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Solubility of mercury in organic liquids

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SOLUBILITY OF MERCURY IN ORGANIC LIQUIDS

by

Edwin Henry Klehr

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

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Of Science and Technology
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I. INTRODUCTION

The purpose of this work was to study the solubility of free mercury in various organic solvents. Benzene, toluene, nitrobenzene, chlorobenzene, bromobenzene, carbon tetrachloride, isooctane, and n-decane were chosen for study, and the variation of solubility with temperature was studied for toluene, n-decane and chlorobenzene.

Measurements of concentration were made by a tracer technique using radioactive mercury-203. In some cases solubilities were both measured directly and inferred from studies of the extraction of free mercury into an aqueous phase from the organic phase.

A correlation of the solubility measurements with the Hildebrand-Scott "solubility parameter" theory, and with the Reed modification of this theory was attempted.

II. REVIEW OF THE LITERATURE

A. Solubility of Mercury Metal

That mercury dissolves to some extent in water was noticed as early as 1908 by Christoff (1). He describes an experiment in which a quantity of water was allowed to flow over a layer of mercury contained in a pycnometer, after which a loss of weight was noted for the mercury. A number of qualitative experiments were then performed in which mercury was detected in aqueous solutions of sulfuric acid, potassium hydroxide, and also organic liquids such as alcohol and benzene. The mercury was detected by the reduction of a solution of gold chloride.

In 1929, Bonhoeffer and Reichardt (2) were able to conclusively demonstrate the presence of free mercury in water by means of ultraviolet absorption. The order of solubility of free mercury was estimated to be roughly that of a noble gas. Similar experiments indicated that hexane also dissolved mercury to a small extent.

In later work (3, 4) Bonhoeffer and Reichardt studied the absorption spectra of mercury dissolved in water, methanol, and hexane as a function of temperature. Two absorption bands were found around 2537 A. U. and the distance between their maxima was seen to increase from hexane to methanol to water, and to decrease with increasing temperature. This later effect was interpreted as a Stark effect due to the action of the electric field of the solvent molecules. They

also measured the solubility of mercury in the three liquids studied:

methanol:	36 mg/100cc at 63° 0.06 mg/100cc at 40°
hexane:	1.05 mg/100cc at 63° 0.27 mg/100cc at 40°
water:	0.1 mg/100cc at 120°

These values were obtained from a method involving the amalgamation of the dissolved mercury on a gold foil.

In 1931, Stock et al. (5), proposed a new method for the determination of traces of mercury which they said could be used to give an exact measurement of as little as 10^{-5} mg of mercury (6). The method involved the electrodeposition of the mercury on a copper wire from a solution of mercuric chloride. After electrodeposition, the mercury was distilled off, collected into a globule and its volume measured under a microscope. By means of this method, the authors detected mercury in nearly every reagent in the laboratory, with the exception of a few things such as tap water and potassium perchlorate.

Stock and co-workers (7) went on to measure the solubility of mercury in air-free water as a function of temperature; in dilute potassium hydroxide, potassium chloride, benzene, blood and egg albumin. The solubility of mercury in air-free water was found to be $0.02\mu\text{g/cc}$ at 30°C; $0.3\mu\text{g/cc}$ at 85°C; and $0.6\mu\text{g/cc}$ at 100°C. It was found to be much higher in the presence of air, which was attributed to air oxidation

of the mercury.

Moser (8) used radioactive tracers to measure the solubility of free mercury in a number of organic solvents. His results and methods are discussed elsewhere in this work.

B. Tracer Technique in Measuring Solubilities

The use of tracers to measure solubilities was first tested by Hevesy and Paneth (9, 10). They used RaD to measure the solubility of PbS and PbCrO₄, and suggested that tracers might prove a useful tool in solubility measurements, especially for salts found to be only slightly soluble.

As early as 1928, Paneth published a book entitled, Radioelements as Indicators (11), in which he discusses the application of tracers in solubility studies; but it has only been in recent years that the tool has received the serious attention it deserves. Reviews of solubility measurements have appeared in 1929 (12) and 1935 (13); Wahl and Bonner offer a convenient summary of work done up to 1949 (14).

Since then, an interesting work has appeared by Schiffman (15), in which he made a critical investigation of the problems involved in the use of radioactive tracers for determining the solubility of sparingly soluble salts. He has considered the instrumental and experimental factors which affect radiation measurements, such as choice of detection instrument, geometry, back-scattering, self-absorption and self-

scattering. The importance of correct glassware treatment and good assaying techniques were emphasized. A probability analysis of counting was given and used to find the limit of detectability of radioactivity, which in turn imposes a lower limit on the concentration range for which a tracer might be useful.

The tracer method was then applied to the determination of the solubility of AgI and AgBr. The reader is referred to the original paper for the results and discussion.

C. Hildebrand-Scott

"Solubility Parameter" Theory

Although it is obvious that the phenomenon of solubility is a very important facet of the field of chemistry, it has only been recently that a chemist has had much to work with beyond "rules of thumb" gathered from experience. "Like dissolves like", while it may be a convenient expression to remember, is quite unsatisfactory when serving as an accurate prediction of just what will be a good solvent for a particular solute.

A somewhat halting start toward modern solution theory was the work of van der Waals (16) and van Laar (17). Van der Waals applied his equation of state to pure components as well as to mixtures, with the characteristic quantities \underline{a} and \underline{b} being composition dependent averages. Once \underline{a} and \underline{b} had been

evaluated for a solution, it was treated exactly in the same manner as a pure component. The properties of non-ideal solutions appeared because of differences in "cohesion" or "covolume", which in turn appeared because of differences in the interactions of different pairs of molecules in the system. On the basis of these assumptions, van der Waals built a detailed and self-consistent theory of multicomponent systems.

It was soon found, however, that the largely empirical van der Waals equation of state could not be expected to yield quantitative values for the thermodynamic properties of liquids. This was in spite of the fundamental work by van Laar (18), who used the van der Waal equations to build a treatment of the vapor pressures of binary liquid mixtures.

More recent theories of solutions almost always have had as a starting point either a perfect gas or an ideal crystal, and then have considered the liquid as either a highly compressed gas or as a slightly imperfect solid. The crucial test for any of these theories has been an explanation of the equilibria between a liquid and its vapor phase, or of a liquid and its solid. If one has described a liquid as a "compressed gas", it may be hard to distinguish between the vapor and the "compressed gas"; and if one has described a liquid as an imperfect solid, it may be hard to be sure just what kind of transition melting is. In other words, these theories have no adequate explanation for the sharpness of melting and boiling points, nor for the magnitude of the heats involved in

the processes.

J. H. Hildebrand and co-workers have formulated a treatment of solutions which avoids leaning on either of the above models. This is the "regular solution", or "solubility parameter" theory which in recent years has been refined and extended to the point where with it one can use the properties of pure, non-polar, non-electrolytes to make some semi-quantitative predictions about the properties of solutions.

It would be beyond the scope of the present work to treat the entire history of the regular solution theory. Three different editions of Hildebrand's The Solubility of Non-Electrolytes have appeared (19), and the historical development is adequately contained in the latest. Consequently, only a few "landmarks" will be mentioned here.

The theory was introduced by papers in 1927 (20) and 1929 (21), in which the simplifying assumption was made that the molecules in a regular solution were distributed randomly, leading to an essentially ideal entropy of mixing, provided that the volume change of mixing was zero. All deviations from ideality were attributed to a heat of mixing, which was then calculated for such a random arrangement. The name "regular" seems to have come from a study of a family of solubility curves of a single solute in a number of solvents, for which a regular behavior was noted (19, Ch. 6).

This assumption of ideal entropy of mixing was later justified by work (22) which pointed out that different

formulations of the entropy of mixing for athermal solutions (free volume method, quasi-lattice method, method of excluded volume) all lead to essentially the same conclusion i. e., that the entropy lies between two limiting values; one the ideal value, and the other a higher maximum value:

$$-(n_1 \ln x_1 + n_2 \ln x_2) \leq \frac{\Delta S^M}{R} \leq -(n_1 \ln \varphi_1 + n_2 \ln \varphi_2);$$

where n_1 = number of moles of component 1,
 x_1 = mole fraction of component 1,
 φ_1 = volume fraction of component 1.

The maximum value is designed to apply to cases of large differences between the molal volumes of the solvent and solute. But since the deviation from the ideal case caused by a molecular volume ratio of two is small, and since most normal substances have molal volumes lying between 60 and 150cc, the molecular size effect was thought not to be significant in most mixtures. This and the fact that differences in intermolecular forces can cause large heats of mixing which usually overshadow small entropy corrections lead Hildebrand to state: "...we shall find that for substances of not too great difference in molal volume, we may, as a good approximation, regard the entropy of mixing as ideal" (19, p. 118).

It remained to calculate the heat of mixing for a solute randomly distributed in a solvent. Scatchard first discussed the problem in 1931 (23). He assumed: 1) the mutual energy of two molecules depends only on the distance between them

and their relative orientation; and not on the nature of the other molecules between or around them, or on the temperature; 2) the distribution of molecules in position and in orientation is random; 3) the change of volume on mixing at constant pressure is zero. Hildebrand (19, p. 123) pointed out that the first assumption is essentially that of the additivity of the energies of molecular pairs, which although not exactly true for dispersion forces, has been quite successful as the basis for nearly all theories of liquids and solutions. The second assumption ignores the ordering effect of molecular shapes, and differences in intermolecular potentials. We shall have more to say about the second and third assumptions later.

These assumptions lead to an expression for the "cohesive energy" of a mole of liquid mixture:

$$-E_m = (c_{11}V_1^2x_1^2 - 2c_{12}V_1V_2x_1x_2 + c_{22}V_2^2x_2^2)/(V_1x_1 + V_2x_2);$$

and for pure components: $-E_1 = c_{11}V_1;$

$$-E_2 = c_{22}V_2.$$

The energy of mixing is then:

$$\Delta E^M = E_m - E_1x_1 - E_2x_2 = (x_1V_1 + x_2V_2)(c_{11} + c_{22} - 2c_{12})\varphi_1\varphi_2;$$

where $\varphi \equiv$ volume fraction of the component in question.

In Hildebrand's notation this becomes:

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

$= (x_1 v_1 + x_2 v_2) (\delta_1 - \delta_2)^2 \varphi_1 \varphi_2$; where δ , the solubility parameter, is defined as:

$$\delta = \left(\frac{\Delta E^V}{V} \right)^{\frac{1}{2}}.$$

Here use is made of the fact that for liquids at ordinary temperatures, the vapor is nearly ideal, and so $-E$ becomes ΔE^V (the energy of vaporization). For a complete derivation of the above equation the reader is referred to Hildebrand's monograph (19, Ch. 7).

The above equation is essentially the same as that first derived by van Laar and Lorenz (24). It was also obtained by Hildebrand and Wood (25) by integrating the intermolecular potential between pairs of molecules using a continuous molecular distribution function.

Since expansion of mixing has been neglected, we may write: $\Delta \bar{H}_1 = \bar{E}_1 + P \Delta V = \Delta \bar{E}_1$; and since $\Delta \bar{S}_1$ for a regular solution is $-R \ln x_1$, we may combine the heat and entropy terms to give the partial molal free energy of mixing for component 1:

$$\Delta \bar{F}_1^M = RT \ln a_1 = RT \ln x_1 + v_1 \varphi_2^2 (\delta_1 - \delta_2)^2;$$

or, if the maximum entropy is to be considered:

$$\Delta \bar{F}_1^M = RT \left[\ln \varphi_1 + \varphi_2 (1 - v_1/v_2) \right] + v_1 \varphi_2^2 (\delta_1 - \delta_2)^2.$$

It should be emphasized that in this derivation the

assumptions of Scatchard have been used; and in the Hildebrand derivation of the same equation, the repulsive terms of the interatomic potential have been simplified, the differences between arithmetic and geometric means have been ignored, and no volume change of mixing and spherical monatomic, nonpolar molecules have been assumed. Nevertheless these equations can and have been used with marked success in estimating vapor pressures of solutions, miscibility relations, solubility of solutes in liquids, osmotic pressure, and a number of other properties.

Scott (26), in his discussion of the "present status of solubility parameter theory", seems pleasantly surprised that in view of the assumptions made the theory has been as useful as it has: "What may seem surprising is that the equation has proved useful at all. Yet it, or its variant with the Flory-Huggins configurational term, has been useful in interpreting qualitatively and often semi-quantitatively a wide variety of nonelectrolyte solutions including those of high polymers; especially so when the components are non-polar and when solubility phenomena are involved. Other theories (e.g., one of the corresponding states variety) often prove more successful for a narrowly restricted group of systems which conform to a special model, but no other has nearly as wide a range of usefulness."

The reasons for this success seem to be: first, that the basic theory does not rest upon a specific model, but

rather upon two simple assumptions about randomness of mixing and molecular interactions; and secondly, that solubility frequently involves free energies far in excess of thermal energies. Here a simple theory has a good chance of showing some degree of success.

It has been found over the years that the simple theory fits most free energy data on binary systems of non-polar, non-electrolytes to within 10-20% of thermal energies, or to within the experimental uncertainty of the solubility parameter itself. Unfortunately, this uncertainty can be quite significant.

Of course, several modifications of the basic equation have appeared--each designed to extend the simple theory to fit a more or less specific case. The only major change in the expression for the entropy of mixing as Hildebrand formulated it has been the substitution of the Flory-Huggins term to allow for differences in size between the two components.

Of the several modifications or extensions proposed, only one will be discussed in this work; that of Reed (27), which is discussed in a later section.

III. MATERIALS AND PROCEDURES

A. Apparatus

Solutions were brought to equilibrium in constant temperature water baths. Temperature was maintained to within $\pm 0.1^{\circ}\text{C}$ by means of an E. H. Sargent Company heating pump in conjunction with a mercury thermoregulator. Agitation was provided by a Burrel wrist action shaker.

Gamma counting was done with a Nuclear-Chicago well-scintillation counter and scaler. A recording spectrometer (Nuclear-Chicago, Model # 1820) was used to reduce the background as low as possible. A spectrum of Hg-203 indicated that optimum operating conditions were a base setting of 230 Kev, and a window width of ten units. The spectrometer was restandardized before each use by means of a standard Cs-137 sample.

Beta counting was done with a Tracerlab-TGC2 Geiger-Mueller end window tube in a Technical Associates Model # AL14A lead housing. Counting was done with a Nuclear-Chicago Model # 165 scaler.

B. Chemicals

Baker and Adamson Reagent grade benzene and nitrobenzene were used. The benzene was repurified by stirring with repeated portions of concentrated sulfuric acid and

redistilling. The nitrobenzene was steam distilled from a dilute sulfuric acid solution and redistilled.

Phillips Petroleum Company Research grade toluene and isooctane, and Pure grade n-decane were used without further repurification.

Eastman Organic Chemicals Eastman grade bromobenzene was found to cause a black deposit on the surface of the mercury after a few hours and a white, finely divided precipitate after a few days. Repurification consisted of shaking with stannous chloride and redistillation. Eastman chlorobenzene was used without further treatment.

Baker Analyzed carbon tetrachloride was shaken with an aqueous solution of sodium sulfite. It was then dried by passing it through a silica gel column and redistilled.

Mercuric nitrate containing Hg-203 was obtained from Oak Ridge National Laboratory. A half-life of 47.0 days obtained from the supply agreed with published values. Finely divided metal, obtained by adding a few drops of hypophosphorous acid to the solution, was coagulated into a globule by stirring with concentrated hydrochloric acid. The globule was washed and dried.

C. Experimental Procedures

To carry out a solubility determination, a globule of active mercury and about 50 ml of organic solvent were shaken

in 100 ml volumetric flasks in the constant temperature water bath. Samples were taken and analyzed until the solution was thought to be at equilibrium.

Analyses were made in two different ways; by G-M counting of solid samples, and by scintillation counting of liquid samples. It was felt that the scintillation method was the more advisable, since it involved fewer and simpler steps. However, the two methods gave about the same precision.

In the solid sample technique, a 0.5 ml aliquot was taken from the solution with a micro-pipette. The pipette was rinsed once, and the sample and rinse were delivered to a 12 ml centrifuge tube. Next 0.2 ml of a 0.04 M mercuric nitrate carrier solution were added. Enough acetone to make one phase was introduced, and the tube was allowed to stand 15 to 30 minutes to ensure complete exchange of the carrier and active mercury. Preliminary experiments had indicated that six to ten minutes would have been sufficient. The acetone and organic solvent were evaporated with a stream of warm air, after which the mercury was precipitated with ammonium sulfide and centrifuged. After careful decantation, a few drops of dilute aqueous sodium hydroxide solution were added to form a slurry which was transferred to a stainless steel planchet, evaporated to dryness, and counted. The method was standardized by applying the same procedure to the original active mercuric nitrate solution. The active mercuric nitrate solution had

previously been standardized by precipitation with sulfide ion, and by titration with potassium thiocyanate. Details of this method of analysis are given by Moser (8).

In the second method, a 0.05 ml aliquot of the solution was delivered to a 5 ml volumetric flask with the rinse. The flask was filled to volume with benzene and the solution transferred to a scintillation counting tube with a rinse, which gave a total volume of 7 ml. This method of analysis was calibrated by employing the same procedure with the original active mercuric nitrate solution. The standardization curves are given in Figures 1 and 2.

In the extraction experiments, 15 ml each of the organic and aqueous phases were put into reaction flasks. The aqueous phase was 0.01 M in nitric acid and 0.007 M in hypophosphorous acid. The flask was agitated in the constant temperature water baths. Analyses of both phases were made by both of the above methods. For the aqueous samples, dilution of the aliquot was done with dilute nitric acid. Here especially the liquid sample technique was to be preferred because of ease and simplicity. Samples were taken until the distribution coefficient remained at a constant value.

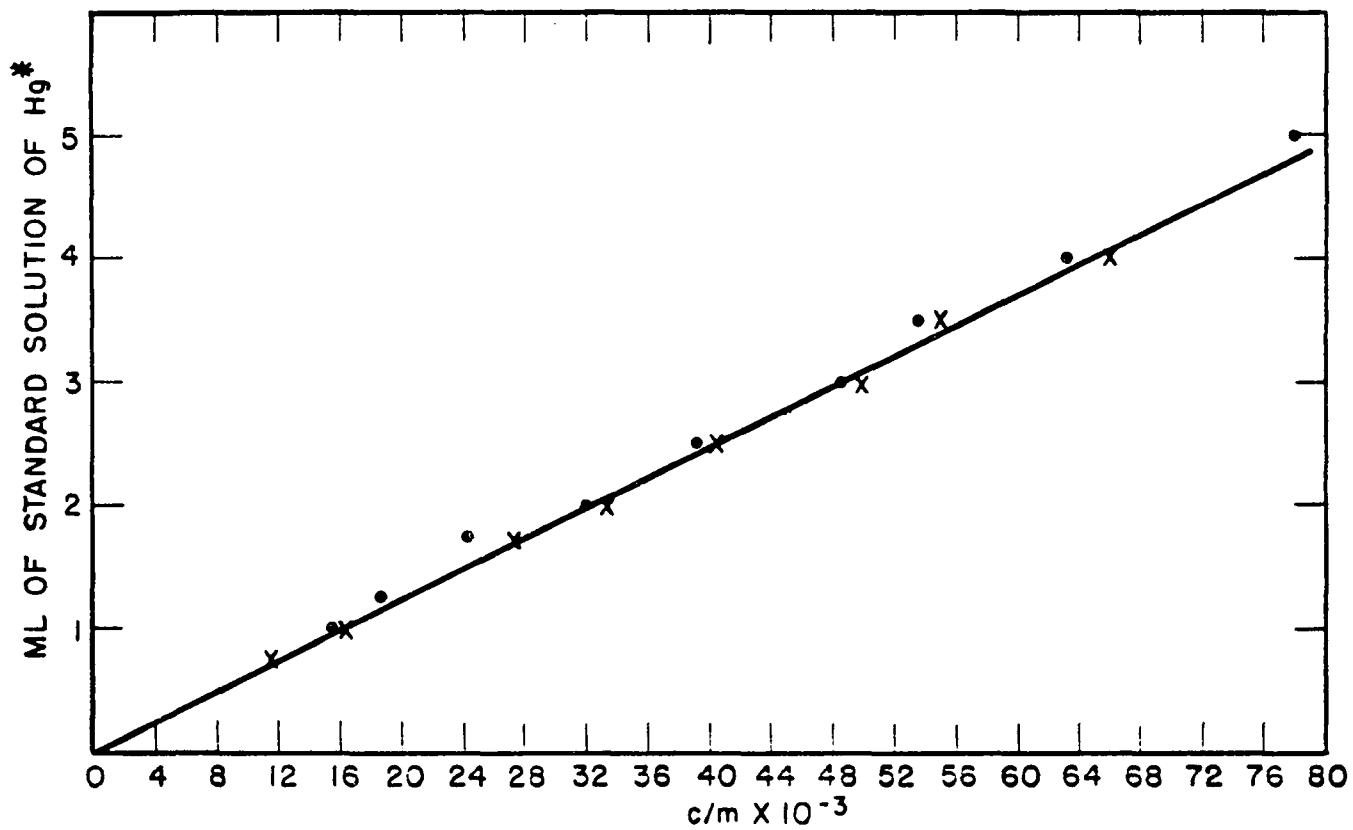


Figure 1. Standardization curve, scintillation counting

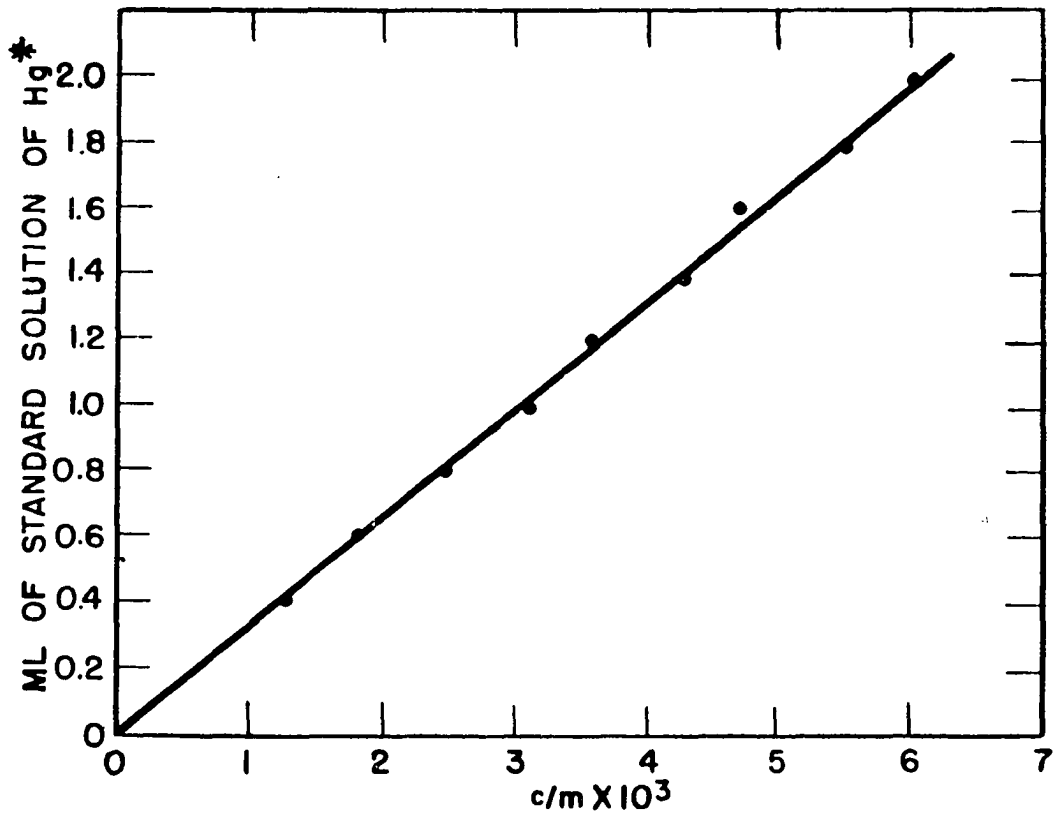


Figure 2. Standardization curve, solid sample counting

IV. METHOD OF INTERPRETING DATA

A. Direct Measurements

In the direct measurement technique, the method of interpreting data is quite simple. It is assumed that the detection device used has the same counting efficiency for any counting sample of the same isotope and obtained in the same manner.

1. Solid samples

Assuming the Geiger-Mueller counter had the same efficiency for any two samples counted, we may write:

$$\text{Eff} = \text{Eff}_s ; \text{ or}$$

$$R/\lambda N = R_s / \lambda N_s ;$$

where the subscript s refers to the standard sample used;

$$R = \text{counts/minute,}$$

$$\lambda N = \text{true disintegration rate,}$$

$$N = \text{total number of mercury atoms in sample,}$$

$$\text{or } N = \text{concentration of mercury in aliquot}$$

multiplied by the volume of the aliquot ($c \times v$).

Consequently, $R/\lambda cv = R_s/\lambda c_s v_s$; which upon rearranging, becomes:

$$c = R v_s c_s / R_s v.$$

The units of c depend on the units used for c_s , which in this study was gram-atoms/liter. The quantity c_s was

determined by sulfide precipitation, and by potassium thiocyanate titration. In all cases, R_s and R were determined at the same time, which obviated any decay corrections.

2. Liquid samples

Using the same reasoning as for the solid samples, we have:

$$c = Rv_s c_s / R_s v.$$

In this case the quantity v_s/R_s was determined for a series of standards of varying v_s (See Figure 1). An average value was taken and used in all the calculations of c , after an appropriate decay correction had been made. Here again the units of c_s and c were gram-atoms/liter. The same standard solution was used to standardize both methods.

B. Extraction Samples and the Indirect Method

Assuming that Henry's Law holds for the solute in both phases, a simplified form of the Nernst distribution law was used:

$$K = \frac{\text{concentration in organic phase}}{\text{concentration in aqueous phase}} \\ = \frac{\text{solubility in organic phase}}{\text{solubility in aqueous phase}}$$

which was rearranged to read:

solubility in organic phase = K (solubility in aqueous phase).

The distribution coefficient K was measured by:

$$K = R_o/R_a;$$

where R_o and R_a were the counting rates of equal aliquots of the organic and aqueous phases. Assuming the solubility of mercury in the aqueous phase to be known (8), one could then calculate the solubility in the organic phase.

Of course, the same assumption about efficiency of counting must be made as in the direct method. Preliminary experiments had shown that the counting rate of a liquid sample was not significantly affected by a change in density of 0.875 to 1.463, all other factors remaining constant. This is not surprising, since a γ -ray was being detected, and one would expect the self-absorption by the samples to be fairly small.

C. Statistics and Experimental Error

The uncertainty quoted for a solubility measurement was calculated as the standard deviation of the average of a series of measurements:

solubility = $a \pm b$; where

$$a = \sum X_i/N;$$

$$b = \frac{\sum (\Delta X_i)^2}{N(N-1)};$$

$$\Delta X_i = a - X_i;$$

N = number of measurements;

X_i = individual measurements.

Because of the simplicity of the procedure, it was felt

that the only probable significant experimental error would involve pipetting the samples. However, preliminary experiments had shown that the precision in pipetting was as great as that of the counting step itself. Consequently, an experimental error greater than 2 or 3% seems unlikely.

V. EXPERIMENTAL RESULTS

A. Studies at 25°C

The solubilities of mercury in the various solvents studied at 25°C are listed in Table 5. The second column contains values obtained from measurements of the distribution coefficient for the organic-aqueous systems. The third column lists values as measured by Moser (8). The agreement between the two methods of measurement, and between Moser's values and those obtained in the present study is quite satisfactory.

B. Variation of Solubility with Temperature

The solubility of free mercury as a function of temperature for toluene, chlorobenzene, and n-decane are given in Table 6 and Figures 3, 4, and 5.

Table 1. Solubility measurements at 25° by scintillation counting

Solvent	Days shaking	Sample number	Counting rate (c/m)	$c \times 10^6$ (g-a/l)	$c_{ave} \times 10^6$	Days included in c_{ave}		
Benzene	2	1	35753	10.3	11.4 ± 0.1	4, 9		
		2	34156	9.8				
	4	1	38500	11.1				
		2	39175	11.3				
		3	4057	11.7				
		4	39851	11.5				
	9	1	38952	11.2				
		2	40399	11.6				
		3	39663	11.4				
		4	40024	11.5				
	Toluene	2	1	47043		8.7	13.4 ± 0.1	4, 5, 8
			2	44121		8.2		
4		1	71061	13.1				
		2	75534	13.5				
5		1	75315	13.5				
		2	74829	13.4				
8		1	74186	13.3				
		2	73644	13.6				
		3	74110	13.3				
		4	74863	13.3				
Chloro-benzene		2	1	56640	11.8	6, 7, 10		
			2	53138	10.1			
	6	1	67695	12.9				
		2	69125	12.4				
	7	1	70035	13.3				
		2	70609	12.6				

Table 1. (Continued)

Solvent	Days shaking	Sam- ple num- ber	Count- ing rate (c/m)	c x 10 ⁶ (g-a/l)	c _{ave} x 10 ⁶	Days included in c _{ave}
	10	1	64180	12.2		
		2	64802	11.6	12.5 ± 0.1	
Bromo- benzene	2	1	60009	17.3		2, 6
		2	58461	16.7		
		3	60564	16.3		
		4	60734	16.4		
	6	1	55626	16.0		16.0 ± 0.3
		2	53656	15.4		
		3	55872	15.1		
		4	55392	15.0		
n-Decane ^a	1	1	15965	4.80		3, 5
		2	16686	5.01		
	3	1	23541	6.76		7.0 ± 1
		2	24344	6.95		
		3	24752	6.68		
		4	24266	6.54		
	5	1	24568	7.05		7.0 ± 1
		2	23212	6.64		
		3	27879	7.51		
		4	22874	6.20		
	5	1	24782	7.01		5, 12, 14
		2	24426	6.99		
		3	25064	6.80		
		4	25304	6.84		
	12	1	24083	6.90		
		2	23915	6.85		
3		24946	6.73			
4		23980	6.48			

^aTwo n-decane solutions were studied.

Table 1. (Continued)

Solvent	Days shaking	Sam- ple num- ber	Count- ing rate (c/m)	$c \times 10^6$ (g-a/l)	$c_{ave} \times 10^6$	Days included in c_{ave}
	14	1	24712	7.07		
		2	28654	8.20		
		3	27705	7.47		
		4	26820	7.24	7.0 ± 0.2	
Isooctane	2	1	12662	2.25		6, 7, 10
		2	11625	2.17		
	6	1	25420	4.54		
		2	25040	4.47		
	7	1	26066	4.81		
		2	25606	4.73		
	10	1	24328	4.52		
		2	24244	4.34		
		3	23400	4.33	4.6 ± 0.1	

Table 2. Solubility measurements as a function of temperature for n-decane

T °C	Days shaking	Sample number	Counting rate (c/m)	c x 10 ⁶ (g-a/l)	c _{ave} x 10 ⁶
0	3	1	4372	2.17	
		2	4463	2.21	
		3	4452	2.21	
		4	4295	2.13	
	6	1	3557	1.87	
		2	3809	2.00	
		3	3901	2.40	
		4	3765	1.97	
10	4	1	4651	2.69	
		2	4672	2.70	
		3	4630	2.67	
		4	4759	2.75	
	8	1	4972	3.08	
		2	4850	3.01	
		3	4855	3.01	
	15	3	1	9518	
2			9004	4.47	
3			9047	4.49	
4			8968	4.46	
6		1	8058	4.22	
		2	9432	4.92	
		3	8024	4.20	
		4	8038	4.21	4.5 ± 0.1
20	7	1	8754	5.05	
		2	8514	4.92	
		3	7639	4.41	
		4	8478	4.90	
	11	1	8102	5.03	
		2	7886	4.90	
		3	8251	5.13	
		4	7746	4.80	

Table 2. (Continued)

T °C	Days shaking	Sample number	Counting rate (c/m)	c x 10 ⁶ (g-a/l)	c _{ave} x 10 ⁶
30 ^a	2 ^b	1	22872	7.40	8.3 ± 0.2
		2	22952	7.44	
		3	22541	7.37	
		4	22839	7.46	
	6	1	25794	8.65	
		2	24653	8.27	
		3	24188	8.15	
		4	24852	8.35	
	8	1	22694	8.32	
		2	22557	8.31	
		3	21559	7.91	
		4	22430	8.21	
	2	1	28301	9.56	
		2	27385	9.36	
		3	26378	8.93	
	6	1	26798	9.00	
		2	26946	9.05	
		3	26821	9.00	
		4	26709	8.98	
	8	1	24779	9.10	
2		23454	8.57		
3		26168	9.55		
4		23550	8.61		
35	4	1	26764	10.2	
		2	26779	10.2	
		3	26657	10.2	
		4	26953	10.2	

^aAt 30°, 35°, and 45° two solutions of n-decane were studied.

^bData of second day not included in calculation of c_{ave}.

Table 2. (Continued)

T °C	Days shaking	Sample number	Counting rate (c/m)	c x 10 ⁶ (g-a/l)	c _{ave} x 10 ⁶
45	6	1	24316	9.85	9.9 ± 0.4
		2	25078	10.2	
		3	22997	9.33	
		4	23003	9.33	
	4	1	24919	9.50	
		2	24429	9.32	
		3	23696	9.05	
		4	23916	9.13	
	6	1	26293	10.7	9.4 ± 0.5
		2	22527	9.14	
		3	22568	9.16	
		4	22125	8.96	
	5	1	32594	13.4	
		2	30881	13.0	
		3	32624	13.4	
		4	32534	13.3	
8	1	29565	13.2	13.3 ± 0.1	
	2	29805	13.3		
	3	29662	13.2		
	4	29467	13.0		
5	1	29760	12.6		
	2	28814	12.2		
	3	30311	12.8		
	4	29264	12.4		
8	1	32789	14.5	13.3 ± 0.3	
	2	31282	14.0		
	3	30480	13.7		

Table 3. Solubility measurements as a function of temperature for chlorobenzene

T °C	Days shaking	Sample number	Counting rate (c/m)	c x 10 ⁶ (g-a/l)	c _{ave} x 10 ⁶
0	3	1	5691	2.82	2.8 ± 0.1
		2	5675	2.82	
		3	5697	2.82	
		4	5589	2.78	
	6	1	5579	2.92	
		2	5321	2.78	
		3	5432	2.84	
		4	5100	2.67	
10	4	1	8679	5.02	5.0 ± 0.1
		2	8116	4.80	
		3	8114	4.80	
	8	1	8331	5.16	
		2	8085	5.02	
		3	8308	5.15	
		4	8030	4.98	
	15	3	1	13183	
2			13091	6.50	
3			13460	6.70	
4			12787	6.35	
6		1	12994	6.80	
		2	12796	6.70	
		3	12821	6.70	
		4	12749	6.65	
20	7	1	14127	8.17	8.4 ± 0.1
		2	14634	8.46	
		3	14362	8.30	
		4	13855	8.00	
	11	1	13402	8.32	
		2	13742	8.51	
		3	13755	8.51	
		4	13744	8.51	

Table 3. (Continued)

T °C	Days shaking	Sample number	Counting rate (c/m)	c x 10 ⁶ (g-a/l)	c _{ave} x 10 ⁶
35	7	1	26192	18.7	
		2	24918	17.8	
		3	24206	19.0	
		4	25254	18.0	
	11	1	26458	19.8	
		2	25757	19.2	
		3	27462	20.5	
		4	28345	21.2	

Table 4. Solubility measurements as a function of temperature for toluene

T °C	Days shaking	Sample number	Counting rate (c/m)	c x 10 ⁶ (g-a/l)	c _{ave} x 10 ⁶	
0	3	1	5759	2.86 ^a	3.4 ± 0.1	
		2	5645	2.79		
		3	5722	2.84		
		4	5877	2.92		
	6	1	6138	3.21		
		2	6341	3.32		
		3	6428	3.36		
		4	6315	3.30		
	10	10	1	6325		3.33
			2	6462		3.41
			3	6592		3.48
			4	6412		3.38
10	4	1	8562	4.95	5.1 ± 0.1	
		2	8605	4.97		
		3	8809	5.09		
	8	1	8588	5.33		
		2	8147	5.08		
		3	8204	5.06		
		4	9066	5.62		
	15	3	1	13434		6.65
2			12932	6.40		
3			13257	6.60		
6		1	12457	6.55		
		2	12818	6.70		
		3	12751	6.65		
		4	12666	6.65		
20		7	1	14769	8.54	
	2		14781	8.54		
	3		14571	8.41		
	4		14774	8.54		

^aData for 3rd day at 0° not included in c_{ave}.

Table 4. (Continued)

T °C	Days shaking	Sample number	Counting rate (c/m)	c x 10 ⁶ (g-a/l)	c _{ave} x 10 ⁶	
30	11	1	13801	8.57	8.5 ± 0.1	
		2	14088	8.75		
		3	13507	8.38		
	2	1	42001	14.2		
		2	39638	13.4		
		3	41935	13.8		
		4	42502	14.4		
	6	1	43607	14.6		
		2	42634	14.3		
		3	43240	14.5		
		4	43005	14.4		
	8	1	39844	14.5		
2		36035	13.2			
3		38438	14.1			
4		36984	13.6			
35	4	1	44484	17.0		
		2	43709	16.7		
		3	43875	16.8		
		4	43758	16.7		
	6	1	38975	15.8		
		2	41199	16.7		
		3	42944	17.0		
		4	38374	15.6		
	45	4	1	63306	26.8	
			2	61077	25.9	
			3	62598	26.4	
			4	63378	26.8	
7		1	61520	27.6		
		2	59934	26.8		
		3	61081	27.4		
		4	57909	25.9		
					26.9 ± 0.2	

Table 5. The solubility of mercury at 25°C

Solvent	Concentration: (gram-atoms/liter) x 10 ⁶			
	Direct measurement	Indirect measurement	Moser ^a	Hildebrand theory ^b
Isooctane	4.6 ± 0.1	4.7		3.4
Carbontetrachloride	7.5 ± 0.1	7.5	7.5 ± 0.3	40
n-Decane	7.0 ± 0.1			9.3
Benzene	11.4 ± 0.3	11.1	12.0 ± 0.6	82
Toluene	13.4 ± 0.1		12.5 ± 0.5	52
Nitrobenzene		8.8	9.3 ± 0.7	157
Chlorobenzene	12.5 ± 0.1			132
Bromobenzene	16.0 ± 0.3			112

^aMoser (8).

^bAs calculated from: $\ln x_1 = -V_1(\delta_1 - \delta_2)^2/RT$.

Table 6. The solubility of mercury as a function of temperature

Concentration: (gram-atoms/liter) x 10 ⁶			Temperature	10 ³ /°K
Toluene	Chlorobenzene	n-Decane	(°C)	
3.4 ± 0.1	2.8 ± 0.1	2.1 ± 0.1	0	3.66
5.1 ± 0.1	5.0 ± 0.1	3.0 ± 0.1	10	3.54
6.6 ± 0.1	6.8 ± 0.1	4.5 ± 0.1	15	3.47
8.5 ± 0.1	8.4 ± 0.1	4.9 ± 0.1	20	3.41
13.4 ± 0.1	12.5 ± 0.1	7.0 ± 0.1	25	3.35
14.4 ± 0.1		8.6 ± 0.1	30	3.30
16.5 ± 0.1	19.3 ± 0.1	9.6 ± 0.1	35	3.25
26.9 ± 0.2		13.3 ± 0.1	45	3.15

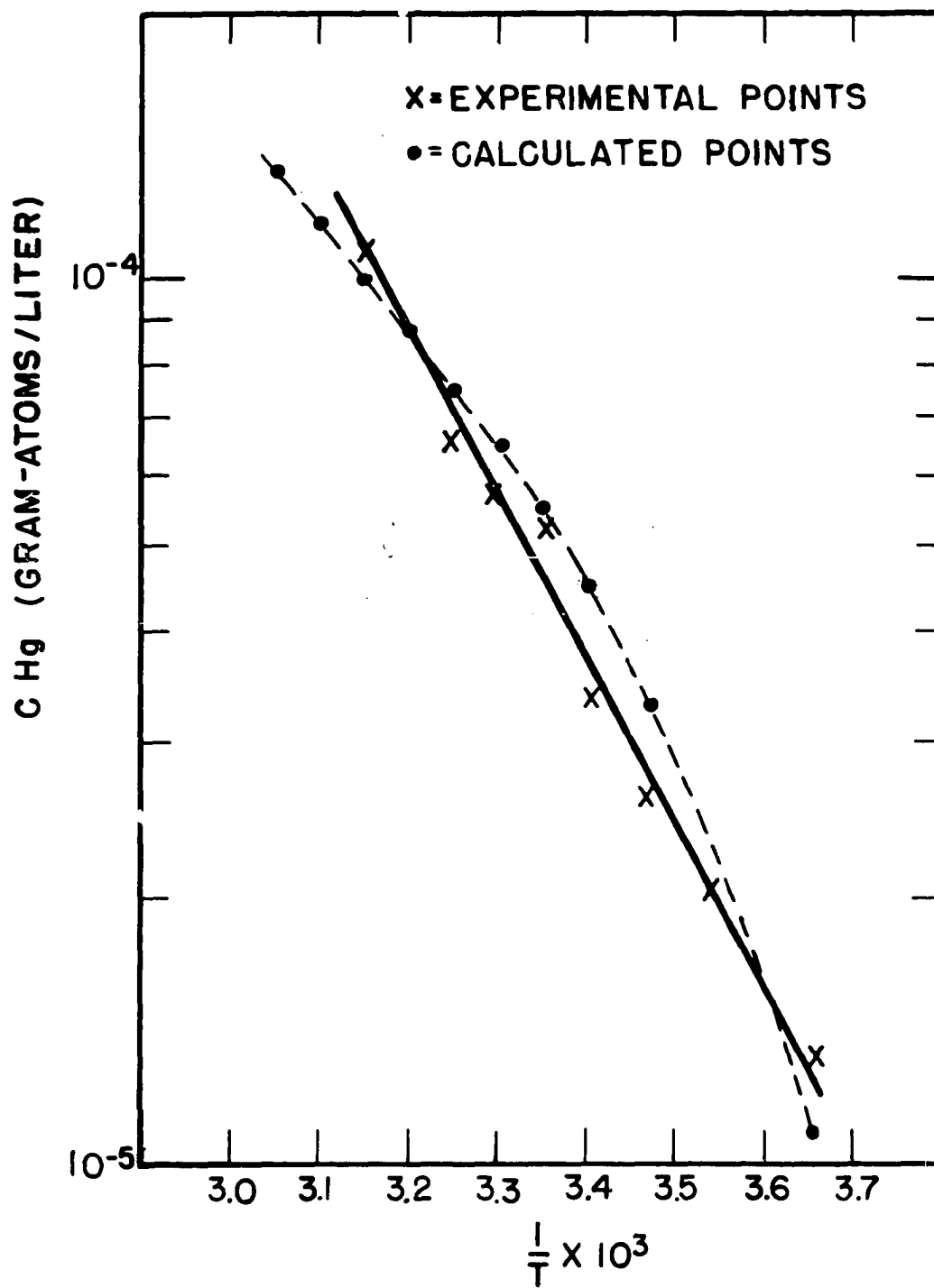


Figure 3. Equilibrium concentration of mercury in toluene
X = experimental points x 4

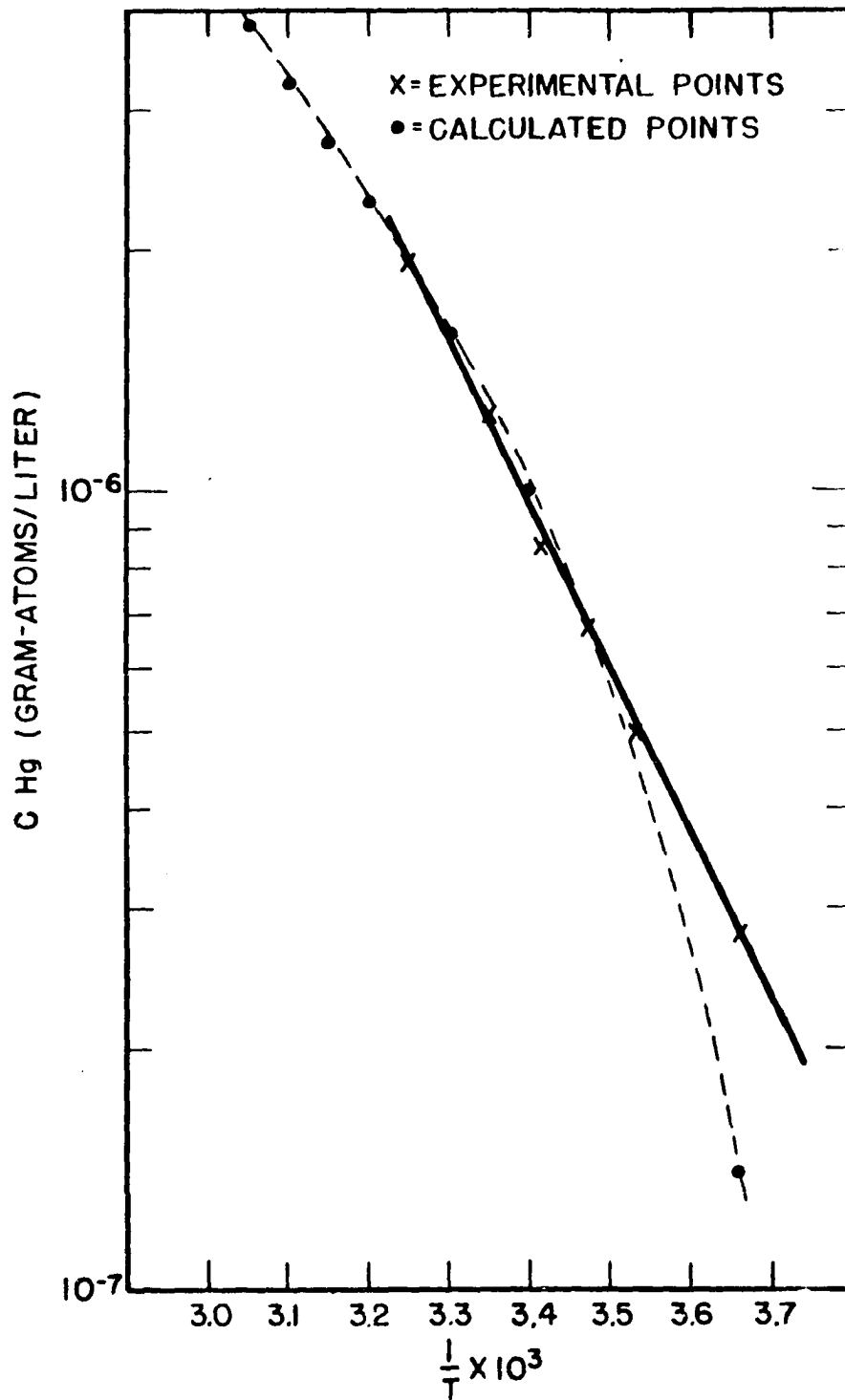


Figure 4. Equilibrium concentration of mercury in chlorobenzene. X = experimental points $\times 10$

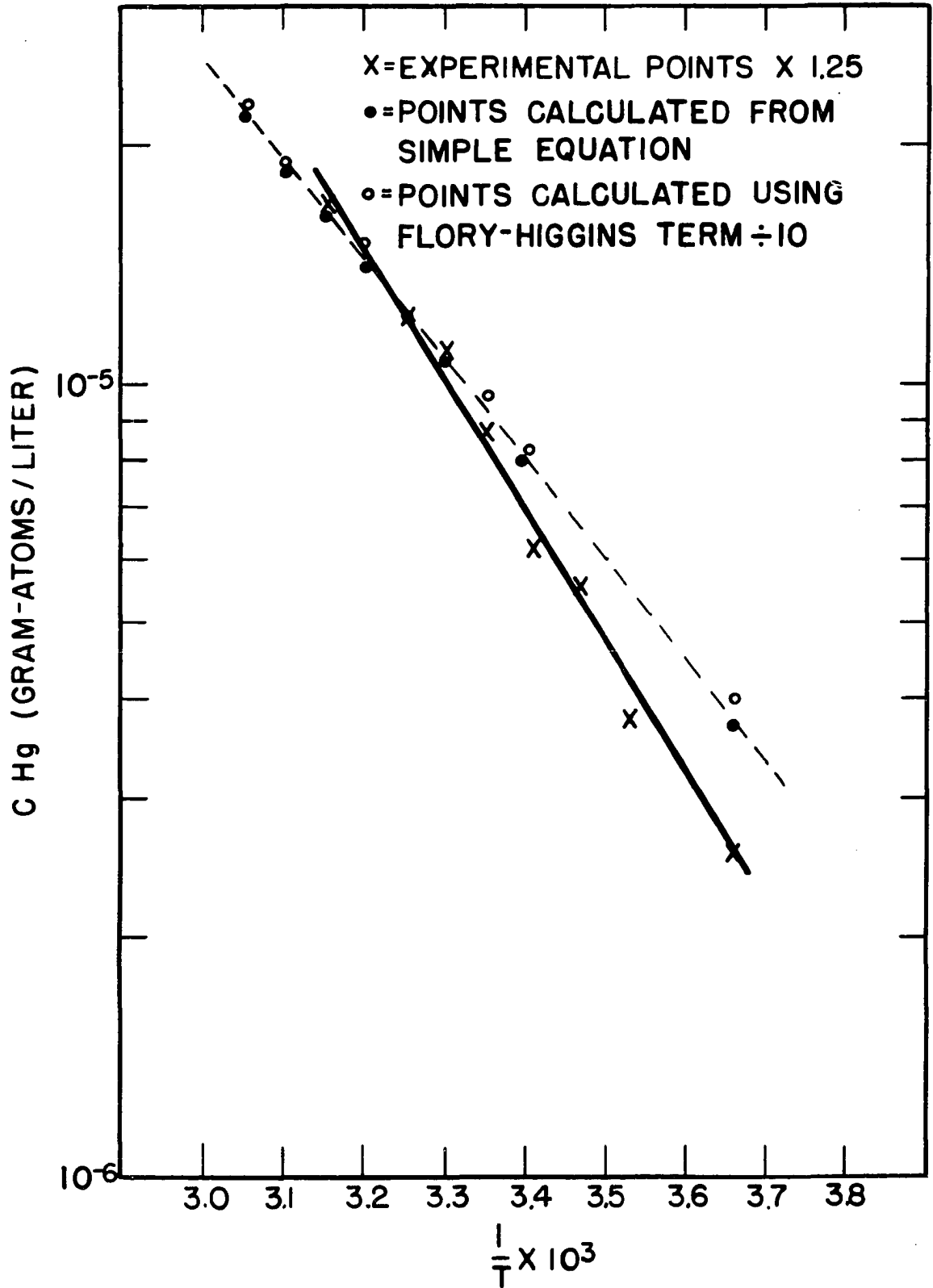


Figure 5. Equilibrium concentration of mercury in n-decane

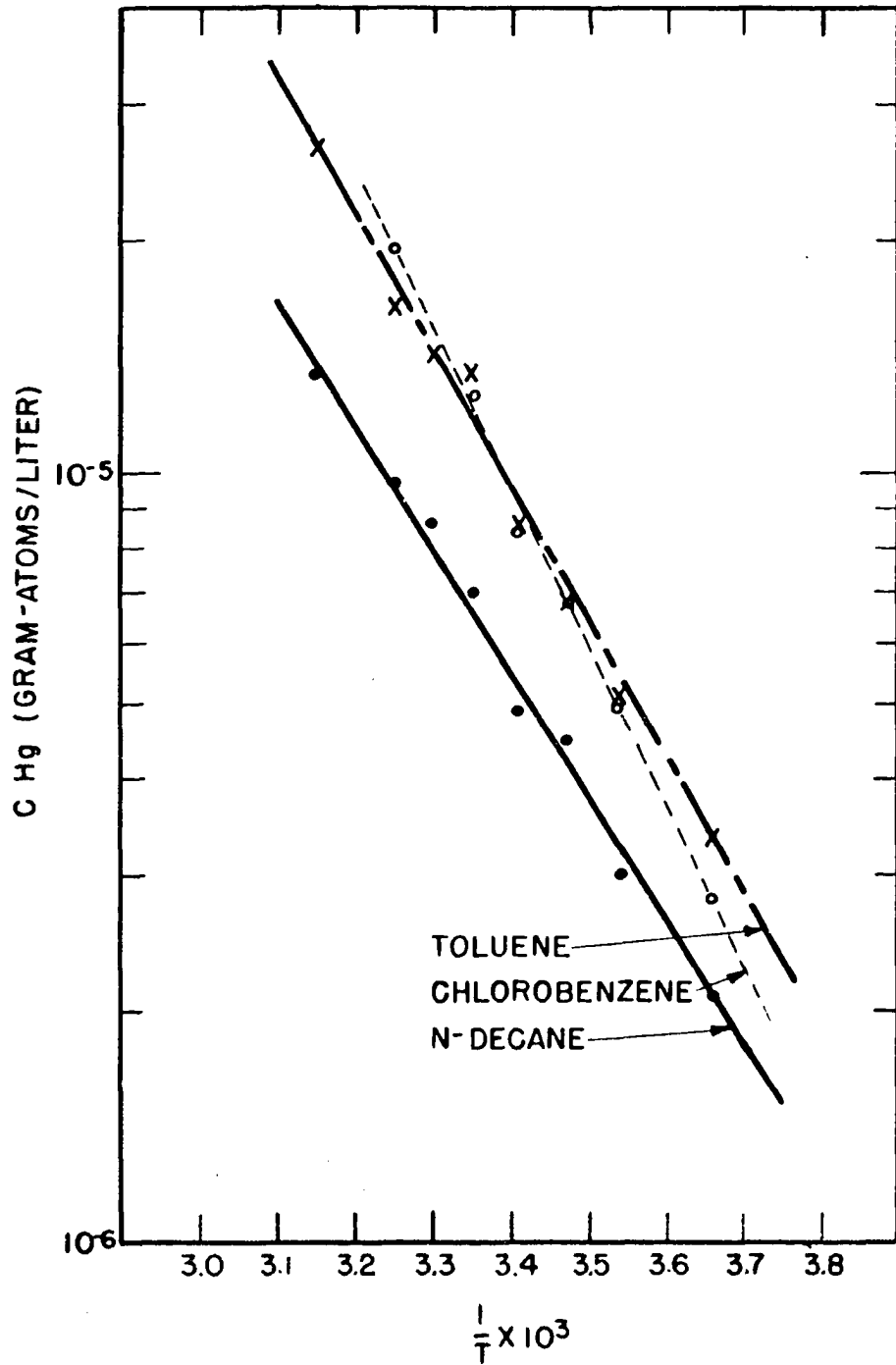


Figure 6. Comparison of equilibrium concentration of mercury in n-decane, toluene and chlorobenzene

VI. CALCULATIONS

We may write Hildebrand's basic equation as:

$$\Delta \bar{F}_1^M = RT \ln x_1 + V_1 \varphi_2^2 (\delta_1 - \delta_2)^2 \quad (\text{subscript 1 refers to}$$

solute). In a saturated solution, the above becomes:

$$\ln x_1 = -V_1 (\delta_1 - \delta_2)^2 / RT.$$

But:

$$x_1 = \frac{c_1}{\frac{1000d}{M_2} + c_1} = \frac{c_1 V_2}{1000};$$

where c_1 is the concentration of solute in gram-atoms/liter, d is the density of the solvent, M_2 the molecular weight of the solvent, and V_2 is its molar volume. Therefore, we may also write:

$$\ln c_1 = \ln(1000/V_2) - V_1 (\delta_1 - \delta_2)^2 / RT.$$

This last equation means that once we evaluate V_1 , V_2 , δ_1 , δ_2 ; we can calculate the expected solubility of mercury in an organic solvent.

A. Evaluation of δ

Of the different methods of evaluating δ given by Hildebrand (19, Ch. 23), the best seems to be the calculation from heats of vaporization. As mentioned earlier, at low vapor pressures, $-E = \Delta E^V$; which we can in turn express as:

$$-E = \Delta E^V = \Delta H^V - RT.$$

The heat of vaporization can be evaluated from calorimetric measurements, or if necessary from the exact Clausius-Clapeyron equation:

$$dp/dT = \frac{\Delta H^V}{T\Delta V^V};$$

and the molal volume for a liquid can be readily evaluated from density measurements.

In the present work δ values were calculated from calorimetric values of ΔH^V when possible, or from the appropriate vapor pressure-temperature relation. Data were taken from the compilation of the American Petroleum Institute (28), and Egloff (29). In all cases the values for δ so obtained agreed well with those quoted by Hildebrand (19, p. 435).

A comparison of the calculated and experimental values for c_1 will be found in Table 5. It is seen that the simple equation fits the experimental values only to within an order of magnitude in most cases.

B. Calculation of Temperature Dependence and Comparison with Experimental Values

The method described above was extended to calculate an expected solubility vs. temperature curve for toluene, chlorobenzene, and n-decane. Here however, use was made of the fact that $\ln \delta$ is a linear function of temperature (19, p. 433);

δ was calculated for those temperatures for which calorimetric values of ΔH^V were available, and intermediate values of δ were obtained by the analytical two point equation for a straight line.

A comparison of the calculated and experimental curves obtained will be found in Figures 3, 4, and 5. It will be noted that in all three cases, it was necessary to multiply the experimental values by an appropriate factor for convenient comparison. It is seen that the experimental values lie along a straight line, while only the calculated curve for n-decane is straight; implying that the experimental ΔH^M is a constant over the temperature range in question, while the calculated value is not.

C. Consistency of δ_{Hg}

It was of interest to study Hildebrand's simple equation by two other approaches. In the first, values of x_1 were used to calculate δ_{Hg} , assuming δ_{solvent} was known. Calculations were made from the equation:

$$\delta_{Hg} = \sqrt{\frac{-2.303RT \log x_1}{V_1}} + \delta_{\text{solvent}}$$

Results are given in Table 7.

For the second approach, the correlation of the solubility in two solvents was studied, using the equation:

Table 7. Internal consistency of δ_{Hg}

Solvent	$-\log x_1$ (exp.)	$(\delta_1 - \delta_2)^{2a}$	δ_2^b	δ_{Hg}^c	$\frac{\log x_1}{\log x_1^*}$	$\left[\frac{\delta_1 - \delta_2}{\delta_1 - \delta_2^*} \right]^d$
Benzene	5.992	551	9.1	33		
Toluene	5.884	539	8.9	32	1.03	0.98
Chlorobenzene	5.895	543	9.7	33	1.02	1.06
Bromobenzene	5.775	532	9.5	33	1.04	1.04
Nitrobenzene	6.044	556	10.0	34	0.99	1.09
Carbontetrachloride	6.139	565	8.5	32	0.98	0.96
Isooctane	6.120	564	6.8	30	0.98	0.77
n-Decane	5.862	540	7.8	31	1.02	0.90

^aValues as given by: $(\delta_1 - \delta_2)^2 = \frac{-2.303RT \log x_1}{V_1}$

^bAssumed values of δ solvent.

^cValues of δ_{Hg} as given by: $\delta_{Hg} = \sqrt{(\delta_1 - \delta_2)^{2a}} + \delta_2^b$.

^dRatio calculated by δ values evaluated as by Hildebrand, (19).

$$(\log x_1)/(\log x_1^*) = \frac{-V_1(\delta_1 - \delta_2)^2/RT}{-V(\delta_1 - \delta_2^*)^2/RT} = \frac{(\delta_1 - \delta_2)^2}{(\delta_1 - \delta_2^*)^2};$$

where the asterisk refers to a second solvent. Benzene was chosen as the "normalization" solvent. The experimental values of $(\log x_1)/(\log x_1^*)$ are compared with $(\delta_1 - \delta_2)^2/(\delta_1 - \delta_2^*)^2$ in Table 7.

A closer inspection of the basic equation reveals that the equilibrium concentration of the solute is given by an exponential term which in turn involves a quadratic expression. This being the case, the concentration will be very sensitive to the values chosen for the solubility parameter; consequently it is of interest to evaluate this effect. We have:

$$\ln c_1 = \ln(1000/V_2) - V_1(\delta_1 - \delta_2)^2/RT.$$

We differentiate this, assuming V_1 , V_2 , T to be constant, obtaining:

$$d \ln c_1 = dc_1/c_1 = -2V_1(\delta_1 - \delta_2)(d\delta_1 - d\delta_2)/RT;$$

$$\delta = \left(\frac{\Delta H^V - RT}{V}\right)^{\frac{1}{2}};$$

$$d\delta = \left(\frac{\Delta H^V - RT}{V}\right)^{-\frac{1}{2}} \frac{d\Delta H^V}{2V};$$

$$= \frac{d\Delta H^V}{2\delta V}.$$

Combining the above equations, and assuming the uncertainties to be small leads to:

$$\Delta c_1/c_1 \approx \frac{-V_1(\delta_1 - \delta_2)}{RT} \left\{ \frac{\Delta(\Delta H_1^V)}{1V_1} + \frac{\Delta(\Delta H_2^V)}{2V_2} \right\}.$$

To evaluate this expression, we take typical values for the involved quantities: $V_1 = 15\text{cc}$; $V_2 = 100\text{cc}$; $(\delta_1 - \delta_2) = 20$; $\delta_1 = 30$; $\delta_2 = 10$; to give us:

$$\Delta c_1/c_1 \approx \frac{1}{2} \left[\frac{\Delta(\Delta H_1^V)}{450} + \frac{\Delta(\Delta H_2^V)}{1000} \right].$$

If we suppose ΔH_1^V and ΔH_2^V were both wrong or uncertain by 100 cal/mole, we would have:

$$\Delta c_1/c_1 \approx \frac{1}{2} \left[\frac{100}{450} + \frac{100}{1000} \right] \approx 16\%;$$

or, if δ_1 and δ_2 were both wrong by 0.2, we would have:

$$\Delta c_1/c_1 \approx \frac{1}{2}(0.2 + 0.2) \approx 20\%.$$

It is felt that these should be maximum errors and it is seen that even as such they would not account for the differences between the calculated and observed values of equilibrium concentrations.

D. Reed's Modification

Reed (27) has published work in which he has attempted to remove some of the assumptions intrinsic in the derivation of Hildebrand's simple equation.

He begins by noting that the equations:

$$\Delta E^M = (x_1 V_1 + x_2 V_2)(c_{11} + c_{22} - 2c_{12}) \varphi_1 \varphi_2; \text{ or:}$$

$$\Delta \bar{E}_1^M = V_1 \varphi_2^2 (\bar{\delta}_1 - \bar{\delta}_2)^2;$$

are valid only if:

$$1) \quad \bar{V}_1 = V_1; \quad \bar{V}_2 = V_2$$

$$2) \quad c_{12} = c_{11} c_{22};$$

that is, only if the partial molal volume of a component in a solution is equal to the molal volume of the pure component, and the "cohesive energy density" of a solution can be expressed as the geometric mean of the pure components.

If one retains assumption 2), but eliminates 1), one arrives at:

$$\Delta E^M = (x_1 \bar{V}_1 + x_2 \bar{V}_2) \varphi_1 \varphi_2 \left[\left(\frac{\Delta E_1^V V_1}{\bar{V}_1^2} \right)^{\frac{1}{2}} + \left(\frac{\Delta E_2^V V_2}{\bar{V}_2^2} \right)^{\frac{1}{2}} \right]^2$$

$$+ \Delta E_1^V (1 - V_1 / \bar{V}_1) x_1 + \Delta E_2^V (1 - V_2 / \bar{V}_2) x_2; \text{ or:}$$

$$\Delta \bar{E}_1^M = \bar{V}_1 \varphi_2^2 (\bar{\delta}_1 - \bar{\delta}_2)^2 + \Delta E_1^V (1 - V_1 / \bar{V}_1), \text{ where } \bar{V}$$

the partial molal volume, and:

$$\bar{\delta} \equiv \left(\frac{\Delta E^V V}{\bar{V}^2} \right)^{\frac{1}{2}}.$$

An elimination of assumption 2) is somewhat more involved. Reed assumes that if both components of the solution are non-polar, the only attractive forces operative are the London

dispersion forces:

$$E_{12} = -k_{12}/r^6 + j_{12}/r^n;$$

$$j_{12} = (6/n)(d_{12}^0)^{n-6}k_{12};$$

where d_{12}^0 is the distance between two unlike molecules when E_{12} is a minimum.

Assuming the only attraction is from dispersion effects, Reed evaluates k_{12} as:

$$-k_{12} = \frac{-3}{2} \alpha_1 \alpha_2 \frac{I_1 I_2}{I_1 + I_2};$$

where $\alpha \equiv$ the polarizability, and $I \equiv$ the ionization potential of the molecule in question. The same assumption also leads to:

$$k_{11} = \frac{3}{4} \alpha_1^2 I_1;$$

$$k_{22} = \frac{3}{4} \alpha_2^2 I_2.$$

Hildebrand (19) has shown that c_{11} ; c_{22} ; and c_{12} can be related to k_{11} ; k_{22} ; and k_{12} .

Using the above expressions, and eliminating Hildebrand's assumption of constant volume of mixing, Reed obtained:

$$c_{11}(V_1/\bar{V}_1)^2 = \frac{2\pi N^2 k_{11}}{\bar{V}_1^2 (d_{11}^0)^3} [S] \quad ;$$

$$c_{22}(V_2/\bar{V}_2)^2 = \frac{2\pi N^2 k_{22}}{\bar{V}_2^2 (d_{22}^0)^3} [S] \quad ;$$

$$c_{12} = \frac{2\pi N^2 k_{12}}{\bar{V}_1 \bar{V}_2 \left(\frac{d_{11}^0 + d_{22}^0}{2}\right)^3} \left[\int \right];$$

where:

$$\left[\int \right] \equiv \left[\int \frac{\rho(y) dy}{y^4} - 6/n \int \frac{\rho(y) dy}{y^{n-2}} \right];$$

and $y = r/d^0$. The quantity d^0 is the distance from the center of a molecule to the first maximum in the density distribution $\rho(y)$ of other molecular centers located around the first molecule. Reed maintained that experimental evidence indicated that $\rho(y)$ vs. y is about the same for various substances, and so could be taken as the same in each of the above equations.

This leads to:

$$c_{12} = (c_{11} c_{22})^{\frac{1}{2}} (\bar{V}_1 / \bar{V}_1) (\bar{V}_2 / \bar{V}_2) \left[\frac{2(d_{11}^0 d_{22}^0)^{\frac{1}{2}}}{d_{11}^0 + d_{22}^0} \right]^3 \left[\frac{2(I_1 I_2)^{\frac{1}{2}}}{I_1 + I_2} \right].$$

We may simplify the above equations by defining:

$q \equiv I_2/I_1$; and $s \equiv d_{22}^0/d_{11}^0$; and further:

$$f_I \equiv \left[\frac{2(I_1 I_2)^{\frac{1}{2}}}{I_1 + I_2} \right] = \frac{2q^{\frac{1}{2}}}{1+q};$$

$$f_d \equiv \left[\frac{2(d_{11}^0 d_{22}^0)^{\frac{1}{2}}}{d_{11}^0 + d_{22}^0} \right]^3 = \left(\frac{2s^{\frac{1}{2}}}{1+s} \right)^3.$$

Substitution of these definitions into the above equation

then leads to:

$$c_{12} = f_I f_d (V_1/\bar{V}_1)(V_2/\bar{V}_2) \sqrt{c_{11}c_{22}}; \text{ or:}$$

$$E^M = (x_1 \bar{V}_1 + x_2 \bar{V}_2) \varphi_1 \varphi_2 \left\{ c_{11} (V_1/\bar{V}_1)^2 + c_{22} (V_2/\bar{V}_2)^2 - 2f_I f_d (V_1/\bar{V}_1)(V_2/\bar{V}_2) \sqrt{c_{11}c_{22}} \right\}$$

$$+ \Delta E_1^V (1 - V_1/\bar{V}_1) x_1 + \Delta E_2^V (1 - V_2/\bar{V}_2) x_2.$$

Finally we would have:

$$\Delta \bar{E}_1^M = \bar{V}_1 \varphi_2^2 \left[(\bar{\delta}_1 - \bar{\delta}_2)^2 + 2 \bar{\delta}_1 \bar{\delta}_2 (1 - f_I f_d) \right] + \Delta E_1^V (1 - V_1/\bar{V}_1).$$

This last equation does not take into account the change in $\bar{\delta}$ with composition.

In the present work, it was not possible to evaluate the partial molal volumes, and so it was felt best to write the last equation as:

$$\Delta \bar{E}_1^M = V_1 \varphi_2^2 \left[(\delta_1 - \delta_2)^2 + 2 \delta_1 \delta_2 (1 - f_I f_d) \right] \quad (\text{assuming}$$

$V = \bar{V}$); and study the effect of the $(1 - f_I f_d)$ term on the calculated equilibrium concentrations of solute.

1. Evaluation of f_I

Ionization potentials for several of the solvents in question were taken from papers by Price (30), Honig (31), and

Morrison and Nicholson (32). The quantity f_I was found to be essentially unity for all cases studied (see Table 8).

2. Evaluation of f_d

The quantity f_d has been defined as:

$$f_d = \left[\frac{2(d_{11}^0 d_{22}^0)^{\frac{1}{2}}}{d_{11}^0 + d_{22}^0} \right]^3 = \left(\frac{2s^{\frac{1}{2}}}{1+s} \right)^3 ;$$

where $s = d_{11}^0/d_{22}^0$. One can evaluate d_{11}^0 and d_{22}^0 from viscosity data or from values of the second virial coefficient, but unfortunately in this case, it was not possible to obtain a consistent set of the necessary values to calculate f_d by either of the two methods. In order to evaluate f_d in a consistent manner for all of the solvents of interest, recourse was had to an approximation given by Hirschfelder, Bird, and Spotz (33):

$$d^0 \cong A(V_c)^{1/3};$$

where A is a constant and V_c is the critical volume. With this in mind, we can evaluate s as:

$$s = d_{11}^0/d_{22}^0 = (V_{c11}/V_{c22})^{1/3};$$

and so arrive at values for f_d . Values for the critical volumes were taken from data by Timmerman (34), the American Petroleum Institute Tables (28), and Lewis (35). Calculations are summarized in Table 8.

Table 8. Effect on predicted solubility of Reed Modification

Solvent	I (ev)	f_I	V_c	f_d	$(\delta_1 - \delta_2)^2$	$2\delta_1\delta_2(1 - f_I f_d)$	$\log x_1$
Benzene	9.24	1.884/1.885	256.5	0.909	472	51	-5.686
	9.43	1.906/1.903					
	9.52	1.916/1.914					
Toluene	8.92	1.852/1.854	316.3	0.885	483	63	-5.933
	9.23	1.884/1.885					
Chlorobenzene	8.8	1.840/1.843	308.0	0.888	448	67	-5.595
Carbontetra- chloride	11.0	2.054/2.053	275.9	0.901	498	52	-5.973
Bromobenzene			323.5	0.881	454	70	-5.690
Isooctane			489.9	0.828	575	72	-7.039
n-Decane	10.19	1.980/1.976	602.0	0.796	528	99	-6.813
Mercury	10.43		56.3				
		$c_1 \times 10^6$	$c_1(s) \times 10^6$	$c_1(e) \times 10^6$	$c(s) \equiv$ Values calculated by simple theory		
		23.1	82.2	11.4	$c(e) \equiv$ Experimental values		
		10.9	52.5	13.4			
		24.9	132.4	12.5			
		19.4	111.6	16.0			
		10.9	40.3	7.5			
		0.55	3.41	4.6			
		0.79	9.27	7.0			

E. Calculation of Heat of Mixing

Heats of mixing for n-decane, toluene and chlorobenzene were calculated according to the integrated equation:

$$\ln K = \ln x = \frac{-\Delta H}{RT} + C.$$

Values of $\log x$ were plotted vs. $1/T$ in Figures 7, 8, 9, and the slopes were determined by the method of least squares. Results are summarized in Table 9.

F. Calculation of Entropy of Solution

The entropy of solution for n-decane, toluene and chlorobenzene were calculated by a method first used by Hildebrand (36, 37, 38). He noted that when solubilities of nonelectrolytes in solutions from which chemical interactions are absent are plotted as \log mole fraction vs. $\log T$, one can obtain practically straight lines. This phenomenon was explained by noting that for a regular solution $\bar{F}-F^S = 0$; consequently, $\bar{S}-S^S = (\bar{H}-H^S)/T$. But:

$$\bar{S}-S^S = \left(\frac{\partial(\bar{F}-F^S)}{\partial T} \right)_x = \left(\frac{\partial(\bar{F}-F^S)}{\partial \ln x} \right)_T \left(\frac{\partial \ln x}{\partial T} \right)_{\bar{F}-F^S};$$

also:

$$\left(\frac{\partial(\bar{F}-F^S)}{\partial \ln x} \right)_T = \left(\frac{\partial(F-F^O)}{\partial \ln x} \right)_T = RT \left(\frac{\partial \ln a}{\partial \ln x} \right)_T;$$

and, therefore, it is true that:

$$\frac{\bar{S}-S^S}{R} = \left(\frac{\partial \ln a}{\partial \ln x} \right)_T \left(\frac{\partial \ln x}{\partial \ln T} \right)_{\bar{F}-F^S}.$$

Table 9. Summary of S^M and H^M calculations

Solvent	$\left(\frac{\partial \ln x}{\partial \ln T}\right)_{\bar{P}-P^0}$	$\frac{\Delta S^M}{(eu)}$	$\int \frac{\ln x}{(1/T)}$	ΔH^M (cal/mol)	$-R \ln x_1(25^\circ)^a$
n-Decane	20.6	41.2	1748	8000	27.1
Chlorobenzene	19.4	38.8	2000	9150	27.2
Toluene	24.4	48.8	2086	9550	27.0

^aIdeal entropy of mixing.

Now $(\partial \ln a / \partial \ln x)$ is very close to one when x is small and the solution obeys Henry's Law. Hildebrand then went on to point out that in many cases, $(\bar{H}-H^S)/T$ is almost a constant over a moderate temperature interval, which would then explain the linear relationship between $\log x$ and $\log T$. This linear relationship, when it occurs, makes possible a "rather accurate" calculation of the entropy of solution by use of the relation:

$$\Delta S = R \left(\frac{\partial \ln x}{\partial \ln T} \right)_{\bar{P}-P^0}.$$

In the present case, $\log x$ is plotted vs. $\log T$ in Figures 10, 11, and 12. It is seen that there is indeed a fairly linear relationship between the two variables. Slopes, calculated by the method of least squares, were used to arrive at values for the entropy of solution. Results are

summarized in Table 9. It should be pointed out that $-R\ln x$ is the ideal entropy of solution at constant volume, while the experimental entropy of solution was measured at constant pressure.

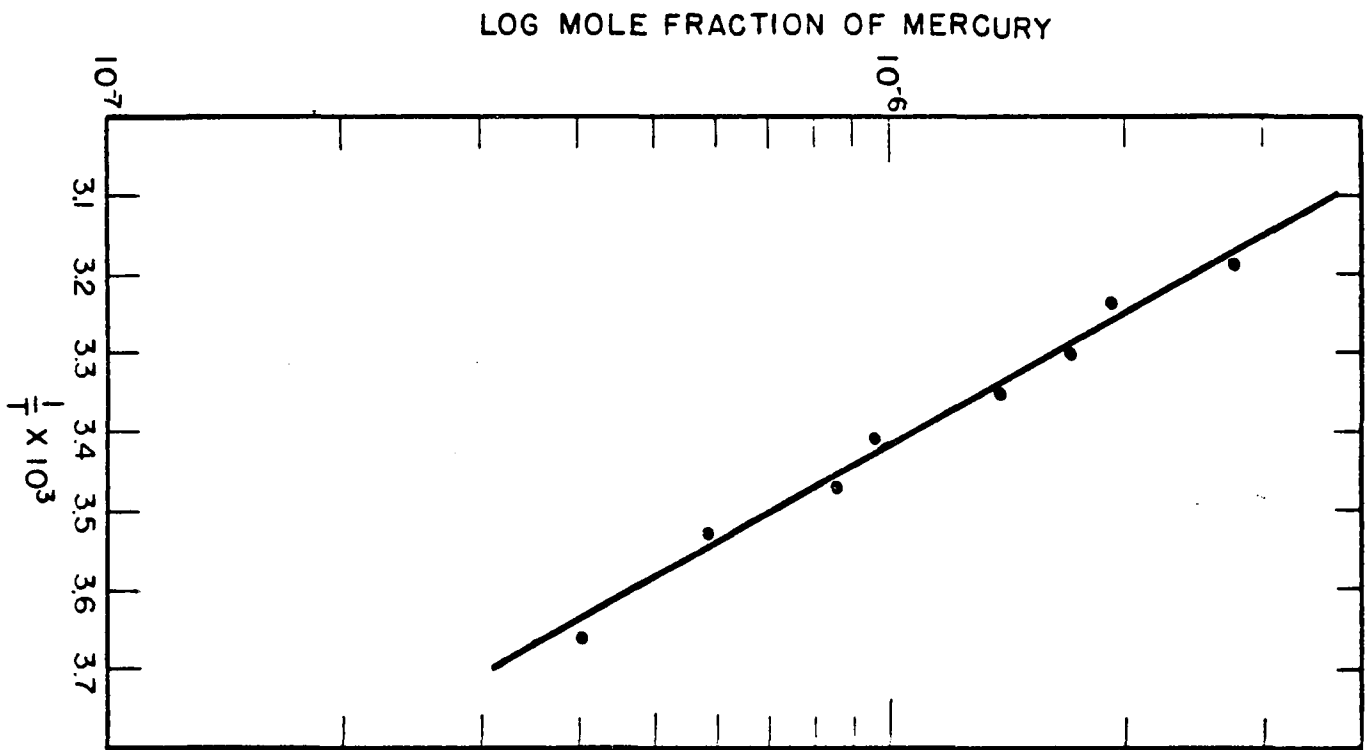


Figure 7. solubility of mercury in n-decane

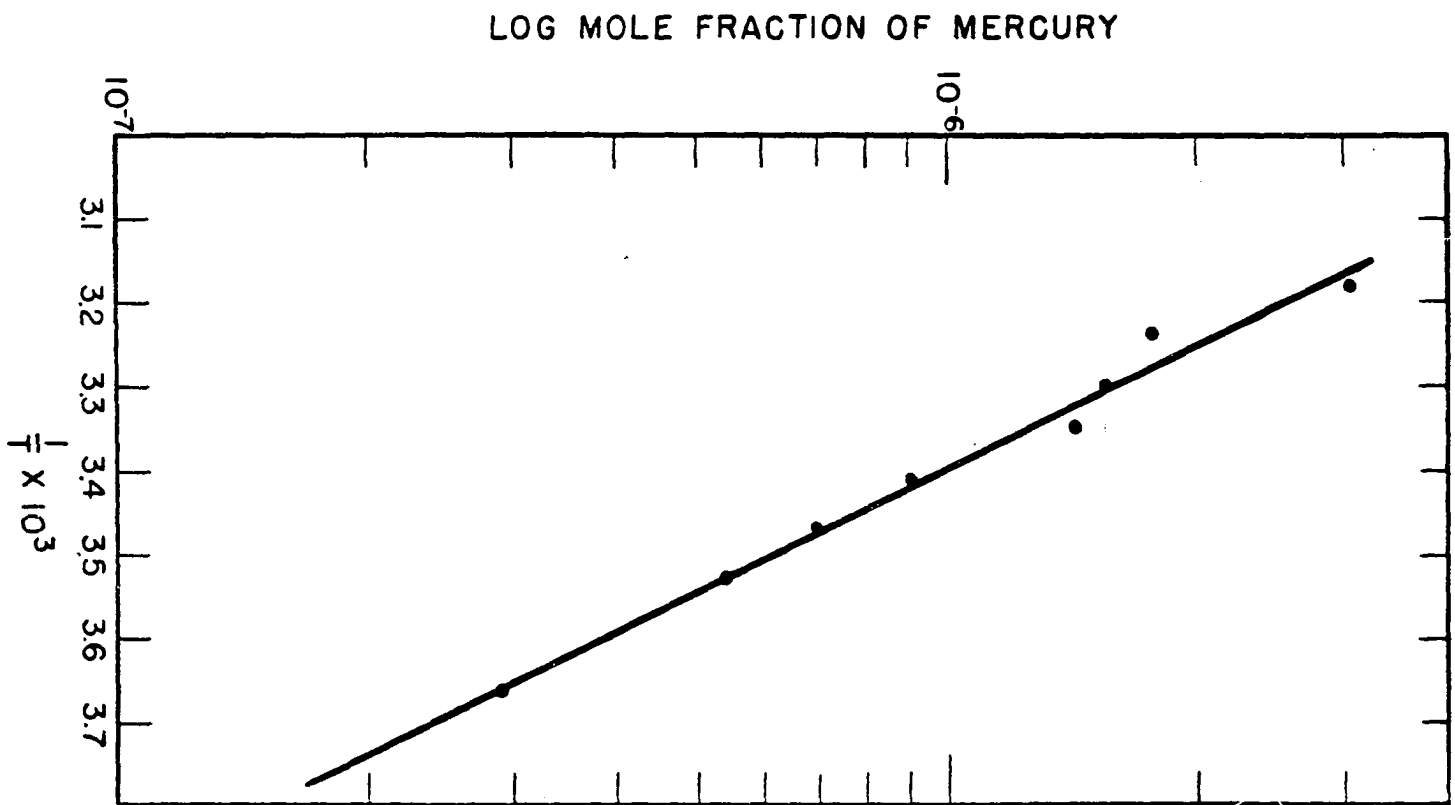


Figure 8. Solubility of mercury in toluene

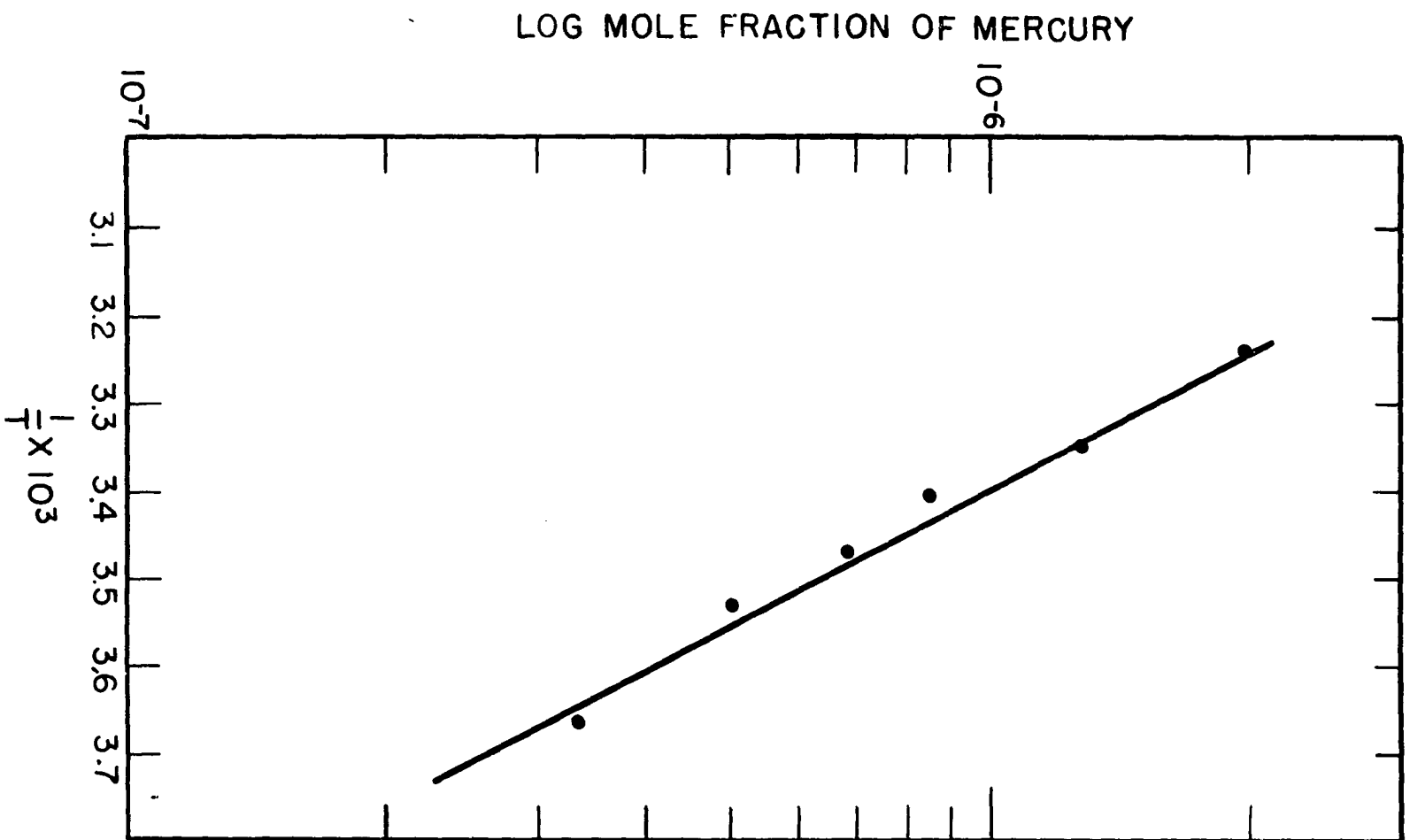


Figure 9. Solubility of mercury in chloro benzene

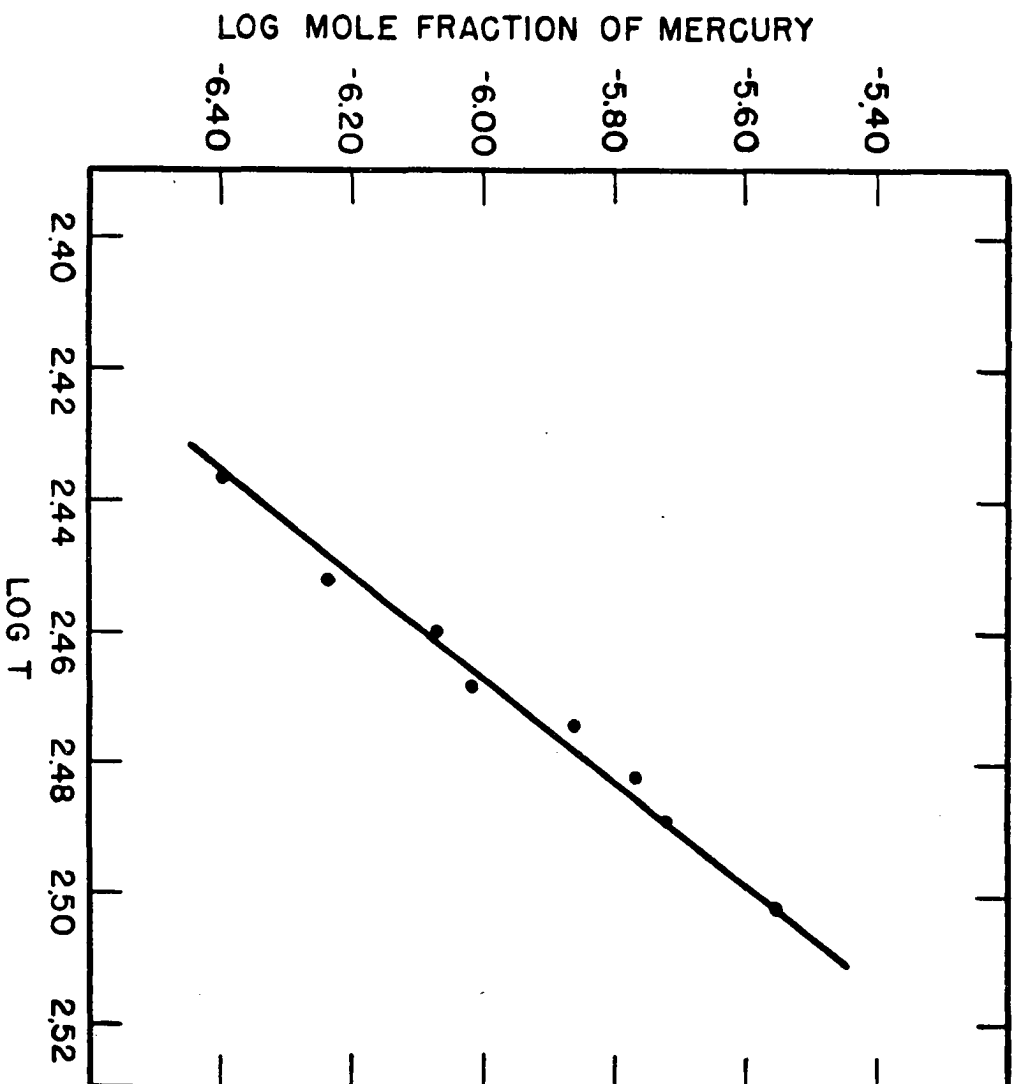


Figure 10. Log mole fraction of mercury in n-decane

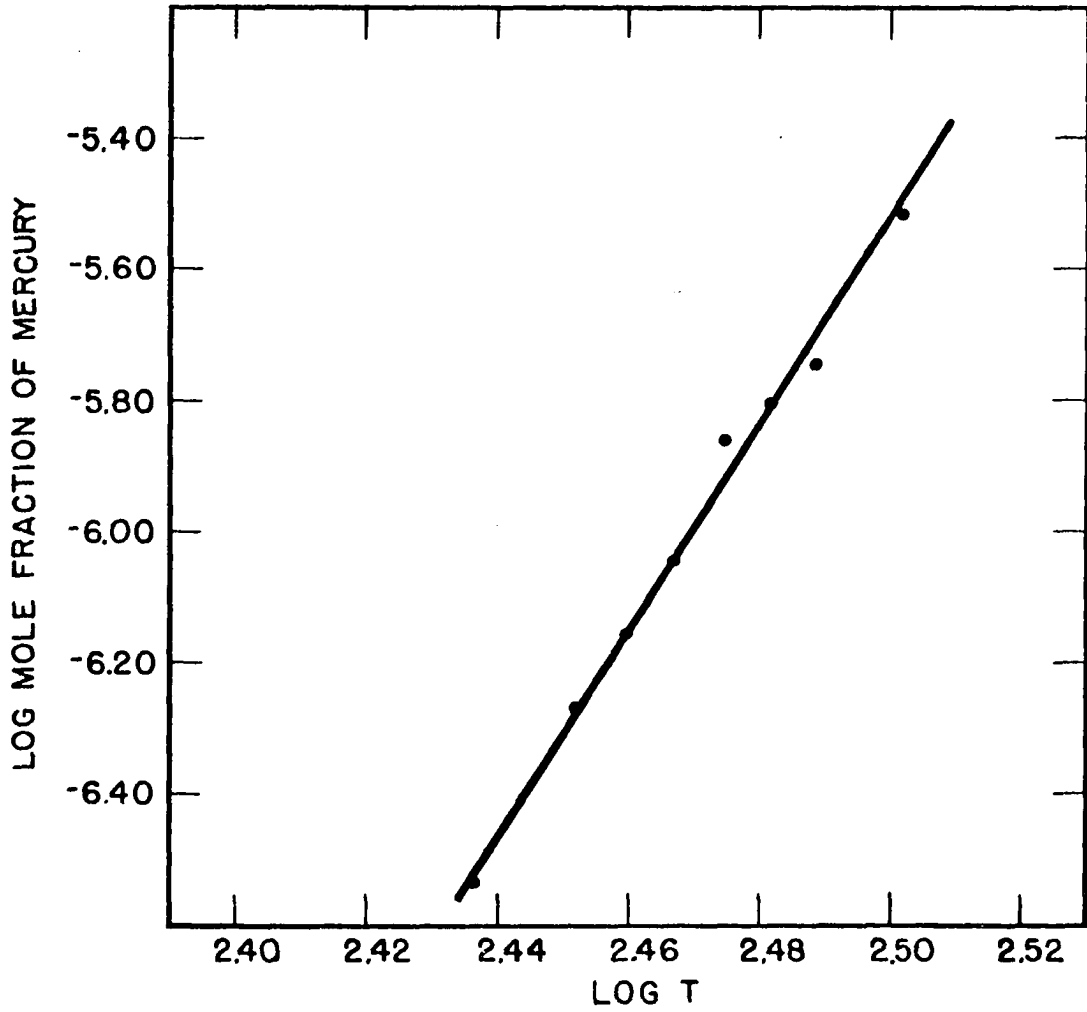


Figure 11. Log mole fraction of mercury in toluene

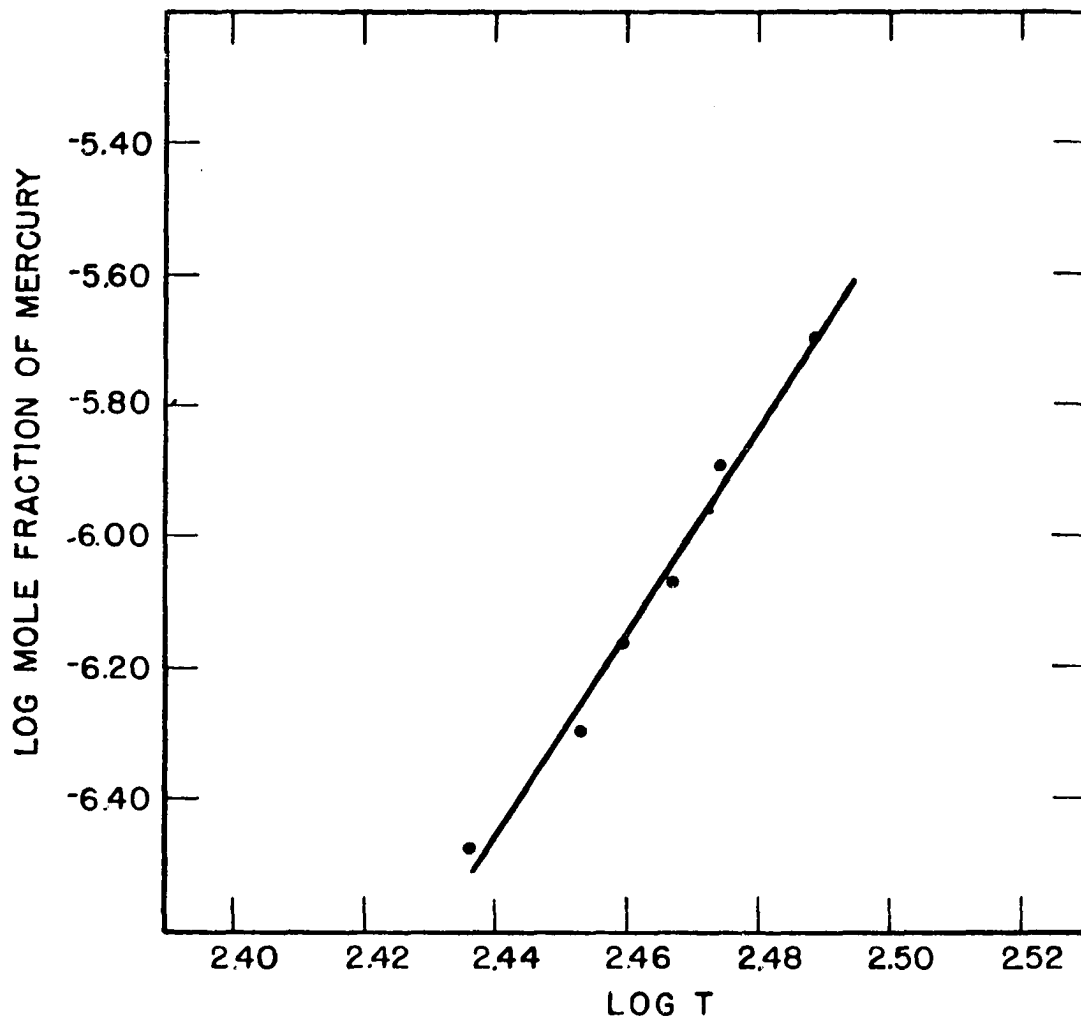


Figure 12. Log mole fraction of mercury in chlorobenzene

VII. DISCUSSION

In general, the Hildebrand-Scott solubility parameter theory has been quite successful in predicting the properties of solutions of non-electrolytes. However, the unusual solvent properties of fluorocarbons have long been recognized as forming "anomalous" cases in solubility parameter application. As with the mercury-organic systems studied, fluorocarbons were found to be much less soluble in hydrocarbons than the theory predicted they would be, which implied that the positive deviation from ideality in these cases was greater than the theory indicated.

Since the first careful measurements on these systems in 1950, a number of different attempts to account for their anomalous behavior have been made. It is of interest to review some of them briefly, since the various mercury-organic systems studied in this work also show a much lower degree of solubility than can be accounted for by differences in solubility parameters.

Among the first of these attempts was that of Simons and Dunlap (39), who proposed a special model for the intermolecular forces between two hydrocarbon molecules. They suggested that, because of the relatively small size of the hydrogen atoms, hydrocarbon molecules can penetrate each other somewhat like meshing gears. Fluorocarbon pairs and hydrocarbon-fluorocarbon pairs were thought not to be able to do this,

and so the interaction energy of a hydrocarbon-hydrocarbon pair would be abnormally large, causing the geometric mean law of interaction energies to be invalid.

This explanation, while somewhat plausible, has been largely discredited. First of all, it depends on the geometry of the hydrocarbon, and consequently one would expect the anomalous cases to be very sensitive to variations in this geometry. This has not been found to be the case. For example, the discrepancies between the observed heats of mixing and those calculated from solubility parameters are about the same for the set of all the isomeric hexanes with perfluoroheptane and perfluoropentane. Secondly, this model indicates that hydrocarbons would have abnormally low solvent powers for all other liquids. This again is not the case; for example, I_2 and $TiCl_4$ are more soluble in hydrocarbons than one would predict from the unmodified theory (40).

Another attempt to fit the hydrocarbon-fluorocarbon data into the simple theory was made by Hildebrand himself (41), who suggested that the solubility data for hydrocarbons could best be fitted by arbitrarily increasing their solubility parameters by about $0.6 \text{ (cal/cm}^3)^{\frac{1}{2}}$. However, this has led to many inconsistencies, in that an increase may fit certain cases well and at the same time make matters worse in other cases. For example, to fit the data on the three systems CH_4 - CF_4 ; CH_4 -Kr; and CF_4 -Kr, one must decrease the δ value for CH_4 by 2.5 units.

Dunlap (42) suggested that the abnormally large heats of mixing for hydrocarbon-fluorocarbon systems could be explained on the basis of the large volume expansion of mixing noted for these systems. However, a correction of heats of mixing to constant volume will not remove the anomalies, since the free energy is a more meaningful quantity in these cases, and the free energy function is very insensitive to volume changes. As a matter of fact, this large volume expansion is also observed in "normal" fluorocarbon solutions; consequently, it can hardly be the cause of any abnormalities in these systems at least.

Scott (40) feels that the failure of the above modifications or explanations indicates that this anomalous behavior of some fluorocarbon solutions must be attributed to a failure of the geometric mean law for the interaction of unlike molecules. Of the possible reasons for the failure of this law, he lists three:

- 1) Polarity The C-F bond must be highly polar and so there should be significant dipole-dipole or dipole-induced dipole interactions between adjacent molecules. A study of the geometry of two fluorocarbon molecules reveals that the net dipole-dipole effect must be one of repulsion; but if this is so, the net interaction energy between two fluorocarbon molecules would be abnormally weak. The interaction between a fluorocarbon-hydrocarbon or a hydrocarbon-hydrocarbon

pair would not be affected by dipole-dipole interactions, and so the over all effect would be that the fluorocarbon-hydrocarbon interaction would be greater than the geometric mean of the interaction of pairs of like molecules. This effect is in the opposite direction from that which Scott was trying to explain.

A consideration of dipole-induced dipole interactions reveals that here also the net effect would be that the fluorocarbon-hydrocarbon interaction should be greater than predicted by the geometric mean law. Consequently, Scott concluded that, "polarity, at least by itself, cannot possibly account for the observed anomalies."

2) Differences in ionization potentials Reed (27) has pointed out that the geometric mean law is valid only if the components have equal ionization potentials, and that the law is actually to be written as:

$$c_{12} = (c_{11}c_{22})^{\frac{1}{2}} \frac{2(I_1I_2)^{\frac{1}{2}}}{I_1+I_2} \left[\frac{2(d_{11}^0d_{22}^0)^{\frac{1}{2}}}{d_{11}^0 + d_{22}^0} \right]^3 =$$

$$(c_{11}c_{22})^{\frac{1}{2}} f_I f_d;$$

if one ignores the differences between partial molar volumes and molar volumes of pure components. Reed has estimated f_I to be about 0.97 and f_d about 0.995 for fluorocarbon-hydrocarbon mixtures. These factors will account for about half of the discrepancy between solubility parameter theory and

experimental results.

According to Scott (40), there is no legitimate reason for disregarding these ionization potential differences, and yet while they offer a reasonably satisfactory account for fluorocarbon-hydrocarbon solutions, they fail to account for the normal behavior of other fluorocarbon solutions. For example, benzene, carbon tetrachloride and iodine have ionization potentials as low or lower than hydrocarbons, and yet they form normal solutions with fluorocarbons.

3) Non-central force fields Another assumption implicit in the geometric mean law is that intermolecular forces can be expressed in terms of a central force field. This is probably valid for monatomic substances, but quite questionable for polyatomic substances such as the fluorocarbons. However, correction for this assumption in the case of fluorocarbons awaits further work. A start has been made by Hamann, Lambert, and Thomas (43), who have calculated an interaction constant between a monatomic molecule and a symmetric polyatomic molecule which is less than the geometric mean law would predict; an effect which is at least in the right direction to explain the fluorocarbon results.

Scott concludes by saying that a satisfactory explanation of the fluorocarbon solubility relations will have to consider ionization potential differences and non-central potential energy functions; however, neither separately nor together do they appear to offer entirely satisfactory answers.

There must be some additional factors not yet recognized.

The present work offers no conclusive answers to the above problem, but it does point out that abnormalities relative to the solubility parameter theory are certainly not limited to fluorocarbon-hydrocarbon mixtures. On the contrary, the discrepancies noted between experimental results and theoretical predictions are greater here than in fluorocarbon solutions.

The Simon and Dunlap interpenetration model seems to be inapplicable to the systems studied here. It utilizes a constant correction term for a hydrocarbon regardless of its geometry. Benzene, toluene, isooctane and n-decane fit into the unmodified theory with a varying degree of success. Consequently, it would be out of order to apply a constant correction term to all of them, since it would not be a large enough correction for some cases, and an over-correction for others.

While Scott's criticism of Hildebrand's method is just, nevertheless, it should be pointed out that according to Table 7, an increase of δ_{Hg} from 31 to 33 would certainly improve the correlation between data and theory. Nevertheless, if one arbitrarily changes a δ value from the value obtained by thermodynamic methods, all physical meaning of the quantity is lost.

Due to the extremely limited solubility of mercury in the organic solvents studied, it was impossible to measure the change of volume on mixing. Because of this, it was not

possible to evaluate Dunlap's suggested explanation involving the effect of a volume expansion on the heat of mixing.

Reed's modification based on a correction of the geometric mean law for differences in ionization potentials seems to offer the best solution to the problem raised by the fluorocarbon anomalies, and the analogous one of mercury-organic solubilities. In the present work it was pointed out that f_I is very close to one; while f_d was considerably less than one for the mercury-organic systems studied. Here also, the use of f_I and f_d helped to bring the theoretical values closer to experimental values; however, it is to be noted that in two cases at least, it amounted to an over-correction. This may be due to the method used to evaluate f_d rather than a case of inapplicability of f_d and f_I . The calculations summarized in Table 7 indicate that the geometric mean law may be invalid even though the ionization potentials involved are nearly equal (i. e., $f_I \cong 1$). The law also depends on a term involving the equilibrium distance between pairs of like molecules, d_{11}^0 and d_{22}^0 . If they differ significantly, f_d differs from one, and the law is invalid. It should be noted that f_d involves a cubed term, and so it is much more sensitive to differences between like pairs than f_I ; which is complicated by the fact that f_d is much more difficult to evaluate than f_I . In the present work the critical volumes were used, so that f_d could be evaluated in a manner that at least would be

consistent for all solvents studied. The use of critical volumes is perhaps adequate for spherical molecules, but it is certainly unsatisfactory for molecules such as n-decane; which could perhaps explain the over-corrections noted above.

Finally, this work offers an interesting application of Hildebrand's method of plotting solubility data. He has pointed out that, for non-electrolytic solutions in which chemical effects are absent, when the logarithm of the mole fraction is plotted vs. the logarithm of the absolute temperature, a straight line can be obtained in many cases. The slopes of these lines can then be used to calculate the entropy of solution.

Straight lines have been obtained for mercury-toluene, mercury-chlorobenzene, and mercury-n-decane systems, which indicates that the technique has a wider range of applicability than previously realized.

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