PART I

THE DISTRIBUTION OF CYCLOHEXENE BETWEEN CARBON TETRACHLORIDE AND AQUEOUS SOLUTIONS OF ACIDS AND SALTS

PART II

THE SOLUBILITY OF SOME NONPOLAR ORGANIC LIQUIDS IN WATER AND IN AQUEOUS SOLUTIONS OF STRONG ACIDS, ALKALI SALTS, AND SILVER NITRATE

THE COÖRDINATION OF SILVER ION WITH BENZENE

PART III

A PROPOSED ENIUM NOMENCLATURE FOR IONIC COMPLEXES INVOLVING CARBON-CARBON MULTIPLE BONDS

Thesis by

Nathan Hart Koenig

In Partial Fulfillment of the Requirements For the Degree of Doctor of Philosophy

California Institute of Technology

Pasadena, California

1950

ACKNOWLEDGEMENTS

The problem of Part I of this thesis and the method for its solution were suggested by Professor Howard J. Lucas. Throughout the entire work of the thesis, he has given generous amounts of time in evaluating the progress of the work and in making detailed suggestions for its continuance. His inquiring spirit and infectious enthusiasm have been a constant source of inspiration.

The investigations of Part II were made possible by a new procedure, stripping analysis, which was suggested by Dr. Frank H. Dickey. I am also greatly indebted to him for beneficial counsel on many occasions.

I am very grateful to Professor John G. Kirkwood and Dr. Frank P. Buff for valuable assistance received during several conferences relating to the theoretical interpretation of the experimental data. I wish to thank Professor Linus Pauling for assistance in developing the schematic representation of the orbitals involved in carbon-carbon multiple bonds and for his critical reading of the remainder of Part III. I also wish to express my appreciation to Professor Ernest H. Swift for constructive criticism of the procedure of stripping analysis and to Professor Stuart J. Bates for suggestions concerning the calculation of equilibrium and thermochemical data for the coördination of silver ion with benzene.

ABSTRACT

It has been shown that cyclohexene distributed at 25° between carbon tetrachloride and dilute aqueous solutions is less soluble in aqueous solutions of alkali salts, hydrochloric acid, and sulfuric acid than in water, but is more soluble in aqueous solutions of perchloric acid and nitric acid. Analysis of the data relative to general salting effects indicates that if aqueous proton-olefin complexes exist, they are present only in very low concentration.

A new procedure, stripping analysis, has been employed to determine the solubility of benzene at 10° and 25° , and of carbon tetrachloride and cyclohexane at 25° in water and in aqueous solutions of strong acids, alkali salts, and silver nitrate. Each of the organic liquids is somewhat more soluble in 3 <u>M</u> perchloric acid than in water, and benzene is much more soluble in 1 <u>M</u> silver nitrate than in water. Qualitative data on the change of solubility with temperature have been obtained by the cloudiness method. The combined solubility data, together with related data for cyclohexene, are discussed in terms of the salting and complexing factors involved.

Equilibrium constants and heats of complex formation have been calculated for the coordination of silver ion with benzene.

The nature of ionic complexes involving carbon-carbon multiple bonds is discussed, and an enium nomenclature is proposed for such complexes because of their distinctive character. The terms "enium" and "onium" are compared.

PART I.	THE DISTRIBUTION OF CYCLOHEXENE BETWEEN CARBON TETRACHLORIDE AND AQUEOUS SOLUTIONS OF ACIDS AND SALTS
	Introduction
	Proton-olefin Complexes
	Method
	Salting-out Effects 4
	Experimental Problems 5
	Materials
	Analysis
	Introduction
	Procedure for Analysis of the Aqueous Layer
	Procedure for Blanks Pertaining to the Analysis of the Aqueous Layer 11
	Effect of Variations in the Procedure for Blanks Pertaining to the Analysis of the Aqueous Layer
	Procedure for Analysis of the Organic Layer
	Procedure for Blanks Pertaining to the Analysis of the Organic Layer 14
	Effect of Variations in the Procedure for Blanks Pertaining to the Analysis of the Organic Layer
	Accuracy and Precision
	Interference by Acids and Salts 17
	Dilution Method
	Acid and Salt Concentrations 19

Page

r	Distribution Procedures	20
	Preliminary Experiments	20
	Procedure Prior to Stirring	21
	Stirring, Settling, and Sampling	24
	Procedure for Distillation of Cyclo- hexene into Carbon Tetrachloride .	26
	Aqueous Phase Transfer Procedure	27
	Distribution-boiling Procedure	30
	Direct Distillation Procedure	31
	Dilution-restirring Procedure	32
r	Distribution Problems	33
	Relative Precision of High and Low <u>K</u> Values	33
	Common Errors	33
	Effect of Peroxide	34
	Stirring and Settling	38
	Effect on Value of K of Variations	
	in Stirring Time, Settling Time, and Amount of Peroxide	40
I	Distribution Data	42
I	Discussion of Results	48
1	References	56
PART II.	THE SOLUBILITY OF SOME NONPOLAR ORGANIC LIQUI IN WATER AND IN AQUEOUS SOLUTIONS OF STRONG ACIDS, ALKALI SALTS, AND SILVER NITRATE. THE COORDINATION OF SILVER ION WITH BENZENE	DS 59

Page

Results and Discussion 6
Solubility Data
Relative Solubilities at 25° 6
Change of Solubility with Temperature 6
Salting Action of Silver Ion 6
Stripping Analysis 6
Related Procedures 6
General Procedure
Stripping and Selective Sorption 7
Condensing, Warming, and Weighing . ?
Materials
Stripping Analyses. I. Benzene 7
Procedure and Data
Run with Known Sample 7
Calculations
Stripping Analyses. II. Carbon Tetrachloride 8
Stripping Analyses. III. Cyclohexane 8
Sulfuric Acid and Salt Solutions 8
Calculations 8
Water and 3 M Perchloric Acid 8
Approximate Solubility of Cyclohexene 8 in Water
Cloudiness Method 8
Coordination of Silver Ion with Benzene 9
Introduction 9
Procedure and Data 9

Page

				00	NIE	1 24	2									
																Page
		Equi	lib	rium	Co	ns	tar	ts	•	•	• •	•	•	•	•	96
		Heat	of	Com	ple	x	For	ma	tio	n	• •	٠	•	•	•	101
	Refer	ences	•	•••	•	•	••	•	•	•	• •	•	•	•	•	103
PART	 A PRO COM MUL	POSED PLEXE: TIPLE	EN 3 II BOI	LUM NVOL NDS	NOM VIN	IEN IG	CLA CAF	BOI	₹E ∛-0	FOI ARI	7 I 301	ON	1C	•	•	106
	Natur Coö	e of (rdina	0le: tion	fini a .	ca	nd.	Ac	ety •	/le •	ni.		•	•	•	•	106
		Intro	oduc	ctio	n	•	• •	•	•	•		•	•	•	•	106
		Quan	tum-	-mec	han	ic	al	In	ter	pre	eta	ti	on	5	•	107
		Supp	ort	ing	Phy	rsi	cal	. Da	ata		• •	•	•	•	•	108
		Symbo	olis	sm .	•	•	• •	•	•	•		•	•	•	•	111
	The E	nium 1	Nome	əncl	atu	ire	•	•	•	•	• •	•	•	•	•	112
		Purp	ose		•	•	• •	•	•	•		•	•	•	•	112
		Gene	ral	Rul	es	in	Na	miı	ng	•	• •	•	•	•	•	112
		Note	s ai	nd E	xan	ıp l	es	•	•	•		•	•	•	•	113
		The	Pro	teni	um	Io	n.	•	•	•		•	•	•	•	115
		"Eni	um#	Com	par	ed	wi	th	۴C	ni)	1m"	•	•	•	•	116
	Refer	ences	•		•	•	• •	•	٠	•	• •	•	•	•	•	118

APPENDIX

Displacement	Vo:	lur	ne	tr	ic	F	las	sk	٠	٠	•	•	٠	٠	•	120
Propositions	•	•	•	•	•	•	•	•	•	•	•	•	•			122

THE DISTRIBUTION OF CYCLOHEXENE BETWEEN CARBON TETRACHLORIDE AND AQUEOUS SOLUTIONS OF ACIDS AND SALTS

PART I

PART I

THE DISTRIBUTION OF CYCLOHEXENE BETWEEN CARBON TETRACHLORIDE AND AQUEOUS SOLUTIONS OF ACIDS AND SALTS

INTRODUCTION

<u>Proton-olefin Complexes</u>. It has often been assumed that the initial step in certain reactions of olefins in aqueous acid solutions is the addition of a proton to an olefin molecule. Presumably this step involves the reaction of a hydronium ion with an olefin molecule, the products being a molecule of water and a proton-olefin complex ion. General discussions of this reaction mechanism have been given (1, 2, 3). The data obtained from kinetic studies of the hydration of olefins (4, 5) and the polymerization of indole (6, 1) have been cited as evidence for the existence of proton-olefin complexes.

According to Whitmore (7, 8), the intermediate complex is a positive ion which is formed by the addition of a proton to the extra electron pair of the double bond, leaving one carbon atom with only six electrons. The complex that Whitmore describes is a carbonium ion, and it would probably be very unstable. Since one of its carbon atoms has only a sextet of electrons, a carbonium ion generally undergoes some further reaction so rapidly that it can not be present in any appreciable concentration. It has been shown, however, that complexes which have a moderate stability in aqueous solution may be formed by the reaction of olefins with silver ion (9, 10) and with mercuric ion (11). Since the complexes may exist in solution in moderate concentration, and since they show no appreciable tendency to undergo rearrangement, it seems unlikely that they are simple carbonium ions. It has been suggested that these complexes have a resonating structure (9, 12) and that they are stabilized by the resonance energy. The proton, like silver ion and mercuric ion, has a strong tendency to form coordination compounds. For example, it can form very stable complexes with water and with ammonia. There is some possibility, then, that a stable complex may be formed by the coordination of a proton with an olefin. The object of the following investigation was to determine whether or not proton-olefin complexes of appreciable stability can exist in aqueous solution.

<u>Method</u>. The study was made by means of the distribution method, which had been used previously to study the silver ion and mercuric ion complexes. The olefin, cyclohexene, was distributed between carbon tetrachloride and an aqueous

- 2 -

acid solution, and the concentration of olefin in each phase was determined by a bromination method. Since an olefin in acid solution may be quantitatively brominated, it is evident that the analysis measures the total concentration of olefin, complexed and uncomplexed. The distribution constant, \underline{K} , is defined as the ratio of the total concentration of olefin in the carbon tetrachloride phase to the total concentration of olefin in the aqueous phase. If the aqueous phase is pure water, the distribution constant is designated as \underline{K}_{m} .

In the following discussion, when a comparison is made of the concentrations of cyclohexene in the aqueous phases of various experiments, it is assumed that the concentrations of cyclohexene in the organic phases of these experiments are equal. In the actual experiments, of course, the concentrations of cyclohexene in the organic phases differed from each other somewhat (rarely over 15%); and the data were analyzed by comparing the various distribution constants, which involved both the organic and the aqueous phases. However, the discussion is simplified by assuming equal concentrations of cyclohexene in the organic phases, since attention may then be focused on the aqueous phases, which are the sites of the postulated complexes.

If a moderately stable complex ion were formed by the addition of a proton to cyclohexene in aqueous acid solutions, a higher (total) concentration of the distributed cyclohexene

- 3 -

would be present in an aqueous phase containing a strong inorganic acid than in a pure water aqueous phase. This assumption is made because a proton-olefin complex ion is polar in character, and it would dissolve in aqueous solutions to a much greater extent than a pure olefin molecule. If, on the other hand, cyclohexene does not form a proton complex, it would ordinarily be expected to have less tendency to dissolve in an aqueous acid solution than in pure water, owing to the salting-out of the nonpolar cyclohexene molecules by the ions of the acid.

Salting-out Effects. It was found, in preliminary distribution experiments, that the aqueous phase concentration of cyclohexene is less in a dilute sulfuric acid solution than it is in pure water. This gave immediate evidence that proton-cyclohexene complexes of moderate stability do not exist in aqueous solution. It did not, however, exclude the possibility that a complex of very low stability may exist. A moderate salting-out effect may outweigh a very small complexing effect. In this case, the concentration of cyclohexene in acid solution would be less than in water. It may be reasoned that the salting-in effect of the hydrogen ion, caused by complex formation, may be exceeded by the salting-out effect of the bisulfate ion.

In order to investigate the possibility that a very low concentration of complex was present, it was necessary to

- 4 -

ascertain the magnitude of the salting-out effect. The salting-out effect was studied by distributing the cyclohexene between carbon tetrachloride and aqueous salt solutions. For each experiment in which the aqueous phase was an acid solution, a corresponding experiment was run in which the aqueous phase was a solution of a sodium or potassium salt of the same acid. Since the acid and the salt contained the same anion, the data essentially represented a comparison of the effect of the hydrogen ion with the effect of the alkali cation. It is generally accepted that sodium and potassium ions have a normal salting-out action. Consequently, it was assumed that these alkali cations would serve as a standard of reference for deciding whether the hydrogen ion merely fitted into the normal pattern of cation salting action, or whether it did indeed have a significant amount of complexing action.

Experimental Problems. The experimental procedures previously used were unsatisfactory for obtaining data of sufficient accuracy for the following investigation. On the basis of the earlier procedures, a value of 3610 ± 10 (13) was reported for \underline{K}_{W} ; and conflicting values, 4305 ± 43 (9) and 4760 ± 20 (13), were reported for the distribution ratio of cyclohexene between carbon tetrachloride and 1 <u>M</u> potassium nitrate. In the following work, the values obtained for water (\underline{K}_{W}) and 1 <u>M</u> potassium nitrate were $38.4 \times 10^2 \pm 0.4 \times 10^2$ and 51×10^2 , respectively.

It seems probable that the values now reported are higher than the values previously reported primarily because the new procedures are more successful in eliminating the errors caused by the presence of peroxide. It will be shown later that the presence of a very small amount of cyclohexene peroxide may cause a large error in the value of the distribution constant. To prevent the formation of peroxide, it was necessary to completely exclude oxygen from the distribution system; and this proved to be the most difficult experimental problem encountered. The development of peroxidefree procedures involved a long series of procedural modifications.

After preliminary experiments indicated that dilute (up to 3 \underline{M}) sulfuric acid solutions had a salting-out effect on cyclohexene, it was considered advisable to run experiments at higher sulfuric acid concentrations. If a coördination factor exists, and if at high acid concentrations this factor increases more rapidly than the salting-out factor, its existence may be detected by such experiments. Before these studies could be made, it was necessary to modify the analytical procedure, in order to eliminate the interference caused by high concentrations of acids. A modified procedure which gave fairly precise results was developed. It was a dilution method in which the acid concentration was reduced prior to

- 6 -

the iodometric determination of the excess bromine.

The concentrations of cyclohexene in the aqueous phase were extremely low, roughly 0.0001 M. Variations in the analytical procedure which are ordinarily permissible because they do not cause appreciable errors in the measurement of moderately low concentrations may give rise to large percentage errors in the measurement of extremely low concentrations. It was therefore necessary to determine accurately the effect of and then to control the various factors which give rise to errors in the analysis.

The extreme dilution of the aqueous phase also made it essential that the distribution components separate into two homogeneous layers. Since the concentration of cyclohexene in the organic phase was 1 M, the presence of a small amount of this phase in the aqueous phase would produce a large error in the value of K. At the high acid and salt concentrations, the difference between the density of the aqueous phase and that of the organic phase was relatively small. If these solutions had been stirred in the usual way, the organic phase would have been very finely dispersed in the aqueous phase, and the process of settling would have been very slow. Long periods of settling are unsatisfactory because there are non-settling factors which cause a slow change in the aqueous phase cyclohexene concentration. A significant improvement in distribution technique was made by introducing the use of an

- 7 -

upflow type of stirrer as a means of obtaining rapid settling despite adverse conditions.

MATERIALS

In general, the inorganic chemicals were of reagent or C.P. grade. The potassium iodide, however, was of USP grade. The bromate-bromide stock solutions (1:10 mole ratio) were made up accurately from reagent grade potassium bromate, dried at 150° , or were standardized with a potassium bromate solution of known concentration by comparing both solutions with one of the sodium thiosulfate solutions. The standard 1 <u>N</u> sodium hydroxide solution, carbonate-free, was periodically checked against a 1 <u>N</u> hydrochloric acid solution which had been standardized with sodium carbonate. The standard silver nitrate solution was made up by weight.

Cyclohexene for the distribution experiments with water, potassium nitrate, sulfuric acid, and sodium bisulfate was prepared by dehydration of purified cyclohexanol with sulfuric acid, followed by distillation from sodium; b.p. 79.5-81.0[°] (uncor.). For later experiments, cyclohexene was prepared from the Eastman Kodak Company best grade material by refluxing with sodium wire for twenty hours and then fractionating. The major part of the distillate, b.p. 81.5-82.5[°] (uncor.), was collected. The cyclohexene was stored under nitrogen, and samples of cyclohexene were withdrawn by nitrogen displacement.

- 8 -

Carbon tetrachloride was prepared from technical material by saturating it with chlorine, exposing the solution to sunlight for several hours, washing with sodium hydroxide solution, drying with calcium chloride, distilling, and collecting the major part of the distillate, b.p. 75.8-76.0^o (uncor.).

The carbon tetrachloride, acetic acid, and potassium iodide were individually tested under conditions similar to those used in the analysis, and were found to have very small or negligible blank values. All of the acids and salts used in the distribution measurements gave very small blank values. In the case of nitric acid, interfering oxides of nitrogen were removed by boiling in the normal course of the distribution procedure.

ANALYSIS

<u>Introduction</u>. The concentrations of cyclohexene in the aqueous and organic phases were determined by specific procedures based on a bromination method described previously (14). The amount of cyclohexene in the sample was calculated from the volume of standard bromate-bromide solution, the comparison ratio of bromate-bromide to thiosulfate as determined in the blank, and the volume of thiosulfate solution required to back-titrate the excess bromate-bromide solution during an analysis. All burets, volumetric pipets, and 3-way stopcock pipets (15) were calibrated. The analysis flasks were shaken

- 9 -

by clamping them to the vibrating arm of a Boerner shaker. Data obtained in the analysis of known solutions of cyclohexene in carbon tetrachloride indicated that the shaking must be vigorous if low results are to be avoided.

Detailed procedures for the analysis of the aqueous and organic layers, and for the corresponding blanks, are given in the following pages. Many possible changes in the analytical procedure (Tables I and II) were investigated before the final procedures were determined. The procedures for the analysis and for the corresponding blank are as similar as possible. This parallel treatment is particularly important in the analysis of the aqueous phase, since large percentage errors may be caused by small variations in such factors as the purity of the materials and the technique of titration. The procedure for analysis of the aqueous layer was used for aqueous samples in which the acid or salt concentration was $1 \leq 0$ r less. Samples containing a higher concentration of electrolyte were analyzed by the dilution method (page 18).

<u>Procedure for Analysis of the Aqueous Layer</u>. An amount of 0.005 <u>N</u> bromate-bromide solution, 25 ml. or less and calculated to be roughly a 50% excess, is pipetted into a 300-ml. standardtapered conical flask. It is washed down with water until the total volume is 26 ml. A stopcock-stopper lubricated with mineral oil is inserted in the neck of the flask, which is then wrapped in a black cloth and evacuated with a water aspirator.

- 10 -

Next, 5 ml. of 3 <u>M</u> sulfuric acid is added, and the flask is allowed to stand for five to fifteen minutes. Then 95 ml. of sample plus 15 ml. of wash water are added from a 3-way stopcock pipet. The flask is then shaken vigorously for five minutes, 10 ml. of a freshly prepared 20% potassium iodide solution is added, and the shaking is continued for thirty seconds. The vacuum is broken, and the stopcock-stopper is removed after washing it free of iodine. The black cloth is removed, and the contents of the flask, while swirled gently, are rapidly titrated with 0.015 <u>N</u> sodium thiosulfate solution. Just before the end-point, 1.5 ml. of 1% starch solution is added.

<u>Procedure for Blanks Pertaining to the Analysis of the Aqueous</u> <u>Layer</u>. 15.00 ml. of 0.005 N bromate-bromide solution is pipetted into a 300-ml. standard-tapered conical flask and is washed down with 11 ml. of water. The subsequent procedure is exactly like that used for the analysis of the aqueous layer except that 110 ml. of water is added instead of 110 ml. of sample plus wash water.

Effect of Variations in the Procedure for Blanks Pertaining to the Analysis of the Aqueous Layer. The data presented in Table I indicate that only a very small or a negligible change in the value of the blank results from a variation of: (a) 4 to 6 ml. in the volume of sulfuric acid; (b) 0.3 to 135 minutes in the interval of time between the addition of

Table I

Effect of Variations in the Procedure for Blanks Pertaining to the Analysis of the Aqueous Layer

Sulfuric acid (ml.)	Standing time (min.)	Shaking time (min.)	(ml.)	Shake KI (sec.)	Sodium thiosulfate (ml.)
5	5	3	8	20	5.23, 5.21,
an an an An an an An an			a internet and a second and as second and a		5.10, 5.10,
5	8	3	8	20	5.17
5	15	3	8	20	5.22, 5.19
5	5	3	20	120	5.18
5	5	3	10	30	5.20
5	0.3	3	10	30	5.22
5	30	3	10	30	5.21
5	135	3	10	30	5.19
4	5	3	10	30	5.21
6	5	3	10	30	5.22
5	15	3	10	30	5.19 ²
5	10	0	5	20	5.17 ^b , 5.13 ^b
5	10	0	5	20	5.21 [°]
5	10	0	5	20	5.02 ^d
5	10	0	5	20	5.20 ^e

a Not darkened (by black cloth).
b Not darkened. Added 2-5 drops mineral oil.
c Darkened. Added 5 drops of mineral oil.
d Not darkened. Added 10 drops of mineral oil and gently swirled (during acid standing period).
e Darkened. Added 10 drops of mineral oil and gently

swirled.

sulfuric acid and the addition of the sample; (c) 8 to 20 ml. in the volume of potassium iodide solution; or (d) 20 to 120 seconds in the time of shaking after the addition of potassium iodide solution. The data also indicate that, in the presence of light, an excessive amount of mineral oil lubricant appreciably decreases the volume of thiosulfate solution required for the titration. Mineral oil was substituted for Lubriseal after it was learned from other experiments that Lubriseal reduces significant amounts of bromine, even in the absence of light.

<u>Procedure for Analysis of the Organic Layer</u>. An amount of O.1 <u>M</u> bromate-bromide solution, 25 ml. or less and calculated to be about a 10 to 15% excess, is pipetted into a 250-ml. standard-tapered conical flask. It is washed down with water until the total volume is 26 ml. A stopcock-stopper lubricated with mineral oil is inserted in the neck of the flæk, which is then wrapped in a black cloth and evacuated with a water aspirator. Next, 5 ml. of 3 <u>M</u> sulfuric acid is added, and the flask is allowed to stand for five to ten minutes. Then 10 ml. of glacial acetic acid is added, followed by the addition from a 3-way stopcock pipet of 1 ml. of sample plus 3 ml. of wash carbon tetrachloride. The flask is then shaken vigorously for five minutes, 15 ml. of a freshly prepared 20% potassium iodide solution is added, and the shaking is continued for thirty seconds. The vacuum is broken, and the stopcock-stopper is removed after washing it free of iodine. The black cloth is removed, and the contents of the flask, while swirled gently, are rapidly titrated with 0.05 M sodium thiosulfate solution. Just before the end-point, 1 ml. of 1% starch solution is added.

<u>Procedure for Blanks Pertaining to the Analysis of the Organic</u> <u>Layer</u>. 10.00 ml. of 0.1 <u>N</u> bromate-bromide solution is pipetted into a 250-ml. standard-tapered conical flask and is washed down with 16 ml. of water. The subsequent procedure is exactly like that used for the analysis of the organic layer except that 4 ml. of carbon tetrachloride is added instead of 4 ml. of sample plus wash carbon tetrachloride.

Effect of Variations in the Procedure for Blanks Pertaining to the Analysis of the Organic Layer. The data presented in Table II indicate that only a very small or a negligible change in the value of the blank results from a variation of: (a) 5 to 7 ml. in the volume of sulfuric acid; (b) 10 to 20 ml. in the volume of acetic acid; (c) 5 to 15 ml. in the volume of potassium iodide solution; or (d) 5 to 30 seconds in the time of shaking after the addition of potassium iodide solution. The data also indicate that, even in the absence of light, long periods of standing subsequent to acidification or excessive amounts of mineral oil appreciably decrease the volume of thiosulfate solution required for the titration. <u>Accuracy and Precision</u>. In the analysis of a known 0.1 <u>M</u> solution of cyclohexene in carbon tetrachloride, the amount of

- 15 -

Table II

Effect of Variations in the Procedure for Blanks Pertaining to the Analysis of the Organic Layer

St aft	anding time er acidified (min.)	Acetic acid (ml.)	Time shaken after KI addn. (min.)	Sodium thiosulfate (ml.)
	5	20	20	20.88 20.87 20.85
	0.3	20	20	20.91
	30	20	20	20.80
	5	10	30	20.92 20.92
	5	10	30	20.91 ^a
	5	10	30	20.89 ^b
	5	10	5	20.90
	0.5	10	30	20.91
	20	10	30	20.95
	90	10	30	20.75
	100	10	30	20.86
	200	10	30	20.74
	15	10	30	20.80 [°]

^a Used 7 ml. of sulfuric acid (instead of 5 ml.).
^b Used 5 ml. of KI solution (instead of 15 ml.).
^c Added 10 drops of mineral oil, at start of experiment.

cyclohexene found was 98% of the theoretical amount. In thirteen determinations of the concentration of an approximately 1 <u>M</u> solution of cyclohexene in carbon tetrachloride, the relative average deviation of a result was 0.5%. It seems likely that the error in the value taken as the volume of the 1-ml. sample was sufficient to account for most of the deviation.

Owing to the extremely low aqueous phase cyclohexene concentrations, the precision of the aqueous phase analysis was not very high. In the experiments performed, the maximum and the minimum concentrations of cyclohexene were 0.0004 M and 0.00004 M. At these concentrations, the amounts of cyclohexene in the 95-ml. samples were equivalent to 5 ml. and to 0.5 ml., respectively, of the 0.015 N thiosulfate solution. In an analysis, the amount of cyclohexene in the sample is proportional to the net volume of thiosulfate solution, which is the difference between the volume of thiosulfate required to titrate the original amount of bromatebromide solution and the volume used in the back-titration. The average deviation of a measurement of the net volume of thiosulfate solution was about 0.02 ml. Accordingly, the relative average deviation of a measurement of the net volume, and hence of a measurement of the concentration of cyclohexene, was about 0.4% at the highest concentration and 4% at the lowest concentration.

- 16 -

Interference by Acids and Salts. High electrolyte concentrations may interfere with the analysis by promoting the decomposition of thiosulfate solution, by increasing the rate of oxidation of iodide ion, and by obscuring the starch-iodine end-point. The decomposition of thiosulfate solutions is accelerated by high acidity (16). This effect may be diminished by gently swirling the titrated solution, so that the thiosulfate may react with the iodine before decomposition sets in. If decomposition does occur, the solution may become noticeably cloudy as a result of sulfur formation. Since sulfurous acid is one of the decomposition products, the usual effect of decomposition is that less thiosulfate solution is required for the titration. If the titrated solution is effectively stirred, the extent of thiosulfate decomposition is not appreciable at acidities below 3 N. The oxidation of iodide ion by dissolved or atmospheric oxygen is also accelerated by high acidity (16), and it is difficult to obtain accurate results if the acidity is greater than 2-3 N.

An attempt was made to overcome the adverse effects of high acidity by means of a neutralization procedure. Strongly acid samples were taken for analysis, and the acid solutions were neutralized prior to the addition of potassium iodide. The following substances were tried as neutralizing agents: sodium acetate, sodium phosphate, sodium sulfate, sodium hydroxide, and borax. In all of these experiments, the

- 17 -

end-point was unsatisfactory. Results of additional experiments indicated that high electrolyte concentrations interfere with the starch-iodine end-point, and that salts and acids of the same concentration have roughly the same effect. Accordingly, neutralization of an acid solution does not eliminate the problem of end-point interference. For uniunivalent electrolytes, the upper limit for good end-points is about 1 M. At higher concentrations, two difficulties are encountered: the end-point color change is gradual, with intermediate violet, red, and pink shades; and the rate of starch-iodine decolorization is low. Owing to the lack of sharpness, it is difficult to get an accurate end-point; and since the decolorization is slow, it is easy to overrun the end-point.

<u>Dilution Method</u>. The procedure which was finally adopted as the most satisfactory way of avoiding the adverse effects of acids and salts was the dilution method. This involves the following changes in the procedure for analysis of the aqueous layer:

A large analysis flask is used. After the sample has been shaken for five minutes during bromination, water is added to reduce the electrolyte concentration to 1 <u>M</u> or less. An increased amount of potassium iodide solution is then added, in order to maintain the usual concentration of iodide ion. 3 ml. of 1% starch solution is used in the titration.

For the distribution experiment involving 8 <u>M</u> sulfuric acid, a 1-liter round-bottomed flask was used for the analysis, and the amounts of dilution water and potassium iodide solution were 550 ml. and 50 ml., respectively. For the distribution experiments in which the concentration of acid or salt was 1 to 3 <u>M</u>, a 500-ml. conical flask was used, and the amounts of dilution water and potassium iodide solution were usually 200 ml. and 25 ml., respectively.

By means of the dilution method, it was possible to obtain reasonably accurate data in the distribution experiment involving 8 <u>M</u> sulfuric acid. The method is not, however, a perfect solution to the problem of interference by electrolytes, since the end-point becomes less sharp as the dilution increases. In the 8 <u>M</u> sulfuric acid experiment, the uncertainty in locating the end-point amounted to about ± 0.08 ml. of thiosulfate solution. This experiment was exceptional, however. In other analyses using the dilution method, the original acid or salt concentration was 1 to 3 <u>M</u>, and in these analyses the end-points were fairly sharp. Due care was taken to compare the analyses with blanks run under very similar conditions.

<u>Acid and Salt Concentrations</u>. In general, the aqueous phase electrolyte concentration was determined by analysis of a sample of convenient size taken from the aqueous layer.

- 19 -

Samples containing an acid or sodium bisulfate were analyzed by titrating with standard 1 <u>N</u> sodium hydroxide solution. The potassium chloride samples were analyzed by titrating with standard silver nitrate solution in the presence of fluorescein indicator. The sodium perchlorate samples were analyzed by evaporating the solution in a weighed dish and drying the residue at 115°. A correction was applied to the weight of the residue for moisture retained at this temperature. The salt concentration in the 1 <u>M</u> potassium nitrate experiment was obtained from the concentration of the original solution, which was made up by weight. An allowance was made for the slight increase in concentration which occurs in the distribution-boiling procedure.

DISTRIBUTION PROCEDURES

<u>Preliminary Experiments</u>. Several variations in apparatus and procedure were employed in the preliminary distribution experiments. Solutions for the organic phase were prepared either by distilling cyclohexene into carbon tetrachloride in the distribution flask or by diluting a known weight of cyclohexene with carbon tetrachloride in an ordinary volumetric flask or a displacement volumetric flask (Appendix). From the observations made and the data collected in these preliminary experiments, it became apparent that it would be necessary to devise more elaborate procedures in order to avoid contamination by oxygen. The data obtained in the preliminary experiments will be discussed in the section dealing with the effect of peroxide.

<u>Procedure prior to Stirring</u>. In the remaining distribution experiments, special precautions were taken to exclude oxygen. The experiments were carried out by a number of procedures, which are interrelated as shown in the following chart:



Distribution constants may be obtained by four main procedures (underlined). The same method is used to prepare the cyclohexene-carbon tetrachloride solution for two of these procedures (solid arrows). After a distribution constant has been obtained by any one of the four main procedures, an additional distribution constant may be obtained by dilutionrestirring of the residual solution (dotted arrows). The four main procedures differ from one another prior to the time that stirring is begun; but all of the subsequent steps stirring, settling, sampling, and analysis - are the same in each procedure.

- 21 -

In the aqueous phase transfer procedure, the aqueous phase is deoxygenated before it is transferred to the distribution flask, whereas in the distribution-boiling procedure the aqueous phase is deoxygenated by boiling it in the distribution flask. In both of these procedures, the cyclohexene-carbon tetrachloride solution is prepared outside the distribution flask. In the direct distillation procedure, however, the cyclohexene is distilled directly into the distribution flask, which contains the carbon tetrachloride.

The distilling apparatus used in the aqueous phase transfer and distribution-boiling procedures fits into the side neck of the distribution flask (figure 1). The distilling flask of this apparatus contains cyclohexene and sodium wire, and the remaining space in the system is filled with nitrogen. The cyclohexene is distilled into carbon tetrachloride contained in the receiver flask. By means of nitrogen pressure, the solution may be forced through a transfer arm, E, into the distribution flask, D, or may be forced up through the sampling tube, F, for analysis. If it is carefully prepared, the solution may be kept fairly free from peroxide for a few days, and portions of the solution may be used in successive runs.

The aqueous phase transfer procedure was the first procedure to be developed which practically eliminated the peroxide complication. It is a very lengthy procedure, however, and it was difficult to arrange a continuous period of time

- 22 -



Figure 1. Distribution-boiling Apparatus

A. To mercury seal

- B. Nitrogen inlet, or outlet to atmosphere (via three-way stopcock)
- C. Upflow stirrer
- D. Distribution flask
- E. Transfer arm
- F. Sampling tube (with tygon tip)
- G. "T" stopcock
- H. Receiver tube
- I. Mercury sintered-glass valve
- J. Distilling head stopcock
- K. Cyclohexene distilling flask

- 23 -

sufficient to make a run. It was then that the shorter distribution-boiling procedure was conceived. It was shown in a determination of \underline{K}_w that this procedure gives essentially the same results as the aqueous phase transfer procedure. The distribution-boiling procedure was then used to determine the distribution constant, at the initial electrolyte concentration, in the early experiments with acid and salt solutions. In the remaining experiments, the distribution constant at the initial electrolyte concentration was determined by the direct distillation procedure. This procedure, the last to be developed, is even shorter than the distribution-boiling procedure, and it too was virtually free from error due to peroxide formation. Detailed procedures are given later (p. 26 ff.).

After a distribution experiment has been completed, the dilution-restirring procedure may be applied. By diluting the residual aqueous layer with oxygen-free water and restirring, the determination of distribution constants at a series of concentrations of the same electrolyte may be greatly accelerated. By observing the rate of the end-point color return, it was found that dilution-restirring may be applied to one cyclohexene-carbon tetrachloride solution as many as three times without serious peroxide effect.

Stirring, Settling, and Sampling. The distribution was carried out in a 500-ml. standard-tapered three-necked flask having a mercury-sealed stirrer in the center neck (figure 1). The

- 24 -

flask was kept in a thermostat at $25.0 \pm 0.1^{\circ}$. The mercury seal was of the conventional type except that a stainless steel tube was held within the inner glass tube by means of a rubber connection. This arrangement provided a metal bearing for the glass stirrer, and was designed to prevent the formation of glass dust which might interfere with settling. The inner glass tube of the seal was fused to a standard-tapered male joint which fitted into the center neck of the distribution flask. The mercury seal stopcock, which was sealed to the glass just above the male joint, led via a 3-way stopcock to the atmosphere (as a pressure release) or to the nitrogen Traces of oxygen were removed from the nitrogen by system. passing it through two wash bottles containing alkaline pyrogallol solution. For preliminary flushing operations, however, nitrogen was taken directly from the nitrogen cylinder.

The stirrer was of the upflow type described by Patterson (17). When the stirrer was rotated, the organic phase was drawn up inside the hollow shaft and sprayed out through the jets in small drops. The jets were placed a little below the aqueous surface, so that the atmosphere in the distribution flask would not be drawn into the issuing stream of droplets by vortex action. The jet tips were turned slightly upward to throw the droplets into the upper regions of the aqueous phase. The total effect was to fill the entire aqueous phase with a mass of swirling droplets, and intimate contact between

- 25 -

the two phases was thereby obtained.

After the solution had been stirred for one-half hour or less, it was allowed to stand while the droplets of the organic phase gradually settled out of the aqueous phase. Samples of each phase were taken after varying periods of settling. The effect of variations in the length of time allowed for stirring and settling will be discussed in later sections.

Sampling of the distribution layers was accomplished by means of a 3-way stopcock pipet, the stem of which was fitted into a one-hole rubber stopper. To obtain a sample, a slow stream of nitrogen was admitted through the mercury seal stopcock. The glass stopper was then withdrawn from the side neck, and the pipet was inserted until the rubber stopper made tight contact with the joint. After the nitrogen pressure had forced up enough liquid to fill the pipet, it was gently withdrawn and replaced by the glass stopper. The stopper was allowed to remain loose for a period of time during which nitrogen continued to flush the vapor space. When the organic phase was sampled, the aqueous phase was prevented from entering the pipet by maintaining a slight nitrogen pressure in the pipet as it was lowered through the aqueous layer.

<u>Procedure for Distillation of Cyclohexene into Carbon Tetra-</u> <u>chloride</u> (Figure 1). A pipet containing the desired volume of carbon tetrachloride is inserted in the tygon tip of the sampling tube, F. The "T" stopcock, G, is opened to the

- 26 -

sampling tube and the receiver tube, H, the stopcock of the mercury sintered-glass valve, I, is opened, and the carbon tetrachloride is run into the receiver flask. Just before the last drop of carbon tetrachloride drains from the pipet, the "T"-stopcock is rotated to connect the receiver tube with the transfer arm, E, which has been previously flushed with nitrogen, and nitrogen entering at the transfer arm is bubbled through the carbon tetrachloride for several minutes.

The "T" stopcock is closed, and the carbon tetrachloride is gently refluxed for fifteen minutes. During the reflux period, a slow stream of nitrogen is passed in from the distilling head stopcock, J, and out through the mercury valve. The carbon tetrachloride is cooled while the stream of nitrogen is continued, so that the mercury will not be drawn into the system. The distilling head stopcock is closed, and the cyclohexene is distilled into the receiver flask until a count of the drops of distillate indicates that a cyclohexene-carbon tetrachloride solution of approximately the desired concentration has been obtained.

Aqueous Phase Transfer Procedure (Figure 2). The transfer flask, A, is initially absent from the apparatus. The distribution flask, D, is flushed with a few liters of nitrogen, over a period of not less than one hour. The nitrogen is admitted through the nitrogen inlet, G, and is released to the atmosphere via the "T" stopcock (beyond H) except for occasional brief

- 27 -



Figure 2. Aqueous Phase Transfer Apparatus

A .	Transfer	flask		D. Distribution flask	
Β.	Transfer	flask sho	rt arm	E. Upflow stirrer	
С.	Transfer	flask lon	g arm	F. To mercury seal	
G.	Nitrogen	inlet, or	outlet to	atmosphere (via 3-way stopco	ck)
Η.	To "T" si	topcock of	distillin	g setup (as in figure 1.)	

2.5 4
intervals when it is released through the stopcock of the transfer flask long arm, C. Meanwhile, about 700 ml. of water is distilled under nitrogen in a separate distillation setup in which the transfer flask is the receiver. The "T" stopcock is closed, and the transfer flask long arm stopcock is opened. The transfer flask is removed from the water distillation setup and quickly placed on the distribution setup. For a few minutes thereafter, nitrogen is bubbled through the water and released through the transfer flack short arm, B.

The transfer flask long arm stopcock is closed, and the short arm is attached to a water aspirator. The water in the transfer flask is warmed slightly and allowed to boil at reduced pressure for twenty minutes. The "T" stopcock is opened meanwhile, so that nitrogen continues to flush the distribution flask. The "T" stopcock is then rotated to connect the distribution flask with the receiver flask containing cyclohexene-carbon tetrachloride solution (see figure 1). Nitrogen is admitted through the distilling head stopcock (J, figure 1), a pressure release is provided via the mercury seal stopcock, and about 20 ml. of the cyclohexene-carbon tetrachloride solution is forced over into the distribution flask.

Nitrogen pressure is applied at the transfer flask short arm, B, the stopcock of the long arm, C, is opened, the mercury seal stopcock is closed, and about 415 ml. of water is forced

- 29 -

over into the distribution flask. While the water is flowing, the transfer arm of the cyclohexene distillation setup is gently withdrawn from the distribution flask, and a glass stopper is inserted loosely in the side neck. When enough water has been transferred, the transfer flask long arm stopcock is closed. Nitrogen is passed in from the mercury seal stopcock while the transfer flask setup is withdrawn from the side neck and quickly replaced by a glass stopper, inserted loosely. The vapor space in the distribution flask is flushed with nitrogen for several minutes, the glass stoppers are tightened, the mercury seal stopcock is closed, and stirring is begun.

Distribution-boiling Procedure (Figure 1). About 415 ml. of the aqueous solution is placed in the distribution flask, D, and the "T" stopcock, G, is opened to the distribution flask and the atmosphere. The solution is boiled for a few minutes, and at the same time it is stirred to prevent bumping. Meanwhile, the vapor space above the solution is flushed with nitrogen entering at the nitrogen inlet, B. The open side neck is then closed with a cork fitted with a thermometer which dips into the solution. The "T" stopcock is closed, and heating is discontinued. The solution, while being stirred, is cooled with an ice-bath until the temperature is 25°. During the cooling, sufficient nitrogen is admitted to keep the pressure in the flask a little above atmospheric pressure. The pressure is indicated by the difference in the levels of mercury in the cuter and inner sections of the seal. The ice-bath is replaced by a 25⁰ thermostat, and the flask is opened to the atmosphere via the mercury seal stopcock.

A slight nitrogen pressure is built up in the cyclohexene distillation apparatus by passing nitrogen in through the distilling head stopcock, J, and out through the mercury sintered-glass valve, I. The tygon tip of the sampling tube, F, is closed by means of a screw clamp. The mercury valve stopcock is closed, and the "T" stopcock is rotated to connect the receiver tube, H, with the transfer arm, E. After about 20 ml. of cyclohexene-carbon tetrachloride solution has been forced over into the distribution flask, the "T" stopcock is rotated to connect the transfer arm with the sampling tube. Nitrogen is passed in through the mercury seal stopcock, and the clamp on the tygon tip of the sampling tube is unscrewed. After the vapor space in the distribution flask has been flushed with nitrogen for several minutes, the mercury seal and "T" stopcocks are closed, and stirring is begun. Direct Distillation Procedure. A glass stopper is inserted in one of the side necks of the distribution flask. A one-hole stopper fitted with a glass tube that extends to the bottom of the flask is placed in the other side neck. Throughout the subsequent operations, the vapor space is flushed with a stream of nitrogen admitted at the seal stopcock (B, fig. 1).

- 31 -

After the empty distribution flask has been flushed with a few liters of nitrogen, the stopper with the glass tube is removed, and 25 ml. of carbon tetrachloride is poured into the flask. The glass stopper is removed, the stirrer is started, and the carbon tetrachloride is gently boiled. After a few minutes, a cork which has a slit in its side is inserted in one of the side necks. The male joint of the condenser which is attached to the cyclohexene distilling flask, K, is inserted in the other side neck. The distillation of cyclohexene is started, and boiling and stirring of the carbon tetrachloride is discontinued. The distillation is continued until a count of the drops of distillate indicates that the distribution flask contains a cyclohexene-carbon tetrachloride solution of approximately the desired concentration. The condenser is removed from the side neck, and a glass stopper is inserted loosely. The slit cork is replaced by a funnel, and about 415 ml. of the aqueous solution, previously boiled and cooled under nitrogen, is poured in through the funnel. This is then replaced by a glass stopper, inserted loosely. After the vapor space in the distribution flask has been flushed with nitrogen for several minutes, the glass stoppers are tightened, the mercury seal stopcock is closed, and stirring is begun.

<u>Dilution-restirring Procedure</u>. The distribution flask contains the residue from the previous distribution experiment. Aqueous samples and additional portions of the aqueous layer were previously withdrawn until the residual aqueous volume was such that a convenient electrolyte concentration would be obtained by dilution. Nitrogen is passed in from the mercury seal stopcock, and the glass stopper in the side neck of the distribution flask is replaced by a funnel. Water, previously boiled and cooled under nitrogen, is added through the funnel until the surface of the liquid is a little above the stirrer jets. The funnel is then replaced by the glass stopper, inserted loosely. After the vapor space has been flushed with nitrogen for several minutes, the glass stopper is tightened, the mercury seal stopcock is closed, and stirring is begun.

DISTRIBUTION PROBLEMS

<u>Relative Precision of High and Low K Values</u>. Since <u>K</u> is inversely proportional to the aqueous phase cyclohexene concentration, and since the concentration of cyclohexene in the organic phase was relatively constant, an increase in the value of <u>K</u> indicated a decrease in the aqueous cyclohexene concentration. Since a decrease in the aqueous phase concentration was accompanied by a corresponding decrease in the precision of the analysis of this phase, the reliability of high <u>K</u> values was generally less than that of low K values.

<u>Common Errors</u>. Some of the common sources of error that increase the value of <u>K</u> are : (a) failure to saturate the aqueous phase with cyclohexene during the stirring period; (b) loss of cyclohexene from the aqueous phase by chemical reaction during the

- 33 -

settling period; and (c) evaporation of cyclohexene into the vapor space that has been desaturated during sampling. Errors that decrease the value of \underline{K} commonly arise from: (a) incomplete settling-out of the organic phase; (b) presence of peroxide in the organic layer prior to stirring; and (c) formation of peroxide during the stirring period.

The Effect of Peroxide. The major experimental difficulty in obtaining accurate distribution constants is that of avoiding peroxide formation. To accomplish this, it is necessary to deoxygenate the distribution materials, combine them in the distribution flask under oxygen-free conditions, and then carry out the subsequent operations of stirring, settling, and sampling without reentry of oxygen. Since nitrogen has approximately the same density as the oxygen that it displaces, the removal of oxygen is a difficult process; and since the gases are invisible, it is not known until the stability of the end-point is observed whether or not the process has been successful. If there has been appreciable peroxide formation, it is difficult to determine the point in the process where the oxygen was not removed, or was allowed to reenter. It was necessary to discard the results of a few experiments performed by the final procedures, because the rapidly drifting end-point indicated that oxygen was admitted by some unknown error in the manipulations.

Cyclohexene at room temperature can react quite readily with atmospheric oxygen (18). The reaction is essentially, if

-- 34 ---

not exclusively, a liquid phase reaction (19). It was formerly thought that a cyclohexene peroxide, in which oxygen is attached to the double bond, was formed. It was later shown (20) that the reaction product is a cyclohexenyl hydroperoxide, in which the OOH group is adjacent to the double bond. One mole of the product absorbs one mole of bromine; moreover, the hydroperoxide group may act as an oxidizing agent (21). The simpler designation "peroxide" is used throughout this paper to denote the hydroperoxide.

In distribution experiments, the peroxide and the cyclohexene of the organic layer dissolve into the aqueous layer almost independently, and since both peroxide and cyclohexene react with bromine during the analysis, the calculated \underline{K} value is low. The peroxide, by virtue of its more polar character, dissolves in the aqueous layer to at least two hundred times as great an extent as the cyclohexene (32). Consequently, a very small amount of peroxide has a large effect on the value of the distribution constant.

The brominated peroxide slowly oxidizes the iodide ion, and the presence of peroxide is revealed by the end-point drift, <u>i</u>. <u>e</u>., the gradual reappearance of the blue starchiodine color. As the peroxide concentration decreases, the rate of iodide oxidation due to this factor eventually becomes so low that it is difficult to distinguish it from the rate of iodide oxidation due to non-peroxide factors, a rate which varies empirically with such factors as acidity, oxygen contact, and lighting conditions. An accurate analysis cannot be readily obtained by allowing the titrated solution to stand until essentially all of the bromine which was reduced by the peroxide is regenerated as iodine, because the reaction is obscured by the presence of iodine due to non-peroxide factors.

To obtain quantitative data on the magnitude of the error due to peroxide, the solutions were rapidly titrated to the end-point, and were then allowed to stand for one hour, under uniform lighting conditions. The amount of color that developed during this period was determined by again titrating to the end-point. The data thus obtained were compared with the data obtained from the corresponding blanks. In general, the comparison indicated that a trace of peroxide was present in the sample. It is therefore likely that most of the <u>K</u> values are very slightly low. It is not likely, however, that the error in any case is large enough to affect the general conclusions based on comparison of the <u>K</u> values.

The data of the preliminary experiments shown in Table III were obtained during the development of peroxide-free procedures. The drifting end-points indicated that moderate amounts of peroxide were present in all of the experiments. The marked effect of peroxide is illustrated by the <u>K</u> values. These were all far below 38.4 x 10^2 , the value found by peroxide-free procedures.

- 36 -

	2)			
Prepn. of 36H10 - CC14 solution	Standing time of soln. prior to stirring	Type of stirring	Stirring time, hr.	Settling time, hr.	Amount of peroxide ^a	K _w x 10-2
Oiluted C ₆ H10 vith CC1 ₄ in volum. flask	2 weeks	Paddle , unbroken layers	P 20	Ч	Эдгет	17
Diluted C ₆ H ₁₀ vith CC1 ₄ in lisplacement volum. flask	5 days	Padûle, unbroken layers	0° 2 C	002 1-00 1-00	Large	ದಿ ದೆ.ಜ ರಿ ಹಿ ರೆ ಜ ಜ ಜ
Diluted C ₆ H ₁ 0 vith CCl ₄ in lisplacement volum. flask	1 to 3 hours	Emulsion by paddle	0° ຄ 0	0°2 1°0	Moderate or Large	28°0 29°0
C6Hlo distld. Into ccl4 in Istrbn. flask	5 days	Emulsion by upflow stirrer	0 80	24 48	Large	22° 8 20°5
o ₆ H ₁ 0 distld. Into ccl ₄ in Istrbn. flask	2 to 5 hours	Emulsion by upflow stirrer	0.70	40	Moderate or large	30 . 4
^a Based on end	l-pt. drift. ^b A	ir atmos., $H_2^{(}$	0 unboiled.	c Under	N2, H20 preb	oiled.

Table III

Distribution of Cyclohexene between Carbon Tetrachloride and Water, $25 \pm 4^{\circ}$. Preliminary Experiments, Illustrating the Marked Effect of Peroxide - 37 -

<u>Stirring and Settling</u>. Since the organic phase cyclohexene concentration was from three thousand to thirty thousand times as great as the aqueous phase concentration, it was essential that the organic phase should settle completely out of the aqueous phase. Since cyclohexene solutions usually undergo slow reactions which affect the value of <u>K</u>, it was also important to avoid long periods of settling and stirring. For meeting all of these requirements, the upflow type of stirrer was especially suitable. The size of the jet tips of the stirrer was such that the organic droplets were small enough to saturate the aqueous phase in a short period of time, yet large enough to settle out rapidly.

The advantages of this type of stirring were greatest at the highest electrolyte concentrations. The increase in the density and viscosity of the aqueous phase caused by the addition of an electrolyte opposes rapid settling. Nevertheless, even when the aqueous phase was 8 \underline{M} sulfuric acid, with a specific gravity (1.44) very close to the specific gravity (about 1.51) of the carbon tetrachloride layer, the aqueous layer was clear after less than one hour of settling. In stirring some of the solutions of high electrolyte concentration, the organic phase was so thoroughly dispersed in the aqueous phase that only twenty minutes was allowed for stirring, instead of the usual one-half hour.

It seems likely that the changes in concentration of the

- 38 -

cyclohexene in the aqueous layer which occur during the settling period are due to some or all of the following processes: (a) settling-out of the organic phase; (b) evaporation of cyclohexene into the vapor phase; (c) diffusion of cyclohexene from the organic phase into the aqueous phase; (d) peroxide formation; and (e) hydration, addition of acid to the double bond, and polymerization. In most of the distribution experiments, a sample of the aqueous phase was taken at some particular time of settling, and one or more samples were taken after certain additional periods of settling. The data thus obtained indicate that if the prescribed procedures are followed there is an initial period of one hour or less in which the organic phase settles out fairly rapidly, and that the concentration of cyclohexene in the aqueous phase changes slowly thereafter.

In general, after the initial settling-out period, the change in concentration in any half-hour interval was no greater than the usual variation in the results of duplicate analyses. Since cyclohexanol would not react with bromine during the analysis (11), the rate of hydration in these solutions is probably low or negligible. It was nevertheless important that the calculation of \underline{K} values be based on samples taken as soon as possible after the initial settling-out period, since slow changes in concentration may in time give rise to large errors in these values. During long periods of

- 39 -

settling in aqueous acid solutions, there was a decrease of 1 to 3% per hour in the value of the cyclohexene concentration calculated from the analytical data.

Effect on Value of K_W of Variations in Stirring Time, Settling <u>Time, and Amount of Peroxide</u>. A number of deductions may be made from Table IV, which gives the values of K_W obtained in experiments with variations in stirring time and settling time, and with small or inconsiderable amounts of peroxide.

(a) The two runs (1 and 3) with the shortest stirring time, ten minutes, were the only experiments in which the \underline{K}_{W} values decreased with an increase in settling time. This suggests that ten minutes of stirring was insufficient to saturate the aqueous layer with cyclohexene, and that the cyclohexene gradually diffused into this layer during the settling period.

(b) The run (2) with the shortest settling time, fifteen minutes, was the only experiment in which there was a substantial increase in \underline{K}_{W} after an additional half-hour of settling. This suggests that the organic phase was still settling out at a moderate rate after a fifteen minute settling period.

(c) In the experiments with a thirty minute stirring time, the effect of peroxide is evident. The highest values of \underline{K}_{W} were obtained in the runs (5 and 7) in which the amount of peroxide was least. On the basis of these two runs, made by different but apparently equally reliable procedures, the

	63			4000	41 -				
TD	x 10-	37.0 35.8 34.7	34 8 36 8 36 4	43 .6 42.8 41.0	34 .7 34 . 9 34 . 9	38° 38° 38°	35 9 35 9 35 9	38.0 38.1 38.0	
ADA NHO ANT TO	Amount of peroxide ^b	Small Small Small	Small Small Small	Winor •••• Small	Small Small Small	Winute Winute	Small Small Small	Minute Minute Minute	
TILDETA ST HOA	Hours settled ^a	002 880	0 8 2 5 • 8 5 • 0 5 • 0	ຄ.ຄ.ຄ ຄ. ຄ. ۲. 0	809 100 100	0°2 1°0	9 ••8 PPO	хо ••0 нно	
TEC HODMADO	(C6H10) in water, <u>w</u>	0.000271 .000280 .000288	.000287 .000272 .000275	.000261 .000266 .000278	.000300 .000299 .000298	.000279 .000278	.000274 .000276 .000274	.000306 .000305 .000306	
DHAVAHOTOKO TO	(c6H10) in cc14, <u>w</u>	1.00đ	1.00đ	1.14 1	1.04 ^f	1.08ª	0.981	1.16 đ	
CZ AR TOT	Winutes stirred	10	30	10	30	30	30	30	
not rigta .AT	Procedure	Modified aq. phase transferc	Dilution of #1 residue, boiled water	Aq. phase transfere	Aq. phase transfere	Aq. phase transfer	Distribution boiling ⁶	Distribution boiling	
STOPT	Run	Ч	જ	63	4	Q	9	2	

Distribution at 250 of Cveloherene between Carbon Tetrachloride and Water Table IV. ^a Refers only to time that aq. layer was sampled. ^b Based on end-pt. drift. ^c Water vacuum-boiled but not predistilled. ^d Av. of analysis from receiver and distribu. flask, diff. 1-2%. ^e Except much shorter period of flushing distribution flask with N₂. ^f Analysis from receiver flask. ^g Prelim. expt. $C_{6}H_{10}$ -CCl₄ soln. 7 days old.

best value for <u>K</u> is 38.4 x $10^2 \pm 0.4 \times 10^2$.

(d) In the experiments with a thirty minute stirring time, little or no change in the value of \underline{K}_{w} occurred for at least one hour after the initial one-half hour settling period. In conjunction with the rest of the data, this suggests that thirty minutes of stirring was sufficient to equilibrate the two phases, that the process of settling-out was essentially completed in the initial thirty minutes, and that other possible processes which alter the cyclohexene concentration did not occur to any appreciable extent for at least one hour thereafter.

DISTRIBUTION DATA

The data obtained in the distribution experiments with acid and salt solutions are given in Tables V and VI. The concentration of cyclohexene in the organic phase did not change appreciably in several hours. The value of the concentration taken for the calculation of <u>K</u> was an average of the experimental values with smaller weight given to values obtained after the first few hours of settling.

The aqueous phase cyclohexene concentration was subject to moderate change in the course of a few hours of settling. The concentration value used to calculate <u>K</u> was generally the known or extrapolated value at 3/4 hour settling time. This choice of time was compatible with the tabulated data, which indicated that 3/4 hour was sufficient for complete settling

- 42 -

Table V

Distribution at 25° of Cyclohexene between Carbon Tetrachloride and Aqueous Acid Solutions

	Org	anic pha	156	Aque	ous pha	180	
Acid concn.	Set- tling time hr.	^C 6 ^H 10 obs. <u>M</u>	concn. value for <u>K</u> <u>M</u>	Set- tling time hr.	°6 ^H 10 obs. <u>₩</u> x	concn. value for <u>K</u> 10^4	x 10 ⁻²
			Sulfuric	acid			
2.96 ⁸	2.2 24.5	0.958 0.954	0.957	0.8 1.2 24.0	1.11 1.16 0.86	1.11	86.2
2.98 ²	3.5 4.0 4.2	0.970 0.959 0.971	0.967	0.8 1.5 5.0	1.12 1.08 1.04	1.12	86.4
1.090	6.0 6.8	0.968 0.964	0.966	1.0 2.0 3.0 4.0	1.73 1.64 1.64 1.49	1.73	55.9
2.40 ^a	2.5	0.970	0.970	0.8	1.29 1.30	1.29	75.2
1.40 ^b	2.0 20.0 21.0	0.985 0.994 0.985	0.986	0.8 1.2 22.8	1.59 1.60 1.29	1.59	62.0
0.36 ^b	2.0 2.2 18.8	0.987 0.995 0.995	0.992	0.5 1.0 20.5	2.28 2.26 1.81	2.27	43.7
8.05 ⁸	1.8 7.8	1.057 1.060	1.058	1.0 3.2 7.0 11.0	0.52 0.49 0.58 0.69	0.52	203
-							

a The distribution-boiling procedure was used.

^b This experiment was performed by dilution-restirring of the experiment preceding it in the table.

Table V (continued)

Distribution at 25° of Cyclohexene between Carbon Tetrachloride and Aqueous Acid Solutions

	Org	anic pha	156	Aque	ous pha	156	
Acid concn.	Set- tling time hr.	C ₆ H ₁₀ obs. <u>M</u>	conon. value for \underline{K}	Set- tling time hr.	°6 ^H 10 obs. ∦ x	concn. value for <u>K</u> 10 ⁴	x 10-3
			Hydrochlo:	ric acid			
3.04 ^a	0.3	1.340 1.344	1.242	0.5	3.05 3.05	3.05	40.7
1.73 ^b	1.6	1.230	1.230	0.5	2.68	2.66	46.2
0.76 ^b	0.3 1.5 21.5 22.0	1.250 1.237 1.251 1.251	1.344	0.5 1.0 20.0	2.85 2.87 2.22	2.86	43.5
3.02 ^a	0.5	0.875 0.875	0.875	0.8	1.95	1.95	44.8
1.97 ^b	0.5	0.884	0.884	0.8	1.76 1.76	1.76	50.2
0.90 ^b	0.3	0.877	0.877	0.5	1.78 1.80	1.79	49.0
0.34 ^b	1.5	0.885	0.885	0.5	2.03	2.02	43.8

a The direct distillation procedure was used.

b This experiment was performed by dilution-restirring of the experiment preceding it in the table.

- 45 -

Table V (continued)

Distribution at 25° of Cyclohexene between Sarbon Tetrachloride and Aqueous Acid Solutions

Acid concn.	Org Set- tling time hr.	anic pl C ₆ H ₁₀ obs. <u>M</u>	hase concn. value for <u>K</u>	Aque Set- tling time hr.	ous ph ^C 6 ^H 10 obs. <u>M</u> x 1	ase concn. value for \underline{K} 10^4	x <u>k</u> 10-2
	×		Perchloric a	loid			
3.00 [®]	0.8	0.979	0.979	1.2	3.58	3.58	27.3
2.21 ^b	* * *		0.994	1.0	3.05	3.05	32.6
1.13 ^b	0.3	1.010	1.010	0.8	2.75	2.75	36.8
			Nitric acid	<i>*</i>		, * * *	
3.06 ^a	4.0	0.935	0.935	0.8	3.43 3.35	3.43	27.3
1.79 ^b	1.5	0.940	0.940	0.5	2.85 2.81	2.83	33.2
0.68 ^b	1.5 17.0	0.949 0.945	0.948	0.5	2.53 2.53 1.27	2.53	37.4
				son the w the	AND TO THE F		

a The direct distillation procedure was used.

b This experiment was performed by dilution-restirring of the experiment preceding it in the table.

- 46 -

Table VI

Distribution at 25° of Cyclohexene between Carbon Tetrachloride and Aqueous Salt Solutions

	Org	anic pha	180	Aque	ous pha	186	
Salt concn.	Set- tling time hr.	obs.	concn. value for <u>K</u>	Set- tling time hr.	C ₆ H ₁₀ obs. <u>M</u> x	value for K 10 ²	x <u>x</u> 10-2
		1	Bodium b	isulfate			
3.02 ^a	5.8	1.048	1.048	0.8 1.5 5.5	0.370 0.436 0.370	0.370	283
0.98 ^b	1.0 19.0	1.060	1.060	0.3	1.285 1.265	1.265	83.8
2.52 ⁸	1.5	1.058	1.058	0.5	0.535	0.530	200
2.06 ^b	15.0 15.5	1.067 1.066	1.067	0.5	0.675	0.670	159
							· · · ·
1.538	8.8 3.8	1.086	1.084	0.8	0.950	0.950	114
0.51 ^b	1.8 2.2	1.086 1.086	1.086	0.5	1.810 1.800	1.805	60.2

a The distribution-boiling procedure was used.

b This experiment was performed by dilution-restirring of the experiment preceding it in the table.

- 47 -

Table VI (continued)

Distribution at 25° of Cyclohexene between Carbon Tetrachloride and Aqueous Salt Solutions

	Org	anic ph	ase	Aque	ous phas	e	
Salt concn.	Set- tling time hr.	C ₆ H ₁₀ obs.	concn. value for \underline{K}	Set- tling time hr.	C ₆ H ₁₀ c obs. f <u>M</u> x 1	onen. alue o <u>r K</u> O	x 10 ⁻²
			Potassium	chloride			
3.02 ^a	0.3	1.011	1.011	0.5	0.775	0.775	131
2.35 ^b	0.3	1.014	1.014	0.5	0.931	0.931	109
1.73 ^b	0.3	1.008	1.009	0.8	1.18 1.16	1.18	85.6
0.87 ^b	0.3	1.016	1.016	0.5	1.73 1.78	1.72	59.0
	· · · · · · · · · · · · · · · · · · ·	а 1 1	Sodium pe	rchlorate			
2.90 ^a	1.5	1.070	1.070	0.8	1.09	1.09	98
1.73 ^b	1.5	1.066	1.066	0.5	1.59	1.59	67.1
× 6	2 4	а 2 2	Potassium	n Nitrate			
1.01°	2.0 2.2	1.194 1.194	1.194	0.5 1.0 1.2	2.36 2.34 2.35	2.35	50.8
a The di	lrect di	stillat	ion proce	dure was	used.		
b This of the end	experime xperimen	nt was t prece	performed ding it i	l by dilut In the tab	ion-rest le.	irring	of
C The di	lstribut	ion-boi	ling proc	edure was	used.		

ŕ

but not for appreciable change by other processes. Although it was shown in experiments with \underline{K}_{W} that 1/2 hour settling time was adequate, 3/4 hour was allowed in the experiments with acid and salt solutions because settling was slower in these solutions than in water.

The tabulated <u>K</u> values and \log_{10} <u>K</u> values, except for the 8 M sulfuric acid experiment, have been plotted in Figures 3 and 4 as a function of the electrolyte concentration. The curves for <u>K</u> all meet the <u>y</u>-axis at approximately 38.4 x 10^{2} , the experimental value of \underline{K}_{w} . Since \underline{K} is plotted so that it increases as the curve descends, points below the value of \underline{K}_{w} , <u>i</u>. <u>e</u>., numerically higher, indicate a salting-out of cyclohexene in the aqueous phase and vice versa. The data for perchloric and nitric acids correspond so well that a single curve satisfies the values for both acids. The two curves for hydrochloric acid represent the data obtained in two series of experiments. In the upper curve, the organic phase cyclohexene concentration was about 1.24 M; in the lower it was about 0.88 M.

DISCUSSION OF RESULTS

It is seen from Figure 3 that the aqueous phase cyclohexene concentration is in every case greater in the acid solution than in the equimolar solution of the corresponding alkali salt. Moreover, the order of anions for increasing



Molarity of Acid or Salt

Figure 3. Plot of Distribution Constant against Aqueous Electrolyte Concentration





Molarity of Acid or Salt

Figure 4. Plot of the Logarithm of the Distribution Constant against Aqueous Electrolyte Concentration aqueous cyclohexene concentration - <u>viz</u>., bisulfate; chloride; perchlorate or nitrate - is essentially the same for the salt curves as for the acid curves. These facts suggest the possibility that the concentration of cyclohexene in the aqueous phase is determined by independent additive effects of the cation and anion.

The relative position and general shape of the curves are compatible with the interpretation that at low electrolyte concentrations the curves reflect primarily a salting action on the aqueous cyclohexene by the individual ions of the electrolyte. A particular ion has nearly the same relative salting action on different nonpolar solutes (23, 24). 1. 11 general, the larger the ion and the smaller its charge, the smaller is the salting-out effect or the greater is the salting-in effect (23, 25). The salting action of hydrogen ion is equivalent to that of a large univalent cation such as rubidium ion (26). Other investigations have shown that the salting-out action of the pertinent cations is in the order: sodium)potassium > hydrogen; for the anions, the salting-out order is: chloride > nitrate > perchlorate (27, 26). The salting action of bisulfate ion has apparently not been investigated previously (28, 24). The analysis of the data for sodium bisulfate and sulfuric acid is somewhat complicated by the presence of divalent sulfate ion from the secondary ionization, which increases with dilution and is greater in sodium bisulfate

- 51 -

solution than in sulfuric acid, where the sulfate ion concentration is reduced by the hydrogen ion from the primary ionization.

In order to examine the data for evidence of a complexing effect in addition to the salting effect, reference is made to the logarithmic curves of Figure 4. Normally, there is a linear relationship between the logarithm of the solubility of the nonelectrolyte and the concentration of the electrolyte (26, 24). This relationship holds guite well for the salt curves up to 1 M, but small deviations from linearity become apparent at higher concentrations. The salt curves may be considered to represent the normal salting pattern, and they thereby provide a standard of reference for deciding whether a complexing factor is involved in the acid curves. Since complexing would increase the total aqueous concentration of olefin, and since the concentration of complex would increase with increasing acidity, the presence of a complexing factor would be indicated in the acid curves by a gradually increasing upward displacement from the line of initial slope.

In cases where the appropriate data are available, the effects of the positive and negative ions of the electrolyte are approximately additive in dilute solution. Thus, the sum of the values of the initial slopes of the sodium bisulfate and perchloric acid curves is roughly equal to the corresponding sum for the sodium perchlorate and sulfuric acid curves. This

- 52 -

additivity is in accordance (26) with the interpretation that the curves are primarily a manifestation of salting effects. At higher concentrations, the curves for sulfuric, perchloric, and nitric acids show slightly greater upward displacement from the line of initial slope than the curves for sodium bisulfate and sodium perchlorate. While these slight differences in curvature suggest the possibility that there is a small complexing factor, the effect is so small that it may readily be the result of undetermined solubility factors or experimental difficulties in determining the distribution constant at high electrolyte concentrations. There is no theoretical basis for an exactly linear relationship in these concentrated solutions (24), and the only conclusion that can be drawn is that the presence of complexes is unlikely unless their concentration is very low.

The basis for the two curves obtained with hydrochloric acid is not evident, but it may be related to the fact that the concentration of cyclohexene in carbon tetrachloride was almost 50% greater in the upper curve. For these curves, the deviation from linearity is pronounced, and the upturn of the curves at higher electrolyte concentration is considerably greater than in the case of potassium chloride. The presence of a minimum in the hydrochloric acid curves definitely suggests the possibility that the curves are the net result of a complexing effect superimposed on a salting-out effect. However, the data as a whole support the interpretation that the minimum is at least partially due to a specific effect not involving proton complexes, since the deviation from linearity in the curves for hydrochloric acid is much greater than in the curves for the other acids, which should be able to form such complexes just as readily. In the case of sulfuric acid, moreover, a comparable minimum was not apparent, since the aqueous cyclohexene concentration was much less in 8 \underline{M} sulfuric acid than in 3 \underline{M} sulfuric acid.

Examples of salting-in of a nonpolar liquid are infrecuently encountered and not well understood (29). It may therefore be felt by some readers that the greater solubility of cyclohexene in perchloric and nitric acids than in water is in itself evidence for complex formation involving the double bond, because there is in this case no other reasonable basis for a salting-in effect. Such a view seems untenable because the results of a later investigation (Part II of this thesis) indicate that cyclohexane, which is similar to cyclohexene but has no double bond, is also more soluble in 3 M perchloric acid than in water. It has also been shown in the later investigation that the salting-in or salting-out of carbon tetrachloride by 3 M perchloric acid, 3 M sulfuric acid, and 3 M sodium perchlorate is roughly parallel to the salting effects on cyclohexene in the distribution system. It is possible that the curves of Figures 3 and 4 are somewhat modified by the presence of varying amounts of carbon tetrachloride in the aqueous phase. The tendency of cyclohexene to dissolve in the aqueous phase presumably increases with an increase in the aqueous phase carbon tetrachloride concentration.

Since cyclohexene is a fairly typical olefin, the analysis of the data obtained with cyclohexene in aqueous solutions indicates that if aqueous proton-olefin complexes exist, they are present in very low concentration. This does not mean that there is no intrinsic affinity between the double bond and a proton, since the proton in aqueous media is strongly attracted to the water molecules.

- 56 -

REFERENCES

- L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 292-294, 308
- G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 232-237, 251
- 3. C. C. Price, "Mechanisms of Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 39-43
- 4. H. J. Lucas and W. F. Eberz, <u>J. Am. Chem. Soc.</u>, <u>56</u>, 460 (1934)
- 5. H. J. Lucas and Y. Liu, J. Am. Chem. Soc., 56, 2138 (1934)
- 6. O. Schmitz-Dumont, K. Hamann, and A. Diebold, <u>Ber.</u>, <u>71B</u>, 205 (1938)
- 7. F. C. Whitmore, Ind. Eng. Chem., 26, 94 (1934)
- 8. K. C. Laughlin, C. W. Nash, and F. C. Whitmore, J. Am. Chem. Soc., <u>56</u>, 1395 (1934)
- 9. S. Winstein and H. J. Lucas, <u>J. Am. Chem. Soc.</u>, <u>60</u>, 836 (1938)
- 10. H. J. Lucas, R. S. Moore, and D. Pressman, <u>J. Am.</u> <u>Chem. Soc.</u>, <u>65</u>, 227 (1943)
- 11. H. J. Lucas, F. R. Hepner, and S. Winstein, <u>J. Am.</u> <u>Chem. Soc.</u>, <u>61</u>, 3102 (1939)
- 12. R. N. Keller, Chem. Rev., 28, 229 (1941)
- 13. H. J. Lucas, F. W. Billmeyer, and D. Pressman, J. Am. Chem. Soc., 65, 230 (1943)
- 14. H. J. Lucas and D. Pressman, <u>Ind. Eng. Chem., Anal. Ed.</u>, 10, 140 (1938)
- 15. H. J. Lucas and W. F. Eberz, <u>J. Am. Chem. Soc.</u>, <u>56</u>, 1230 (1934)

16. E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1946, pp. 79-81

REFERENCES

- 17. J. A. Patterson, Ind. Eng. Chem., Anal. Ed., 6, 171 (1934)
- 18. H. N. Stephens, J. Am. Chem. Soc., 50, 568 (1928)
- 19. H. N. Stephens, J. Am. Chem. Soc., 58, 219 (1936)
- 20. R. Criegee, Ann., 522, 75 (1936)
- 21. E. H. Farmer and A. Sundralingam, J. Chem. Soc., 121 (1942)
- H. Hock and O. Schrader, <u>Naturwissenschaften</u>, <u>24</u>, 159 (1936)
- 23. S. Glasstone, "Textbook of Physical Chemistry," second ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, pp. 699, 729
- 24. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 397-400, 565
- 25. P. S. Albright, J. Am. Chem. Soc., 59, 2098 (1937)
- 26. P. M. Gross, Chem. Rev., 13, 91 (1933)
- 27. D. Pressman, L. Brewer, and H. J. Lucas, <u>J. Am. Chem. Soc.</u>, <u>64</u>, 1117 (1942)
- 28. M. Randall and C. F. Failey, <u>Chem. Rev.</u>, <u>4</u>, 271, 285, 291 (1927)
- 29. J. O'M Bockris and H. Egan, <u>Trans. Faraday Soc.</u>, <u>44</u>, 151 (1948)

PART II

THE SOLUBILITY OF SOME NONPOLAR ORGANIC LIQUIDS IN WATER AND IN AQUEOUS SOLUTIONS OF STRONG ACIDS, ALKALI SALTS, AND SILVER NITRATE

THE COORDINATION OF SILVER ION WITH BENZENE

PART II

THE SOLUBILITY OF SOME NONPOLAR ORGANIC LIQUIDS IN WATER AND IN AQUEOUS SOLUTIONS OF STRONG ACIDS, ALKALI SALTS, AND SILVER NITRATE

THE COÖRDINATION OF SILVER ION WITH BENZENE

INTRODUCTION

The experiments were initiated as a result of problems presented by the previous study of postulated proton-olefin complexes (1). In that investigation, it was found that cyclohexene distributed between carbon tetrachloride and aqueous solutions was more soluble in an aqueous phase containing perchloric acid or nitric acid than in a pure water aqueous phase. In connection with the distribution experiments, it was of interest to know the solubilities of carbon tetrachloride in certain aqueous solutions. The desired solubilities have been determined by a new procedure, stripping analysis, which has also been employed to determine various aqueous solubilities of benzene and cyclohexane. The relative solubility of cyclohexene in 3 \underline{M} perchloric acid and the change of this solubility with temperature have been compared to the corresponding data for cyclohexane in 3 <u>M</u> perchloric acid, where complexing involving the double bond is excluded, and for cyclohexene in 1 <u>M</u> silver nitrate, where such complexing definitely occurs. Related solubility data have also been obtained, with the object of gaining a better understanding of the relation between salting and complexing factors in the aqueous solubility of nonpolar liquids.

In stripping analysis, the organic liquid is stripped from its aqueous solution by passing a current of nitrogen through the solution. The gas stream is passed through a column of Drierite, which removes the water vapor, and then through a weighed trap, where the organic vapor is frozen out of the nitrogen. Stripping analysis has been employed to determine the solubility of benzene at 10° and 25°, and of carbon tetrachloride and cyclohexane at 25° in water and in aqueous solutions of strong acids, alkali salts, and silver nitrate. Qualitative data on the change of solubility with temperature have been obtained by the cloudiness method. In this method, it is noted whether cloudiness develops when the temperature of a saturated solution is altered.

RESULTS AND DISCUSSION

Solubility Data. The best values for the various solubilities are given in Table I. Except as indicated in the footnotes, the solubilities apparently have not been determined previously.

Table I

Solubility of Some Organic Liquids in Water and in Aqueous Solutions

		Benzene	, 25 ⁰	Benzen	e, 10 ⁰
		grams/liter	moles/liter	grams/liter	moles/liter
Wat	er	1.73 ^a	0.023	1.71 ^a	0.022
1 <u>M</u>	KNO_3	1.37	.018 ^b	1.32	.017
1 <u>M</u>	$AgNO_3$	5.01	.064 [°]	5.77	.074
3 M	$NaClO_4$	0.77	.010		
3 <u>M</u>	HClO4	2.13	.027	1.76	.023
3 <u>M</u>	H_2 SO ₄	0.81	.010		

			Carbon Tetra	chloride, 25 ⁰	Cyclohex	ane, 25°
			grams/liter	moles/liter	grams/liter	moles/liter
Wa	ate	er	0.76 ^d	0.0049	0.060±.010	0.0007
1	M	kno ₃	.67	.0044	$.049 \pm .010$.0006
1	M	AgN03	.71	.0046	.052±.010	.0006
3	M	$NaClO_4$.29	.0019	.019±.015	•0003
3	dented to	HC104	.93	.0060	.072±.010	.0009
3	M	H2804	.39	.0025	$.026 \pm .015$.0003

The approximate solubility of cyclohexene in water at 25° is 0.25 grams/liter.

a Seidell (2) reports the average of determinations by four workers as follows: 1.80 g./1000 g. of water at 25° and 1.63 g./1000 g. at 10° . A more recent value (3) is b 1.74 g./l. at 25°. The literature value is 0.0165 moles/liter (3).

c The literature value is 0.062 moles/liter (3).

d The literature values are $0.77 \text{ g./1000 g. of water at 15° (4),} 0.77 \text{ g./1000 g. at 25° (5), and 0.81 g./1000 g. at 30° (4).$

The solubility in grams per liter of solution is based upon the value or average of values given in subsequent tables. In a few instances, a very small extrapolation was made on the basis of the usual linear relationship between the logarithm of solubility and the concentration of electrolyte (6, 7), because the experimental solubility was not determined in an electrolyte solution of the exact integral molarity shown in the table. Values in moles per liter are expressed to a lower precision than values in grams per liter because they are calculated from the latter values and not directly from the experimental data. In the data on the solubility of benzene at 10°, the electrolyte concentration is expressed in moles per liter at approximately 25°, the temperature at which the concentration was determined.

<u>Relative Solubilities at 25°</u>. The relative solubilities of Table II have been calculated from the solubilities in grams per liter given in Table I. The solubility of each organic liquid in the specified solution is expressed as a percentage of the solubility of that liquid in water. The values for cyclohexene are based upon previous experiments (1) on cyclohexene distributed between carbon tetrachloride and aqueous solutions, and represent a comparison of the distribution ratio between carbon tetrachloride and water to the distribution ratio involving the acid or salt solution.

Aside from the solubilities in 1 M silver nitrate, the

- 62 -

- 63 -

Table II

Relative Solubility at 25° of Some Organic Liquids in Aqueous Solutions of Acids and Salts^a

	Water	KNO3 1 M	AgNO3 1 M	NaClO ₄ 3 <u>M</u>	HC104 3 M	_{H2} SO4 3 <u>м</u>
Benzene	100	79	290	45	123	47
Carbon tetra- chloride	100	88	93	38	122	51
Cyclo- hexane ^b	100	82	87	32	120	43
Cyclo- hexene ^c	100	76	7 × 10 ^{3 d}	38	141	44

a The values for each organic liquid are relative to a value

of 100 for the solubility of that liquid in water. ^b The reliability (estimated at ± 10) of the cyclohexane values is considerably less than that of the other values.

C These values refer to the relative solubility of cyclohexene in the aqueous layer of a distribution system in which the organic layer is an approximately 1 M solution of cyclohexene in carbon tetrachloride.

d This value is based upon the data of Winstein and Lucas (8).

data reveal a general parallelism in the action of the different acids and salts on the various organic solutes. This corresponds to normal salting behavior, in which the relative influence of a given electrolyte is almost independent of the nonpolar substance salted (9, 7). The relative solubilities are compatible with the usual salting effects of the ions involved (1).

Since the four chemically different organic liquids are

all somewhat more soluble in 3 <u>M</u> perchloric acid than in water, the change in solubility apparently involves primarily a salting effect rather than chemical complex formation. This view is in harmony with the fact that helium and argon are also more soluble in aqueous solutions of perchloric acid than in water (10). In particular, since there is a salting-in effect with cyclohexane, which is similar to cyclohexene but has no double bond, the increased solubility of cyclohexene in 3 <u>M</u> perchloric acid cannot be attributed solely to complex formation involving the double bond.

The experimental results indicate that the relative solubility in 3 M perchloric acid is somewhat greater for cyclohexene than it is for cyclohexane. This again (1) suggests the possibility that the salting-in effect with cyclohexene may be partially explained by the presence of a very low concentration of proton-olefin complex. The difference in relative solubility is small, however, and it may also reasonably be ascribed to other possible causes such as experimental variations, effect of changes in the aqueous carbon tetrachloride concentration on the distribution of cyclohexene, and small variations in salting effect based upon differences in the organic solutes. The experimental data for 3 M sulfuric acid do not support the interpretation that this salting-in effect involves the presence of protonolefin complexes, since the relative solubility of cyclohexene

- 64 -
in 3 \underline{M} sulfuric acid is about the same as or less than that of the other organic liquids in 3 \underline{M} sulfuric acid.

In each case, the organic solute is more soluble in 3 M perchloric acid than in 3 M sodium perchlorate. Since the acid and salt have a common anion, and since the salting-out action of sodium ion is much larger than that of hydrogen ion (6), the change in solubility is in the expected direction. In each case, also, the relative solubility in 3 M perchloric acid is greater than in 3 M sulfuric acid. The direction of this solubility change is the same as that in the only available example of a comparable change of anion - i.e., the relative solubility of distributed cyclohexene in 3 M sodium perchlorate, 38%, is greater than that in 3 M sodium bisulfate, 13% (1). Although it seems reasonable from these data that the organic solutes should be more soluble in 3 M perchloric acid than in 3 M sodium perchlorate or 3 M sulfuric acid, it is not evident from a theoretical standpoint why they should be more soluble in 3 M perchloric acid than in water. There is as yet no completely satisfactory theory of salting effects, and the current theoretical equations require salting-out of a nonpolar substance in aqueous solutions (7, 11). It is noteworthy that even a saturated hydrocarbon, cyclohexane, is salted into 3 M perchloric acid.

The high relative solubilities of benzene and cyclohexene in 1 \underline{M} silver nitrate are in marked contrast to the other solubilities in Table II, and this indicates that some type of complexing action is involved. There are reasons why this solubility effect should not be attributed to a salting-in action rather than complex formation. First, since cyclohexane and carbon tetrachloride are salted out in 1 M silver nitrate, the effect with benzene and cyclohexene is contrary to the general parallelism of salting effects. A reasonable basis for the solubility differences exists. Silver ion often forms complexes with nucleophilic substances, and cyclohexene and benzene display nucleophilic properties in general. Secondly, cyclohexene and benzene are salted out in 1 M potassium nitrate. Since potassium ion and silver ion are similar in size (12), the solubilities in 1 M potassium nitrate and 1 M silver nitrate should be approximately equal (as is the case with cyclohexane and carbon tetrachloride) if no complexing were involved. Finally, it will be shown in the next section that the data on change of solubility with temperature indicate that complex formation is involved in the case of cyclohexene and benzene in 1 M silver nitrate.

Change of Solubility with Temperature. Data pertaining to the change of solubility with temperature are presented in Tables III and IV. Data obtained by the cloudiness method (Table III) generally show the sign of the temperature coefficient of solubility, which is positive if the solubility of the liquid increases with increasing temperature. In Table IV, the

-- 66 **

- 67 -

Table III

Temperature Coefficient of Solubility of Some Organic Liquids in Water and in Aqueous Solutions

	Water	KNO3 1 <u>M</u>	$\frac{\text{AgnO}_3}{1 \text{ M}}$	HCIO4 3 M
Benzene	Positive	Positive	Negative	Positive
Carbon tetra- chloride	Positive	Positive	Very small	Positive
Cyclo- hexane	Positive	Positive	Small	Positive
Cyclo- hexene	Positive	Positive	Negative	Positive

Table IV

Some Relative Solubilities of Benzene in Water and in Aqueous Solutions at 25° and at 10° a

	Water	KNO3 1 M	AgNO3 1 M	нс 10 4 З <u>М</u>
25 ⁰	100	79	290	123
10 ⁰	99	76	334	102

^a All values are relative to a value of 100 for the solubility of benzene in water at 25°.

solubility data for benzene at 10° and 25° have been expressed as a percentage of the solubility of benzene in water at 25° .

Since a stable complex is ordinarily formed by an exothermic reaction which proceeds more readily at lower temperatures. complex formation often results in a negative temperature coefficient of solubility. Accordingly, the temperaturesolubility data for cyclohexene and benzene in 1 M silver nitrate suggest that stable complexes are present in these solutions. On the other hand, the data for the 1 M potassium nitrate solutions and for cyclohexane in 3 M perchloric acid indicate that the solubility change for the solutions which do not contain complexes is in the same direction as the temperature change. All of the 3 M perchloric acid solutions have a positive temperature coefficient. Since the temperature effect for solutions of cyclohexene and benzene in 3 M perchloric acid is evidently like that of electrolyte solutions where complexing is improbable rather than that of silver nitrate solutions, it seems unlikely that aqueous acid solutions of benzene and cyclohexene contain proton complexes unless these are present in very low concentration. Salting Action of Silver Ion. The salting action of silver ion apparently has not been investigated previously (13, 7). Since the radius of silver ion, 1.26Å, is slightly less than that of potassium ion, 1.33Å (12), and since both ions are singly charged, it would be expected that the salting-out

- 68 -

action of silver ion would be slightly greater than that of potassium ion, providing that eighteen-shell ions conform to the usual salting pattern. The experimental data on the solubility of cyclohexane in 1 M silver nitrate and 1 Mpotassium nitrate indicate that the salting action of silver ion is, in fact, roughly equal to that of potassium ion. This provides experimental justification for the explicit or implicit assumption by other investigators (8, 3) that silver nitrate and potassium nitrate have approximately equal salting action.

The experiments on the solubility of carbon tetrachloride in 1 <u>M</u> silver nitrate were of particular interest because of the possibility that they might reveal a weak coordination of silver ion with the unshared electron pairs of the chlorine atoms. The ability of silver salts to accelerate reactions involving alkyl halides (14) suggests the possibility that an intermediate complex of this type does exist. Carbon tetrachloride is salted out in 1 <u>M</u> silver nitrate at 25^o to a slightly smaller extent than in 1 <u>M</u> potassium nitrate, and the change of solubility with temperature of carbon tetrachloride in 1 <u>M</u> silver nitrate is very small. These facts indicate that if there is any complexing action, it is very limited in extent.

STRIPPING ANALYSIS

Related Procedures. Although stripping analysis is an original

- 69 -

procedure, its basic elements are well known. Volatile substances are sometimes removed by stripping (also called desorption) in industrial processes (15). Stripping procedures are occasionally employed in analysis; for example, hydrogen sulfide in aqueous solution may be volatilized by a current of air and then chemically absorbed (16). The most closely related procedure is apparently one developed by Clifford (17), who combined stripping with selective absorption in a method for determining the water dissolved in a nonpolar solvent. The water is stripped from the solution by a current of nitrogen, and the vapors are passed through calcium chloride, which removes all of the moisture but none of the organic vapor. The separation of a condensable vapor from a gas stream by freezing-out is also a familiar process, and one which may be very efficient (18).

<u>General Procedure</u> (Figure 1). The empty weighed trap is placed on the joint of the Drierite column, and a moisture guard tube is attached to the capillary tip of the trap. After the stripping apparatus has been flushed with a stream of nitrogen, the trap is submerged in the cooling-liquid contained in the Dewar flask, and the nitrogen stream is interrupted. The tip of the pipet containing the sample is held inside the addition tube by a rubber connection, and the sample is run into the gas washing bottle. The sample is stripped for a specified period of time by nitrogen flowing at a definite



Figure 1. Stripping Apparatus

- A. Gas washing bottle B. Sintered tube C. Addition tube D. Drierite column E. Trap F. Dewar flask

*

The nitrogen stream is stopped, the capillary tip of rate. the trap is sealed with a small flame, and the Dewar flask is The trap is lowered from the column and immediately removed. closed with a loosely fitting rubber stopper. The frost on the trap is washed off with water, and the trap is submerged in an acetone-bath for ten minutes. The stopper is tightened, and the trap is carefully wiped with a towel and reweighed. Stripping and Selective Sorption. The length of time required to strip a substance from its aqueous solution varies empirically with such factors as the original amount of substance, the volatility of the substance, the volume of solution, the rate of nitrogen flow, the size of the nitrogen bubbles, and the dimensions of the vessel. If the required time is not known, stripping should be continued for a reasonable interval after fresh condensate can no longer be detected. Confirmation that no appreciable additional condensate is forming is obtained if a new trap shows no gain in weight after a further period of stripping. After the minimum time of stripping has been determined for a given set of conditions, the time and conditions should be duplicated when analyzing other samples containing the same or somewhat smaller amounts of the substance.

In a typical run with benzene, after an initial period of fifteen to thirty minutes in which no condensate was visible, condensate was formed very rapidly. The rate of formation then gradually decreased, so that after about two more hours fresh condensate was no longer detectable. After a total stripping time of about four hours, the residual solution was stripped for one hour or more into a new trap, which did not gain in weight. Additional evidence that the amount of benzene in the residue was very small or negligible was obtained from a similar run in which there was practically complete recovery of the benzene in a known sample.

When the gas stream passes through the Drierite, a very efficient drying agent (18), the water is selectively removed. The Drierite was of the indicating variety, and the twentyinch column was usually recharged after about one-half of the Drierite had become hydrated. In the sections on benzene and cyclohexane, blank runs with pure water are described. The results indicate that no significant amount of water is carried into the trap. Since water vapor weighs less than nitrogen, a trace of water carried into the trap will decrease its final weight. The maximum possible decrease, about 0.4 mg., would occur if there were just enough water (0.6 mg.) to saturate all of the vapor space (27 ml.) in the trap.

To insure removal of any unflushed organic vapor, the Drierite was usually flushed with nitrogen for one-half hour prior to stripping a new sample. Before making a run which involved a change in the organic substance, the Drierite column was recharged. Then, in general, the Drierite was

- 73 -

conditioned; i.e., it was saturated with respect to the new substance by stripping a dilute solution of the substance through the Drierite. Evidence that no appreciable additional amount of organic material was retained in runs with conditioned Drierite was furnished by the results of the run with a known benzene sample and by the fact that good checks were obtained in duplicate runs with various saturated solutions. Condensing, Warming, and Weighing. The body of the trap was six to seven inches long, and the over-all length was eleven inches. The trap weight was about 44 g. The vapor space was 27 ml. in trap no. 1 and 24 ml. in trap no. 2. The trap was held firmly to the Drierite column by springs, but the joints were not lubricated. Liquid air was employed as the coolingliquid in the runs with carbon tetrachloride, which has a vapor pressure of 0.14 mm. at -70°C (19). In the runs with cyclohexane and benzene, which have somewhat lower vapor pressures, the Dewar flask contained a dry ice-acetone mixture at -78°C. The vapor pressure of benzene is 0.1 mm. at -58°C, the lowest temperature for which data is available (19). The temperature of the nitrogen leaving the trap is not known exactly, but a calculation based on an estimate of this temperature and the corresponding vapor pressure of benzene indicates that the amount of benzene carried beyond the trap was 1 to 2 mg.

During the warming period, the loosely fitting rubber

- 74 -

stopper acts as a filter to absorb organic vapor from the slowly escaping nitrogen, which must squeeze through at least one-half inch of an imperceptible passage between the rubber and the glass. After it is removed from the trap, the stopper generally starts to lose weight slowly by evaporation of the organic vapor which was absorbed during the warming and weighing periods. To prevent a possible loss in weight during the next run, the stopper was usually placed in an oven at 110° for a few minutes - but not longer lest it become hygroscopic. The stopper was used only if its weight was substantially constant for at least one hour; moreover, it was weighed shortly before it was inserted in the trap.

Normally the empty trap was left on the balance until the change in weight in twenty minutes was less than 0.1 mg. After the first one-half hour of the final weighing, the change in weight of the stoppered trap, if it had been carefully wiped to remove excess moisture, was less than 0.1 mg. per ten minutes. In general, the accepted weight was recorded after the trap had been on the balance for one hour. The average change in the humidity of the balance room during a run was only about 2%. It has been suggested that the effect of humidity changes be minimized by using an appropriate counterpoise exposed to the same influences as the trap.

MATERIALS

The inorganic chemicals were of reagent or C.P. grade.

- 75 -

The salt solutions were made up by weight, and the acid solutions were standardized with 1 M sodium hydroxide. Carbon tetrachloride and cyclohexene were purified by the methods described previously (pp. 8-9). The benzene, originally of reagent grade, was recrystallized twice by freezing and then distilled. The final product froze very sharply at 5.42°.

The freezing point of cyclohexane, 6.55° (20), is very sensitive to impurities (21). The best commercial grades of cyclohexane are likely to contain benzene and methyl cyclopentane impurities (22). In the experiments with 3 M sulfuric acid and 3 M sodium perchlorate (runs 32 and 33) and in the early experiments with water and 3 M perchloric acid (runs 26 through 31), the cyclohexane was Eastman Kodak Co. best grade material, m.p. 3-5°. Prior to runs 27 through 31, this cyclohexane was extracted with 3 M perchloric acid. In experiments subsequent to run 33, the cyclohexane was recrystallized three times by freezing, extracted twice with 3 M perchloric acid, dried with potassium carbonate, and distilled. The freezing point of the final product was 6.4-6.3°, which corresponds to less than 0.1 mole per cent of impurities. It will be shown later (Table VIII) that the purification resulted in a decrease in solubility.

STRIPPING ANALYSES. I. BENZENE

<u>Procedure and Data</u>. The saturated solution was prepared in a 125-ml. long-necked flask held in a constant-temperature

- 76 -

The benzene, 10 to 15 ml. in the neck of the water-bath. flask, was dispersed very finely in the aqueous phase for thirty minutes by means of a downflow stirrer (23). The liguid was transferred to a 125-ml. centrifuge bottle and centrifuged for five minutes at 1700 r.p.m. If the solution was saturated at 25° and room temperature was below 25°, the benzene was kept in solution during the centrifuging period by slightly warming the centrifuge bottle just before it was filled. A volume of sample containing about 0.1 g. of benzene was taken for analysis. To prevent benzene from contaminating the sample, a little air was blown through the pipet as it was lowered through the benzene layer. The solution was stripped in a 125-ml. gas washing bottle according to the general procedure, usually for four hours at about 28 ml. per minute.

The stripping analyses are outlined in Table V. In most of the runs with water, sodium chloride and sodium thiosulfate were added so that the stripping conditions would be very similar to those of the runs with silver nitrate. Calculation of the solubility involved a correction based upon the known sample. The values obtained in duplicate runs indicated that the precision of a result was about $\frac{1}{2}\%$. A water blank was run after run 44, when only eight inches of fresh Drierite remained in the column. Nitrogen was passed through 100 ml. of water for 4.0 hours at 29 ml. per minute into trap no. 2,

- 77 -

Stripping Analyses. The Solubility of Benzene in Water and in Aqueous Solutions of Acids and Salts

Run	Aqueous phase	Satn. temp. C.	Sample volume ml.	Strpg. time hr.	N ₂ rate ml/mir	Trap 1 no.	Trap gain mg.	Ben- zene g./1.
22	Water	22	200.0	6.0	24	1	318.5	1.67 ^a
35	Water	25.0	60.0 ^b	4.0	25	1	97.8 [°]	1.73
59	Water	25.0	60.0 ^b	4.0	27	2	98.0	1.73
44	Water	10.0	65.0 ^b	4.0	28	2	105.0	1.70
60	Water	10.0	60.0 ^b	4.0	30	1	96.7	1.72
24	3.01 HClO ₄	22	100.0	3.6	29	1	194.2	2.00 ^d
57	3.00M HC104	25.0	50.0	3.5	30	2	100.1 ^e	2.12
41	3.00 <u>M</u> HC104	10.0	50.0	3.0	28	2	81.7 ¹	1.75
42	3.00M HC104	10.0	50.0	3.0	26	2	75.8 ^g	1.78
36	3.01 H ₂ SO ₄	25.0	100.0	4.0	27	1	74.7	0.81
37	2.90 Naclo ₄	25.0	100.0	5.8	81	2	73.4	0.79
58	1.00M KNO3	25.0	75.0	4.0	27	2	97.2 ^h	1.37
43	1.00M KNO3	10.0	75.0	4.0	28	1	92.7	1.32

a Approx. value; exploratory run. Sample prepared in a 300-ml. flask and stripped in a 250-ml. gas washing bottle. Trap gained 318.5 mg. in 6.0 hr.; then stripped for 3.0 hr. into new trap, which gained 4.7 mg. (solubility calcd. from combined b gain). Also added 10 ml. of sat. NaCl and 20 ml. of sat. Na2S203.

Then stripped for 4.0 hr. into a new trap, which lost 1.4 mg. d Approximate value; exploratory run.

e Then made alkaline with NaOH and stripped for 1.0 hr. into a new trap, which lost 1.0 mg.

f Then stripped for 2.0 hr. into a new trap, which lost 1.2 mg. g Then stripped for 1.2 hr. at 33 ml./min. into new trap, which

gained 3.7 mg. (solubility calculated from combined gain).

h Then stripped for 1.0 hr. into a new trap, which lost 0.2 mg.

which decreased in weight by 1.2 mg.

Run with Known Sample. About 1.5 g. of benzene was weighed to 0.1 mg. in a small glass-stoppered vial and was then frozen by placing the vial in dry ice. The vial was unstoppered and quickly transferred to a 2-liter glass-stoppered bottle containing a known weight of water. The vapor space in the stoppered bottle was 25 ml. The benzene was completely dissolved in the course of two hours of vigorous shaking. The solution was cooled to 10°, and a 100.0-ml. sample was taken for stripping. The small amount (about 5 mg.) of benzene in the 25-ml. vapor space of the bottle was taken into account in calculating the amount (66.5 mg.) of benzene in the sample. The sample was added to 4 g. of sodium chloride and 8 g. of sodium thiosulfate, and the solution was stripped into trap no. 2 for 3.0 hours at 29 ml. per minute. The gain in weight of the trap was 60.7 mg. An additional 1.0 hours of stripping into a new trap resulted in a loss in weight of 0.5 mg.

<u>Calculations</u>. Although the gain in weight of the trap was 5.8 mg. less than the amount of benzene in the known sample, calculations indicate that the trap contained all but about 1.5 mg. of the benzene. The apparently unrecovered remaining 4.3 mg. was actually the difference between the final weight of nitrogen in the trap and the original weight of air. When stripping was begun, the moist air in the trap was

- 79 -

replaced by dry nitrogen. This caused a loss of 0.7 mg. in the weight of the trap (no. 2, 24 ml. vapor space). At the end of stripping, about 3.6 mg. of nitrogen was displaced from the trap by benzene vapor. Since the benzene frozen in the upper regions of the trap slowly drained to the bottom during the warming-up period, it could readily saturate practically all of the vapor space in the trap. Vaporization of benzene into the upper neck was indicated by the gain in weight of the stopper during the weighing period. The vapor pressure of the benzene at room temperature, 26°, was about 100 mm. Accordingly, it displaced the nitrogen from about 100/750 = 2/15 of the vapor space in the trap. This was 3.2 ml. of nitrogen, or 3.6 mg. The 1.5 mg. of unrecovered benzene may have been left in the solution in the gas washing bottle or may have been carried beyond the trap by the nitrogen stream.

The weight of benzene in the various samples was obtained from the trap gain by adding 5.8 mg., in runs using trap no. 2, or 6.3 mg., in runs using trap no. 1 (27 ml.). In runs 22 and 42, in addition to the above correction, 4.9 mg. and 3.7 mg., respectively, were added to the small amounts of benzene recovered by additional stripping. These amounts were insufficient to saturate the space in the trap, and the correction applied was of the type discussed in the calculations for cyclohexane.

STRIPPING ANALYSES. II. CARBON TETRACHLORIDE

The following procedure was employed in all runs except run 55. The saturated solution was prepared in a 500-ml. flask fitted with a mercury-sealed upflow stirrer (23) and held in a thermostat at 25.0° . A mixture of 25 ml. of carbon tetrachloride and 410 ml. of the aqueous solution was stirred for 0.75 hour. After a settling period of at least 0.75 hour, two 100.0-ml. samples were taken from the clear aqueous phase. Since there was no addition tube on the gas washing bottle in run 19 and the preceding runs, the samples for these runs were transferred with a minimum loss of organic vapor by inserting the pipet in a one-hole cork which fitted loosely in the neck of the gas washing bottle.

The solution was stripped for 4.0 hours at about 24 ml. per minute into trap no. 1. Following this, the nitrogen stream was decreased to a very low rate, and the Dewar flask was lowered until only the lowest bulb of the trap remained submerged in the liquid air. After about one-half hour, the nitrogen stream was stopped completely, the capillary tip of the trap was sealed, and the Dewar flask was removed. The trap was lowered from the column and immediately closed with a loosely fitting rubber stopper. After about two minutes, when the carbon tetrachloride was melted and the exterior frost was gone, the stopper was tightened, and the trap was submerged in an acetone-bath for ten minutes. The trap was then wiped with a towel and weighed. The stopper and the empty trap had been weighed previously and allowed to stand until their weight varied less than about 1 mg. per hour.

A modified procedure was followed in run 55 in order to avoid the possibility of low results due to the slow reaction of carbon tetrachloride with silver ion to form silver chloride or due to the presence of a carbon tetrachloride-silver ion complex that might hinder stripping. The saturated solution was prepared in a 250-ml. centrifuge bottle from 40 ml. of carbon tetrachloride and 140 ml. of 1 M silver nitrate. The liquid was stirred vigorously for thirty minutes and was forthwith centrifuged for three minutes at 1700 r.p.m. In the next few minutes, a 100.0-ml. sample of the clear aqueous phase was placed in the gas washing bottle, and 30 ml. of saturated sodium chloride solution was added to precipitate the silver ion as silver chloride. Most of the precipitate was dissolved thereafter by the addition of 60 ml. of saturated sodium thiosulfate solution.

The main runs are presented in Table VI. These runs were preceded by thirteen runs in which a satisfactory procedure for stripping analysis was being developed. In the runs shown in Table VI, the warming and weighing technique differed somewhat from that described in the section on stripping analysis. Because of this and because the solubility was calculated on the basis of the run with a known sample of benzene, the results are probably slightly less reliable than those of the runs with benzene.

Table VI

Stripping Analyses. The Solubility at 25° of Carbon Tetrachloride in Water and in Aqueous Solutions

Run	Aqueous phase	Prepn. Stirred, hr.	of soln. Settled, hr.	Trap gain, mg.	0014, g./l.
15	Water	0.75	1.25	146.2	0.73
14	3.00 M HC104	.75	0.75	180.2	.93
16	2.98 <u>M</u> HC104	.75	1.25	179.9	.93
18	2.96 <u>M</u> H ₂ 80 ₄	.75	1.25	71.6	.39
19	2.90 \underline{M} NaClO ₄	.75	1.75	52.7	.30
17	1.00 \underline{M} AgNO ₃	.75	1.25	136.5	.71
55	1.00 \underline{M} AgNO ₃	.50		68 .7	.75 ^a
56	1.00 M KNO3	.75	1.25	127.7	.67

^a Since this value was obtained by a special procedure (p. 82), the value of Table I was taken from run 17.

STRIPPING ANALYSES. III. CYCLOHEXANE

<u>Sulfuric Acid and Salt Solutions</u>. The saturated solution was prepared in a 300-ml. long-necked flask held in a water-bath at 25[°]. The cyclohexane, 12 to 15 ml. in the neck of the flask, was dispersed very finely in the aqueous phase for thirty minutes by means of a downflow stirrer. The aqueous solution and cyclohexane were divided between two 200-ml. centrifuge bottles and were centrifuged for ten minutes at 1700 r.p.m. A 100-ml. sample was taken from each bottle. To prevent cyclohexane from contaminating the sample, a little air was blown through the pipet as it was lowered through the cyclohexane layer. The 200 ml. of solution was stripped by the general procedure in a 250-ml. gas washing bottle for 3.0 hours at about 28 ml. per minute.

The analytical data are given in Table VII. Special care was taken to attain equilibrium in the initial weighings and to employ a uniform technique at all other times when handling or weighing the trap or stopper. Nevertheless, because of the extremely small weight change in these runs, the results are regarded as semi-quantitative in significance. They indicate that the salting-out effect is in the order: 3 M sodium perchlorate > 3 M sulfuric acid > 1 M potassium nitrate, which is roughly equal to 1 M silver nitrate.

<u>Calculations</u>. An approximate value for the weight of cyclohexane in the sample was obtained from the gain in weight of the trap in the following manner. First, 0.7 or 0.8 mg. was added to correct for the replacement of air by nitrogen. In general, the cyclohexane in the trap was completely vaporized during warming, but the amount of vapor was not sufficient to

- 84 -

- 85 -

Table VII

Stripping Analyses. The Solubility at 25° of Cyclohexane in Some Aqueous Solutions

Run	Aqueous phase	N2 rate, ml./min.	Trap no.	Trap gain, ^{mg} .	Cyclo- hexane, g./l.
32	3.01 \underline{M} H ₂ SO ₄	28	1	1.6	$0.026 \pm .015$
33	2.90 <u>M</u> NaClO ₄	26	1	0.8	$.020 \pm .015$
51	1.00 <u>M</u> $AgNO_3$	29	1	4.6	$.048 \pm .010$
75	1.00 \underline{M} AgNO ₃	30	2	5.7	.056±.010
72	1.00 <u>M</u> KNO3	27	2	8.2	.070 ^a
73	1.00 <u>M</u> KNO3	27	2	5.2	$.052 \pm .010$
74	1.00 M KNO3	27	2	4.5	$.046 \pm .010$

^a This value was discarded because it disagreed with the values of runs 73 and 74 and because it was higher than the value for water (Table I).

saturate the available space. Since the ratio of the molecular weights is 28 to 84, the displaced nitrogen was one-third as heavy as the cyclohexane. Hence the net gain in weight was the weight of cyclohexane in the trap minus one-third of this weight, or the weight of cyclohexane in the trap was one and one-half times the gain in weight of the trap (previously corrected for the replacement of air by nitrogen). Finally, 1.5 mg. was added to correct for unrecovered cyclohexane. This correction was taken to be the same as that determined in the known sample of benzene, because the vapor pressures of cyclohexane and benzene were approximately equal. In run 72, the amount of cyclohexane in the trap was more than sufficient to saturate the available vapor space, and the solubility was calculated in the same way as in the runs with benzene.

<u>Water and 3 M Perchloric Acid</u>. The data are presented in Table VIII in the form of a comparison between corresponding experiments with water and 3 <u>M</u> perchloric acid. The basic procedure was the one followed in the previously described cyclohexane experiments, but it was modified in most cases as noted in the table. The runs are divided on the basis of the purity of the cyclohexane. The effect of purification was to lower the solubility in both water and perchloric acid without greatly altering the comparison ratio. In a blank run with water, the trap decreased in weight by 0.5 mg.; in three blank runs with 3 <u>M</u> perchloric acid, the trap decreased in weight by 1.4 mg., 0.6 mg., and 1.3 mg.

In runs with neutral solutions of purified cyclohexane, the residues from sampling and stripping were usually tested for the presence of peroxide with ferrous thiocyanate solution. If peroxide was present, its concentration was no greater than 0.0001 <u>M</u>, the concentration of the tertiary butyl hydroperoxide control. In the experiments with precautions against peroxide formation, the solution materials were

- 86 -

Table VIII

Stripping Analyses. Comparison of the Solubility at 25° of Cyclohexane in Water and in 3 M Perchloric Acid

Water 2.99±0.01 M Perchloric Acid

Tr	ap gai	n,	Tr	ap gain	a, **			
Run	mg.	Notes	Run	mg.	14	otes		
		Eastman Kodak Co.	Cyclo	hexane	, M.P. 3	- 5 ⁰		
26	6.7	New Drierite,	27	8.4				
28	8.0	unconditioned	29	9.4				
30	7.9		31	9.1				
		Purified Cycl	ohexan	e, M.P	• 6.4 ⁰			
45	4.4 ^a	Perox. Precautions; no peroxide test						
46	6.2 ^b	Perox. precautions: no peroxide found	47	8.7b	Proced.	like	run	46
54	7.1	Proced. like run 46 but peroxide found						
70	6.3 ^b	Proced. like run 46; no peroxide found	71	8.4 ^b	Proced.	like	run	46
49	6.4	Added NaClO4	48	7.6	Neutral	ized	(NaOI	I)
52	7.0	Stirred 2 hr; setld.	50	6.6 ^a	Proced.	like	run	52
		z nr.; perox. 10und	53	7.2	proced.	like	run	52

a The absence of cyclohexane layer was noticed after centrifuging; experiment continued, but low result anticipated.

^b This was one of the values taken to calculate the solubility for Table I.

previously boiled and cooled under nitrogen and were shielded from light during stirring and stripping. Peroxide formed during the stirring period would be expected to alter the properties of the aqueous phase so that more cyclohexane would dissolve. Formation of peroxide during stripping would tend to decrease the amount of organic material volatilized by the nitrogen stream.

In one pair of runs (48 and 49), the solutions were practically identical during stripping. A slight excess of sodium hydroxide solution was added to the perchloric acid sample in run 48, and an equivalent amount of a solution of sodium perchlorate and sodium hydroxide was added to the water sample in run 49. Another set of runs (50, 52, and 53) was made to investigate the effect of a fourfold increase in stirring time plus a one-half hour period of settling prior to centrifuging. An over-all inspection of the results of corresponding experiments in Table VIII strongly indicates that cyclohexane is more soluble in 3 <u>M</u> perchloric acid than in water.

APPROXIMATE SOLUBILITY OF CYCLOHEXENE IN WATER

Decxygenated water (90 ml.) and cyclohexene (10 ml.) freshly distilled from sodium were vigorously stirred at 25^o for five minutes in a 100-ml. long-necked flask wrapped in a black cloth. The liquid was quickly transferred to a 125-ml.

- 88 -

centrifuge bottle and centrifuged for a few minutes. Then, without delay, a 50-ml. sample of the aqueous phase was analyzed by a bromination procedure (24). The slowly drifting end-point indicated that peroxide was present. A correction was made for the error due to peroxide (1) by calculating the solubility from the total volume of thiosulfate required to reach the initial end-point and to decolorize the solution after one-half hour of standing, at which time the end-point drift was extremely slow. The value of the solubility obtained in duplicate experiments was 0.25 ± 0.01 grams per liter. Further experiments on the solubility of cyclohexene in aqueous solutions were not undertaken because of the necessity of developing special techniques to avoid errors due to peroxide formation.

CLOUDINESS METHOD

Except for cyclohexene in 1 M silver nitrate, the following procedure was applied to all of the sixteen combinations of Table III (p. 67). A saturated solution was prepared by stirring the components at 60-70°. After a short settling period at 70-75°, a sample of the clear aqueous phase was taken with a warmed 15-ml. pipet. The sample was run into a warmed 10-ml. mixing cylinder until it contained sufficient liquid to leave almost no vapor space when the stopper was inserted. The cylinder was kept stoppered throughout the subsequent procedure.

A positive temperature coefficient of solubility was indicated if the liquid became cloudy when the cylinder was placed in cold water. The temperature effect was reversible, since the liquid alternated from clear when heated to cloudy when cooled. The liquid was heated until it became clear and then allowed to cool slowly by loss of heat to the atmosphere. After a time, a cloudy zone appeared at the bottom of the liquid and slowly expanded upward until the entire liquid was cloudy. Much later, a clear zone originated at the bottom and gradually progressed upward until all of the liquid was clear. When the liquid was momentarily shaken, small liquid droplets descended into the solution and then rose back to the surface.

The following procedure was applied to the four 1 Msilver nitrate solutions. Saturated solutions were prepared at about 5°. A clear aqueous phase sample was pipetted into a cooled 10-ml. mixing cylinder, which was stoppered when full. A negative temperature coefficient in the vicinity of room temperature was indicated if the liquid in the cylinder turned cloudy when heated. The temperature effect was reversible. When the ice-cold clear solution was allowed to stand at room temperature, a cloudy zone appeared at the top of the liquid and slowly expanded downward until the entire liquid was cloudy. Much later, the cloudiness slowly

- 90 -

contracted upward until the entire liquid was clear, with droplets of a second phase visible at the surface.

Experiments in addition to those of Table III indicated that the temperature coefficient of solubility is negative for benzene in 0.5 M silver nitrate and positive for benzene in 1 M perchloric acid, 3 M sulfuric acid, 3 M potassium chloride, and 3 M sodium perchlorate. The change of solubility with temperature of carbon tetrachloride in 1 M silver nitrate is very small, since only a very slight cloudiness developed upon altering the temperature of solutions saturated at either 5° or 65°. The sign of the temperature coefficient was not indicated because the cloudiness might have been due to dispersed silver chloride. For a solution of cyclohexane in 1 M silver nitrate saturated at either 5° or 65°, there was no appreciable cloudiness when the temperature was altered. The amount of dissolved cyclohexane was so small, however, that the separation of a second liquid phase might not have been detected, and all that can be stated is that the change of solubility with temperature is small.

COÖRDINATION OF SILVER ION WITH BENZENE

Introduction. In their investigation of the coordination of silver ion with unsaturated compounds, Winstein and Lucas (8) concluded that the ability of phenol to form complexes with silver ion in aqueous solution probably resides in the benzene

- 91 -

ring. Recently, Andrews and Keefer (3) measured spectrophotometrically the solubilities at 25° of benzene and other aromatic hydrocarbons in aqueous solutions of silver nitrate and potassium nitrate of total ionic strength 1 <u>M</u>. The data were interpreted on the assumption that each hydrocarbon formed a monosilver and a disilver complex. The reported equilibrium constants for benzene, calculated as aqueous phase concentration ratios, were 2.41 and 0.212 for the first and second argentation reactions, respectively.

Evidence that complex formation takes place in aqueous silver nitrate solutions containing benzene has been presented previously (p. 65). Since benzene is salted out in 1 <u>M</u> potassium nitrate and cyclohexane is salted out in 1 <u>M</u> silver nitrate (Table II), the coördination apparently involves silver ion and the unsaturation of the benzene ring. It has been postulated that the silver ion is centrally located above the plane of the ring (8) in a position where it can form bonds involving the π electrons of the ring (3).

In the experiments that follow, stripping analysis has been employed to determine the solubility of benzene at 25° in aqueous silver nitrate solutions up to 4 <u>M</u> and the solubility at 10° in 0.5 <u>M</u> and 1 <u>M</u> silver nitrate. These data, together with data for the solubility of benzene in water at 10° and 25° (Table I), have been plotted in Figure 2. Since the curves intersect at a point very close to the y-axis, benzene



Silver Nitrate, Molarity

3.00

4.00

2.00

Figure 2. Solubility of Benzene in Aqueous Solutions of Silver Nitrate

1.00

2.00

0

0

- 93 -

has exactly the same solubility at 10° as at 25° in the very dilute silver nitrate solution at this point. In this case, the increase in solubility with decreasing temperature caused by complex formation has been compensated by the decrease in solubility with decreasing temperature characteristic of solutions of benzene in water.

The solubility data have been interpreted on the assumption that a one-to-one silver-benzene ion is the only complex species present. Equilibrium constants and heats of complex formation have been calculated for the heterogeneous reaction of aqueous silver ion with liquid benzene and for the homogeneous reaction of aqueous silver ion with benzene dissolved in the aqueous phase.

<u>Procedure and Data</u>. To facilitate stripping, the benzene was liberated from the silver-benzene complex ion by a reaction which produced the more stable silver-thiosulfate complex ion, $Ag(S_2O_3)_2$. Attempts to complex silver ion by direct addition of thiosulfate ion are accompanied by the formation of a precipitate of silver sulfide (25). The presence of a precipitate was considered undesirable because stripping might be hindered by the adsorption of benzene on the surface of the solid. In the procedure adopted, the silver ion was first completely precipitated by sodium chloride solution, and the silver chloride was then completely dissolved by the addition of sodium thiosulfate solution. The thiosulfate solution was

- 94 -

made very slightly alkaline with sodium hydroxide, in order to avoid decomposition of thiosulfate by the acidic silver nitrate solution.

With the following exceptions, the procedure in all but the two exploratory experiments was the same as the procedure for benzene described previously. The saturated solution was prepared in a 40 to 60 ml. long-necked flask. In general, the silver ion concentration was determined from a portion of the solution by titrating it against an aliquot portion of standard sodium chloride solution in the presence of fluorescein indicator. The solutions saturated at 25° were centrifuged in the laboratory and were normally below this temperature when sampled; the solutions saturated at 10° were centrifuged in a cold room at 5° .

After diluting the sample in the gas washing bottle to 60 ml. by addition of water, 10 ml. of saturated sodium chloride solution was added. The Dewar flask was temporarily lowered, and the solution in the gas washing bottle was swirled several times by moving the stripping apparatus in a circular path. Following this, 20 ml. of slightly alkaline saturated sodium thiosulfate solution was added, and the solution was again swirled until all or almost all of the silver chloride was dissolved.

A blank was run on a solution prepared from 20 ml. of 1 M silver nitrate, 40 ml. of water, 10 ml. of saturated sodium

- 95 -

chloride solution, and 20 ml. of slightly alkaline saturated sodium thiosulfate solution. Nitrogen was passed through the solution for 4.0 hours at 29 ml. per minute into trap no. 2, which decreased in weight by 0.8 mg. The stripping analyses are outlined in Table IX. The solubility was calculated in the same way as in the previous benzene runs. The values obtained in duplicate runs indicated that the precision of a result was about 1%.

Equilibrium Constants. The symbols to be employed are defined as follows:

- Bo liquid benzene (organic phase) in equilibrium with aqueous silver nitrate
- Ba uncomplexed benzene in aqueous silver nitrate Bw benzene in the aqueous phase of water saturated with benzene

Ag⁺ uncomplexed silver ion in aqueous silver nitrate BAg⁺ silver-benzene complex ion in aqueous silver nitrate

<u>a</u> activity (used with a subscript indicating the substance)

<u>f</u> molar activity coefficient (used with a subscript indicating the substance)

[] molarity of the substance enclosed

K Thermodynamic equilibrium constant of the

heterogeneous reaction: $Ag^{+} + Bo = BAg^{+}$

- 96 -

- 97 -

Table IX

Stripping Analyses. The Solubility of Benzene in Aqueous Silver Nitrate Solutions

Run	Total Ag	Satn. temp. °C.	Sample volume ml.	Strpg. time hr.	N2 rate ml./min.	Trap no.	Trap gain mg.	Ben- zene g./l.
65	0.248	25.0	44.96	4.0	29	1	106.5	2.51
34	0.495	25	100.0	3.0	29	1	283.5	3.30 ^a
38	0.499	25.0	30.00	4.0	25	2	95.2	3.37
23	1.00	23	100.0	3.0	27	l	486.0	4.92 ^b
64	0.993	25.0 [°]	25.00	4.0	29	2	148.4	6.17 ^d
66	0.997	25.0 ⁰	15.00	4.0	29	2	68.5	4.95
67	0.987	25.0	15.00	4.0	27	2	69.5	5.02
68	2.00	25.0	10.02	4.0	29	1	75.9	8.20
69	4.00	25.0	10.02	3.5	31	2	133.2	13.87
39	0.497	10.0	19.96	4.0	27	1	71.4	3.89
62	0.534	10.0	25.00	4.0	28	2	92.3	3.92
40	0.993	10.0	15.00	4.0	28	1	79.6	5.73
63	0.993	10.0	19.96	3.7	29	1	108.4	5.75

^a Approximate value; exploratory run. Sample stripped without added electrolyte for 3 hr. (trap gained 283.5 mg.); then added excess NaCl to residue and stripped for 42 hr. into emptied trap, which gained 33.9 mg. (solubility calculated from combined gain).

- b Approximate value; exploratory run. No electrolyte was added to the sample. c The solution was at 26° when sampled.

d This value was discarded because it disagreed not only with the values of runs 66 and 67 but also with the values of runs 40 and 63 (since solubility decreases with increase in temp.)

 $[BAg^+]/[Ag^+]$, evaluated equilibrium constant of the heterogeneous reaction: $Ag^+ + Bo = BAg^+$ thermodynamic equilibrium constant of the homogeneous reaction: $Ag^+ + Ba = BAg^+$ $[BAg^+]/[Ag^+][Bw] = K_o/[Bw]$, evaluated equilibrium

constant of the homogeneous reaction: $Ag^{+} + Ba = BAg^{+}$ Since the equilibrium system involves benzene in two phases, there is an equilibrium constant for the reaction of aqueous silver ion with benzene in the organic phase as well as in the aqueous phase. The respective thermodynamic equilibrium constants are:

$$\underline{\mathbf{K}}^{*} = \frac{\underline{\mathbf{a}}_{BAg^{+}}}{\underline{\mathbf{a}}_{Ag^{+}}} = \frac{[BAg^{+}]\underline{\mathbf{f}}_{BAg^{+}}}{[Ag^{+}]\underline{\mathbf{f}}_{Ag^{+}}}$$
(1)

$$\frac{\mathbf{K}^{*}}{\mathbf{a}} = \frac{\frac{a}{\mathbf{B}\mathbf{A}\mathbf{g}^{+}}}{\frac{a}{\mathbf{A}\mathbf{g}^{+}}\frac{a}{\mathbf{B}\mathbf{a}}} = \frac{\left(\mathbf{B}\mathbf{A}\mathbf{g}^{+}\right)\mathbf{f}}{\left(\mathbf{A}\mathbf{g}^{+}\right)\mathbf{f}}\frac{a}{\mathbf{A}\mathbf{g}^{+}}\frac{a}{\mathbf{B}\mathbf{a}}}$$
(2)

To evaluate the equilibrium constants with the available data, certain approximations are necessary. It is assumed that the activity coefficient of silver ion, f_{Ag} , is approximately equal to the activity coefficient of silver-benzene complex ion, f_{BAg} . This assumption is made because the

K_

K*

Ka

activity coefficients of two similarly charged ions in a solution of some particular ionic strength are approximately equal, especially if the solution is dilute (26); and because information as to the activity coefficient of the silverbenzene complex ion is not available.

Since the mole fraction of water in the organic phase is not over 0.002 (27), and since the activity of pure benzene is taken as unity, $\underline{a} = 1$ to a very good approximation. The activity of the aqueous benzene is essentially the same in all of the silver nitrate solutions, since these solutions are in equilibrium with practically pure benzene. This constant activity is also the activity of benzene in the aqueous phase of pure water saturated with benzene. Since a very dilute solution of a liquid dissolved in another liquid with which it is only partially miscible obeys Henry's law guite well (28), the activity of the aqueous benzene, \underline{a} , is approximately Ea equal to the molarity of benzene in the aqueous phase of water saturated with benzene, [Bw], for a standard state chosen so that activity becomes equal to molarity as the solution approaches infinite dilution (29). Substitution of $\underline{a}_{Bo} = 1 \text{ and } \underline{f}_{Ag'} = \underline{f}_{BAg'}$ in equation 1 reduces it to [BAg']/[Ag'], which defines \underline{K}_{0} ; and substitution of $\underline{\alpha}_{Ba} = [Bw]$ and $\underline{f}_{Ag^{\dagger}} = \underline{f}_{BAg^{\dagger}}$ in equation 2 reduces it to [BAg*]/[Ag*][Bw], which defines $\frac{K}{a}$. Thus, $\frac{K}{b}$ is approximately equal to $\frac{K}{b}$, and $\frac{K}{a}$ is approximately equal to \underline{K}^* .

- 99 -

The values of \underline{K}_0 and \underline{K}_a are shown in Table X. The aqueous phase molar concentrations of total silver ion, $[Ag^++BAg^+]$, and of total benzene, $[Ba + BAg^+]$, are based upon the values given in Table IX. In two instances, a small linear extrapolation was made to determine the concentration of total benzene at the concentration of total silver ion in Table X. The aqueous concentrations of uncomplexed benzene were calculated by means of the logarithm of solubility versus electrolyte concentration relationship (6, 7) from the solubility of

Table X

Equilibrium Constants for the Coördination of Silver Ion with Benzene

[Ag ⁺ + BAg ⁺]	[Ba+ BAg ⁺]	[Ba], calcd.	(BAg ⁺]	[Ag ⁺]	K	K
			25 ⁰		<i>v</i>	CL.
0.248	0.0322	0.0209	0.0113	0.237	0.0476	2.15
0.499	.0431	.0197	.0234	0.476	.0492	2.22
0.997	.0640	.0176	.0464	0.951	•0487	2.20
2.00	.1050	.0139	.0911	1.91	.0476	2.15
4.00	.1776	.0087	.1689	3.83	.0441	1.99
			10 ⁰			
0.497	0.0490	0.0192	0.0298	0.467	0.0638	2.91
0.993	.0735	.0169	.0566	0.936	•0604	2.76
- 101 benzene in water and in 1 <u>M</u> potassium nitrate (Table I) on

the assumption that the concentration of uncomplexed benzene is the same in equimolar solutions of potassium nitrate and silver nitrate. Approximately equal concentration in 1 <u>M</u> potassium nitrate and 1 <u>M</u> silver nitrate is to be expected because it was previously shown that this relationship holds in the case of cyclohexane (p. 84) and because relative salting action is almost independent of the nonpolar substance salted (9, 7). At higher concentrations of silver nitrate, a moderate error in the calculated value of the concentration of uncomplexed benzene would have very little effect on the value of the equilibrium constant, since this concentration is subtracted from a much larger concentration in making the calculation.

The relatively small variation in the value of the equilibrium constants over a wide range of silver ion concentrations suggests that the principal reaction involved is the formation of a one-to-one complex. However, a minor reaction yielding a disilver complex may occur without being apparent because of approximations made in calculating the equilibrium constants. Moreover, since the activity of benzene in both phases is essentially constant, the data would not reveal the existence of a reaction yielding a monosilver-polybenzene complex. <u>Heat of Complex Formation</u>. Table XI shows the values of the heat of complex formation, $\Delta \underline{H}$, for the heterogeneous and - 102 -

homogeneous reactions. $\Delta \underline{H}$, assumed to be constant over the small temperature range, was calculated from the respective \underline{K} and \underline{K} values by means of the integrated form of the equation $\underline{dln}\underline{K}/\underline{dT} = \Delta \underline{H}/\underline{RT}^2$. The heat of formation of the silver-benzene complex is roughly one-half of the heat effect, 6 kcal., attending the formation of one mole of silver-cyclohexene complex in an aqueous solution in equilibrium with a 1 M solution of cyclohexene in carbon tetrachloride (8).

Table XI

Heat of Complex Formation for the Coördination of Silver Ion with Benzene

Heterogeneous Reaction: $Ag^+ + Bo = BAg^+$

[AgN0₃] $K_{0,10}^{/K}$, 25° -AH, kcal. 0.50 1.297 2.90 1.00 1.240 2.40

Homogeneous Reaction: $Ag^{+} + Ba = BAg^{+}$

[AgNO₃] $\frac{K}{a,10^{\circ}/K}a,25^{\circ}$ -AH, kcal. 0.50 1.312 3.03 1.00 1.255 2.53

- 103 -

REFERENCES

- 1. Part I of this thesis
- 2. A. Seidell, "Solubilities of Organic Compounds," third ed., Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1941, p. 368
- 3. L. J. Andrews and R. M. Keefer, <u>J. Am. Chem. Soc.</u>, <u>71</u>, 3644 (1949)
- 4. P. M. Gross and J. H. Saylor, <u>J. Am. Chem. Soc.</u>, <u>53</u>, 1744 (1931)
- 5. P. M. Gross, J. Am. Chem. Soc., 51, 2362 (1929)
- 6. P. M. Gross, Chem. Rev., 13, 91 (1933)
- 7. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 51-59, 397-400, 565
- 8. S. Winstein and H. J. Lucas, <u>J. Am. Chem. Soc.</u>, <u>60</u>, 836 (1938)
- 9. S. Glasstone, "Textbook of Physical Chemistry," second ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, pp. 699, 729
- 10. G. Åkerlöf, J. Am. Chem. Soc., 57, 1196 (1935)
- 11. J. O'M. Bockris and H. Egan, <u>Trans. Faraday Soc.</u>, <u>44</u>, 151 (1948)
- 12. L. Pauling, "The Nature of the Chemical Bond," second ed., Cornell University Press, Ithica, N. Y., 1940, p. 346
- 13. M. Randall and C. F. Failey, <u>Chem. Rev.</u>, <u>4</u>, 271, 285, 291 (1927)
- 14. L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 138
- 15. "Rogers' Industrial Chemistry," edited by C. C. Furnas, sixth ed., Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1942, p. 66
- 16. E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1946, pp. 422-425

- 104 -

REFERENCES

17.	C. W. Clifford, Ind. Eng. Chem., 13, 628, 631 (1921)
18.	A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, pp. 5, 13-16
19.	N. A. Lange, "Handbook of Chemistry," sixth ed., Handbook Publishers, Inc., Sandusky, Ohio, 1946, p. 1399, 1407
20.	A. F. Forziati, A. R. Glasgow, C. B. Willingham, and F. D. Rossinni, <u>J. Research Nat. Bureau Standards</u> , <u>36</u> , 129 (1946)
21.	W. F. Seyer, M. M. Wright, and R. C. Bell, <u>Ind. Eng. Chem.</u> , 31, 759-60 (1939)
22.	E. L. Eckfeldt and W. W. Lucasse, <u>J. Phys. Chem.</u> , <u>47</u> , 164 (1943)
23.	J. A. Patterson, Ind. Eng. Chem., Anal. Ed., 6, 171 (1934)
24.	H. J. Lucas and D. Pressman, <u>Ind. Eng. Chem., Anal. Ed.</u> , <u>10</u> , 140 (1938)
25.	F. Ephraim, "Inorganic Chemistry," by P. C. L. Thorne and E. R. Roberts, fourth ed., rev., Nordeman Publishing Co., Inc., New York, N. Y., 1943, p. 556
26.	(a) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 379
	(b) A. A. Noyes, J. Am. Chem. Soc., 46, 1116 (1924)
27.	C. Black, G. G. Joris, and H. S. Taylor, <u>J. Chem. Phys.</u> , <u>16</u> , 537 (1948)
28.	(a) J. A. V. Butler, D. W. Thomson, and W. H. MacLennan, J. Chem. Soc., 674 (1933)
	(b) M. Randall and H. P. Weber, <u>J. Phys. Chem.</u> , <u>44</u> , 917 (1940)
29.	S. Glasstone, "Thermodynamics for Chemists," D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 354

A PROPOSED ENIUM NOMENCLATURE FOR IONIC COMPLEXES INVOLVING CARBON-CARBON MULTIPLE BONDS

PART III

PART III

A PROPOSED ENIUM NOMENCLATURE FOR IONIC COMPLEXES INVOLVING CARBON-CARBON MULTIPLE BONDS

Nature of Olefinic and Acetylenic Coordination

<u>Introduction</u>. It has long been known that olefins may combine with certain salts to form complex substances of comparatively low stability (1). It was only about a decade ago, however, that chemists began to understand, in the terms of modern structural theory, the nature of the coördination between a cation and a carbon-carbon double bond.

x+	X	X	x ⁺
>0=0<	>å—o<	>a-q<	>0-0<
I	II	III	IV
"double bond	carbo	nium ions	evelie

"double bond carbonium ions cyclic ionic" form positive ion

The picture of an ion whose structure was intermediate between III and IV was first advanced by Roberts and Kimball (2), as a postulated intermediate in the halogenation of ethylenes. In studies which showed that silver ion coordinates with unsaturated compounds, Winstein and Lucas (3) independently developed the concept, during a conference with Professor Linus Pauling, that the complex was a resonance hybrid receiving contributions from structures I, II, and III. Lucas and co-workers (4, 5, 6) later extended the concept of a resonance hybrid to include all four structures, with reference to the olefin complexes of bromine, mercury, and silver. It should be noted that the cyclic positive ion, IV, involves donation of a pair of electrons from \underline{X} , so that this structure would make only a small contribution for strongly electrophilic cations and be non-existent for coördination with a proton.

Quantum-Mechanical Interpretations (7, 8, 9, 10) It is probable that in a carbon-carbon multiple bond one of the bonds is similar to the carbon-carbon single bond in ethane, while the other bond or bonds are of weaker bonding power, thereby giving rise to the well-known unsaturated properties of alkenes and alkynes. The carbon-carbon bond in ethane is called a $\sigma\sigma$ bond or a σ bond. It involves the overlap of one s-p hybrid bond orbital from each carbon atom. The primary bond in a double or triple bond is also a $\sigma\sigma$ bond. It is to be noted that the amount of p character in the s-p hybrid orbitals of this $\sigma\sigma$ bond may be different from the amount in the $\sigma\sigma$ bond of ethane. The other part of a double bond involves a p orbital from each carbon atom, and is called a $\pi\pi$ bond or a π bond. In forming a triple bond each carbon atom uses two p orbitals, which are at right angles to each other. Thus the

- 107 -

double bond is made up of one $\sigma\sigma$ bond and one $\pi\pi$ bond, whereas the triple bond consists of one $\sigma\sigma$ bond and two orthogonal $\pi\pi$ bonds. Figure 1 is an original schematic representation of this interpretation of the carbon-carbon double bond and triple bond, showing the approximate orbitals in the manner used by Pitzer (11). The $\pi\pi$ bond or bonds are shown separately from the $\sigma\sigma$ bond, so that the difference in their character may be more readily seen.

The strength of a bond is approximately proportional to the amount of overlap of the orbitals, so that a $\pi\pi$ bond is only about 70% as strong as a or bond. Rotation about the carboncarbon axis is not restricted by the $\sigma\sigma$ bond, because of its cylindrical symmetry about this axis. Rotation is restricted by the $\pi\pi$ bond, however, since there is a maximum overlap, and hence stability, when the π orbitals lie in the same plane. Whereas the σ orbitals overlap to a maximum extent directly between the carbon nuclei, the olefin π orbitals have lobes extending above and below the plane of the molecule, so that they may also overlap favorably with the orbitals of atoms coming in from above or below. Similarly, the two π orbitals of each carbon atom in a triple bond extend out from the carbon nucleus in four orthogonal lobes, so that their spatial distribution is well suited to coordination with other atoms. Supporting Physical Data. It was believed until recent years that the donated electrons of the coordinated link type of bond must be initially non-bonding electrons, but there is

- 108 -



DOUBLE BOND SECTIONS

-109-

nothing in molecular orbital theory to warrant this limitation (12, 13). It is true that donation of lone electron pairs is more commonly observed, but this is because such electrons are usually more weakly bound than bonding electrons. For donation by bonding electrons to occur, it is essential that these electrons have especially low ionization potentials. Electrons in olefins fulfill this condition. The π electrons of ethylene lie in an orbital of ionization potential 10.5 volts while the lone pair electrons of ammonia lie in an orbital of ionization potential 10.8 volts (13, 14). Donation of the π electrons of ethylene may be expected, therefore, just as ammonia may donate its lone pair of electrons.

The available energy data also supports the possibility of a significant amount of coördination involving the double bond. Winstein and Lucas (3) found the Δ <u>H</u> of complex formation of one molecule of cyclohexene and of methylethylene with silver nitrate in aqueous solution to be -6 kcal., a value comparable to -6.7 kcal., one-half the Δ <u>H</u> for the coördination of two ammonia molecules with one silver ion, in aqueous solution. Baughan, Evans, and Polanyi (15) have calculated that the proton affinity of ethylene, about 174 kcal., is only about 10 kcal. less than the proton affinity of water.

The Raman spectra of aqueous solutions of silver-olefin complexes were studied by Taufen, Murray, and Cleveland (16).

- 110 -

Their data support the conclusion that complex formation in some way involves the double bond. That the double bond has not been broken, but merely weakened, is indicated by the presence of a line still in the double bond region, but of definitely smaller displacement than in the original compound. We new line corresponding to a metal-carbon linkage could be discerned.

<u>Symbolism</u>. A number of special symbols have been used to indicate the distinctive nature of the double bond and its coördination compounds.



Hückel (7) suggested the use of I or II to represent the double bond, and referred to the π electrons as "electrons of the second kind." Mulliken (17) prefers to call them "unsaturation electrons." Werner (18) proposed that III be used for the conventional double bond formulation. Price (19) has suggested that the intermediate in several typical elefinic reactions is an association complex with the π electrons of the double bond, represented by a symbol such as IV. Dewar (20) has used V to represent the " π complex" which is postulated as an intermediate in various rearrangements of aromatic systems. Walsh (13) prefers the symbol VI, by which he means that the two electrons of the original π bond now bind the three nuclei. In IV, V, and VI the present author is using X as a generalized cation, to represent various specific cations described in the above references.

The Enium Nomenclature

<u>Purpose</u>. Thus it is seen that in the past decade there have been rapid strides in our knowledge of a type of coordinate link which differs from the classic type involving a lone electron pair. It seems likely that our knowledge of this type of linkage, and in particular of its applications in understanding the mechanisms of organic reactions, will become of increasing importance. Suggestions have been made for characteristic symbols to represent these complexes. A distinctive nomenclature to represent this type of linkage would, likewise, be very valuable; and it is important that such a nomenclature be adopted before the present unsystematic names become too well established.

<u>General Rules in Naming</u>. It is proposed that ionic complexes which may be reasonably considered to have a resonance contribution from the double bond ionic structure I be named enium complexes, provided that the usual name of the donor compound

- 112 -

ends in "ene".



For example, since II is one of the resonance structures of the complex ion that seems to be responsible for the increased aqueous solubility of cis-2-pentene which occurs when silver nitrate is present (6), the ion would have an enium name. The enium name consists of the acceptor ion, a hyphen, and the Geneva name of the donor molecule with its final "e" replaced by the suffix "ium". Thus II would be "silver-cis-2-pentenium ion." Complexes wherein the double bond is replaced by a triple bond would receive corresponding "ynium" names. Notes and Examples. The enium and ynium nomenclature is based on two facts. First, "ene" and "yne" are used in the Geneva system to represent the double bond and triple bond, respectively. Secondly, Chemical Abstracts (21) suggests that "ium compounds" are "compounds containing an organic cation". "Carbenium" ion is used by some authors in the place of "carbonium" ion, but the latter is the one now accepted by Chemical Abstracts. No other usage of enium or ynium, which might cause confusion with the proposed nomenclature, has been found.

The double bond may be part of a ring system, as in the "silver-cyclohexenium" ion (3). Either the cis or the trans configuration of an olefin may be involved in coordination. In the case of the 2-pentenes, "silver-cis-2-pentenium" ion is more readily formed than the "silver-trans-2-pentenium" ion (6). With dienes, complexes have been observed with either one or two silver ions coordinated with one unsaturated molecule; for example, "silver-dimethylbutadienium" and "disilver-dimethylbutadienium" ions (3). If the acceptor ion has more than one valence state, this may be indicated by "ie" or "ous". "Mercuric-cyclohexenium" and "hydroxymercuriccyclohexenium" complexes have been investigated (5). If the mercurous complex exists, it would be a "mercurous-cyclohexenium" ion. An alternate method of indicating the oxidation state of the cation is by means of Roman numerals. For example, the mercurous and mercuric complexes of cyclohexene would be, respectively, "mercury(I)-cyclohexenium" and "mercury(II)cyclohexenium" ions.

Whenever convenient, and where confusion is not likely to arise, a simplified or group name may be used, in which the name of the donor molecule, or acceptor ion, is omitted in forming the enium name. For example, "argentenium" ion would be a simplified name for referring, in context, to the complex ion of silver with some specific olefin. Or "argentenium" ions might be used to refer to a group of metal-olefinic complexes

- 114 -

each of which contains silver. In the shortened name of a cation such as mercury, the oxidation states may be indicated by shortening "ic" to "i", and "ous" to "o". The respective ions would be "mercuri-enium" and "mercuro-enium", the hyphen being inserted to separate the successive vowels. An example of where it would be convenient to omit the cation would be in saying that both silver and mercuric ions are known to form "cyclohexenium" complexes. Another case would be the use of the term "benzenium" complexes in a discussion of postulated mechanisms for aromatic reactions.

The Protenium Ion. By analogy with the nomenclature of metals, a possible enium name for an olefin-hydrogen ion complex would be "hydrogenenium". The name "protenium" is advocated instead, primarily because it seems more euphonious. There is also some justification for basing the name on the word proton, inasmuch as the complex involving this bare nucleus is unique. It was noted, for example, that it is here impossible to write a cyclic resonance form, since the proton has no electrons to furnish for the formation of a three-membered ring. Pitzer (22) has suggested the name "protonated double bond" in connection with the structure of diborane. While this may be regarded as an alternative name for a "diprotenium" complex, it is felt that the enium system is more convenient to use as a generalized nomenclature. The protenium ion has been postulated as an intermediate in acid catalyzed olefinic reactions (19). The corresponding ion involving a triple bond would be a "protynium" ion.

"Enium" Compared with "Onium". Positive bromo-olefin complexes have been postulated as reaction intermediates by Winstein and Lucas (4). They indicate that the structure of these complexes is exactly analogous to that of the previously mentioned silver complexes in regard to the contributing resonance forms, although the proportion of the various forms differs. Their name for the complex is (cyclic) "bromonium" ion (23). However, not all organic cations are named as "onium" compounds. Other "ium" compounds (organic cations) such as "inium" (e.g., pyridinium), "olium" (e.g., imidazolium) and "ylium" (e.g., pyrylium) are recognized (21). In fact, Lucas, Hepner, and Winstein use the name "mercurinium" (5) in naming the analogous bivalent mercury complexes. It is therefore recommended that the name "bromenium" be substituted for "bromonium", inasmuch as the former makes it obvious that this ion has distinctive character arising from the double bond ionic resonance contribution. Similarly, it is recommended that the names "chlorenium", "iodenium", and "halenium" be substituted for the corresponding "onium" names (23). "Mercuric-cyclohexenium" would be used instead of "cyclohexenemercurinium" (5). The structural difference between donation of bonding electrons, in enium complexes, and donation of a lone electron pair, in most compounds with an "onium" name, would be indicated by a slight modification in nomenclature. Diphenyl iodonium iodide is a stable substance in which the positive iodine has been an electron donor. A positive iodine-olefin complex, which is likely to be unstable except in aqueous solution, would be distinguished as an "iodenium" ion, in which the iodine may be considered primarily as an acceptor of the double bond electrons. It would be unnecessary to refer to a "cyclic" chloronium intermediate (24), since "chlorenium" would by definition involve the cyclic arrangement.

In discussions of the role of neighboring groups in replacement reactions, Winstein and co-workers (25) have so commonly represented postulated intermediate enium complexes in the three-membered ring form that it is well to stress here that the ring form is only a resonance contribution to a hybrid ion and not an exact description of the actual ion. As noted by Price (19), a ring structure is not necessary as an explanation of the stereochemistry of these reactions. Because of the spatial distribution of the π electrons, the hybrid structure may retain sufficient double bond character to resist rotation.

- 118 -

REFERENCES

, 1.	R.	N.	Keller, <u>Chem. Hev.</u> , <u>28</u> , 329 (1941)
2.	I.	Rot	perts and G. E. Kimball, <u>J. Am. Chem. Soc.</u> , <u>59</u> , 947 (1937)
3.	s.	Wir	stein and H. J. Lucas, <u>J. Am. Chem. Soc.</u> , <u>60</u> , 836 (1938)
4.	s.	Wir	stein and H. J. Lucas, <u>J. Am. Chem. Soc.</u> , <u>61</u> , 1576 (1939)
5.	H.	J.	Lucas, F. R. Hepner, and S. Winstein, J. Am. Chem. Soc., <u>61</u> , 3102 (1939)
6.	H.	3.	Lucas, R. S. Moore, and D. Pressman, J. Am. Chem. Soc., 65, 227 (1943)
7.	E.	Hüc	ckel, <u>Z. Elektrochem.</u> , <u>43</u> , 752 (1937)
8.	L.	Pau	ling, "The Nature of the Chemical Bond," second ed., Cornell University Press, Ithica, N. Y., 1940,
9 10 1 10 4 1			pp. 89-90
9.	9.	Gla	Sectone, "Theoretical Chemistry," D. Van Nostrand Company, Inc., New York, N. Y., 1944, pp. 103-104
10.	H.	Eyı	ring, J. Walter, and G. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 225
11.	ĸ.	s.	Pitzer, J. Am. Chem. Soc., 70, 2140 (1948)
12.	A.	D.	Walsh, J. Chem. Soc., 89 (1947)
13.	A.	D.	Walsh, <u>Nature</u> , <u>159</u> , 165, 712 (1947)
14.	₩.	C.	Price, <u>Chem. Rev.</u> , <u>41</u> , 257 (1947)
15.	E.	c.	Baughan, M. G. Evans, and M. Polanyi, Trans. Faraday Soc., 37, 377 (1941)
16.	H.	J.	Taufen, M. J. Murray, and F. F. Cleveland, J. Am. Chem. Soc., 63, 3500 (1941)
17.	R.	s.	Mulliken, J. Chem. Phys., 7, 339 (1939)
18.	Α.	E.	A. Werner, <u>Nature</u> , <u>160</u> , 644 (1947)

- 19. C. C. Price, "Mechanisms of Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 39-43
- 20. M. J. S. Dewar, J. Chem. Soc., 406, 777 (1946)
- 21. Chem. Abstracts, 39, 5937 (1945)
- 22. K. S. Pitzer, J. Am. Chem. Soc., 67, 1126 (1945)
- 23. S. Winstein and H. J. Lucas, <u>J. Am. Chem. Soc.</u>, <u>61</u>, 2845 (1939)
- 24. H. J. Lucas and C. W. Gould, <u>J. Am. Chem. Soc.</u>, <u>63</u>, 2541 (1941)
- 25. S. Winstein and E. Grunwald, <u>J. Am. Chem. Soc.</u>, <u>70</u>, 828 (1948)

APPENDIX

- 120 -

DISPLACEMENT VOLUMETRIC FLASK

The displacement volumetric flask (Figure 1) is an apparatus for preparing and sampling a volatile solution. The vapor space above the solution does not increase during sampling; hence the concentration of the solution does not change by differential evaporation of the solution components. The apparatus was designed for cyclohexene in carbon tetrachloride solutions (p. 20), but it was used only in preliminary experiments because it was noticed that a black deposit gradually appeared on the surface of the mercury beneath the solution.

The flask is made by drawing out the neck of a standardtapered conical flask and is calibrated in the same way as an ordinary volumetric flask. The stopper is made by sealing a capillary stopcock into a tube bearing a microstopcock, and fusing the bottom of the tube to a standard-tapered male joint which fits the neck of the flask. When the stopper is inserted, the lower end of the capillary stopcock tube is slightly below the surface of the solution, and the vapor space above the solution is just enough to allow convenient mixing of the solution components. The stopper is held firmly in the neck of the flask by springs. When mercury is added through the microstopcock, pressure is created and the solution is forced up through the capillary stopcock.



Figure 1. Displacement Volumetric Flask

- A. Entering mercury B. Displaced solution C. Capillary stopcock D. Graduation mark

PROPOSITIONS

1. I predict that a determination of the temperature coefficient of solubility for benzene in 0.2 <u>M</u> silver nitrate would reveal that there is a reversal in the sign of the coefficient somewhere between 10° and 70° .

2. Although an organic substance is less soluble in an aqueous salt solution than in water, the possibility is not excluded that a low concentration of water-soluble ionic complexes of the organic substance is present. It would be of interest to investigate the existence of such "hidden complexes" by experiments comparing the solubility of the organic substance in different salt solutions at various concentrations and temperatures.

3. Stripping analysis determinations of the solubilities of cyclohexane, carbon tetrachloride, and benzene in hydrochloric acid solutions would give a valuable indication as to whether or not proton complexing is the basis for the minimum in the distribution constant versus acid concentration curve of cyclohexene distributed between carbon tetrachloride and hydrochloric acid.

4. The experiments of Andrews and Keefer indicate that the coördination of silver ion with benzene in aqueous solution involves primarily complexes in which one silver ion is combined with one or more molecules of benzene. I propose that information in regard to the relative proportions of different monosilver-polybenzene species could be obtained

- 122 -

by experiments combining the spectrophotometric analysis method of Andrews and Keefer with the distribution method of Winstein and Lucas (1).

5. Ingold and co-workers have shown that the rate of bromination of substituted ethylenes in methylene chloride at low temperatures in absence of light increases with an increase in the total number of methyl groups attached to the double bond carbon atoms. I propose that these results support the assumption that the rate-determining step involves a bromenium ion rather than a simple carbonium ion (2).

6. The electrophilic nature of vinyl sulfones has been used to account for the ease with which they undergo addition of such nucleophilic reagents as amines or mercaptans. It appears that the mercaptans, although weaker bases toward a proton, add to vinyl sulfones more readily than do the amines. I propose that this unusual behavior may be explained on the basis of the stabilizing effect of a cyclic intermediate in the case of the mercaptans (3).

7. Smyth and co-workers have suggested that the dipole moment of diphenylselenium dichloride reflects the effect of contributing resonance structures having a positive charge on the benzene ring and a negative charge on the chlorine atom. I propose that the effect of resonance contributions be further investigated by determining the dipole moment of dibiphenylylselenium dichloride, which could probably be prepared by the chlorination of biphenylyl selenide (4). 8. Additional teaching emphasis on the following valence rules would make it easier for students to learn the formulae of chemical compounds.

(a) With the exception of nitrogen, when there is more than one stable valence state of a regular element, in contrast to a transition element, these valences differ only by an even number.

(b) A consequence of electron-pairing is that compounds containing only non-metallic elements are restricted to those having an even total number of atoms of the nitrogen and halogen families. (For this rule hydrogen may be classified with the halogens.)

9. Experiments indicate that the nearer the polar group is to the end of a straight-chain sodium alcohol sulfate, the greater the detergent power of an aqueous solution of the compound. I propose an explanation for this effect based upon the relationship between the location of the polar group and the stability of the micelles which are responsible for detergent action (5).

10. It is of interest to compare the conventional Grotrian energy level diagram with an alternative spiral arrangement of atomic energy levels.

- 125 -

REFERENCES

1.	(a)	s.	Winstein and H. J. Lucas, <u>J. Am. Chem. Soc.</u> , <u>60</u> , 836 (1938)
	(b)	L.	J. Andrews and R. M. Keefer, <u>J. Am. Chem. Soc.</u> , <u>71</u> , 3644 (1949)
2.	(a)	C.	K. Ingold and E. H. Ingold, <u>J. Chem. Soc.</u> , 2354 (1931)
	(b)	s.	V. Anantakrishnan and R. Venkataraman, <u>Chem. Rev.</u> , <u>33</u> , 27 (1943)
3.	(a)	с.	C. Price, "Mechanisms of Reactions at Carbon- Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 47
	(b)	Μ.	A. Stahmann, C. Golumbic, W. H. Stein, and J. S. Fruton, <u>J. Org. Chem.</u> , <u>11</u> , 719 (1946)
4.	(a)	0.	Behaghel and K. Hofmann, Ber., 72, 697 (1939)
	(b)	с.	P. Smyth, A. J. Grossman, and S. R. Ginsburg, J. Am. Chem. Soc., <u>62</u> , 192 (1940)
	(c)	ĸ.	A. Jensen, Z. anorg. allgem. Chem., 250, 245 (1943)
5.	(a)	E.	E. Dreger, G. I. Keim, G. D. Miles, L. Shedlovsky, and J. Ross, <u>Ind. Eng. Chem.</u> , <u>36</u> , 610 (1944)
	(b)	R.	W. Mattoon, R. S. Stearns, and W. D. Harkins, J. Chem. Phys., <u>16</u> , 644 (1948)
	(c)	J.	W. McBain and H. McHan, <u>J. Am. Chem. Soc.</u> , <u>70</u> , 3838 (1948)