The Association of Silver Ion with Cis and Trans Isomers.

Thesis by
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The Association of Silver Ion with Cis and Trans Isomers.

Introduction

The compounds of low stability which ethylenic linkages form by "addition" or "coordination" are distinctly different in type from the stable addition compounds produced by their reaction with the usual reagents such as the halogens. Such coordination compounds have been described previously, for example, the complex salts of hydrocarbons with aluminum and ferric chlorides[1], the loose addition compounds of olefins with hydrogen bromide, of the type $C_2H_4 \cdot HBr$[2], with zinc chloride, of the type $C_5H_{10} \cdot ZnCl_2$[3], and the addition compounds of aromatic hydrocarbons with nitro compounds[4].

Winstein and Lucas[5] have given a discussion of other loose chemical compounds formed by the olefinic double bond and in this same article report on various studies on the coordination of silver ion with unsaturated compounds, in an effort to understand better the nature of the bond in these olefin-metal complexes. Their work was a continuation of that of Eberz, Welge, Yost and Lucas[8]. By means of distribution measurements, in a method described below, a study was made of the coordination complexes which silver ion forms with (a) the monoölefins trimethylethylene, 2-pentene, 1-hexene, cyclohexene and propenylbenzene; (b) the diolefins dimethylbutadiene and biallyl; (c) the unsaturated oxygenated compounds allyl alcohol, crotyl alcohol, crotonaldehyde, crotonic acid and phenol Complex ions of three different types were observed, viz., combinations of one silver ion with one unsaturated molecule, two silver ions with one unsaturated molecule and one silver ion with two unsaturated molecules. Equilibrium constants were obtained for the reactions of silver ion with all these compounds at 25 degrees, and with trimethylethylene, cyclohexene and phenol at 0 degrees. For trimethylethylene and cyclohexene it was found that $\Delta H = 6.0$ kcal. It was shown also, by shaking portions of given mixtures of the 2-butenes with aqueous 1N silver nitrate, conversion of the treated and untreated samples into the dibromobutanes and studying the second order reaction rate constants, k_2, for the reaction of potassium iodide with the dibromides[6], that neither cis-2-butene nor trans-2-butene isomerizes in the presence of silver ion. This important proof is used in the development of the present work.

In addition, it has been shown that no detectable amount of silver enters the carbon tetrachloride phase. Such a reaction as

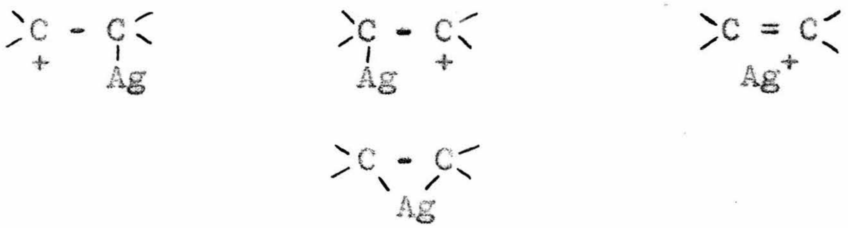
$$Ag^+ + B + H_2O = Ag.B.OH + H^+ \quad ..... \qquad (2)$$

does not occur, for a solution of 1N silver nitrate gives a pH of 5.3 before and after saturation with isobutene. A hydrated complex has, however, been shown to exist in the case of mercury and cyclohexene[10].

In aqueous solution the following ions failed to form complexes with an olefin: Cd^{++}, Co^{++}, Cr^{+++}, Cu^{++}, Fe^{+++}, Ni^{++}, Pb^{++}, Tl^+, Zn^{++}. The inability of these ions to form complexes with ethylenic compounds, these authors suggested, may be due to the greater strength of their water-coordination bond over their olefin-coordination bond since, when the complex is formed, the reaction is probably the replacement of a coordinated water molecule by the ethylene molecule, as shown below. The silver ion in water apparently has two water molecules coordinated with it:-[7]

$$B + (H_2O)_2 \cdot Ag^+ \underset{}{\overset{K_1}{\rightleftharpoons}} B(H_2O)Ag^+ + H_2O \qquad (1)$$

These authors proposed a structure for the ethylenic silver ion complex, according to which the ethylenic compound can occupy one of the two coordination positions of silver by acting as the donor of an electron pair. A covalence joins the silver atom to one of the carbon atoms, and a positive charge appears on the other. Resonance involving two such bonded forms, an unbonded form, and also possibly the three membered carbon-carbon-silver ring is believed to account for the stability of the complex.



The resonance energy, about 10 kcal., is enough greater than the strain energy, probably 3 to 4 kcal.[5], to lead to an expectation of moderate stability. Formation of a hybrid structure made up of contributions from these four forms need not necessarily go through an intermediate containing an activated double bond.

In the case of two compounds, biallyl and dicyclopentadiene, solid silver complexes were obtained.

Using a combination of the symbols of the above authors and those of Eberz, Welge, Yost and Lucas[8], the distribution method may be described with the aid of the following notation:

B = unsaturated substance

(Bt) = total concentration of unsaturated substance in aqueous phase in moles per litre.

(B) = uncomplexed unsaturated material in aqueous phase in moles per litre.

(BAg) = concentration of species $(B.Ag)^+$ in aqueous phase, in moles per litre.

(Ag^+) = concentration of free silver ion in aqueous phase in moles per litre.

(Agt) = total silver concentration in aqueous phase in moles per litre.

$(B)_c$ = concentration of unsaturated material in carbon tetrachloride in moles per litre.

μ = ionic strength = normality

$K_D = (B)_c/(B)$ = distribution ratio of the unsaturated material between carbon tetrachloride and 1 N potassium nitrate (3)

$$K = \frac{(BAg)}{(B)(Ag^+)} \tag{4}$$

The procedure consists in distributing the unsaturated organic compound B between carbon tetrachloride and 1 N potassium nitrate, and then combining the resulting distribution ratio with other data obtained by distributing B between carbon tetrachloride and 1 N silver nitrate, or a solution of $\mu = 1$ of both potassium nitrate and silver nitrate. The data required are the concentrations of B in the two phases and the concentration of the silver salt in the aqueous phase.

Combining equations (3) and (4) above we get

$$K = \frac{K_D\,(BAg)}{(B)_c(Ag^+)} \tag{5}$$

But

$$(Agt) = (Ag^+) + (BAg)$$

and

$$(Bt) = (B) + (BAg)$$

and therefore

$$(Ag^+) = (Agt) - (Bt) + (B)$$

From (5) then

$$K = K_E = \frac{K_D\left[(Bt) - (B)\right]}{(B)_c\left[(Agt) - (Bt) + (B)\right]}$$

and

$$K_E = \frac{K_D\left[(Bt) - (B)_c/K_D\right]}{(B)_c\left[(Agt) - (Bt) + (B)_c/K_D\right]} \tag{6}$$

All of the quantities in K_E, the evaluated constant, we can determine experimentally.

In this theory we assumed, for K, that one mole of B coordinates with one mole of silver. What we really have in K_E then is the first argentation constant of B. Winstein and Lucas[5] called this constant K_1. $K_1 = K$ when only this reaction occurs in the aqueous phase:

$$B + Ag^+ \overset{K_1}{\rightleftharpoons} BAg^+ \tag{7}$$

Subsequent reactions may occur, as brought out for the butadienes, and for phenol, for example, by the above authors[5], but in this work we are dealing with a monomolecular complex and shall use $K_E = K_1$ for the evaluated complex constant.

Another constant K_o has been evaluated.

$$K_o = \frac{K_1}{K_D} \qquad (8)$$

It is especially useful in the case of hydrocarbons. As seen by combining (3), (4) and (8),

$$K_o = \frac{(BAg)(B)}{(B)(Ag^+)(B)_c} = \frac{(BAg)}{(Ag^+)(B)_c} \qquad (9)$$

K_o is the equilibrium constant for the reaction between B, dissolved in carbon tetrachloride, and aqueous silver ion to give the complex ion BAg^+. K_o is essentially independent of K_D because (B) is small compared to (Bt). K_D is usually very high in hydrocarbons going up to 9000 for 1-hexene and consequently involves somewhat more error for them. Hence K_o finds great usefulness in the present work in the analysis of a mixture of isomers by the silver association constants, for in this case greater accuracy is required than is present in K_D or K_E.

In comparing the stability of different olefin complexes, Winstein defined unit activity of B as the activity of B in a 1 molar solution of B in carbon tetrachloride. K_o gives a measure of the silver association in terms of this concept. This amounts to choosing a standard state for all the olefins with about the same activity relative to the liquid state.

The influence of partial miscibility of the carbon tetrachloride and water upon K_1 causes this latter constant to be lower than the value for carbon tetrachloride-free water due to the increase in solubility of an olefin in water on saturating the water with carbon tetrachloride. But K_o is not subject to this error.

It must be assumed that potassium and silver ions are equivalent in their effect upon the activity of the unsaturated substance. Thus, exclusive of the silver complex, K^+ and Ag^+ would have the same "salting out" effect on B from the aqueous phase. Hence, this present work is based on a constant ionic strength $\mu = 1$.

Analysis of mixtures of the normal butenes by means of the second order reaction rate constants for the reaction of potassium iodide with the dibromides has been studied[15].

Whether or not silver ion coordinates to different degrees with cis and trans geometrical isomers has been of keen interest. The concept held forth possibilities in the light of determining the composition of unknown mixtures of cis and trans isomers by means of the size of the constant K_o. With this in view the present work was undertaken. Its scope is divided roughly into

(a) improvement of the apparatus and technique of the past to facilitate the accuracy required for the isomers.

(b) search for available unsaturated isomers which lend themselves to a method of analysis by bromination.

(c) measurements upon pure cis and trans 2-pentene.

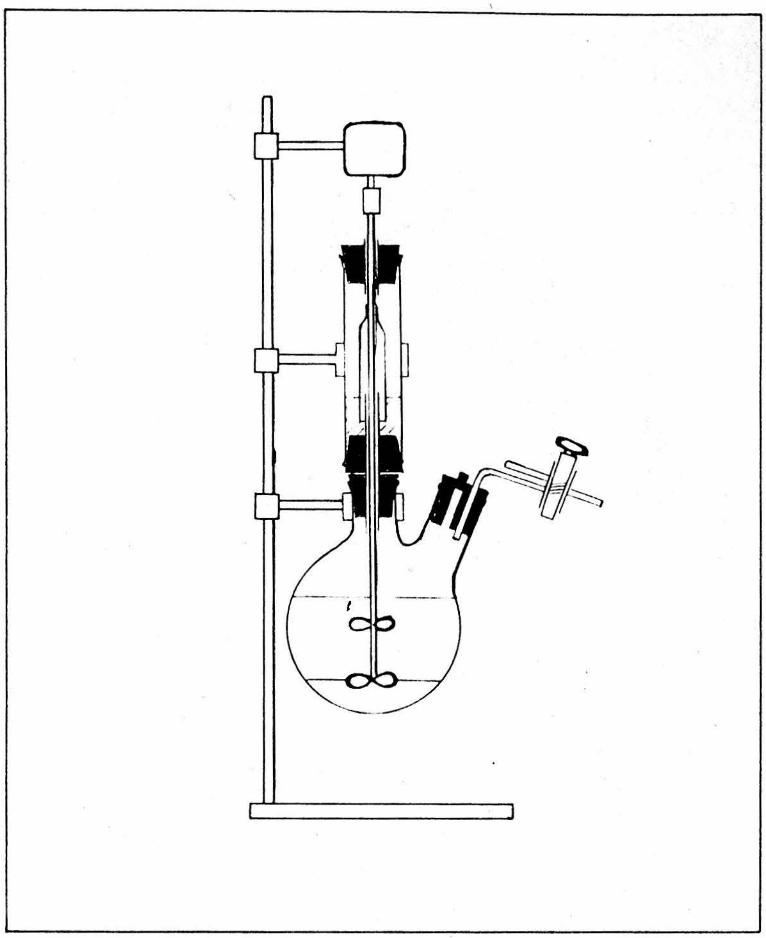


Figure 1.

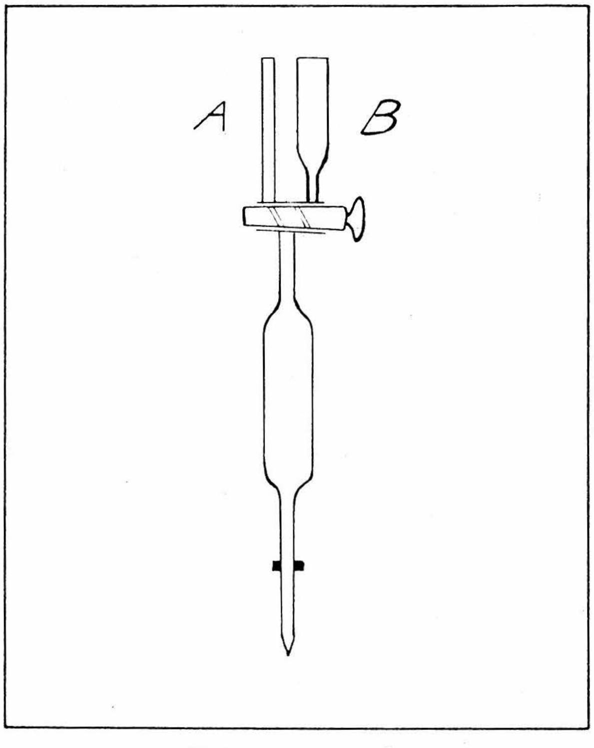


Figure 2.

Experimental

Materials.

The standard silver nitrate solutions were made up by weight, as were the standard bromate-bromide solutions. Inorganic chemicals were C.P. or reagent grade.

The carbon tetrachloride used was purified of oxidizing materials by saturating it with chlorine and allowing the solution to remain in sunlight over a period of two weeks. It was then shaken with strong KOH, dried with $CaCl_2$, $Ca(OH)_2$ added and distilled. The initial distillate was returned to the batch and the main fraction collected at 75.5°C. (uncorr.) with no range.

The isobutene used was prepared by refluxing tertiary butyl alcohol with crystallized oxalic acid and the evolved butene was passed through three spiral wash bottles each containing water to remove the alcohol, next through a tower containing soda lime and calcium chloride and then into an ampoule where it was condensed and sealed off.

Cyclohexene was made available by Franklin Hepner. It was distilled off sodium in a nitrogen atmosphere and gave no indication of peroxide on testing with potassium iodide, dilute sulfuric acid and starch.

The 2-butene was prepared by dehydrating primary butyl alcohol with concentrated sulfuric acid over kieselguhr, passing the evolved butene first through concentrated sodium hydroxide solution, through dilute sulfuric acid and then through a soda lime and calcium chloride tower to the cooled ampoule.

The diethyl fumarate and maleic acid used were Eastman material.

The 2-pentene mixture of isomers was prepared by dehydration of commercial secondary amyl alcohol by concentrated sulfuric acid over kieselguhr and the pentene distilled off over a range 39° - 43° C. It was shaken with sodium hydroxide solution then dried over calcium chloride and redistilled with a range 35.5° - 36.5° C.

Analysis

The analytical method used was essentially that of Davis, Crandall and Higbee[9] as adapted in the previous silver work[5,8] with some modification,[10] in particular the use of a nitrogen atmosphere in all the distributions and nitrogen to force up the sample. Five minutes was allowed for each bromination.

For the dilute solutions, 0.05 N bromate-bromide and 0.02 N thiosulfate were used, but 0.25 N bromate-bromide and 0.2 thiosulfate were employed where needed. Five minutes of shaking[5] with a small excess of bromate-bromide solution is sufficient for analysis of both phases with all these substances. Exceptions were attempted in the work on ethyl fumarate as discussed below. In the analysis of solutions of silver nitrate enough potassium bromide was added to precipitate all the silver and enough iodide later to allow for any metathesis of silver bromide to iodide. This gave an end-point somewhat like that in the iodometric copper analysis. During bromination the analysis flasks were wrapped in black cloth.

All distributions were carried out in a thermostat at

25.0° ± .03° C. The apparatus for the distribution measurements as first carried out is shown in Fig. 1. In the 2-pentene work it was found necessary (see below) to change this apparatus to one with ground glass joints ~~(Fig. 3)~~. Sampling of the two phases was carried out by means of calibrated pipets[11] of the style shown in Fig. 2. The distribution flasks, usually 200 ml., were first filled with nitrogen, the solutions poured in, and again nitrogen passed through by means of the 3-way stopcock shown in Fig. 1. The samples were forced into the pipets by means of nitrogen.

One hour in the thermostat after stirring mechanically for twenty minutes was usually allowed for the establishment of equilibrium between the phases. In the 2-pentene work described below the effects of varying stirring and settling times were studied. Difficulty was encountered as usual[5] in determining large distribution ratios accurately because a trace of the concentrated phase in the dilute phase gives rise to large errors and because of the small amount of standard bromate-bromide solution consumed by even a 100 ml. sample of the dilute phase.

Results

Iso butene.

Concentrations are in moles per litre throughout this work. In the runs with the gases isobutene and 2-butene, carried out to study the techniques previously employed, the unsaturated substance was distilled at room temperature into the two-phase system in the distribution flask, previously filled with nitrogen, while stirring mechanically for five minutes. The amount of gaseous sample was gauged from the level of the liquid in the ampoule.

Table I gives some typical results for isobutene distributions between carbon tetrachloride and water showing good agreement and no appreciable drift over a time of settling up to five hours. This result is of interest in the work below with 2-pentene, when the drift over much longer periods was studied. Previous authors[8] reported a value of 606 for this K_W, at a slightly higher isobutene concentration, having used isobutene instead of nitrogen to force their samples into pipets. The agreement with the present value of 586 is fairly good.

Cyclohexene.

In checking Winstein's work[5] on the potassium nitrate constants K_D, a value of 4225 was obtained with 5% deviation for cyclohexene. Winstein's value was 4305. In connection with these distributions of cyclohexene the effects of peroxide formation were noticeable. In peroxide containing samples the titres drifted in the direction of the liberation of more iodine and too much bromine was used up. With freshly distilled samples the end-points were sharp. It is considered possible that the cyclohexene peroxide makes bromine substitution easy.

2-Butene.

With 2-butene distributions more variation was encountered since runs were allowed to settle as long as 20 hours. Table II gives some typical results. The increase in K_D with time of settling is to be expected and was studied under the 2-pentene work below. The true value of K_D in this case is probably about 800 since a very small amount of organic phase in the aqueous phase would cause the drop to 743. Using $K_D = 800$ the silver constant K_E for this 2-butene mixture of isomers was found to be 48.7 and $K_o = .0608$.

Diethyl Fumarate.

Since the cis-trans isomers dimethyl maleate and dimethyl fumarate were available for study, an investigation was made upon the bromination analysis of diethyl fumarate solutionsto ascertain whether or not these esters lend themselves to analysis. In the absence of light the ethyl fumarate in carbon tetrachloride did not add bromine to any extent. (See Runs 35 and 45, Table III). According to Lucas and Pressman[12] maleic and fumaric acids can be analysed quantitatively by bromination for 30 minutes in the presence of mercuric ion. An investigation was carried out using mercuric sulfate solutions to catalyse the addition of bromine to diethyl fumarate. Varying success was attained. Mercuric sulfate 0.2 N solution was prepared by dissolving the C.P. Baker's solid in 6 N sulfuric acid and diluting to the desired

Table I.

Iso butene Distributed Between Carbon Tetrachloride and Water.

Run. No.	Stirring time m.	Settling time m.	aqueous (B)	$CCl_4(B)_c$	K_w
3	5	5	.000467	.264	566
8	5	5	.000476	.275	578
9	5	10	.00107	.622	582
10	5	15	.000974	.574	590
11	5	15	.000776	.465	600
12	5	20	.000740	.443	600
13	15	60	.000725	.423	585
14	15	30	.000595	.349	587
16	10	300	.00119	.692	582

Average $K_w = 586 \pm 8$

Table II.

2-Butene Distributed Between Carbon Tetrachloride and 1N KNO_3

Run No.	Stirring time m.	Settling time h.	aqueous (B)	$CCl_4(B)_c$	K_D
33	10	1.5	.000807	.648	803
29	10	2.7	.000829	.663	800
30	10	3.0	.000618	.459	743
33	10	20	.000775	.735	948

Probable $K_D = 800$

volume. This solution as used was 3 N in sulfuric acid. It was found necessary to wait for five minutes before adding the mercuric sulfate to the solution of sample in the brominating mixture. If added right away, the mercury ties up the bromide ion. Time must be allowed for the bromine to be liberated. The complex of Hg^{++} and Br^- however is very necessary because if it is broken up with sodium chloride solution before adding the sample the catalytic effect of the mercury disappears. It does not matter whether the mercury solution is added before or after the sample. After the shaking period sodium chloride solution was added, to liberate free bromine from its mercuric sulfate complex. As previously suggested[12] it was necessary to have the molar ratio of mercuric ion to final bromide ion greater than unity to obtain the maximum catalytic effect. Glacial acetic acid was used to increase the solubility of the ester in the aqueous phase.

With mercuric sulfate present the analysis was about 10% efficient. Addition of acetic acid enhanced this to a small degree depending on the time allowed for bromination and, as shown in Table III, on the amount of acetic acid added. Doubling the mercuric ion concentration (Run 46, Table III) had no increased effect.

To obtain a check on the solutions and on the work of Lucas and Pressman[12] a standardized solution of maleic acid was prepared and analysed with mercuric sulfate catalyst. Results as shown in Table IVa were quite satisfactory. Blanks were run on the acetic acid but the amount of bromine used up was only 0.001 ml. per ml. C.P. acetic acid used. Merck's reagent acetic acid used up .0002

Table III.

Ethyl Fumarate in CCl_4

(All in darkness)

Run No.	35	41	42	43	44	45	46
Milliequivs. ester	18.40	1.973	1.973	1.973	1.973	1.973	1.973
Acetic acid, ml.	0	20	30	25	25	20	20
0.2 N $HgSO_4$, ml.	0	15	15	15	15	0	30
Shaking time m.	30	30	30	30	60	30	30
Milliequivs. found	0.0	.465	.498	.448	.623	.051	.473
Efficiency %	---	24	25	23	32	2	24

Table IVa.

Maleic Acid in H_2O

Run No.	54	55
Milliequivs. acid	.4206	.4206
0.2 N $HgSO_4$, ml.	10	5
Shaking time, m.	30	20
Milliequivs. found	.4211	.4149
Milliequivs. error	+.0005	-.0057
Efficiency %	99.9	98.8

ml. of bromine per ml. of acid. These blank corrections were no worry as long as the bromination of the ester was inefficient.

Samples of the diethyl fumarate were made up in C.P. and in Merck reagent acetic acid in order to eliminate carbon tetrachloride altogether from the analysis. The samples were washed into the analysis flasks with about 20 ml. of the same grade acetic acid as is the solution. See Table IV*b*. Bromine substitution is possible (as in Run 59, Table IV*b*) but very slight. It is entirely a matter of relative rates. The acetic acid blank is here important. For example, in Run No. 60, where the blank was .0127 milli equivalents, the efficiency of bromination was actually 97 %. The acetic acid correction varies with time, that is, the longer the time of shaking the more bromine is used by the acetic acid. Hence, a shaking period of 70 minutes is too long to be practical. Two alternatives now presented themselves; conducting the brominations at a higher temperature, or increasing the concentrations of the solutions involved. Higher temperature work would be impractical if high enough (see Runs 68 and 69) and would lead to other additional sources of error. Increasing the concentrations also decreases the accuracy of analysis. From runs 66 and 67 it is seen that upon increasing the bromine concentration, the per cent bromine addition is, actually, not increased at all (compare 67 with 62 and 57). Run 69 was the most efficient obtained. The acetic acid blank also varies with the amount of wash liquid, which must be kept constant. This blank should be run with about one third the amount of bromate[12] as in the actual run, in order to approximate the average bromine

Table IVb.

Diethyl Fumarate in Acetic Acid. (about 25 ml)

Run No.	47	48	49	50	56
Grade CH_3COOH	CP	CP	CP	CP	Reagent
Milliequivs ester	.1093	.1093	.1093	.1093	.1109
0.2 N $HgSO_4$ ml.	5	5	5	5	10
Shaking time m.	30	40	40	40	20
Daylight or darkness	DK	DK	DK	Light	Light
Milliequivs. found	.04258	.0477	.0496	.0502	.0858
Efficiency %	39	44	45	46	77
Corrected (d) efficiency %	--	--	--	--	--

Run No.	57	58	59	60	61
Grade CH_3COOH	Reagent	Reagent	Reagent	Reagent	Reagent
Milliequivs ester	.1109	.1109	.1109	.1109	.1109
0.2 N $HgSO_4$ ml.	10	10	10	10	10
Shaking time m.	30	40	50	70	20
Daylight or darkness	Light	Light	Light	Light	Dark
Milliequivs. found	.0936	.1038	.1155	.1198	.0723
Blank				.0127	
Efficiency %	84	94	104	108	65
Corrected (d) efficiency %	--	--	--	97	--

Table IV*b*(cont.)

Run No.	62	63	64	65	66^a
Grade CH_3COOH	Reagent	R	R	R	Reagent
Milliequivs ester	.1109	.1109	.1109	.1109	.1109
0.2 N $HgSO_4$ ml.	10	10	10	10	5
Shaking time m.	30	40	50	70	30
Light or Darkness	DK	DK	DK	DK	DK
Milliequivs. found	.0929	.0928	.1020	.1096	$.0789^b$
Efficiency %	84	84	92	99	--
Corrected (d) efficiency %	--	72	--	87	71

Run No.	67^a	$68^{a,c}$	$69^{a,c}$
Grade CH_3COOH	Reagent	R	R
Milliequivs ester	.1109	.1109	.1109
0.2 N $HgSO_4$ ml.	5	5	5
Shaking time m.	30	20	30
Light or Darkness	Light	Light	Light
Milliequivs. found	$.0930^b$	$.0805^b$	$.1026^b$ → = (.1118 −.0092)
Efficiency %	--	--	100.8
Corrected (d) efficiency %	84	73	92

a = analytical solution strengths doubled

b = milliequivalents corrected for acetic acid blank

c = carried out on a bath at 30° C.

d = corrected for acetic acid blank

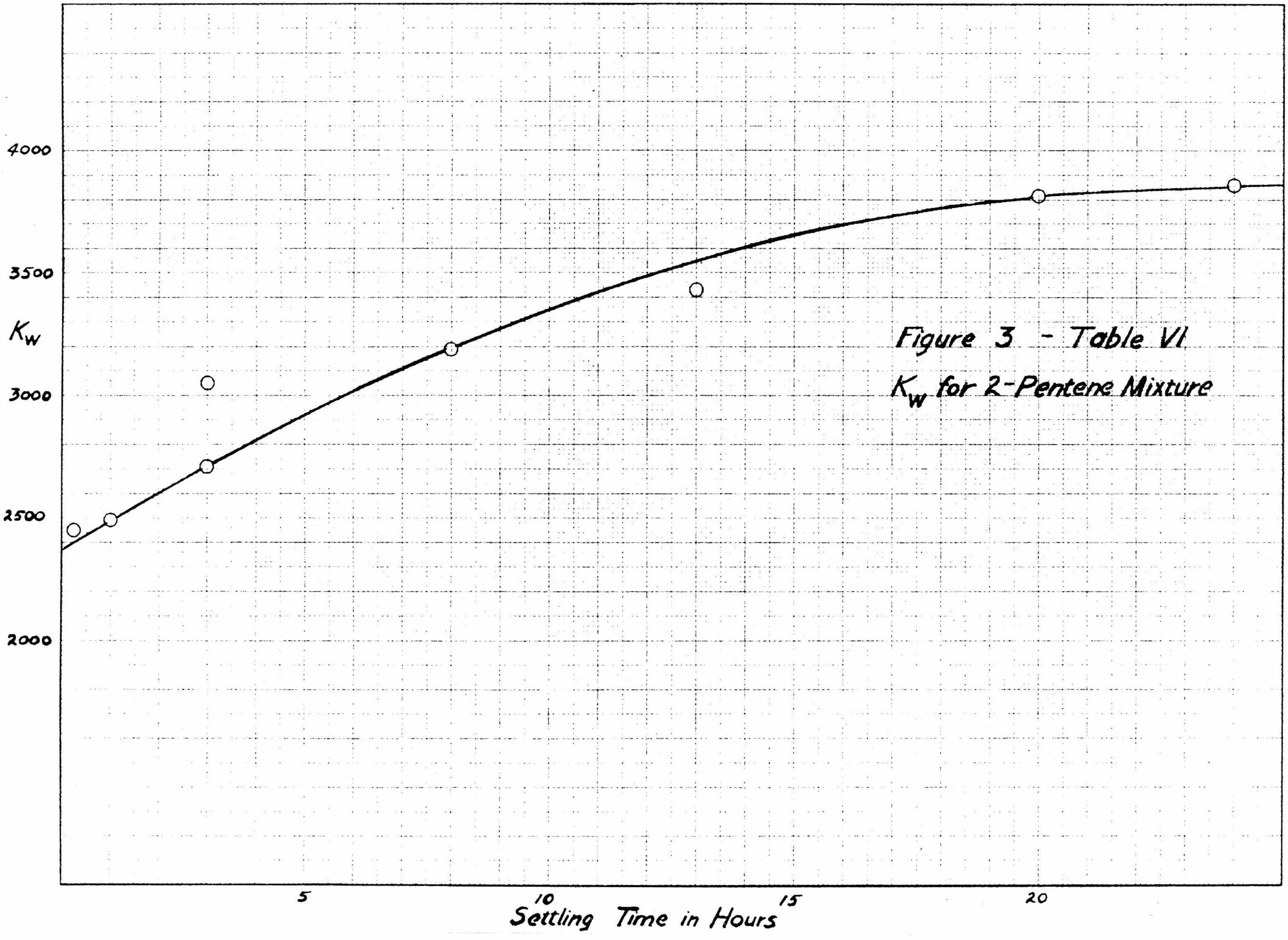


Figure 3 - Table VI

K_W for 2-Pentene Mixture

concentration. That is, the amount of acetic acid used in the blank should be an amount arbitrarily weighted considering an average concentration of bromine after allowing for the ester using some. This was not always done. Since the blank error becomes so critical, and must in the final analysis be estimated, the procedure does not hold any promise for the requisite accuracy of the isomer work.

It might be possible to obtain better and more consistent analytical results by deliberately hydrolysing the ester solutions for a ten or twelve hour period in strong acid and then analysing for the fumaric and maleic acids[12].

2-pentene mixture

The 2-pentene, micro boiling point = 36.1° C. (uncorr.), was always kept under nitrogen. The first apparatus used with the 2-pentene mixture, all of which in this work came from the same preparation, was that shown in Figure 1. This apparatus contained two rubber stoppers exposed to the solution vapor. Runs were made with 1 N potassium nitrate, with 1 N silver nitrate, and with water as the aqueous phase in this apparatus and drifts in the constants were noted as shown for K_W in Table VI and Figure 3. K_W increased with time of settling. This was considered due to loss of 2-pentene from the water phase and vapor into the rubber stoppers. Good agreement was obtained with K_D (Table V.) for a settling time of 45 minutes. All the runs with 2-pentene were made in a 200 ml. flask using 10 ml. of a carbon tetrachloride solution of the pentene and 175 ml. aqueous phase.

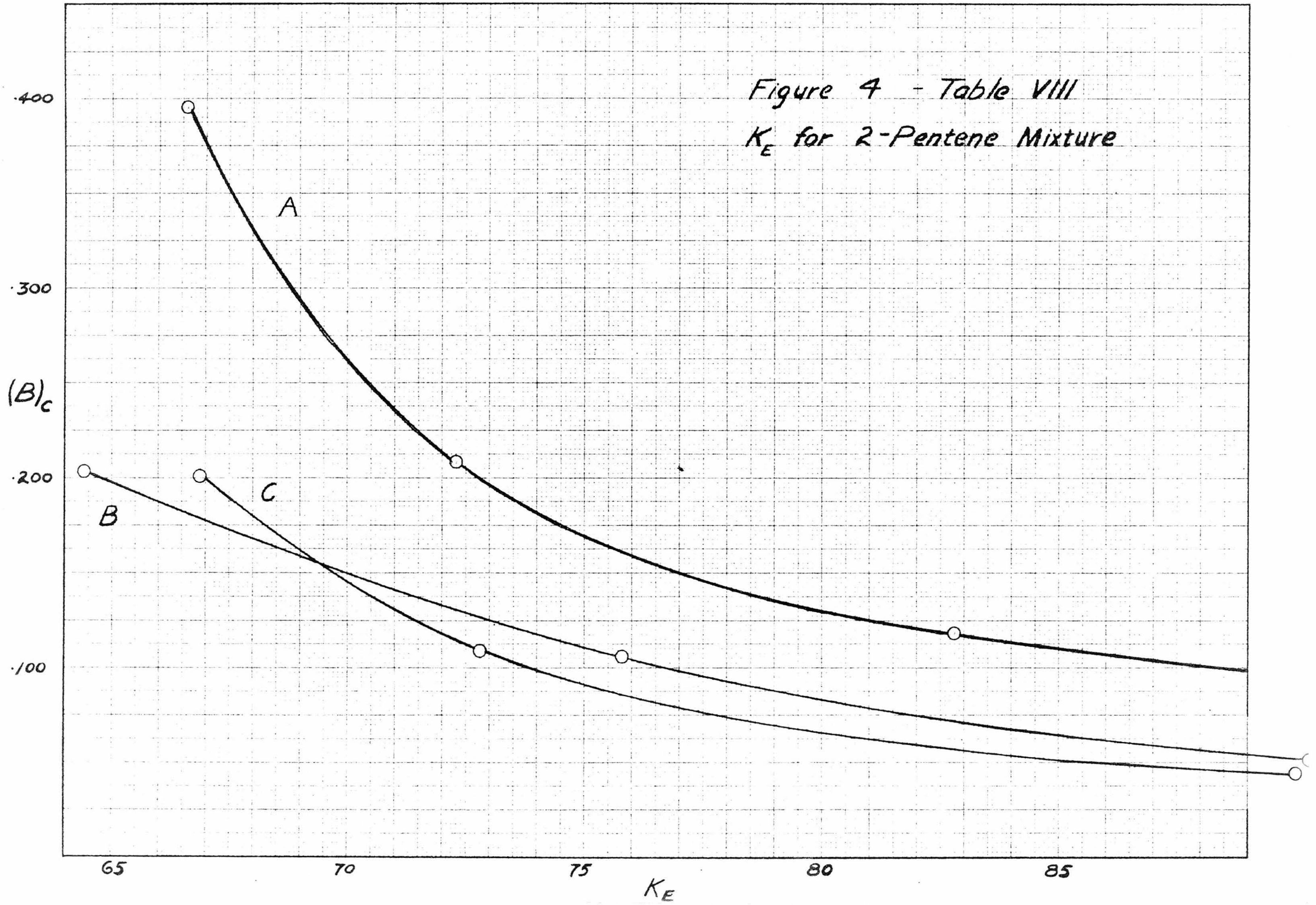


Figure 4 - Table VIII

K_E for 2-Pentene Mixture

In determining the silver association constants with this 2-pentene mixture another type of drift was encountered, - not a drift with time of settling (also present however) but a drift in K_E upon dilution of a run and redetermination of the constant upon the diluted phases using the same procedure. This increase in K_E is shown in Table VIII. and illustrated in Figure 4. The three curves A, B and C represent dilutions of three different initial distributions. At first this upward drift in K_E was considered due to a need for longer stirring time since, after the first sampling is made and more carbon tetrachloride added, the 2-pentene must traverse the interface in the other direction, that is, from the aqueous phase into the carbon tetrachloride phase, in order to reach the previous equilibrium. This would require the breakdown of the complex BAg^+, which is in the aqueous phase, and hance might be expected to require longer stirring and settling. However, as illustrated below in the general theory for the distribution of a mixture of two substances between water and carbon tetrachloride, constancy in K_E upon sampling, dilution, stirring and resampling is not to be expected since it is quite a different proportion of the isomers that remains in the solution. Because of the very great solubility of the pentene in the carbon tetrachloride phase this effect is not more pronounced in the present case. That the stirring time is nevertheless an important factor is shown by runs 117 and 118 (Table IX) where increasing the stirring time brought K_E down quite considerably. The concentration of pentene in carbon tetrachloride was varied 100 % (Table VIII) in initial runs with no observed change in K_E,

Table V:

K_D-2-pentene mixture between 1 N KNO_3 and CCl_4

Rubber Stoppers △

Run No.	75	76	97
Stirring time m.	20	20	20
Settling time m	45	45	45
(B)	.0001366	.0001255	.0000556
$(B)_c$	.5280	.5230	0.226
K_D	3890	4170	4070

Ground Glass Joints □

Run No.	114	112	115
Stirring time m.	20	20	20
Settling time h.	1	3	15
(B)	.0001054	.0001127	.0001137
$(B)_c$	.451	.454	.453
K_D	4270	4030	3990

Average K_D = 4070 ± 100

Table VI.

K_w-2-pentene mixture between water and CCl_4

Rubber stoppers

Run No.	103	101	100	106	104	105	102	80
Stirring time m.	20	20	20	20	20	20	20	20
Settling time h.	0.25	1.00	3.0	3.0	8.0	13.0	20.0	24.0
(B)	.000201	.000196	.000161	.000172	.000155	.000143	.000129	.0001245
$(B)_c$	.493	.488	.489	.465	.494	.490	.492	.480
K_w	2450	2490	3050	2710	3190	3430	3820	3860

Table VII.

K_w,-2-pentene mixture between water and CCl_4

Ground Glass Equipment

Run No.	111	108	110	109
Stirring time m.	20	20	20	20
Settling time h.	1	4	5	9
(B)	.000156	.000147	.000157	.000142
$(B)_c$	.453	.452	.453	.450
K_w	2910	3070	2890	3170

For glass, Average K_w = 3074 ± 141

showing that the complex BAg$^+$ is, as previous authors believed[5], monomolecular.

The loss of pentene into the rubber stoppers was overcome by construction of ground-glass equipment similar to the apparatus in Figure 1 but with the lower bearing of the mercury-seal stirrer sealed directly into the male part of a 24/40 joint. During distributions, a ground-glass stopper was kept in the side arm. While sampling, the same type of rubber-stoppered 3-way stopcock was used as previously but loss of pentene into the rubber during the sampling alone was negligible. Considerable difficulty was encountered in getting suitable glass bearings and ground-in stirring rods that would eliminate whip and breaking of the rod and permit the high speed of stirring necessary. It was necessary to regrind the stirring rods and remold the bearings about every two hours of use. Further investigations using this type of equipment would justify exploring the possibilities of using a graphite-lubricated ground-glass joint in the distribution flask having the stirring rod ring-sealed into the male joint.

All three types of distributions were repeated with the ground-glass equipment. Table V and Table VII show how the settling time drift was eliminated. The potassium nitrate runs are shown in Table V. Since all three of these K_D runs with rubber settled ~~in~~ less than one hour, it is justifiable to take the average of all six runs 4070 for K_D for this 2-pentene mixture. All the silver constants (Tables VIII and IX) are calculated on the basis $K_D = 4070$. Table IX gives the silver association results

Table VIII.

Silver Association Constants for 2-pentene mixture
between 1N $AgNO_3$ and CCl_4
$K_D = 4070$ △
(Rubber Stoppers)

Initial Run No.	77	78	82	81	86
Stirring time m.	20	20	20	20	20
Settling time m.	60	60	60	60	60
$(B)_t$	.00690	.00695	.00660	.00677	.00656
$(B)_c$	.417	.412	.404	.403	.396
K_E	66.7	68.2	65.7	67.6	66.7
K_o	.0164	.0167	.0162	.0166	.0164

Table VIII (cont.)

	A^a	B^a	C^a
Initial Run No.	87	91	92
Stirring time m.	20	20	20
Settling time m.	60	60	60
$(B)_t$	.00655	.00327	.00335
$(B)_c$	.396	.204	.201
K_E	66.6	64.4	66.9
K_o	.0164	.0159	.0165

K_E Average initial runs = 66.6 ± 0.8

K_o Average initial runs = .0164 ± .0002

Second run No.	88	93	94
Stirring time m.	20	20	20
Settling time m.	60	60	60
$(B)_t$	.00375	.00202	.00199
$(B)_c$	.209	.107	.109
K_E	72.3	75.8	72.8
K_o	.0178	.0186	.0179

K_E average second runs = 73.6 ± 1.4

K_o average second runs = .0181 ± .0003

Third run No.	90	95	96
Stirring time m.	20	20	20
Settling time m.	80	60	80
$(B)_t$	.00243	.00110	.000950
$(B)_c$	.118	.0496	.0428
K_E	82.8	90.3	90.0
K_o	.0203	.0222	.0221

K_E average third runs = 87.7 ± 3.3

K_o average third runs = .0215 ± .0008

[a] These columns, A, B and C, represent successive dilutions of initial runs and are shown graphically in Figure 4.

with ground-glass equipment, showing that previous __initial__ runs with rubber stoppers can justifiably be included in values of K_E and K_o for this mixture of the 2-pentene isomers. The K_E drift was again noted and, as mentioned above, increased time of stirring for the diluted runs had a marked effect in reducing the upward drift. However, longer stirring had a likewise marked effect in increasing the mortality of glass rods and bearings.

Table IX.

Silver Association Constants for 2-pentene mixture between

1 N. $AgNO_3$ and CCl_4

(Ground Glass Equipment) $K_D = 4070$

Run No.	116	117[a]	119	121	118[b]
Stirring time m.	20	40	40	20	60
Settling time h.	1.0	1.0	1.0	11	1.0
$(B)_t$	.00580	.00344	.00588	.00583	.00188
$(B)_c$	.355	.193	.361	.358	.109
K_E	65.8	71.6	65.7	65.8	69.2
K_o	.0162	.0176	.0161	.0162	.0170

(a) dilution of No. 116

(b) dilution of No. 117

Average of all initial K_E runs = 66.4 ± 0.8

Average of all initial K_o runs = $.0163 \pm .0002$.

Silver Association with Cis and Trans 2-Pentene.

Materials.

The pure 2-pentene isomers were separated by M. J. Schlatter of this laboratory[13] and had the physical properties shown in Table X. Densities at 20° C. and 25° C., the boiling point at 744 mm. and the refractive index at 20° C. were kindly furnished by Mr. Schlatter.

Method.

Solutions of the isomers were made in carbon tetrachloride and kept under nitrogen as with the mixture and with the ground glass equipment a standard procedure for all runs was carried out, stirring for 20 minutes and settling one hour. Results are given in Tables XI and XII and are summarized in Table XIII.

Data.

Tables X, XI, XII and XIII.

Discussion.

Estimations of the composition of the 2-pentene mixture by interpolating between the values of K_W, K_D and K_E for the pure isomers are invalid because of the average deviation (A.D.) of these results. However K_O does not contain the errors of the other constants,

$$K_o = \frac{K_E}{K_D} = \frac{(Bt) - (B)_c/K_D}{1 - (Bt) + (B)_c/K_D} ,$$

and estimates of the mixture composition should be as good as the

Table X.

Physical Properties of Cis and Trans 2-pentenes (13)

Isomer	Density D_4^{25}	Density D_4^{20}	BP 744 mm.	Ref. Index n^{20}
Cis	0.6504	0.6554	36.06° C.	1.3828
Trans	0.6426	0.6475	35.48° C.	1.3798

Table XI. Trans 2-pentene

	between 1N KNO_3 and CCl_4			between water and CCl_4		
K_D				K_W		
Run No.	123	125	126	132	133	134
Stirring time m.	20	20	20	20	20	20
Settling time m.	60	60	60	60	60	60
(B)	.0000864	.0000916	.0000853	.0001454	.0001443	.0001434
$(B)_t$	.501	.497	.484	.477	.482	.477
K_D or K_W	5780	5420	5670	3290	3340	3330

Average K_D = 5620 ± 140 Average K_W = 3320 ± 20

Silver Association Constants - between 1N $AgNO_3$ and CCl_4

Run No.	129	130	131	144[a]
Stirring time m.	20	20	20	20
Settling time m.	60	60	60	60
$(B)_t$	.00455	.00467	.00459	.00399
$(B)_c$	.409	.414	.405	.361
K_E	61.8	62.7	62.8	61.4
K_o	.0110	.0112	.0112	.0109

Average K_E = 62.2 ± 0.6

Average K_o = .0111 ± .0001

[a] Run 144 was carried out on the same carbon tetrachloride solution of trans 2-pentene after standing under nitrogen two weeks.

Table XII Cis 2-pentene

K_D	between 1N KNO_3 and CCl_4			K_W between H_2O and CCl_4		
Run No.	135	136	137	138	139	140
Stirring time m.	20	20	20	20	20	20
Settling time m.	60	60	60	60	60	60
(B)	.000135	.000130	.000129	.000179	.000187	.000186
$(B)_c$	.477	.478	.464	.472	.480	.479
K_D or K_W	3530	3690	3600	2630	2570	2580

Average K_D = 3607 ± 56 Average K_W = 2593 ± 24

Silver Association Constants - between 1N $AgNO_3$ and CCl_4

Run No.	141	142	143
Stirring time m.	20	20	20
Settling time m.	60	60	60
$(B)_t$	.00983	.00970	.00963
$(B)_c$	.311	.310	.314
K_E	114.2	112.7	110.7
K_o	.0316	.0313	.0308

Average K_E = 112.5 ± 1.2

Average K_o = .0312 ± .0003

Table XIII

2-Pentene Summary

	Trans			Mixture			Cis		
	Total runs		A.D.	Total runs		A.D.	Total runs		A.D.
K_W	3	3320	± 20	4	3010	±110	3	2593	± 24
K_D	3	5620	±140	4	4070	±145	3	3607	± 56
K_E	4	62.2	±0.6	11	66.4	±0.8	3	112.5	± 1.2
K_o	4	.0111	±.0001	11	.0163	±.0002	3	.0312	±.0003

Table XIV.

2,3-Dibromopentane	Dielectric Constant ϵ	% threo	Refractive Index n^{20}
100 % threo	6.51	100	1.5089
mixture from 2-pentene mixture	5.70[a]	75.0	1.5088
100 % erythro	5.43	0	1.5087

[a] Reading was 5.69

Correction to permit straight line interpolation = .014

Corrected straight line reading = 5.70

deviation in K_o, i.e. 1 %.

From the K_o values,

$$\frac{\text{trans 2-pentene}}{\text{cis 2-pentene}} = \frac{.0312 - .0163}{.0163 - .0111} = \frac{149}{52} = \frac{74.1}{25.9}$$

and thus the 2-pentene mixture preparation is 74.1 % of the trans isomer and 25.9 % of the cis.

Corroboration of this result was obtained by preparing the 2,3-dibromopentane of the 2-pentene mixture, carefully drying and distilling it, and measuring the dielectric constant ϵ of this mixture of erythro and threo dibromopentanes, using the cell of C. Gould, Jr. and his calibration of the same[14]. By checking the value of ϵ with M. J. Schlatter's graph of dielectric constant plotted against mixture composition for these 2,3 - dibromopentanes, the mixture of dibromopentanes was found to be 75.0 % of the threo and 25.0 % of the erythro isomer, or 75.0 % trans 2-pentene in the original preparation. The 0.9 % difference in the values for percentage trans is partly due to a racemization[13] of up to 3 % in making the dibromide. However, there is a 1 % deviation in K_o. The refractive index of the dibromopentane[13] was also determined as a check on its purity. A summary is given in Table XIV. Figure 5 shows graphically the composition of any pure mixture of cis and trans 2-pentene for the observed value of the silver association constant K_o based on the assumption that it is a linear function in the mixture. The validity of interpolating, thus to obtain the composition of the mixture upon this assumption is illustrated in the general theory below.

Distribution Between Water and CCl_4 of Two Substances and Their Mixture

B = mols of unsaturated substance per litre, subscript W represents the water phase and C the carbon tetrachloride phase. Prime and double prime represent the two substances.

Define K'_W and K''_W by

$$\frac{B'_W}{B'_c} = K'_W \ (10) \quad \text{and} \quad \frac{B''_W}{B''_c} = K''_W \ (11)$$

If x = mol fraction, does $K_W = x'K'_W + (1 - x')\ K''_W$?

Now $B'_W = K'_W B'_c$ and $B''_W = K''_W B''_c$

$$\therefore B'_W + B''_W = K'_W B'_c + K''_W B''_c$$

and $B'_W + B''_W = B^e_W$ (evaluated by experiment) (12)

Similarly,

$$B'_c + B''_c = B^e_c \text{ (evaluated by experiment)} \qquad (13)$$

Now

$$\frac{B^e_w}{B^e_c} = K_w = \frac{B'_w + B''_w}{B'_c + B''_c} \qquad (14)$$

$$= \frac{K'_w B'_c + K''_w B''_c}{B'_c + B''_c}$$

$$= \frac{K'_w\ B'_c}{B'_c + B''_c} + \frac{K''_w B''_c}{B'_c + B''_c}$$

$$= x'_c \cdot K'_w + x''_c \cdot K''_w$$

$$= x'_c \cdot K'_w + (1 - x'_c)\ K''_w$$

$$= x'_c \cdot K'_w + K''_w - K''_w \cdot x'_c$$

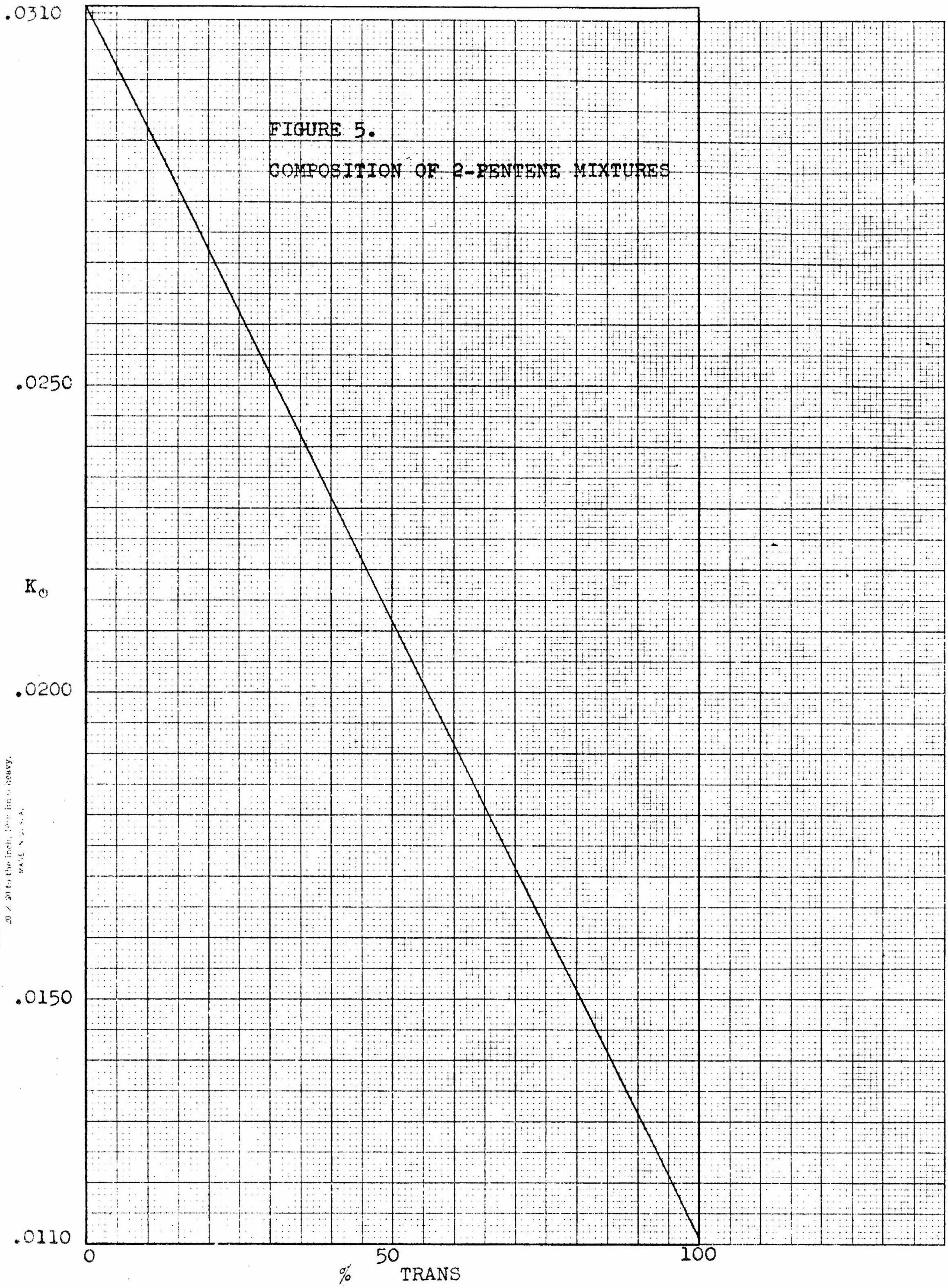


FIGURE 5.

COMPOSITION OF 2-PENTENE MIXTURES

and

$$x_c' = \frac{K_W - K_W''}{K_W' - K_W''} \qquad (15)$$

which is the mol fraction of first isomer in carbon tetrachloride phase.

Similarly,

$$x_c'' = \frac{K_W - K_W'}{K_W'' - K_W'}$$

The silver association constants can be treated similarly.

$$B + Ag \rightleftharpoons BAg$$

$$\text{Observed } K_E = \frac{(BAg)}{(B)(Ag)} \quad \text{for the mixture.} \qquad (16)$$

For the components:

$$K_E' = \frac{(B'Ag)}{(B')(Ag)} \quad (17) \text{ and } K_E'' = \frac{(B''Ag)}{(B'')(Ag)} \qquad (18)$$

$$\text{The observed } K_E = \frac{(B'Ag + B''Ag)}{(B' + B'')(Ag)} \qquad (19)$$

$$= \frac{B'Ag}{(B' + B'')\ Ag} + \frac{B''Ag}{(B' + B'')\ Ag}$$

$$= \frac{B'}{B' + B''}\ \frac{(B'Ag)}{(B')(Ag)} + \frac{B''}{B' + B''}\ \frac{(B''Ag)}{(B'')(Ag)}$$

Since these B concentrations are in the water phase,

$$K_E = x_W' \cdot K_E' + x_W'' \cdot K_E'' \qquad (20)$$

$$K_E = x_W'\ K_E' + (1 - x_W')\ K_E''$$

$$= x_W'\ K_E' + K_E'' - K_E'' x_W'$$

$$x_W' = \frac{K_E - K_E''}{K_E' - K_E''} \qquad (21)$$

Discussion of Other Cis Trans Possibilities

Cis and trans dichlorethylenes suggested themselves by their availability but it was found that these isomers are very difficult to keep free of oxidizing materials. Even kept under carbon dioxide they generate oxidizing substances which with acid and potassium iodide give the deep blue starch color. Hence it would be extremely difficult to obtain more or less permanent end-points in titration.

Maleic and fumaric acids can be brominated quantitatively by means of mercuric ion catalysis[12] but maleic acid, unlike fumaric is quite soluble in water. In fact the distribution would probably favor the water phase enormously, causing many difficulties. At a higher ionic strength, say 4 or 5, and if the distribution is not too greatly in favor of the water, and with added nitric acid to keep the organic silver salts in solution, it may be possible to obtain good silver association constants.

This work on the cis and trans 2-pentenes may lead to the determination of K_o for the other four pentenes and, further, may lead to a study of the effects of various substituent groups on an ethylenic carbon atom with regard to making electrons more or less available for the silver complex.

Summary.

Preliminary analytical and distribution work was carried out with isobutene, 2-butene, cyclohexene and diethyl fumarate.

The silver association constants of a preparation mixture of 2-pentenes were measured by the distribution method and the same technique was applied to the pure cis and trans 2-pentene isomers. For the cis, the silver constant $K_o = .0312 \pm .0003$; for the trans, $K_o = .0111 \pm .0001$. For the mixture of 2-pentenes used, $K_o = .0163 \pm .0002$, leading to the conclusion that the mixture was 74.1 % trans and 25.9 % cis 2-pentene.

By dielectric constant measurements on the dibromide preparation from the 2-pentene mixture, using the results of previous work in this laboratory, the mixture composition was found to be 75.0 % of the trans isomer. The agreement between the two methods is approximately as good as the experimental error in K_o, namely 1 %.

The silver complex with cis 2-pentene is almost three times as strong as the silver trans complex.

This apparatus and method should have a wide usefulness in dealing with mixtures of cis and trans isomers and in studying the effects on the silver complex of various substituents on an ethylenic carbon atom.

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References.

1. (a) Henderson and Gangloff, Journal of the Am. Chem. Soc., 39, 1420 (1917);

   (b) Hunter and Yohe, ibid., 55, 1248 (1933);

   (c) Egloff, Wilson, Hulla and Van Arsdell, Chem. Rev., 20, 345 (1937).
2. Maass and Wright, J. A. C. S., 46, 2664 (1924).
3. Kondakow, Chem. Listy, 24, 1 (1930)
4. Taylor and Baker, "Sidgwick's Organic Chemistry of Nitrogen", Oxford University Press, New York, N. Y., 1937, p. 264.
5. Winstein and Lucas, J.A. C. S., 60, 836 (1938).
6. Dillon, Young and Lucas, J.A. C. S., 52, 1953 (1930).
7. Schmidt and Keller, Z. physik. Chem. A141, 331 (1929).
8. Eberz, Welge, Yost and Lucas, J.A. C. S. 59, 45 (1937).
9. Davis, Crandall and Higbee, Ind. Eng. Chem., Anal. Ed., 3, 108, (1931).
10. Lucas, Hepner and Winstein, J.A. C. S., 61, 3102 (1939).
11. Lucas and Eberz, J. A. C. S., 56, 460 (1934).
12. Lucas and Pressman, Ind. and Eng. Chem., 10, 140 (1938).
13. Lucas and Schlatter, unpublished work.
14. Lucas and Gould, unpublished work.
15. Dillon, Young and Lucas, J. A. C. S. 52, 1953 (1930).