.81	4.41	84.52
	9.20	4.52	1.76	4.16	84.25
C-2	8.15	5.32	1.28	4.73	84.02
	8.20	5.30	1.26	4.66	83.97
	8.25	5.16	1.28	4.63	84.08
	8.85	4.22	1.27	4.02	84.41
	9.05	3.72	1.27	3.82	84.71
	9.80	3.40	1.27	3.07	84.27
C-3	8.00	5.15	1.11	4.71	84.16
	8.65	4.30	1.08	4.03	84.34
	8.82	3.75	1.08	3.86	84.72
	9.05	3.48	1.08	3.63	84.77

$pSe^{-2} = pSe_{tot} + pk_2 - pH.$

$-p\phi_{22} = pK_{sp} + 2\ pK_w + pSe^{-2} - pHg_{tot} = 84.24 \quad \sigma = \pm\ 0.32$

$-p\beta_{22} = -(2\ pk_2 + p\phi_{22})$

$= 61.04.$

TABLE NO. 7.9

Complex $[Hg(HSe)_2(OH)]^-$, $p\phi_{21}$, $p\beta_{21}$

(Experimental Data after pk_1 of H_2Se from Table 7.4).

C.No.	pH	pHg_{tot}	pSe_{tot}	pHg_c	pSe^{-2}	$-p\phi_{21}$
C-2	4.15	7.39	1.30	7.60	8.83	75.99
	4.22	7.45	1.28	7.70	8.73	75.86
	4.55	7.35	1.25	7.56	8.33	75.93
	4.60	7.45	1.27	7.73	8.30	75.78
	4.65	7.35	1.27	7.60	8.15	75.81
	4.67	7.44	1.37	7.71	8.33	75.90
	4.70	7.54	1.31	7.94	8.23	75.60
	4.85	7.55	1.23	8.04	8.00	75.42
	4.90	7.47	1.32	7.82	8.04	75.73
C-3	4.92	6.82	1.18	6.89	7.88	76.52
	4.95	6.98	1.18	7.08	7.84	76.32
	5.20	6.92	1.18	7.11	7.58	76.28

$$Se^{-2} = \frac{k_1 k_2 \cdot Se_{tot}}{[H^+]^2 + k_1 [H^+]}$$

$$[Hg_c] = [Hg_{tot}] - [Hg(HSe)(OH)] - [Hg(HSe)_2(OH)_2^{-2}].$$

$$-p\phi_{21} = pK_{sp} + pK_w + pSe^{-2} + pH - pHg_c.$$

$$= 75.96 \qquad \sigma = \pm 0.31.$$

$$-p\beta_{21} = -(2\,pk_2 + p\phi_{21})$$

$$= 52.76.$$

The Solubility Product Constant, MnSe:

$$(Mn^{+2}).(Se^{-2}) = K_{sp}$$

From the experimental data (fig. 7.5) where M_{tot} corresponds to the presence of the free Mn^{+2} ions in solution, the solubility product constant is calculated. The results are presented in table 7.10.

$$M_{tot} = Mn^{+2}$$

$$Se_{tot} = Se^{-2} \cdot \left[\frac{(H^+)^2}{k_1 . k_2} + \frac{(H^+)}{k_2} \right]$$

$$K_{sp} = (Mn^{+2}) . \left[\frac{Se_{tot} . k_1 . k_2}{(H^+)^2 + k_1 (H^+)} \right]$$

$$pK_{sp} = 12.15 \qquad \sigma = \pm 0.40$$

Mn(HSe)(OH):

The concentration of this complex is obtained from the experimental data when the solubility curves assume a slope of zero both as a function of pH and pSe_{tot}. The calculations are presented in table 7.11, the Mn_{tot} for the pH range 10 - 13, are averaged out since the complex species is the same in all the conditions after this pH value.

$$\phi_{11} = \frac{(Mn(HSe)(OH))}{(Mn^{+2}).(H^+).(Se^{-2}).(OH^-)}$$

$$= \frac{(Mn_{tot})}{K_{sp} . K_w}$$

$$-p\phi_{11} = 19.66 \qquad \sigma = \pm 0.20$$

$$-p\beta_{11} = -(pk_2 + p\phi_{11})$$

$$= 8.06.$$

TABLE NO. 7.10

Solubility Product of MnSe

(Experimental Data from C_1, C_2, C_3, Table 7.5).

pH	pMn^{+2}	pSe^{-2}	pK_{sp}
C-1			
4.22	3.13	8.64	11.77
4.32	3.31	8.57	11.88
4.42	3.32	8.44	11.76
4.55	3.85	8.29	12.14
4.77	4.40	7.98	12.38
4.80	4.60	8.05	12.71
5.30	5.10	7.49	12.59
5.40	4.65	7.38	12.03
C-2			
4.37	3.40	9.19	12.59
5.40	3.82	8.18	12.00
C-3			
4.57	3.35	8.52	11.87

$$pK_{sp} = pMn^{+2} + pSe^{-2}$$

$$= 12.15 \quad \sigma = \pm 0.40$$

$$Se^{-2} = \frac{k_1 k_2 . Se_{tot}}{[H^+]^2 + k_1 [H^+]}.$$

TABLE NO. 7.11

Complex [Mn(HSe)(OH)], $p\phi_{11}$, $p\beta_{11}$

(Experimental Data pH, 10-13, Table 7.5).

C.No.	pMn_{tot} (average)	$-p\phi_{11}$	$-p\beta_{11}$
C-1	6.50	19.65	8.05
C-2	6.58	19.57	7.97
C-3	6.39	19.76	8.16

$$-p\phi_{11} = -pMn_{tot} + pK_{sp} + pK_w = 19.66 \qquad \sigma = \pm 0.20.$$

$$-p\beta_{11} = -(pk_2 + p\phi_{11}) = 8.06.$$

Discussion of the Results:

The literature available on the solution chemistry of the inorganic selenides is very scanty. Metallic selenides have been precipitated by dropping the soluble metal salt into a saturated solution of H_2Se in an oxygen free atmosphere. The selenides formed by precipitation are reported to be similar in character to the sulphides but are relatively unstable in air and can not be dried without some decomposition.

Moser and Atynski (86) have shown that like its thio-compound, Hg_2Se also does not exist. They always found HgSe and Se whenever mercurous compound was reacted with the solution of H_2Se. These authors have also reported the preparation of MnSe and Ag_2Se by the same general reaction mentioned above. It is their observation that the Ag_2Se probably forms complexes with hydroxides, sulphides, and selenides. However, detailed information on this aspect is unavailable. Fabre and Diacon (86) have also successfully employed the soluble alkali selenides in the preparation of MnSe. It is apparent from the earlier literature that the precipitated selenides maintain the stoichiometry in the solid phase irrespective of the method of preparation.

The System HgSe:

The comparative studies on the solution chemistry of HgSe have now shown clearly the parallel character of this system with that of its corresponding sulphide. The initial solubility slope of zero once again proves that a hydrated species Hg(HSe)(OH) does occur in the equilibrium. This shall remain constant and other complexes, if formed, will have their concentrations added to this. That is to say, if any other complex is formed in concentration higher than the hydrated species, the solubility curves will indicate changes in the experimental slopes, which will identify the new complex. As solubility of HgSe increases around pk_1 of H_2Se, this clearly implies that solubility increases only because of the appearance of a new complex forming species HSe^- in the equilibrium. The experimental data show that one HSe^- ion is added in the new complex. The second complex can now be written as,

$$(Hg(HSe)(OH)) + (HSe^-) \rightleftharpoons (Hg(HSe)_2(OH)^-)$$

This assumption like the earlier case of HgS neatly explains the solubility plateau immediately after the pk_1 of H_2Se. If the non-hydroxy species is postulated as $Hg(Se)_2H$, similar to $Hg(S_2)H$, discussed in the corresponding HgS system, the solubility slopes must decrease after pk_1 till pk_2 of H_2Se. The experimental results thus support the formation of mixed hydroxy-complex both in HgS and now, as seen here, in the HgSe system.

The continuous increase of the HgSe solubility after pH 6 can only be accounted for by assuming the formation of yet another complex in the system. The experimental slope of the HgSe solubility as a function of Se_{tot} still remains one (fig. 7.4) thereby assuring that the amount of HSe^- ions in the new complex also remain the same as in the previous one. Experimentally the conditions remain similar except that the concentration of free OH^- ions is increased because of the increased alkalinity. It is easy to visualize now that the reaction for the new complex formation proceeds as follows,

$$(Hg(HSe)_2(OH))^- + (OH^-) \rightleftharpoons (Hg(HSe)_2(OH)_2^{-2})$$

This treatment is justified since the charge of the complex is raised only by one unit. The di-hydroxy di-seleno complex formation is also favoured on the basis that the solubility increases in the pH regions where HSe^- is still the only complexing ligand present in appreciable concentration. It is possible to write the same complex shown above as $HgSe_2^{-2} \cdot 2H_2O$, i.e. dihydrated form of the species $HgSe_2^{-2}$. The last mentioned form has been favoured strongly by several authors for the sulphide system, which has been fully discussed earlier (chapter VI). From our experiences may we now conclude confidently that mixed hydroxy seleno-complex formation is the characteristic property of the mercury selenide system as well.

The System Ag_2Se:

In this system the parallel character is not observed to the same extent as in mercury selenide. The ligand HSe^- seems to favour little complex formation with Ag^+, which was very pronounced in the Ag_2S system. However, the increase in the Ag_2Se solubility in region beyond pk_2 of H_2Se is a clear indication that Se^{-2} ions participate in the complex formation in this case. This is another example found in this study where the complexing is demonstrated unambiguously for the deprotonated species of the precipitating ligand acids. SeO_3^{-2} complexing has already been discussed earlier (chapter V).

The complex $Ag_2(HSe)(OH)$ is formed in the initial stage of precipitation and extends till the pH region of 10, when Se^{-2} becomes the predominent complex forming ligand. This observation leaves no doubt on the earlier assumption that H_2Se or HSe^- complexes are not formed in acidic medium.

The pH solubility slope of Ag_2Se beyond pk_2 is one (fig. 7.1) which means that only one OH^- ion enters the complex. The Se_{tot} solubility slope is -1.5, at a constant pH, which implies that two Se^{-2} ions participate in the complex species.. The complex formation reaction may be written as,

$$(Ag^{+}) + 2(Se^{-2}) + (OH^{-}) \rightleftharpoons (Ag(Se)_2(OH))^{-4}$$

Gubeli and Ste-Marie (59) have found that in pure hydroxy system, Ag(OH) complex formation is strong in alkaline conditions. It may be easily proved that in this selenide system the solubility of Ag_2Se does not increase because of any pure hydroxy complex like Ag(OH). If it were so, the solubility with respect to pH will conform to a slope of one, but it shall continuously diminish with a slope of 0.5 with increasing Se_{tot} in the medium. The observed solubility trend is actually reverse in this respect so that the formation of a pure silver hydroxy complex is ruled out. It may further be demonstrated that the solubility does not increase because of the formation of pure seleno complexes, e.g. $Ag(Se)_n^{1-2n}$, with n having an integral value. In such an event the pH effect on the solubility would be minimum. This may be seen clearly in silver selenite complexing (chapter V), where the solubility curves attain a horizontal slope of zero immediately after the pk_2 of H_2SeO_3. The formation of monohydroxy di-seleno complex of silver is therefore beyond doubt and it may be regarded as a special characteristic of the system Ag_2Se.

<u>The System MnSe</u>:

MnSe has shown parallel solubility character compared to its sulphide. This system too has the presence of free Mn^{+2} ions in the initial phase of precipitation followed by the formation of the complex species Mn(HSe)(OH). This demonstrates that Mn has little tendency to form coordination complexes with the ligands of H_2S or H_2Se. The experimentally determined solubility product of MnSe compares well with the theoretically calculated value of Buketov *et al.* (85). However, the regular trend of the sulphides being more soluble than the selenides is lost here, since the solubility product of the MnS has been found lower than its selenide in this study. A similar discrepancy was noticed by Ste-Marie (23) in the ZnS and ZnSe systems under similar experimental conditions, who also observed their K_{sp} values reversed in order. It is difficult to advance any specific reason for such a behaviour, perhaps it will be necessary to investigate the entire series from Mn to Zn to look for a possible explanation for this odd observation.

Original Contributions to the Solution Chemistry of Metal Chalcogenides.

This investigation on the solution chemistry of the sparingly soluble metal chalcogenides has revealed the formation of aqueous complexes of varying stabilities. A close study of the heterogeneous equilibria has shown that the stability of the complex, in general, increases with the increasing insolubility of the parent compound. This observation demonstrates that aqueous coordination complexes of exceptionally high stabilities are possible irrespective of the solubility of the original compound.

The theoretical treatment has been developed for the solubility equilibrium data, which may be utilized for the identification of a variety of complexes in solution. The versatility of the method lies in the extreme simplicity and clarity with which the constitutions of the possible complexes can be established unambiguously. Particularly it is true for the mixed complexes, which have been observed for the first time in such systems. This approach thereby offers an alternate route to explore the complicated inorganic systems involving weak acids precipitations, which in turn also function as the complexing ligands.

The uncertainties on the ionization constants of H_2Se and H_2SeO_3 have been cleared successfully. The solubility product constants of their silver and mercury compounds have been established experimentally for a medium of controlled ionic strength. In general, the experimental technique can be adopted for such determinations at any desired ionic strength.

The aqueous selenite complexes of silver have been observed for the first time in this study. Though the complexes are weak in character yet their formation has been demonstrated positively from the experimental data.

The thio-complexing characteristics of the transition and B character elements have been elucidated fully. The transition elements have shown very feeble coordination behaviour. A new complex $Co(HS)_4^{-2}$ has been detected in the CoS system. The solubility trends indicate that the complexing characteristics in the series increase with the increasing atomic number of the element.

The stoichiometries of the previously known sulphide complexes of the Ag_2S and HgS systems have been corrected through this investigation. In the Ag_2S system, in unbuffered conditions, the formation of two species, $Ag_2(HS)(OH)$ and $Ag(HS)_2^-$ could be proved convincingly with little evidence for the higher complexes. While in the HgS system it has been established in accordance with the theory that the experimental data can best be explained, if only the formation of mixed thio-hydroxy complexes is assumed for certain. Further it has been illustrated that the complex formation in this case proceeds in a stepwise fashion.

The systematic studies on the seleno-complexes have been initiated for the first time in this work. Comparative studies in case of HgSe have shown a behaviour similar to its counterpart HgS. The system Ag_2Se on the other hand has exhibited a totally different behaviour compared to its corresponding system Ag_2S. However, the formation of a unique complex $Ag(Se)_2(OH)^{-4}$ has been observed. The system MnSe has exhibited a parallel character compared to its corresponding MnS system, with little tendency towards coordination with either of the ligand species of the H_2Se.

The reliability of the calculated results is shown by the concordant values obtained for the formation constants of those systems that have been investigated by other workers as well, e.g. the complex $Ag(HS)_2^-$ and the solubility products of the metal sulphides. One may therefore conclude with confidence that the new constants derived in this study for the selenide and selenite complexes are also true. The constants obtained are, however, the concentration stability constants valid at unit molar ionic strength. The experimental technique, nevertheless, permits the evaluation of these constants at another higher ionic strength; such measurements in turn may be utilized in the determination of the thermodynamic constants.

Finally, as far as the author is aware the aqueous complexes of the metal selenite and selenide systems have been investigated and successfully established for the first time. Probably this investigation is the first detailed report on the experimental studies on the solution chemistry of the metal selenides.

Summary of the New Results

Dissociation Constants of Ligand Acids at $\mu = 1.0$ $NaClO_4$ and 25°C

Acid	pk_1	σ	pk_2	σ
H_2Se	3.48	± 0.22	11.60	± 0.18
H_2SeO_3	2.26	± 0.09	8.12	± 0.28

Solubility Product Constants of the Insoluble Compounds at $\mu = 1.0$ $NaClO_4$ and 25°C

Compound	pK_{sp}	σ
Ag_2S	49.03	± 0.20
Ag_2Se	53.79	± 0.08
Ag_2SeO_3	15.58	± 0.12
HgS	51.94	± 0.31
HgSe	56.61	± 0.22
MnS	13.11	± 0.07
MnSe	12.15	± 0.40
FeS	17.80	± 0.18
CoS	21.50	± 0.27

Stability Constants of the Aqueous Complexes at μ = 1.0 $NaClO_4$ and 25°C.

Complex	$-p\beta_{complex}$	σ
$[Ag(SeO_3)^-]$	2.42	± 0.12
$[Ag\ (SeO_3)_2^{-3}]$	3.76	± 0.05
$[Ag_2(HS)(OH)]$	41.89	± 0.16
$[Ag(HS)_2^-]$	16.97	± 0.06
$[Hg(HS)(OH)]$	44.62	± 0.23
$[Hg(HS)_2(OH)^-]$	47.15	± 0.17
$[Hg(HS)_2(OH)_2^{-2}]$	53.37	± 0.06
$[Mn(HS)(OH)]$	7.46	± 0.20
$[Fe(HS)(OH)]$	13.78	± 0.13
$[Co(HS)(OH)]$	15.33	± 0.10
$[Co(HS)_4^{-2}]$	14.88	± 0.22
$[Ag_2(HSe)(OH)]$	48.49	± 0.10
$[Ag(Se)_2(OH)^{-4}]$	24.07	± 0.19
$[Hg\ (HSe)(OH)]$	51.18	± 0.22
$[Hg\ (HSe)_2(OH)^-]$	52.76	± 0.31
$[Hg(HSe)_2(OH)_2^{-2}]$	61.04	± 0.32
$[Mn(HSe)(OH)]$	8.06	± 0.20

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