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Herbert Charles Moser
Iowa State College

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RADIOCHEMICAL STUDIES OF MERCURY AND ITS IONS IN DILUTE SOLUTIONS

by

Herbert Charles Moser

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In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

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I. INTRODUCTION

The purpose of this study is to elucidate some of the chemical characteristics of mercury and its ions in dilute solutions. The tracer technique of determining low concentrations is applied by using radioactive mercury 203 in a threefold area of investigation.

The problem of the stability of dimeric mercurous ions in dilute aqueous solutions is studied. The principal aim of this endeavor is that of resolving between dissociation of the dimers into individual mercurous ions and dismutation into mercuric ions and dissolved free mercury. The two processes are alternate mechanisms describing the instability of the mercurous dimer in dilute solutions. Use is made of the extraction of dissolved free mercury into organic solvents to measure the extent of dismutation.

The demonstration of the existence of free mercury as a solution species led to an interest in measuring the limited solubility of mercury in a number of solvents. In general mercury is thought of as completely insoluble in liquids, but with the use of radioactive mercury tracer the solubility is found to be within easily detectable concentrations in all of the solvents tested. A correlation of the solubility measurements with existing quantitative theory is attempted.

In a third area of study, equilibria between mercuric iodide and iodide ions are investigated. Although these equilibria have been the subjects of a number of investigations, it was thought desirable to see if an approach using radioactive mercury tracer to determine low concentrations would give results similar to those obtained in other ways. The extraction of mercuric iodide into benzene is used to measure the equilibrium constants for the combination of mercuric iodide and iodide ions to form triiodo and tetraiodo complexes of mercury (II).

II. REVIEW OF LITERATURE

A. Properties of the Mercurous Ion

It is not the intention of this review to list all of the publications which describe the behavior of the mercurous ion. Mention will be made of only those studies having results relevant to the present problem, namely, the stability of the mercurous ion in dilute solutions.

It has been shown in a number of ways that mercurous ions exist in the form of dimers in aqueous solutions. Following are perhaps the most convincing arguments concerning this unique behavior.

Ogg (1) and Abel (2) have shown that, in systems of mercury metal and aqueous solutions of mercuric and mercurous nitrates, the concentration ratio of mercury (II) to mercury (I) is always constant and independent of total mercury concentration in solution. The existence of a dimeric form of mercury (I) in the equilibrium:

$$Hg_2^{++} \rightleftharpoons Hg(1) + Hg^{++}$$

with an equilibrium constant:

$$K = \frac{[Hg^{++}]}{[Hg_2^{++}]}$$

explains these observations. If the mercurous ions were monomeric the equilibrium constant would have the form:

$$K = \frac{[Hg^{++}]}{[Hg^{+}]^2} \quad ,$$

and the ratio $[Hg(II)]/[Hg(I)]$ would not be constant.

Ogg (1) also conducted experiments in which he treated silver nitrate solutions of varying concentrations with metallic mercury. When this is done reduction of some of the silver takes place and aqueous solutions of silver nitrate and mercurous nitrate remain. The free silver formed by the reduction of silver ions is amalgamated by the mercury metal. Alternate equations describing the reaction can be written:

$$Hg + Ag^{+} \underset{}{\overset{K_1}{\rightleftharpoons}} Hg^{+} + Ag$$

$$\text{or } 2Hg + 2Ag^{+} \overset{K_2}{\rightleftharpoons} Hg_2^{++} + 2Ag$$

with equilibrium constants:

$$K_1 = \frac{[Hg^{+}][Ag]}{[Hg\ ][Ag^{+}]}$$

$$\text{and } K_2 = \frac{[Hg_2^{++}\ ][Ag]^2}{[Hg\ ][Ag^{+}]^2} \quad .$$

In these expressions $[Hg\ ]$ and $[Ag]$ are the concentrations of mercury and silver in the amalgams. Ogg's experiments were conducted in dilute silver nitrate solutions and the resulting amalgams were mercury rich. Thus the free mercury concentrations remained essentially constant. Measurements of the concentrations of mercury and silver in the aqueous phase and silver in the amalgam sufficed to demonstrate the dimeric state of mercury (I). It was found that for an eightfold variation of mercury (I) concentration, values of $[Hg_2^{++}][Ag]^2/[Ag^+]^2 = K_2[Hg]^2$ changed only 20 per cent. However with the same variation of mercury (I) concentration, values of $[Hg^+][Ag]/[Ag^+] = K_1[Hg]$ changed threefold.

Using an entirely different approach, Woodward (3) obtained further evidence supporting the dimeric state of the mercurous ion. In a study of the Raman spectrum of a nearly saturated solution of mercurous nitrate containing nitric acid, he found, in addition to bands of the water and lines due to the nitrate ion, a strong Raman frequency ($\Delta\nu = 169$ cm^{-1}) which he ascribed to the mercury-mercury link.

Other experiments could be cited which demonstrate the dimeric state of the mercurous ion, but those mentioned above suffice to verify this behavior. The remaining part of the review will be concerned with the results of studies regarding the stability of the dimer.

The instability of these dimeric ions with respect to the formation of liquid mercury and mercuric ions is well established. Ogg (1) and Abel (2) observed this behavior quantitatively in solutions of mercurous and mercuric nitrates in the presence of mercury metal. By making separate analyses for mercury (I) and mercury (II) they were able to report concentration ratios, $[Hg(I)]/[Hg(II)]$, of 240 at 25° (2) and 224 (1). The experimental temperature was not specified for the latter value. Using these measurements, values of 120 and 112 are calculated for the equilibrium constant:

$$K = \frac{[Hg_2^{++}]}{[Hg^{++}][Hg(l)]} \quad .$$

Other estimates of K have been made from e.m.f. measurements. If the standard oxidation potentials of the couples:

$$2Hg \rightleftharpoons Hg_2^{++} + 2e \qquad (E_1^o)$$

$$\text{and } Hg_2^{++} \rightleftharpoons 2Hg^{++} + 2e \qquad (E_2^o)$$

are known, a value of K can be calculated. Thus at 25°C:

$$\log K = \frac{E_1^o - E_2^o}{0.059} \quad .$$

a value of K as high as 166 (4) has been reported, but more recent measurements favor the somewhat lower figures 129.2 ± 1.0 (5), 88 ± 3 (6) and 83.4 (7). The wide variance in experimental answers can be understood when one considers that only a 1 millivolt change in the measurement of $E_1^o - E_2^o$ makes a difference of about six in the calculated equilibrium constant.

Higginson (8) added a new consideration about the instability of the mercurous dimer by suggesting that it dissociates in very dilute solutions to form Hg^+ ions. He studied the ultra-violet absorption spectra of mercurous perchlorate solutions and observed that, in solutions having concentrations lower than 10^{-6} M in mercurous perchlorate, there is a significant departure from Beer's law. To explain this effect he assumed a dissociation of the dimer to give relatively transparent monomeric mercurous ions. A dissociation constant within the limits 10^{-8} to 10^{-6} was reported. No other experimental value appears to have been published although values of 10^{-31} and 10^{-18} have been inferred from other observations and calculations (8).

Cartledge (9) predicted the presence of Hg^+ ions as intermediates in Eder's reaction:

$$K_2C_2O_4 + 2HgCl_2 = Hg_2Cl_2 + 2KCl + 2CO_2 \ .$$

He calculated a standard oxidation potential of -1.71 volts for the half cell reaction:

$$Hg(l) \rightleftharpoons Hg^+(aq) + e \ .$$

The calculation was carried out by approximating an ionic radius and an energy of hydration of the Hg^+ ion. Using the estimated value above and the standard oxidation potential of the Hg, Hg_2^{++} couple, a value of +42 kcal was determined for the ΔF of dissociation. This leads to a dissociation constant of 10^{-31}.

Kolthoff and Barnum (10) studied the anodic reaction of cysteine ($HOOC-CH(NH_2)-CH_2-SH$) at the dropping mercury electrode. They predicted the formation of HgSR at the anode with a resulting mercurous ion concentration in solution of approximately 10^{-20} M. They further suggested that at this small concentration practically all of the mercury (I) was present as Hg^+ ions. The dissociation constant would have to be larger than 10^{-18} to be consistent with the latter statement.

The possibility of another mechanism describing the instability of the mercurous ion was brought out in an interesting calculation by Sidgwick (11). He proposed the following reaction in view of the very slight solubility of mercury metal in water:

$$Hg(aq) + Hg^{++} \rightleftharpoons Hg_2^{++} ,$$

with an equilibrium constant:

$$K = \frac{[Hg_2^{++}]}{[Hg^{++}][Hg]aq} .$$

Using Stock's (12) value of 1 x 10^{-7} M for the solubility of mercury and a value of 116 for the concentration ratio $[Hg_2^{++}] / [Hg^{++}]$, he calculated an equilibrium constant of 1.16 x 10^9 for the above reaction. The equilibrium constant of the dismutation equation:

$$Hg_2^{++} \rightleftharpoons Hg^{++} + Hg(aq)$$

would be the reciprocal of this quantity or 8.6 x 10^{-10}.

In conclusion, dissociation and dismutation have been proposed as alternate mechanisms describing the instability of the mercurous ion. Since Higginson's experiments, the ultra-violet absorption spectrum of mercuric perchlorate has been published by Buck, Singhadeja, and Rogers (13). Implications of this cast considerable doubt upon Higginson's explanation of the deviations from Beer's law encountered in very dilute solutions of mercurous perchlorate. A comparison of the results of the two studies is worth-while.

In the absorption spectrum of mercuric perchlorate (13) maxima are shown at almost exactly the same wavelengths as those given by Higginson for mercurous perchlorate. The molar extinction coefficient at the wavelength of maximum absorption is one-half the value of that for mercurous perchlorate. Under these circumstances it would be extremely difficult to use absorption spectra to distinguish between the two mechanisms of dissociation or dismutation. The occurrence of either process would lead to similar deviations from Beer's law if dissolved free mercury and Hg^+ are both relatively transparent.

B. The Limited Solubility of Mercury Metal

Bonhoeffer and Reichardt (14) studied the ultra-violet absorption spectrum of water that had been heated in the presence of metallic mercury. The spectrum of n-hexane that had been similarly treated was also studied. Absorption bands characteristic of dissolved mercury were found in both solvents, and the solubility was noted as about equal to that of the inert gases. In a later publication (15) these same authors reported values for the solubility of mercury in methanol, n-hexane, and water. Analyses were made gravimetrically by amalgamating the dissolved mercury on a gold

Table 1. Reported Values for the Solubility of Mercury Metal

Solvent	Temperature °C	Solubility mg/100 cm^3	Investigators
Methanol	40	0.06	Reichardt and Bonhoeffer (15)
	63	36	Reichardt and Bonhoeffer (15)
Hexane	40	0.27	Reichardt and Bonhoeffer (15)
	63	1.03	Reichardt and Bonhoeffer (15)
Benzene	room	0.15-0.20	Stock _et_ _al_. (12)
Water	25-28	0.003	Pariaud and Archinard (19)
Water	30	0.002-0.003	Stock _et_ _al_. (12)
Water	85	0.03	Stock _et_ _al_. (12)
Water	100	0.06	Stock _et_ _al_. (12)
Water	120	0.1	Reichardt and Bonhoeffer (15)

foil. These values along with other solubility measurements mentioned in this review are given in Table 1.

Reichardt and Bonhoeffer (15, 16) were able to demonstrate quite conclusively that dissolved free mercury was present in their solutions. The spectral absorption curves showed two absorption bands in the region of the mercury resonance line at 2537Å. The distance between the maxima of the bands was found to increase with the polarity of the solvent. This observation was interpreted as a Stark effect due to the action of the electrical field of the solvent molecules.

Stock et al. (12) determined the solubility of mercury in air-free water and benzene. They found that the presence of air in water affected the solubility considerably, but a similar behavior was not found in the case of benzene. The method of analysis was apparently similar to one reported earlier (17, 18) in which mercury was electrolytically deposited on a copper wire from a solution containing mercuric chloride. It was then distilled out of the wire and made into a tiny globule. Finally the volume of the globule was determined under a microscope. They asserted that an exact determination could be made on as little as 10^{-5} mg (7.3×10^{-10} cm^3) and a lower limit of 2×10^{-6} mg could be detected.

Pariaud and Archinard (19) measured the solubility of mercury in triple distilled, degassed water at a temperature of 25-28°C. The concentration of mercury in solution was determined colorimetrically with diphenyethiocarbazone (dithizone). Their article might be criticized because no mention is made of oxidizing the dissolved mercury during the course of the analysis. Unless reference to this step was just neglected, their value for the solubility did not include the contribution due to the dissolved free element.

C. Mercuric Iodide-Iodide Ion Equilibria

The mercuric iodide-iodide ion equilibria have been the subject of a number of investigations. Sherrill (20) concluded that two principal complexes were present in solutions containing mercuric iodide and potassium iodide. From e.m.f. measurements of cells with a mercury electrode in a solution of HgI_2 and KI, he inferred that the predominant complex was $HgI_4^{=}$ in the concentration range studied (0.04 - 1.0M KI,0.0025 - 0.3M HgI_2). In other studies he used the catalytic effect of iodide ions upon the decomposition of hydrogen peroxide to measure the iodide ion concentration in solutions of hydrogen peroxide, mercuric iodide and potassium iodide. In these solutions (0.03125M KI, 0 - 0.01315M HgI_2) he concluded that the principal complex ion was $Hg_2I_7^{\equiv}$. Measurements of the freezing points of solutions of mercuric iodide and potassium iodide were also explained by assuming $HgI_4^{=}$ and $Hg_2I_7^{\equiv}$. Sherrill studied the distribution of mercuric iodide between benzene and aqueous potassium iodide solutions. By assuming that $HgI_4^{=}$ and HgI_2 were the predominant aqueous species, values for the equilibrium constant K_2 of the reaction:

$$HgI_2 + 2I^- \rightleftharpoons HgI_4^{=}$$

$$K_2 = \frac{\left[HgI_4^{=}\right]}{\left[HgI_2\right]\left[I^-\right]^2}$$

were calculated. They varied from 5.9×10^5 to 31×10^5, and 7.3×10^5 was considered the best value.

Garrett (21) measured the solubility of mercuric iodide in potassium iodide solutions. His results were interpreted by assuming the presence of the aqueous species HgI_2, HgI_3^- and $HgI_4^=$. Using the equilibrium constants from this study and the value of Tananaev and Pilipenko (22) for the solubility of mercuric iodide (a value accepted by Garrett), the following constants are calculated at 25°C:

$$K_1 = \frac{[HgI_3^-]}{[HgI_2][I^-]} = 3600$$

$$\text{and } K_2 = \frac{[HgI_4^=]}{[HgI_2][I^-]^2} = 2.7 \times 10^5 .$$

By electrometric methods Qvarfort and Sillén (23) have determined a large number of the constants associated with mercury (II) and iodide ion equilibria. In order to obtain values for K_1 and K_2 a number of different measurements had to be made: the potential of a mercury electrode in solutions of mercuric iodide and potassium iodide, the redox potential of Hg_2^{++} - Hg^{++} in iodide solutions using a platinum electrode, the potential of a mercury electrode in solutions of mercurous mercury and added iodide, and the solubility of mercuric iodide. In spite of the complexity of the method, their values of $K_1 = 6100 \pm 2400$ and $K_2 = (1.03 \pm 0.11) \times 10^6$ are not widely variant from those calculated from Garrett's data.

From optical measurements Fromherz and Lih (24) reported $K_2 = 1.1 \times 10^5$ and Job (25) reported $K_2 = 0.8 \times 10^8$ at 16°C. In both of these studies only the higher complex $HgI_4^=$ was considered.

III. MATERIALS AND PROCEDURE

A. Solutions and Solvents

1. Aqueous solutions

Solutions used in this study were made up with water that was doubly distilled from alkaline potassium permanganate.

A 0.1 M nitric acid solution was prepared using Baker and Adamson C. P. reagent grade nitric acid. It was analyzed by titration with a standard sodium hydroxide solution. Solutions of 0.01 M and 0.001 M nitric acid were made from the 0.1 M solution.

Solutions of 0.047 M mercuric nitrate, 0.1 M potassium nitrate and 0.1 M potassium iodide were prepared from "Baker Analyzed" reagent grade chemicals. Nitric acid was added to the mercuric nitrate solution to prevent hydrolysis of the mercuric ions. The solution was standardized volumetrically with potassium thiocyanate and gravimetrically by precipitation of the sulfide. Potassium iodide and potassium nitrate were treated as primary standards. Gravimetric analysis of a solution of potassium iodide prepared from the same reagent for earlier work had established a purity of about 99.6 per cent reported as KI. The hypophosphorous acid used in the study was Baker and Adamson U.S.P. grade containing 30 - 32 per cent acid.

2. Solutions containing radioactive mercury

A 0.31 M solution of mercuric nitrate in 1.56 M nitric acid containing radioactive mercury 203 was obtained from the Oak Ridge National Laboratory. In order to maintain a high specific activity the tracer was used in the experiments without dilution with stable mercury except during analysis. When shipped the mercury had a very high specific activity, approximately 50 millicuries/g. Mercury 203 decays to stable thallium 203 by the emission of a beta particle of maximum energy 0.20 mev (26) and a gamma ray of energy 0.28 mev (27). The isotope has a half life of 48 days (28).

A stock solution of mercurous nitrate was prepared from the radioactive mercuric nitrate solution by dilution with 0.01 M nitric acid and shaking with a drop of metallic mercury. Mercury metal was prepared from the solution of radioactive mercuric nitrate by reduction with hypophosphorous acid. After precipitation the finely divided metal was coagulated into a globule by the addition of a small amount of concentrated hydriodic acid and finally washed thoroughly. The final mercurous ion concentration in the stock solution was approximately 1.8×10^{-3} M. In one instance another more dilute solution was made from this just prior to use.

A stock solution of radioactive mercuric nitrate was prepared by dissolving 7.343 mg of metallic mercury, prepared as mentioned above, with nitric acid and diluting to a final volume of 10 ml. This solution was further diluted for use in the study.

3. Organic solvents

Phillip's Pure Grade n-hexane and Eastman Spectro Grade cyclohexane were used in distribution studies with dilute mercurous nitrate solutions. The presence of unidentified impurities in these solvents made their use impractical without quite extensive purification. When they were used without any treatment at all, it was found that the oxidized forms of mercury extracted into them from the highly dilute mercurous nitrate solutions. This is not too surprising, because of the pronounced tendency of mercuric ions to form complexes. In fact some extraction from dilute mercuric nitrate solutions was found using n-hexane even after prolonged refluxing of the solvent with both concentrated sulfuric acid and a solution of potassium permanganate.

After a large number of attempts at purifying the solvents, the following treatment appeared adequate to remove the interfering impurities. The solvents were shaken with both concentrated sulfuric acid and a solution of alkaline potassium permanganate, then were passed through a column packed with dry, activated alumina, and finally redistilled. In the case of cyclohexane a silica gel column was also used in the purification. When samples of the purified solvents were shaken with a solution of 3.4×10^{-4} M mercuric nitrate in 0.01 M nitric acid, no mercury was found in the organic phase. If the concentration of mercury in the organic phase had been 2×10^{-9} M or more it would have been detected radiochemically. The purified solvents were also used for the determination of the solubility of mercury metal.

Baker and Adamson, reagent grade, thiophene-free benzene was used without further purification for the mercuric iodide distribution experiments and for mercury solubility measurements.

In addition to the solvents already mentioned, Eastman toluene (from toluene sulfonic acid), Eastman Spectro Grade carbon tetrachloride, and Baker Purified nitro-benzene were used in mercury solubility measurements. If the toluene was not treated impurities in it were found to react with mercury forming a black deposit on the surface. Purification was carried out by shaking with an aqueous solution of sodium hydroxide, passing through a column packed with dry silica gel, and redistilling. Using the treated toluene, the solubility of mercury was found to remain essentially constant during a seven day period and no visible evidence of a reaction was apparent even after two weeks. However, a black surface deposit was noticed after about three weeks. The treatment of carbon tetrachloride was similar to that for toluene except that an aqueous solution of sodium sulfite was used. The added purification of this solvent was done to insure the absence of any free chlorine. Nitrobenzene was used without any further treatment.

B. Apparatus

All solutions were allowed to equilibrate in E. H. Sargent and Company water baths capable of maintaining constant temperatures to within ± 0.1°C. The experimental solutions were placed in 10 - 50 ml volumetric glass stoppered flasks for equilibration, and agitation of the solutions was provided by a Burrell model DD shaker.

Radiochemical analyses were made using a Tracerlab type TGC-2/1B84 Geiger-Mueller counting tube incorporated with a Nuclear Instrument and Chemical Corporation model 164 scaling unit. The counting tube had a mica end window of 1.8 mg/cm^2 thickness. Counting data were all taken using the same lead housing, plastic counting mount, and aluminum sample holder.

C. Experimental Procedures

1. Distribution experiments with dilute mercurous nitrate solutions

Dismutation constants were obtained by the procedure of extracting the dissolved free mercury from dilute aqueous solutions of mercurous ions with *n*-hexane and cyclohexane.

The dilute aqueous solutions of mercurous nitrate were made by extensively diluting the stock solution with 0.01 M nitric acid to concentrations in the 10^{-5} M to 10^{-8} M range. The dilutions were made by adding micro-pipet aliquots to 5 or 10 ml of 0.01 M nitric acid. Distribution was carried out by shaking equal volumes of the aqueous solutions and purified n-hexane or cyclohexane. After the mixtures were equilibrated at 25°C by shaking in a water bath for 12 to 15 hours, both phases were analyzed for mercury concentration.

Cleanliness was of utmost importance since the experiments involved such dilute solutions of mercury. The equilibration flasks were always cleaned in the same way. They were rinsed with a warmed solution of alcoholic potassium hydroxide and then distilled water from the tap. Next they were rinsed with concentrated nitric acid and again several times with distilled water from the tap. Finally they were rinsed five times with double distilled water, inverted on a lintless tissue, and allowed to drain dry. The pipets were cleaned in a similar fashion shortly before use excepting that rinsing with alcoholic potassium hydroxide was omitted unless the pipet showed signs of draining improperly. They were generally dried with suction.

As mentioned earlier, 12 to 15 hours of equilibration time were allowed in these experiments. In order to verify this procedure identical solutions of dilute mercurous nitrate in 0.001 M nitric acid were extracted for different lengths of time with purified n-hexane. The results are given in Table 2. The distribution ratio D is the quotient of the total mercury concentration in the aqueous phase divided by the concentration of mercury in the organic phase.

Table 2. Time Dependence of the Distribution Ratio

Time in Hours		D
0.5		7.4
1		7.1
2		6.6
6	(average of two determinations)	6.7
13		6.6

Another experimental condition, the use of solutions 0.01 M in nitric acid, is justified in the following way. The procedure was designed to use solutions in which the oxidized forms of mercury were uncomplexed. First of all nitric acid is preferred to perchloric acid because of its lower limit of maximum chloride content. Baker and Adamson, reagent grade perchloric acid (70 - 72 per cent) has a maximum chloride content of 0.001 per cent, while their C. P. grade nitric acid has a maximum limit of only 0.00001 per cent chloride. In view of the tendency of the mercuric ion to form chloro complexes, the advantage of the acid with a lower chloride content is evident. The concentration was set at 0.01 M because at lower acidity the mercury ions hydrolyze and at higher nitrate concentrations they form nitrato complexes.

The proper nitric acid concentration can be calculated using the published values of the hydrolysis and complexing constants. The following reactions and corresponding equilibrium constants need to be considered:

$$Hg^{++} + H_2O \overset{K_1}{\rightleftharpoons} HgOH^+ + H^+ \qquad K_1 = 2 \times 10^{-4} \quad (29)$$

$$Hg^{++} + 2H_2O \overset{K_2}{\rightleftharpoons} Hg(OH)_2 + 2H^+ \qquad K_2 = 5 \times 10^{-7} \quad (29)$$

$$Hg(NO_3)_2 \overset{K_3}{\rightleftharpoons} Hg^{++} + 2NO_3^- \qquad K_3 = 1.0 \quad (30)$$

$$Hg(NO_3)^+ \overset{K_4}{\rightleftharpoons} Hg^{++} + NO_3^- \qquad K_4 = 1.3 \quad (30)$$

$$Hg_2^{++} + H_2O \overset{K_5}{\rightleftharpoons} Hg_2OH^+ + H^+ \qquad K_5 = 1 \times 10^{-5} \quad (31)$$

$$Hg(NO_3)_2 \overset{K_6}{\rightleftharpoons} Hg_2^{++} + 2NO_3^- \qquad K_6 = 0.5 \quad (30)$$

$$Hg_2NO_3^+ \overset{K_7}{\rightleftharpoons} Hg_2^{++} + NO_3^- \qquad K_7 = 1.05 \quad (30)$$

If all of the chemical species of mercury (I) and (II) are included in the equilibrium reactions given above, the total concentration of mercury (II), $\left[Hg(II)\right]_{tot}$, is given by:

$$\left[Hg(II)\right]_{tot} = \left[Hg^{++}\right] + \left[HgOH^+\right] + \left[Hg(OH)_2\right] + \left[HgNO_3^+\right] + \left[Hg(NO_3)_2\right]$$

$$= \left[Hg^{++}\right] + \frac{K_1\left[Hg^{++}\right]}{\left[H^+\right]} + \frac{K_2\left[Hg^{++}\right]}{\left[H^+\right]^2} + \frac{\left[NO_3^-\right]\left[Hg^{++}\right]}{K_4} + \frac{\left[NO_3^-\right]^2\left[Hg^{++}\right]}{K_3}.$$

Since $[Hg^{++}]$ is a common factor to each term:

$$[Hg(II)]_{tot} = [Hg^{++}]\left\{1 + \frac{K_1}{[H^+]} + \frac{K_2}{[H^+]^2} + \frac{[NO_3^-]}{K_4} + \frac{[NO_3^-]^2}{K_3}\right\} .$$

Thus
$$\frac{[Hg^{++}]}{[Hg(II)]_{tot}} = \frac{1}{1+ \frac{K_1}{[H^+]} + \frac{K_2}{[H^+]^2} + \frac{[NO_3^-]}{K_4} + \frac{[NO_3^-]^2}{K_3}} .$$

Similarly for mercury (I):

$$\frac{[Hg_2^{++}]}{[Hg(I)]_{tot}} = \frac{1}{1 + \frac{K_5}{[H^+]} + \frac{[NO_3^-]}{K_7} + \frac{[NO_3^-]^2}{K_6}} .$$

In the last equation $[Hg(I)]_{tot}$ is the total mercury (I) concentration expressed as moles of Hg_2^{++} per liter.

The calculated variations of the fractions $[Hg^{++}]/[Hg(II)]_{tot}$ and $[Hg_2^{++}]/[Hg(I)]_{tot}$ with nitric acid concentration are given in Table 3.

Table 3. Fractions of Mercury (I) and Mercury (II) in Uncomplexed Form in Nitric Acid Solutions

Conc. of HNO_3 moles/liter	$[Hg^{++}]/[Hg(II)]_{tot}$	$[Hg_2^{++}]/[Hg(I)]_{tot}$
0.1	.92	.90
0.01	.96	.99
0.001	.59	.99

Since the objective of this work was the study of the equilibrium between the simple ions, a concentration of nitric acid was selected in which a maximum fraction of the involved ions were uncomplexed, specifically, 0.01 M nitric acid.

In the absence of oxidized forms of mercury the distribution of the dissolved free element between aqueous 0.01 M nitric acid and the solvents n-hexane and cyclohexane was measured. A drop of radioactive mercury was shaken with 10 ml of the solvents for 1 - 2 days. Then 5 ml was withdrawn with a pipet and added to 5 ml of 0.01 M nitric acid. After equilibration in a constant temperature bath, samples from the aqueous and organic phases were analyzed for mercury.

Care was not taken to use water saturated with the organic solvents and vice versa because the mutual solubility of the two phases is quite small. Reported solubility measurements of water in the solvents and conversely are given in Table 4.

Table 4. Solubility of Organic Solvents in Water and the Solubility of Water in Organic Solvents

Solvent	Solubility in H_2O g solvent/100 g H_2O	H_2O Solubility in g H_2O/100 g solvent
n-hexane	0.014 at 15.5°C (33)	0.011 at 20°C (32)
Cyclohexane	not reported	0.010 at 20°C (32)
Benzene	0.175 at 25°C (34)	0.05 at 26°C (32)

2. Mercury solubility determinations

Use was made of radioactive mercury tracer of known specific activity to determine the solubility in aqueous solutions and several organic solvents.

A globule of mercury metal prepared from radioactive mercuric nitrate by reduction with hypophosphorous acid was equilibrated with 5 - 10 ml of liquid by shaking in a constant temperature bath. Aliquots of the liquids were withdrawn from time to time for about two weeks, and the mercury concentration was determined radiochemically.

3. Distribution measurements with mercuric iodide solutions

In this area of study benzene was used to extract mercuric iodide from aqueous solutions.

Micro-pipet aliquots of the stock solution of mercuric nitrate were added to 10 ml aqueous solutions containing potassium iodide, nitric acid and potassium nitrate. A 10 ml aliquot of thiophene-free benzene was added to each of the aqueous solutions, and the mixtures were equilibrated by shaking in a constant temperature bath for 12 - 15 hours. Following this, both phases were analyzed for mercury concentration. The length of time necessary to reach equilibrium was not established experimentally. From the results of the other distribution experiments 12-15 hours were thought to be sufficient.

The iodide dependence of the distribution was determined by varying the potassium iodide concentration over a range 0.001 to 0.02 M while keeping the ionic strength at 0.03 and the nitric acid concentration at 0.01 M. The effect of varying the acidity was determined by varying the nitric acid concentration over the range 0.001 to 0.02 M. In this case the potassium iodide concentration was 0.01 M and the ionic strength was again 0.03.

The distribution of mercuric iodide between benzene and an aqueous solution not having an excess of potassium iodide was determined. Approximately 4 mg of mercuric iodide containing radioactive mercury was prepared by adding a stoichiometric amount of potassium iodide to mercuric nitrate carrier containing added mercury tracer. The mercuric iodide precipitate was washed several times with distilled water and transferred into a mixture of 10 ml of benzene and 10 ml of an aqueous solution of 0.01 M nitric acid and 0.02 M potassium nitrate. After equilibration as mentioned in the other cases, samples were taken from both phases for analyses.

D. Analyses

1. Method of mounting the radioactive samples

Before the tracer technique of determining low concentrations could be applied, a satisfactory method of mounting the radioactive samples had to be found. The method had to give reproducible results with a given amount of radioactive mercury even when the solution environments were not the same. A serious limitation was imposed by the low energy (E_{max} = 0.21 mev) of the beta rays from mercury 203. Very thin counting samples were needed to avoid serious self absorption of the beta particles within the sample. Direct evaporation of aliquots from the solutions was unsatisfactory because some of the solutions contained enough dissolved salts to make the self absorption high.

Several other mounting methods were tested using a solution of mercuric nitrate with added mercury tracer:

a. Precipitation as mercuric sulfide and mounting on filter paper.

b. Dissolving the sulfide precipitate with a small amount of hydriodic acid and evaporation of the solution on a stainless steel planchet.

c. Solution of the sulfide precipitate with aqua regia and evaporation of the solution on a glass slide.

d. Electrodeposition of the metal on platinum and copper planchets.

e. Precipitation as mercuric sulfide and mounting on stainless steel planchets.

The last method was found to be the most satisfactory. A small amount of precipitate could be mounted rapidly and quite simply.

Method e was used to mount radioactive mercury tracer in the present studies in order to determine the concentrations of mercury in the solutions. Following is a description of the procedure. The solution containing radioactive mercury was added to 0.2 ml of mercuric nitrate carrier (0.047M) contained in a centrifuge tube. Excess ammonium sulfide and 2 - 3 drops of Aerosol O T solution were added, and the mercuric sulfide precipitate was coagulated by stirring with a glass rod. Following high speed centrifugation 2.21 mg of mercuric sulfide were firmly packed on the bottom of the centrifuge tube. The supernatent liquid was discarded, and the centrifuge tube was rinsed with distilled water, care being taken not to disturb the precipitate. Approximately 0.5 ml of dilute sodium hydroxide ($\sim$0.01M) was added and the precipitate finely dispersed in it. The small amount of sodium hydroxide greatly facilitated the dispersion. The finely divided precipitate was transferred to a stainless steel planchet using a long tipped dropping pipet. Flaming the planchets before use allowed the solution to spread over the surface more uniformly. A thin ring of lacquer evaporated on the periphery of the planchet was sufficient to retain the liquid. The mounting was completed by slowly evaporating the sample to dryness under a heat lamp. The surface density of the mercuric sulfide precipitate in a sample prepared in this way is approximately 0.6 mg/cm^2. The open samples were counted by placing them 0.5 cm from the counting tube window.

The counting rates of duplicate samples mounted as described above generally agreed to within 2 per cent. As a general test of the reliability of the method samples containing the same amount of radioactivity but differing weights of mercuric sulfide were prepared. The variation of the counting rate with sample thickness is plotted in Figure 1. The general shape of the curve is explained by considering two effects. With samples of low thickness, increasing the weight of precipitate increases the self scattering of the beta particles and as a consequence the counting rate is increased. At higher thickness increasing the weight increases the self absorption of the beta particles and the counting rate is decreased.

2. Specific activity determinations

The stock solution of radioactive mercuric nitrate (7.343 mg Hg/10 ml) was diluted with 0.01 M nitric acid to a final concentration of 3.67×10^{-5} M. Two 0.05 ml samples containing 18.4×10^{-7} milligram atoms of mercury were mounted for counting. These samples were counted every day that concentrations were to be determined. The quotient of their average counting rate divided by 18.4×10^{-7} was taken as the specific activity in counts per minute per milligram atom.

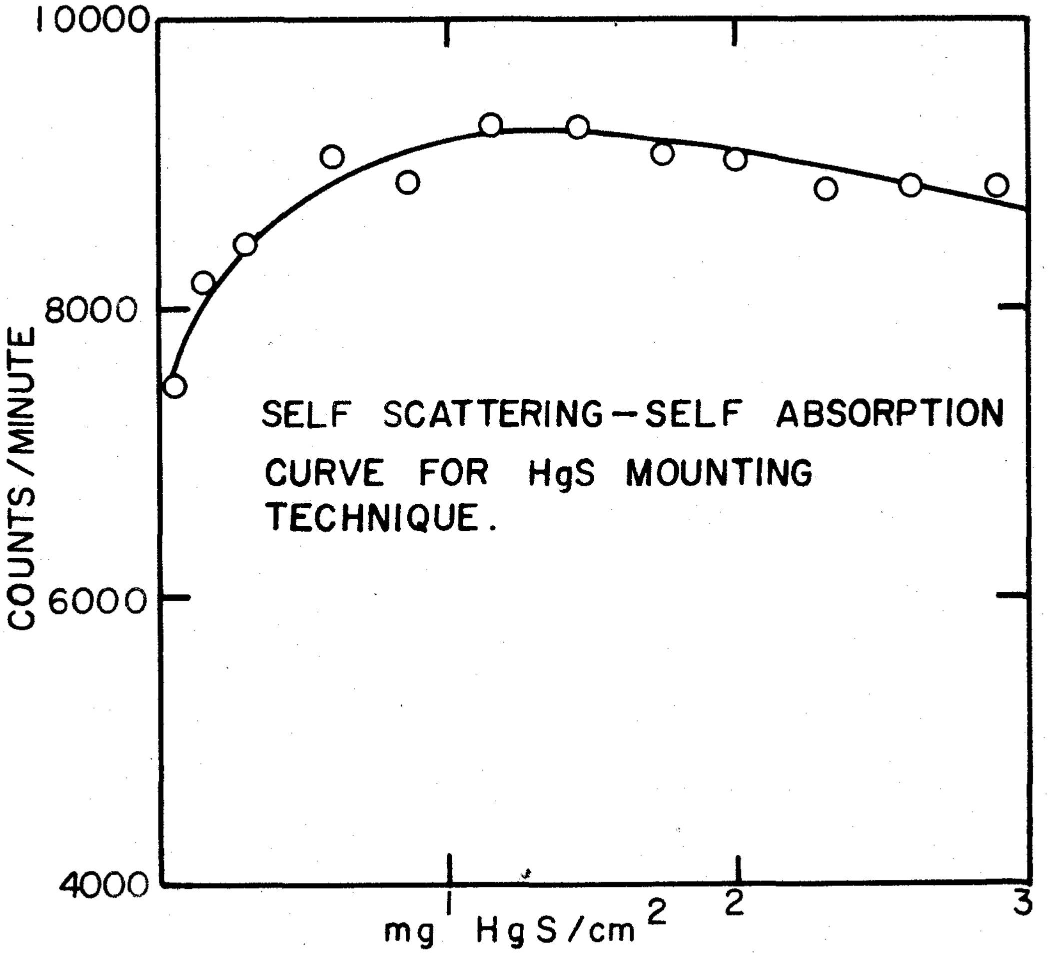

Figure 1. Self scattering-self absorption curve for counting samples containing radioactive mercury 203.

3. Analyses of the aqueous solutions

The determination of the mercury concentration in the aqueous solutions involved subjecting an aliquot of the solution to radiochemical analysis to determine the activity in counts per minute per milliliter. The concentration in gram atoms per liter was then calculated as the quotient of the activity per milliliter divided by the specific activity. In the case of the mercurous nitrate solutions and solutions of free mercury containing only nitric acid as additional solute, aliquots of the active solutions were simply added to 0.2 ml of carrier and the sulfide precipitated and mounted. With solutions containing 0.1 and 0.01 M hypophosphorous acid enough hydrogen peroxide was added to prevent reduction of the carrier to mercury metal. Precipitation and mounting were then carried out in the usual manner. In analyzing tracer solutions of mercury (II) containing iodide, excess potassium iodide was added to the carrier-aliquot mixture before precipitating the sulfide.

For the radiochemical analyses to be reliable it is essential that the mercury in the tracer solutions exchange completely with the mercuric nitrate carrier. Wolfgang and Dodson (35) found the rate of exchange between mercury (I) and mercury (II) ions to be immeasurably fast. Results of an experiment conducted in the present work indicate that exchange between mercury (I) and dissolved free mercury is extremely fast, but the exchange may have been induced in the separation process. Exchange between mercury (II) and dissolved free mercury should also be fast because the reaction:

$$Hg^{++} + Hg(aq) = Hg_2^{++}$$

is probably very rapid (35) and the equilibrium point lies far to the right (11). All of the mercury in the mercury (II) iodide solutions was in the same chemical form before precipitation.

4. Analyses of the organic solutions

The problem of analyzing the organic solutions was similar to that encountered with the aqueous solutions excepting that the organic solvents were immiscible with the aqueous mercuric nitrate carrier. To circumvent this difficulty enough acetone was added to the mixture of solvent and carrier to make it one phase. The solution was allowed to stand for several minutes to insure complete exchange, and this was followed by evaporation of the acetone and solvent. Mounting of the mercury in the aqueous residue was then carried out in the usual way. It was discovered that the addition of a small amount of hydrochloric acid prevented the formation of difficultly soluble solids during the evaporation process. Volatilization of mercuric chloride was inhibited by only moderate heating during the evaporation. A stream of warmed air was passed over the solution to hasten the process.

In analyzing the nitrobenzene solutions some of the solvent remained with the aqueous residue after evaporation. The problem was not serious, however, because the excess solvent did not interfere with the precipitation of the sulfide.

IV. METHOD OF INTERPRETING DATA, EXPERIMENTAL RESULTS, AND DISCUSSION

A. Distribution of Mercury between Dilute Mercurous Nitrate Solutions and Non-polar Solvents

1. Method of interpreting data

Non-polar organic solvents such as *n*-hexane and cyclohexane were used for the distribution experiments in order to eliminate extraction of ionic forms of mercury. The selective extraction of dissolved free mercury is essential for quantitative interpretation of the distribution measurements. In the following discussion, a functional relationship is developed which relates measurable quantities, such as the concentration of mercury in each phase, to equilibrium constants of the prevailing chemical reactions.

If only free mercury is extracted into the organic phase, a distribution ratio D and a distribution constant D^o can be defined as:

$$D = \frac{[\mathrm{Hg}]_{tot,aq}}{[\mathrm{Hg}]_o}$$

$$\text{and } D^o = \frac{[\mathrm{Hg}]_{aq}}{[\mathrm{Hg}]_o}$$

In these expressions $[\mathrm{Hg}]_{tot,aq}$ is the total concentration of mercury in all forms in the aqueous phase in gram atoms per liter and $[\mathrm{Hg}]_{aq}$ and $[\mathrm{Hg}]_o$ are the concentrations of free mercury in the aqueous and organic phases. Providing dismutation and dissociation both occur in dilute solutions of mercurous ions:

$$Hg_2^{++} \overset{K}{\rightleftharpoons} Hg(aq) + Hg^{++}$$

$$K = \frac{[Hg]_{aq}[Hg^{++}]}{[Hg_2^{++}]}$$

and $$Hg_2^{++} \overset{k}{\rightleftharpoons} 2Hg^{+}$$

$$k = \frac{[Hg^{+}]^2}{[Hg_2^{++}]} \quad .$$

If these two equilibria adequately describe the behavior of mercury in the experimental aqueous solutions (i.e. if anion complexing, etc., do not occur) then:

$$[Hg]_{tot,aq} = [Hg]_{aq} + [Hg^{++}] + [Hg^{+}] + 2[Hg_2^{++}] \quad . \qquad (1)$$

The quantities on the right side of Equation 1 can be expressed in terms of the concentration of mercury in the organic phase $[Hg]_o$, the dismutation constant K, the dissociation constant k, and the distribution constant D^o in the following manner.

If a sample of pure mercurous nitrate in the absence of any free mercury or mercuric nitrate is diluted to a certain volume and extracted with an equal volume of an organic solvent, then:

$$[Hg]_{aq} = D^o[Hg]_o$$

and $$[Hg^{++}] = [Hg]_{aq} + [Hg]_o$$

$$= (1 + D^o)[Hg]_o \quad .$$

Further
$$2\left[Hg_2^{++}\right] = \frac{2\left[Hg\right]_{aq}\left[Hg^{++}\right]}{K}$$
$$= \frac{2D^o(1 + D^o)\left[Hg\right]_o^2}{K}$$

and
$$\left[Hg^+\right] = \sqrt{k}\left[Hg_2^{++}\right]^{\frac{1}{2}}$$
$$= \left\{\frac{kD^o(1 + D^o)}{K}\right\}^{\frac{1}{2}}\left[Hg\right]_o \quad .$$

Equation 1 under these conditions then can be written:

$$\left[Hg\right]_{tot,aq} = D^o\left[Hg\right]_o + (1 + D^o)\left[Hg\right]_o + \left\{\frac{kD^o(1 + D^o)}{K}\right\}^{\frac{1}{2}}\left[Hg\right]_o + \frac{2D^o(1 + D^o)}{K}\left[Hg\right]_o^2 \quad .$$

But since
$$\frac{\left[Hg\right]_{tot,aq}}{\left[Hg\right]_o} = D \quad ,$$

then
$$D = 1 + 2D^o + \left\{\frac{kD^o(1 + D^o)}{K}\right\}^{\frac{1}{2}} + \frac{2D^o(1 + D^o)}{K}\left[Hg\right]_o \quad . \qquad (2)$$

Equation 2 is more properly written using the individual activity coefficients of the ions:

$$D = 1 + 2D^o + \frac{\gamma_{Hg^{++}}^{\frac{1}{2}}}{\gamma_{Hg^+}}\left\{\frac{kD^o(1 + D^o)}{K}\right\}^{\frac{1}{2}} + \frac{\gamma_{Hg^{++}}}{\gamma_{Hg_2^{++}}}\frac{2D^o(1 + D^o)}{K}\left[Hg\right]_o \quad . \qquad (3)$$

with the activity coefficient of dissolved free mercury taken as unity.

Examination of Equation 3 will show that a plot of the variation of D with $[\mathrm{Hg}]_o$ can be used to evaluate the equilibrium constants k and K. If D^o and the ionic activity coefficients are known, a value of K can be determined from the slope and k can be estimated from the intercept at zero $[\mathrm{Hg}]_o$.

2. Experimental results and discussion

Experimental data are tabulated in Tables 5 and 6 for the distribution of mercury between the solvents _n_-hexane and cyclohexane and dilute aqueous mercurous nitrate solutions. Graphical representations of the data are given in Figures 2 and 3.

Table 5. Experimental Results of the Distribution of Mercury between Purified _n_-hexane and Dilute Mercurous Nitrate Solutions

$[\mathrm{Hg}]_{tot,aq} \times 10^7$ g atoms/l	$[\mathrm{Hg}]_o \times 10^7$ g atoms/l	D	% Extraction into Organic Phase
0.21	0.18	1.17	46
0.61	0.42	1.45	41
1.25	0.70	1.79	36
2.84	1.16	2.44	29
6.84	1.95	3.50	22
7.59	2.18	3.48	22
7.82	2.26	3.46	23
14.6	2.92	5.0	17
17.0	2.70	6.30	14
17.4	2.76	6.30	14
27.4	3.64	7.53	12
35.8	4.17	8.58	10
96	6.16	15.6	6

Table 6. Experimental Results of the Distribution of Mercury between Purified Cyclohexane and Dilute Solutions of Mercurous Nitrate

$[Hg]_{tot,aq} \times 10^7$ g atoms/l	$[Hg]_o \times 10^7$ g atoms/l	D	% Extraction into Organic Phase
0.76	0.57	1.33	43
0.98	0.64	1.52	39
1.69	1.01	1.67	37
4.61	1.90	2.42	29
8.45	2.55	3.32	23
10.8	2.75	3.93	20
11.4	3.02	3.78	21
14.9	3.30	4.52	18
20.6	3.90	5.28	16
32.4	4.56	7.11	12
48.5	5.38	9.02	10

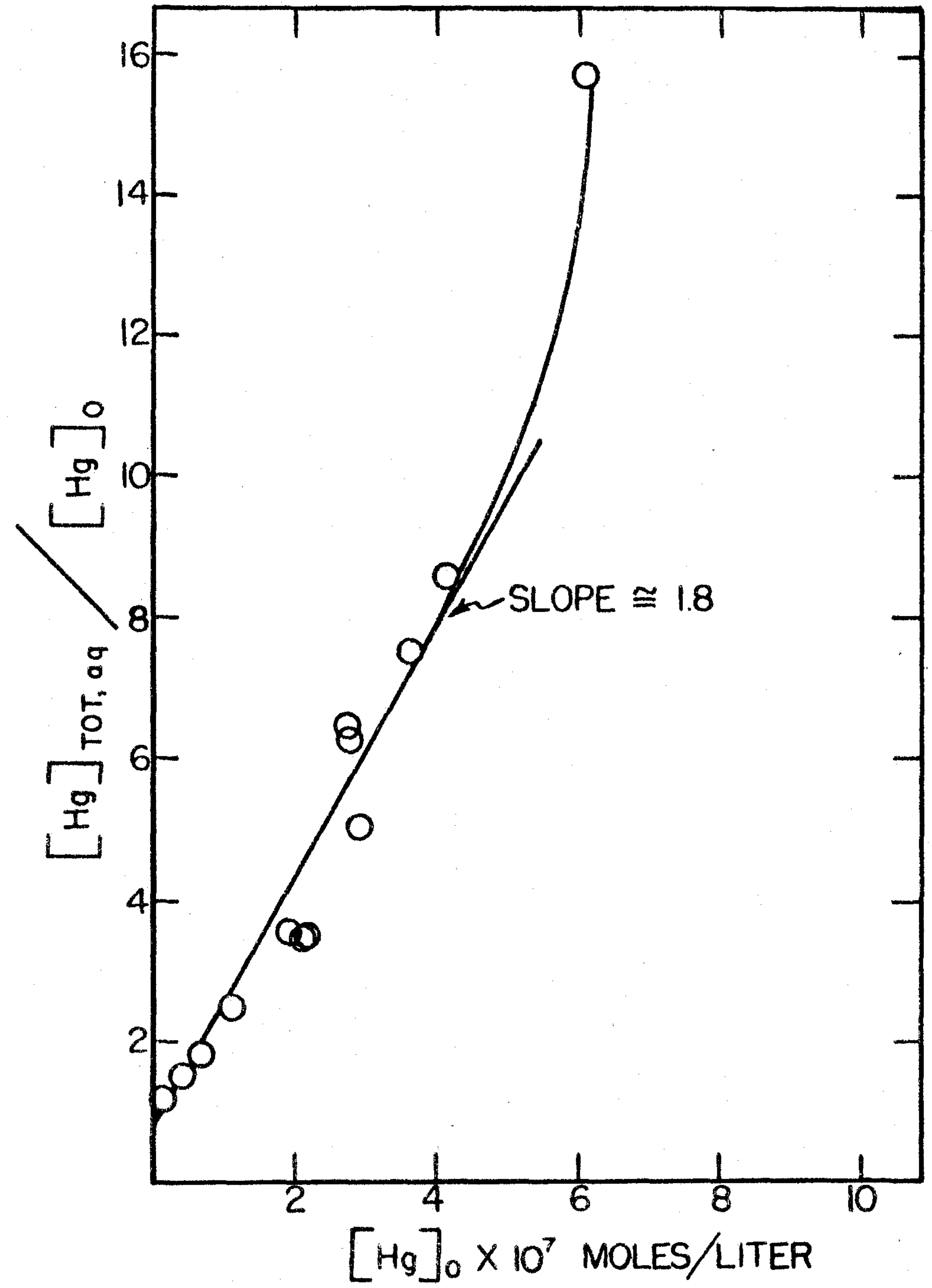

Figure 2. Distribution of mercury between purified n-hexane and dilute mercurous nitrate solutions.

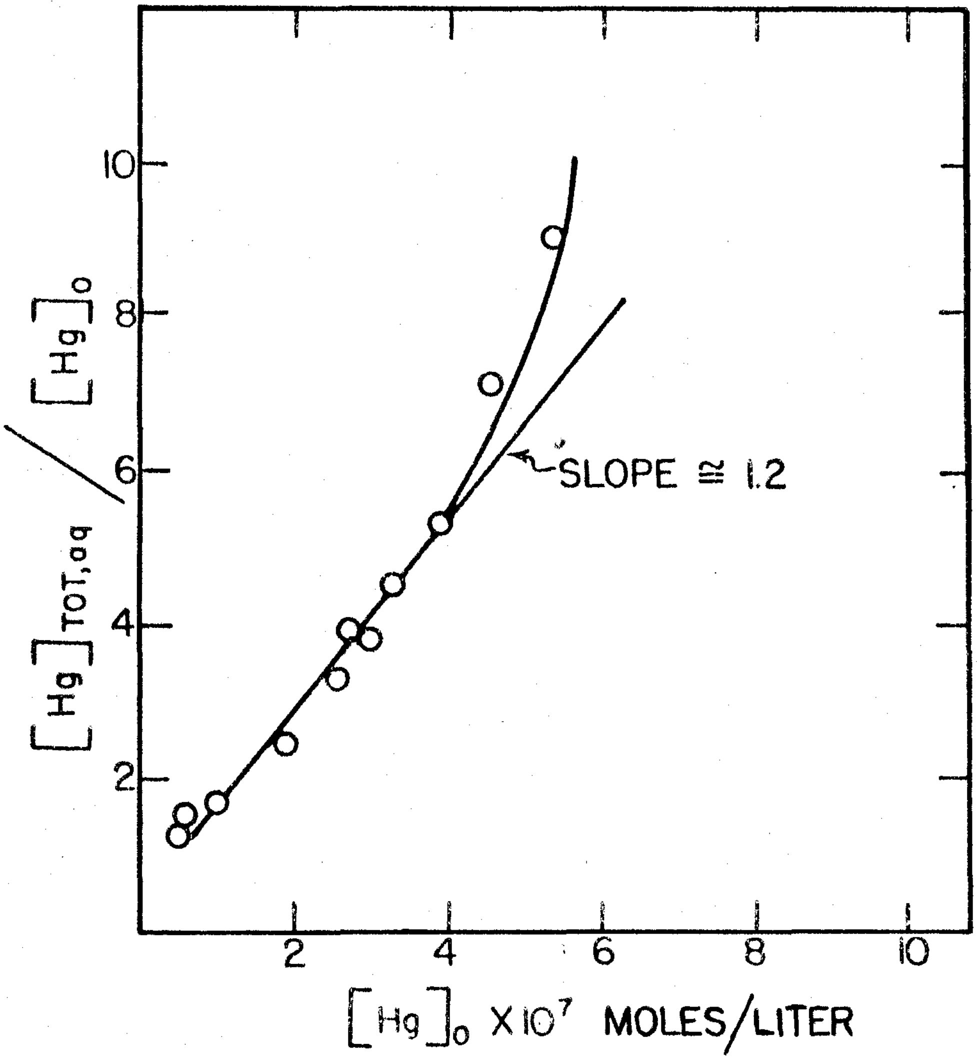

Figure 3. Distribution of mercury between purified cyclohexane and dilute mercurous nitrate solutions.

The increasing slope of the curves at higher values of $[\mathrm{Hg}]_o$ can be explained qualitatively by considering that the stock solution of mercurous nitrate contained a small amount of mercuric nitrate. This is required by the equilibrium between the three oxidation states of mercury. As long as the amount of mercury (II) produced in the dismutation is large compared to the amount already present (so that $[\mathrm{Hg}^{++}] = (1 + D^o)[\mathrm{Hg}]_o$), the linear dependence is held. When this is not the case an increasing slope is expected.

Table 7 contains measurements of the distribution constant D^o and values of the dismutation constant K which were calculated from the slopes of the curves in Figures 2 and 3. The activity coefficient ratio $\gamma_{\mathrm{Hg}^{++}}/\gamma_{\mathrm{Hg}_2^{++}}$ was taken as unity in the calculations.

Table 7. Values for the Dismutation Constant Calculated from Distribution Measurements

Solvent	Slope	D^o	K
n-hexane	1.8×10^7	0.048	5.6×10^{-9}
Cyclohexane	1.2×10^7	0.031	5.3×10^{-9}

The n-hexane experiments were performed first while the mercury had a higher specific activity than in the later experiments with cyclohexane. Hence lower concentrations could be measured in the n-hexane experiments, and it was possible to obtain experimental values very close to the ordinate axis. The intercept was found to be approximately 0.8.

If a measurable dissociation of the mercurous dimer is taking place in the solutions, the effect would be to increase the ordinate intercept by the amount:

$$\frac{\gamma^{\frac{1}{2}}_{\mathrm{Hg}^{++}}}{\gamma_{\mathrm{Hg}_2^{++}}}\left\{\frac{kD^{\circ}(1 + D^{\circ})}{K}\right\}^{\frac{1}{2}} .$$

Estimated values of this expression for different values of the dissociation constant k have been calculated and are given in Table 8. Values of K and D° were taken from the n-hexane experiments because of a more accurate intercept at zero $[\mathrm{Hg}]_0$. The ratio $\gamma^{\frac{1}{2}}_{\mathrm{Hg}^{++}}/\gamma_{\mathrm{Hg}^{+}}$ was estimated to be

Table 8. Calculated Ordinate Intercepts Corresponding to Different Values for the Dissociation Constant

k	$\frac{\gamma^{\frac{1}{2}}_{\mathrm{Hg}^{++}}}{\gamma_{\mathrm{Hg}^{+}}}\left\{\frac{kD^{\circ}(1 + D^{\circ})}{K}\right\}^{\frac{1}{2}}$	Predicted Ordinate Intercept
10^{-6}	2.7	3.8
10^{-7}	0.86	2.0
10^{-8}	0.27	1.4
0	0	1.1

0.91 using Kielland's (36) calculated individual activity coefficients at ionic strength 0.01. The values $\gamma_{Hg^{++}}$ and $\gamma_{Hg^{+}}$ were taken as 0.67 and 0.90 with $\gamma_{Hg^{+}}$ being assumed equal to $\gamma_{Tl^{+}}$ or $\gamma_{Ag^{+}}$.

The observed ordinate intercept of 0.8 is obviously not very precise, but it does indicate that the value of k is not greater than 10^{-7} and is probably somewhat less. In fact, the data can be explained best without considering the occurrence of dissociation at all.

It is interesting to compare the determinations of K in Table 7 with those obtained by calculations similar to the one carried out by Sidgwick (11). Thus the dismutation constant K can be calculated from:

$$K = \frac{[Hg]_{aq}\,[Hg^{++}]}{[Hg_2^{++}]}$$

if values of the solubility of mercury metal and the ratio $[Hg^{++}] / [Hg_2^{++}]$ are known for aqueous systems involving mercury (I) and mercury (II) in equilibrium with liquid mercury.

In this connection measurements of the solubility of mercury metal were made using a tracer technique which was quite sensitive in the low concentration range encountered. A value of 3.0×10^{-7} g atoms/liter was found at 25°C.

Using this value of the solubility together with the reported values for the ratio $[Hg^{++}] / [Hg_2^{++}]$ (see page 6 for reciprocals of this ratio), values in the range of

1.8×10^{-9} to 3.6×10^{-9} are calculated for the dismutation constant K. The most recent measurements of the ratio $[Hg^{++}]/[Hg_2^{++}]$ give answers favoring the larger value of K and should perhaps be considered the most reliable.

However even the larger values of K calculated above are smaller than the 5.3×10^{-9} and 5.5×10^{-9} obtained in the distribution experiments, but it is felt that the agreement is reasonable considering the assumptions that were made and the low concentrations encountered.

B. Mercury Solubility Measurements

1. Brief discussion of the "solubility parameter" theory

The change in free energy when two substances are mixed can be expressed as:

$$\Delta F^M = RT(x_1 \ln x_1 + x_2 \ln x_2) + \Delta F^E \qquad (4)$$

per mole of solution. In Equation 4, x_1 and x_2 are the mole fractions of the components and ΔF^E is an excess free energy term which is equal to zero when the two components form an ideal solution.

Hildebrand and Scott (37) have related ΔF^E to thermodynamic properties of the pure components for substances forming "regular" solutions. The term "regular" solution was originated by Hildebrand, and the principle has been stated as (38, p. 69):

> A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal

solution of the same composition, the total volume remaining unchanged.

In harmony with this notion the molar energy of mixing can be expressed as (37):

$$\Delta E^M = \Delta F^E$$

$$= (x_1V_1 + x_2V_2)\varphi_1\varphi_2 \left\{\frac{\left[\Delta E_1^V\right]^{\frac{1}{2}}}{V_1} - \frac{\left[\Delta E_2^V\right]^{\frac{1}{2}}}{V_2}\right\}^2 \quad (5)$$

where V_1, V_2 are the molar volumes of components 1 and 2,

ΔE_1^V, ΔE_2^V are their energies of vaporization per mole,

and φ_1, φ_2 are their volume fractions $\varphi_1 = \dfrac{x_1V_1}{x_1V_1 + x_2V_2}$.

The quantities $(\Delta E_1^V/V_1)^{\frac{1}{2}}$ and $(\Delta E_2^V/V_2)^{\frac{1}{2}}$ have been called "solubility parameters" and are frequently designated as simply δ_1 and δ_2.

Equations 4 and 5 can be combined to give:

$$\Delta F^M = RT(x_1 \ln x_1 + x_2 \ln x_2) + (x_1V_1 + x_2V_2)\varphi_1\varphi_2(\delta_1 - \delta_2)^2. \quad (6)$$

The partial molal free energies of mixing are then:

$$\Delta \bar{F}_1^M = RT \ln x_1 + V_1\varphi_2^2 (\delta_1 - \delta_2)^2 \quad (7)$$

$$\Delta \bar{F}_2^M = RT \ln x_2 + V_2\varphi_1^2 (\delta_1 - \delta_2)^2 \quad (8)$$

The derivation of Equation 6 was not dependent upon any solution model, such as the "hole" or "liquid a disordered solid" models, but principally upon three simplifying assumptions: complete randomness, equating the energy of interaction of a pair of unlike molecules to the geometric mean of the interaction energies of like pairs, and no volume change on mixing. As formulated the equation can be expected to apply only to solutions of non-polar, non-associated liquids.

In some cases the first term of Equation 6 is replaced by the Flory-Huggins term, $x_1 \ln \varphi_1 + x_2 \ln \varphi_2$, which is designed to account for the disparity in sizes of the component molecules. However, this substitution is not universally accepted as revealed by the following quotation (39, p. 46):

> This formulation is not exactly right for the solutions of long chain polymers for which it was designed, and the wisdom of its application to solutions of ordinary molecules seems doubtful, at least to this writer; it is almost certainly an overcorrection for the size effect.

While Equation 6 lacks rigor due to the assumptions made in its derivation, it has nevertheless been used quite successfully to interpret solubility data of non-electrolytes. It has the desirable feature, from an experimental point of view, of relating the free energy of mixing to measurable thermodynamic properties of the pure components thus allowing its application to actual solutions.

2. <u>The solubility equation applied to solutions of mercury and organic solvents</u>

Mercury is designated as component 1 and the solvent as component 2. For liquid mercury in equilibrium with dissolved mercury:

$$\Delta\bar{F}_1 = 0 \quad .$$

Equation 7 can then be written:

$$RT \ln x_1 = -\varphi_2^2 V_1(\delta_1 - \delta_2)^2 \quad . \qquad (9)$$

Since the solubility of mercury metal is extremely limited with $x_2 \gg x_1$ and $x_2V_2 \gg x_1V_1$, Equation 9 can be further simplified to:

$$RT \ln x_1 = -V_1(\delta_1 - \delta_2)^2 \quad . \qquad (10)$$

The concentration of mercury is designated as C_1 g atoms per liter so that:

$$x_1 = \frac{C_1}{C_1 + \frac{1000d}{M_2}}$$

$$\cong \frac{C_1M_2}{1000d}$$

$$\cong \frac{C_1V_2}{1000}$$

where d is the density of the solution, M_2 is the molecular weight of the solvent, and V_2 is its molar volume. Equation 10 can now be written:

$$RT \ln \frac{C_1V_2}{1000} = -V_1(\delta_1 - \delta_2)^2$$

$$\text{or } C_1 = \frac{1000}{V_2} e^{-V_1(\delta_1 - \delta_2)^2/RT} \quad . \qquad (11)$$

The mercury solubilities determined in this study are recorded in Table 9 and compared with the corresponding values calculated with the use of Equation 11. The

Table 9. The Solubility of Mercury in Organic Solvents at 25°C

Solvent	V_2 ml/mole	$\left[\frac{\Delta E^V}{V_2}\right]^{\frac{1}{2}}$	$C_1 \times 10^6$ Calculated g atoms/l	$C_1 \times 10^6$ Observed g atoms/l
n-hexane	132	7.30	6.2	6.1-6.7
Cyclohexane	109	8.20	21	11.0 ± 0.2
Carbon Tetrachloride	97	8.6	37	7.5 ± 0.3
Toluene	107	8.90	48	12.5 ± 0.5
Benzene	89	9.15	72	12.0 ± 0.6
Nitrobenzene	103	10.0	157	9.3 ± 0.7
Mercury	14.8	31		

"solubility parameter" values used in the calculations were those given by Hildebrand and Scott (37).

Values calculated using the Flory-Huggins term were not recorded in Table 9 because the agreement between them and the observed solubilities was not as good as that found using Equation 11.

For the most part the results of this experiment agree only to an order of magnitude with the calculated solubilities. In most other cases the "solubility parameter" theory gives better correlation than this. In one other area in particular, however, it has proved to be largely inadequate. Heats and free energies of mixing of hydrocarbon-fluorocarbon mixtures are invariably higher than those predicted by the theory. Hence the observed solubilities are much smaller than predicted. Similar solubility behavior was generally found for the mercury-organic solvent mixtures studied in the present work.

It has been suggested by Reed (40) that the "solubility parameter" theory is inadequate for hydrocarbon-fluorocarbon mixtures for two reasons: it does not take into account the large volume expansions on mixing, and the geometric mean assumption for interaction energies between pairs of unlike molecules is not valid for substances having considerably different ionization potentials. These factors may also be important in explaining the deviations between calculated and observed values of the present study, but the first one cannot be measured because the solubility of mercury is so slight, and the second alone will not explain the difference. For instance the ionization potentials of cyclohexane and carbon tetrachloride are the same (41, 42); yet the calculated mercury solubility in cyclohexane agrees much better with the experimental value than a similar comparison with carbon tetrachloride as solvent.

3. Measurements of mercury solubility in aqueous solutions

Equilibrium mercury solubilities in aqueous solutions determined in this study are given in Table 10. Graphical

Table 10. Equilibrium Solubilities of Mercury in Aqueous Solutions

Solution	Temperature °C	Conc. Hg x 10^7 g atoms/liter
Direct Determinations		
0.1M H_3PO_2	25	3.0 ± 0.3
0.01M H_3PO_2, 0.01M HNO_2	25	2.9 ± 0.1
0.001M H_3PO_2, 0.01M HNO_3	25	3.0 ± 0.1
Inferred Solubilities		
0.01M HNO_3 (D^o)(solubility in n-hexane)	25	2.9 - 3.2
0.01M HNO_3 (D^o)(solubility in cyclohexane)	25	3.4

representation of the solubility versus time is given in Figure 4 for two solutions. In aqueous solutions containing only nitric acid or perchloric acid the direct determination of the solubility showed an increase from day to day. This behavior is illustrated in Figure 4. It was found that the addition of a small amount of hypophosphorous acid completely eliminated this effect.

The day to day increase in solubility found in solutions containing only nitric acid or perchloric acid can be explained by a continuous oxidation process of the free metal. This reaction is maintained by the irradiation of

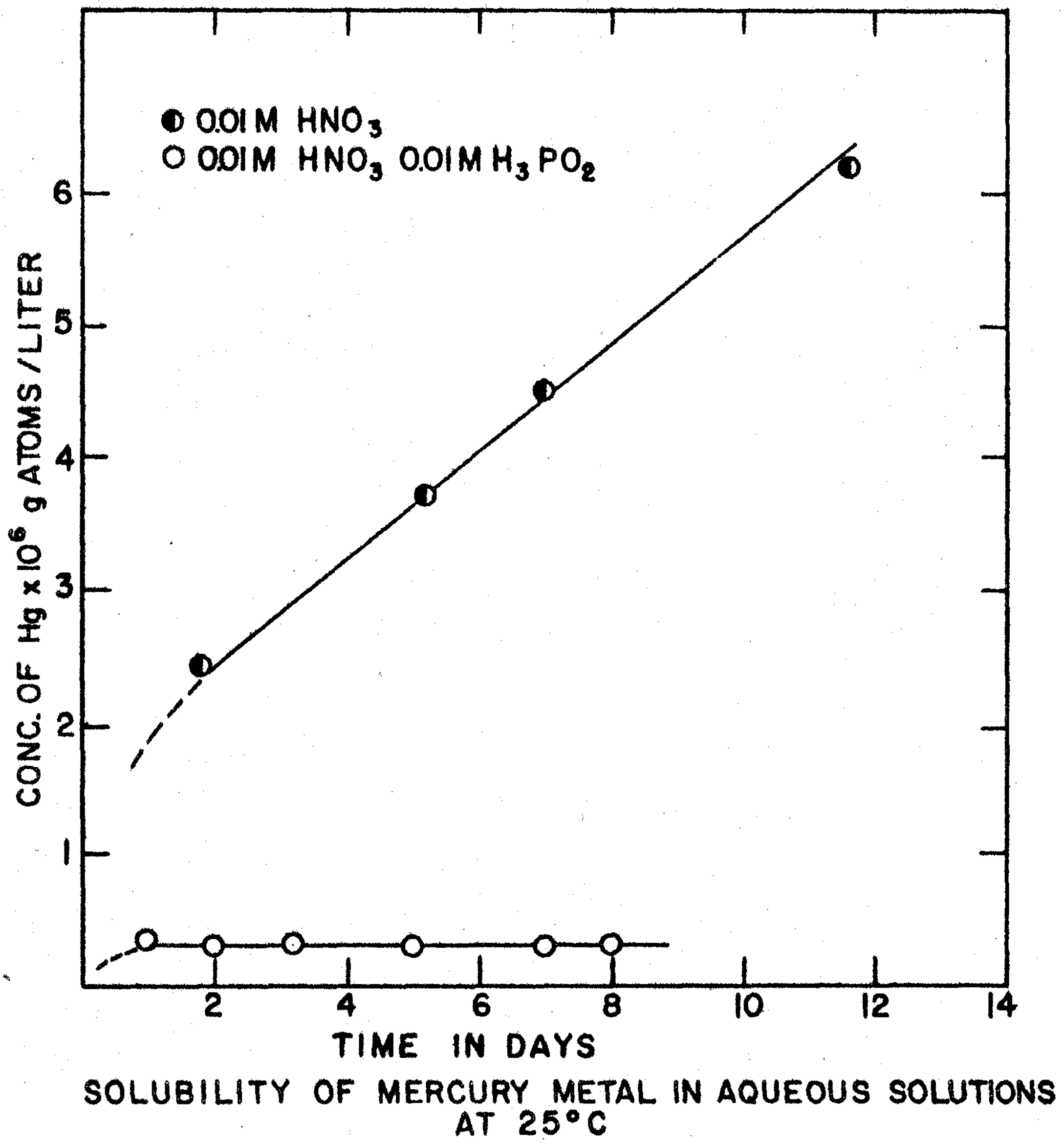

Figure 4. Time dependence of the solubility of mercury.

the water with gamma rays and beta particles being emitted by the drop of radioactive mercury. Water molecules under the action of such high energy radiation are decomposed to form hydrogen peroxide and molecular hydrogen with considerable evidence that hydrogen and hydroxyl radicals are also produced, possibly as intermediates in the formation of the first two (43, 44). The presence of the reactive hydroxyl radicals in irradiated water makes it a good oxidant. In fact an equivalent reduction potential of +0.95 volts has been estimated by Dainton and Collinson (45) for such solutions.

The action of hypophosphorous acid in helping to attain equilibrium is probably due to the effectiveness of this reducing agent in scavenging the oxidizing hydroxyl radicals.

The mercury solubility was found to be essentially independent of hypophosphorous acid concentration. This indicates that the measurements are actually representative of the concentration of free mercury in solution and not a measure of the solubility of some oxy-phosphorous salt of mercury.

Unlike other studies (12, 19), care was not taken to use air-free water. Even though slightly larger solubilities were found in this study than those given in the literature, the added precaution of removing all of the air from the solutions was thought unnecessary when using a reducing medium. Stock *et al*. (12) found that the solubility of mercury in aqueous solutions increased when air was present, but this effect cannot be used to explain the difference in solubility measurements reported in the literature and found in this study. For if air oxidation had occurred in the solutions used in this study, the solubility would have increased from day to day in the solutions being shaken in the presence of air. The procedure used in this study is further justified by comparing the values inferred from solubilities in _n_-hexane and cyclohexane with those obtained directly.

The presence of air did not affect the solubility of mercury in benzene (12), and it is reasonable to expect a similar behavior with _n_-hexane and cyclohexane. Thus the solubility measurements in the organic solvents can be taken as indicating the concentration of dissolved free metal (the concentrations of Hg were found to be essentially constant with time after about 2 days) and can be multiplied by the distribution constants of dissolved free metal between water and the solvent to give results similar to those obtained directly.

C. Mercuric Iodide-Iodide Ion Equilibria

1. Method of interpreting data from mercuric iodide distribution measurements

In addition to studies of mercurous ion behavior and mercury solubility, the somewhat unrelated mercuric iodide-iodide ion equilibria were also investigated. Use was made of the extraction of mercuric iodide into benzene from aqueous solutions to measure the extent of formation of the triiodo and tetraiodo complex ions of mercury (II). A method of interpreting measurements of the distribution of mercuric iodide will be discussed next.

It is assumed that mercuric iodide dissolved in benzene or aqueous solutions exists in the form of HgI_2 molecules in the concentration range used. This can be justified on the basis of experimental evidence. For instance Kohlrausch and Rose (46) found the conductivity of mercuric iodide solutions to be extremely small. Their value of 1×10^{-6} M for the solubility of HgI_2 is much smaller than the 1.32×10^{-4} M (22) and 7.4×10^{-5} M (47) reported by other workers using methods not employing conductivity measurements. This indicates that the molecules of HgI_2 are only slightly dissociated to produce conducting ionic species. Also the large values of $K_1 = 7.3 \times 10^{12}$ and $K_2 = 6.6 \times 10^{23}$ reported (23) for the equilibria:

$$Hg^{++} + I^- \xrightleftharpoons{K_1} HgI^+$$

$$\text{and } Hg^{++} + 2I^- \xrightleftharpoons{K_2} HgI_2 \quad ,$$

indicate only a slight dissociation of mercuric iodide.

The degree of ionization of the HgI_2 molecules calculated using the above values for K_1 and K_2 was found to be negligible even in the most extreme case of the present study. Thus molecules of HgI_2 were calculated to be only 0.1 per cent ionized in a 1×10^{-5} M mercuric iodide solution which did not have added potassium iodide to suppress the ionization.

Dissolved mercuric iodide is undoubtedly in the form of HgI_2 molecules in benzene also. The possibility of the existence of ionic species in a non-polar solvent is remote so that dissociation can be disregarded. Further, molecules such as $HHgI_3$ and H_2HgI_4 need not be considered as possible species in the benzene phase. For if they were present in the organic phase the extraction of mercury from mercuric nitrate-potassium iodide solutions would be hydrogen ion concentration dependent. Experimentally, as indicated in Table 11, the extraction from solutions containing excess potassium iodide was found to be essentially independent of hydrogen ion concentration.

Table 11. Extraction of Mercury from Dilute Mercuric Nitrate Solutions Containing Excess Potassium Iodide[a]

$[H^+]$ moles/liter	$[Hg]_{tot,o}/[Hg]_{tot,aq}$ [b]
0.001	0.39
0.006	0.37
0.010	0.39
0.020	0.38

[a] $[I^-]$ = 0.001 moles/liter; ionic strength = 0.03

[b] $[Hg]_{tot,o}$ and $[Hg]_{tot,aq}$ are the total concentrations of mercury in the benzene and aqueous phases.

A functional relationship between measurable quantities and association constants of prevailing equilibria can be developed and tested experimentally. Consider the equilibria:

$$HgI_2 + I^- \underset{}{\overset{K_1}{\rightleftharpoons}} HgI_3^- \qquad (12)$$

$$\text{and } HgI_2 + 2I^- \overset{K_2}{\rightleftharpoons} HgI_4^= \qquad (13)$$

with equilibrium constants:

$$K_1 = \frac{\gamma_1 [HgI_3^-]}{\gamma_0 [HgI_2] \gamma_- [I^-]}$$

$$\text{and } K_2 = \frac{\gamma_2 [HgI_4^=]}{\gamma_0 [HgI_2] \gamma_-^2 [I^-]^2} \quad .$$

In the above expressions γ_-, γ_0, γ_1, and γ_2 are the activity coefficients of the species I^-, HgI_2, HgI_3^-, and $HgI_4^=$. Brackets denote concentrations in moles/liter.

Extraction measurements can be used to evaluate K_1 and K_2. If HgI_2 is the only form of mercury extracting into benzene, an extraction ratio E and an extraction constant E^o can be defined by:

$$E = \frac{[HgI_2]_o}{[Hg]_{tot,aq}}$$

$$\text{and } E^o = \frac{[HgI_2]_o}{[HgI_2]_{aq}} \quad .$$

The subscripts denote the phase, and $[Hg]_{tot,aq}$ is the total concentration of mercury in all forms in the aqueous phase.

If Reactions 12 and 13 are the only ones occurring in the aqueous phase then:

$$[Hg]_{tot,aq} = [HgI_2]_{aq} + [HgI_3^-] + [HgI_4^=] \qquad (14)$$

Since $[HgI_2]_{aq} = \dfrac{[HgI_2]_o}{E^o}$,

$$[HgI_3^-] = \frac{K_1 \Upsilon_o \Upsilon_-}{\Upsilon_1}[HgI_2]_{aq}[I^-]$$

$$= \frac{K_1 \Upsilon_o \Upsilon_-}{E^o \Upsilon_1}[HgI_2]_o[I^-],$$

and $[HgI_4^=] = \dfrac{K_2 \Upsilon_o \Upsilon_-^2}{\Upsilon_2}[HgI_2]_{aq}[I^-]^2$

$$= \frac{K_2 \Upsilon_o \Upsilon_-^2}{E^o \Upsilon_2}[HgI_2]_o[I^-]^2 ,$$

Equation 14 can be written:

$$[Hg]_{tot,aq} = \frac{1}{E^o}[HgI_2]_o + \frac{K_1 \Upsilon_o \Upsilon_-}{E^o \Upsilon_1}[HgI_2]_o[I^-] + \frac{K_2 \Upsilon_o \Upsilon_-^2}{E^o \Upsilon_2}[HgI_2]_o[I^-]^2$$

$$= \frac{[HgI_2]_o}{E^o}\left\{1 + \frac{K_1 \Upsilon_o \Upsilon_-}{\Upsilon_1}[I^-] + \frac{K_2 \Upsilon_o \Upsilon_-^2}{\Upsilon_2}[I^-]^2\right\}. \qquad (15)$$

Equation 15 can be rearranged to yield:

$$\frac{E^o\,[Hg]_{tot,aq}}{[HgI_2]_o} - 1 = \frac{K_1\gamma_o\gamma_-[I^-]}{\gamma_1} + \frac{K_2\gamma_o\gamma_-^2[I^-]^2}{\gamma_2}$$

$$= \frac{E^o}{E} - 1 = \frac{K_1\gamma_o\gamma_-[I^-]}{\gamma_1} + \frac{K_2\gamma_o\gamma_-^2[I^-]^2}{\gamma_2} \ . \qquad (16)$$

The last form, Equation 16, can be reduced to a simpler expression for graphical interpretation:

$$\frac{E^o - E}{E[I^-]} = \frac{K_1\gamma_o\gamma_-}{\gamma_1} + \frac{K_2\gamma_o\gamma_-^2}{\gamma_2}[I^-] \ . \qquad (17)$$

K_1 and K_2 can be determined from the intercept and slope of a plot of $(E^o - E)/E[I^-]$ versus $[I^-]$ if values of the activity coefficients are known.

2. Results

Experimental data are given in Table 12 of the variation of the extraction ratio E with iodide ion concentration. In the experiments the concentration of mercury was small compared to the iodide concentration so that the fraction of iodide ions undergoing combination was small and could be neglected. The ionic strength was kept at 0.03 in all of the solutions with the hydrogen ion concention held at 0.01 M. Graphical representation of the data is given in Figure 5. The satisfactory linearity of the plot verifies the use of Equation 17 to interpret the measurements.

Table 12. Distribution of Mercury between Benzene and Aqueous Mercuric Nitrate-Potassium Iodide Solutions at 25°C

E	$[I^-]$ moles/liter	$\frac{E^o - E}{E\,[I^-]}$
47.2 (E^o)	0	
6.97	0.001	5,760
3.33	0.002	6,590
1.47	0.004	7,770
0.527	0.008	11,100
0.391	0.010	12,000
0.287	0.012	13,600
0.176	0.016	16,700
0.121	0.020	19,500

Values of $(5.05 \pm 0.12)10^3$ and $(7.24 \pm 0.11)10^5$ were determined for the intercept and slope of Figure 5 by applying the method of least squares for equally weighted measurements. Only the ordinate values were assumed liable to error. The above figures can be considered as non-thermodynamic values of K_1 and K_2 and thus compared with the values 6100 ± 2400 and $(1.03 \pm 0.11)10^6$ which were determined using electrometric measurements (23) in solutions of the same acidity and ionic strength.

For an estimation of the thermodynamic values of K_1 and K_2 some assumptions regarding the activity coefficients are necessary.

Since aqueous HgI_2 is an uncharged species and its concentration is always small, γ_o is assumed equal to unity. Also it is assumed that the activity coefficients γ_-, γ_1, and γ_2 can be calculated for solutions of ionic strength 0.03 using the Debye-Hückel expression:

$$\log \gamma_i = \frac{-Az_i^2 \mu^{\frac{1}{2}}}{1 + Ba_i \mu^{\frac{1}{2}}} \,.$$

In this expression γ_i = activity coefficient of ion i

A = a constant, 0.5092 at 25°C (48)

B = a constant, 0.3286×10^8 at 25°C (48)

a_i = "effective diameter" of ion i in solution

z_i = charge of the ion

and μ = the ionic strength of the solution.

Kielland (36) has estimated the "effective diameter" of the iodide ion to be 3×10^{-8} cm which leads to a value of approximately 0.84 for γ_-. Estimates of a_i for several complex ions are also given (36). Thus it appears reasonable to assign "effective diameters" of 4×10^{-8} cm and 4.5×10^{-8} cm for HgI_3^- and $HgI_4^=$ which lead to activity coefficients of 0.85 and 0.52 respectively.

Using values of the activity coefficients given above, the ratios $\gamma_0 \gamma_- / \gamma_1$ and $\gamma_0 \gamma_-^2 / \gamma_2$ are calculated to be approximately 1 and 1.4 respectively. Corresponding thermodynamic values of K_1 and K_2 are then $(5.0 \pm 0.1)10^3$ and $(5.1 \pm 0.1)10^5$.

The results of this study were obtained using solutions in the concentration range 10^{-7} M to 10^{-5} M in mercury and are in fair agreement with those reported from measurements at higher concentrations. An interesting extension of the present work would be that of performing distribution experiments in the 10^{-9} M concentration range to check for anomalous behavior. Measurements at this low concentration range could be made by using tracer of very high specific activity.

V. SUMMARY

The behavior of the mercurous ion has been studied in dilute aqueous solutions. The ion was found to be unstable toward dismutation according to the equation:

$$Hg_2^{++} \overset{K}{\rightleftharpoons} Hg^{++} + Hg(aq) \quad .$$

Values of 5.3×10^{-9} and 5.6×10^{-9} have been measured for the dismutation constant K at 25°C by making use of a radioactive tracer technique in which mercury was distributed between non-polar solvents and dilute aqueous solutions of mercurous nitrate.

The above values for the dismutation constant are in fair agreement with the values 1.8×10^{-9} to 3.6×10^{-9} which were calculated by a different approach. The latter figures were obtained as the product of the reported concentration ratios $[Hg^{++}] / [Hg_2^{++}]$, in the presence of liquid mercury, and the solubility of the metal in aqueous solutions determined in this study (3.0×10^{-7} g atoms/liter).

Although the possibility of dissociation of the mercurous dimer into monomeric mercurous ions cannot be completely excluded, the results of this study can be satisfactorily interpreted without considering this effect. The results indicate that a dissociation constant as large as 1×10^{-7} is highly unlikely.

The solubility of mercury in several organic solvents was determined and compared with solubilities calculated with Hildebrand's "solubility parameter" equation. The agreement was reasonable with saturated hydrocarbons as solvents, but with carbon tetrachloride, benzene, and benzene derivatives as solvents the observed solubilities were considerably smaller than those predicted by the solubility equation.

Mercuric iodide-iodide ion equilibria have been studied at 25°C. Use was made of the extraction of mercuric iodide into benzene from dilute aqueous solutions of mercuric nitrate containing excess potassium iodide to study the following equilibria:

$$HgI_2 + I^- \xrightleftharpoons{K_1} HgI_3^-$$

$$\text{and } HgI_2 + 2I^- \xrightleftharpoons{K_2} HgI_4^= \quad .$$

K_1 and K_2 were determined to be $(5.0 \pm 0.1)10^3$ and $(5.1 \pm 0.1)10^5$ respectively.

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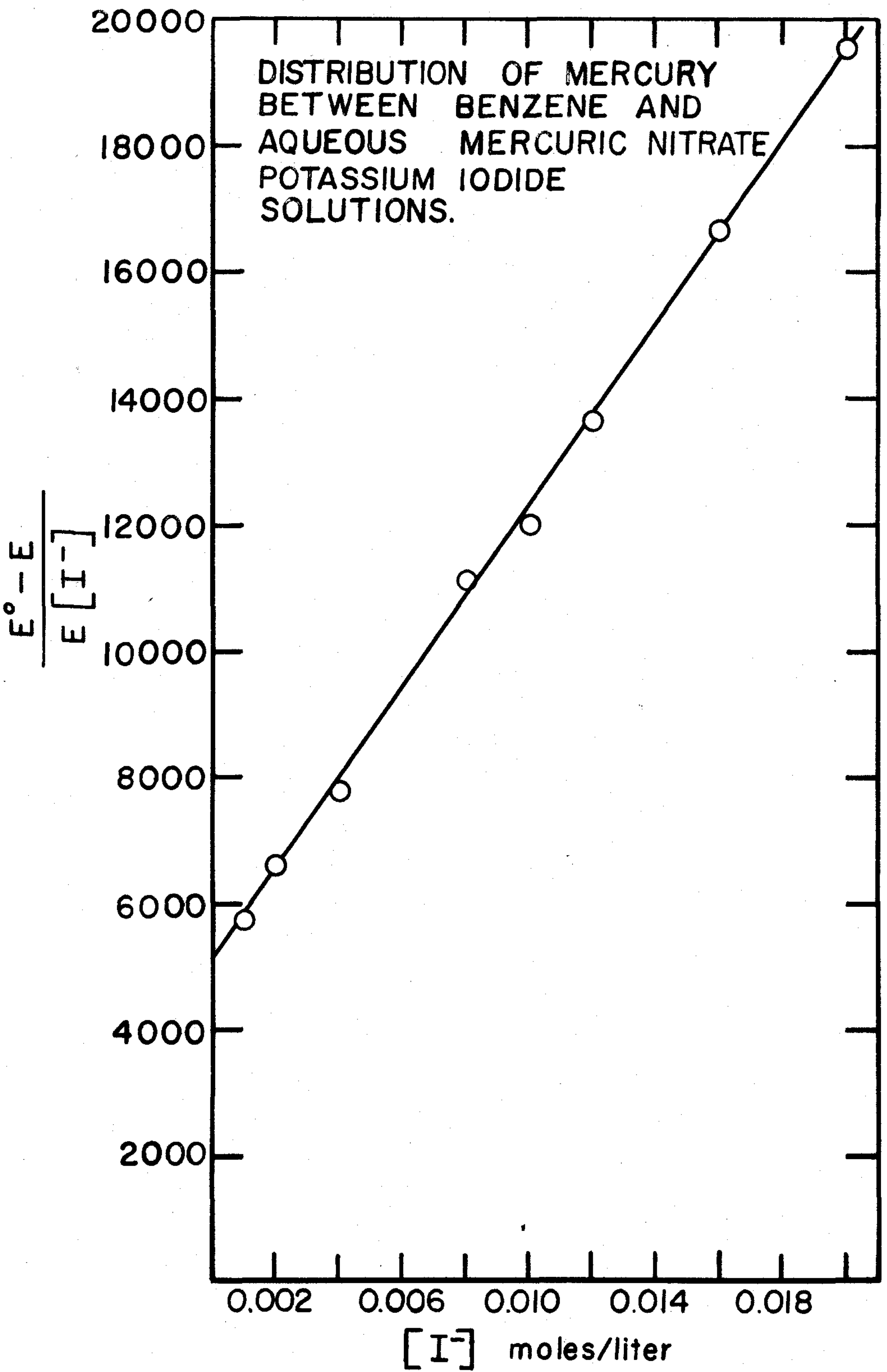

Figure 5. Distribution of mercury between benzene and aqueous $Hg(NO_3)_2$-KI solutions at 25° C.