THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report

of

Committee on Thesis

The undersigned, acting as a Committee
of the Graduate School, have read the accompanying
thesis submitted by Minerva Morse
for the degree of   Master of Science.
They approve it as a thesis meeting the require-
ments of the Graduate School of the University of
Minnesota, and recommend that it be accepted in
partial fulfillment of the requirements for the
degree of   Master of Science.

W. H. Hunter
Chairman

C. H. Bailey

Anthony Zeleny

May 18 1920

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report

of

Committee on Examination

This is to certify that we the
undersigned, as a committee of the Graduate
School, have given Minerva Morse
final oral examination for the degree of
Master of Science . We recommend that the
degree of Master of Science be conferred
upon the candidate.

Minneapolis, Minnesota

.....May 18.....192 0.   *W. H. Hunter*
                                    Chairman
                          C. H. Bailey

                          Anthony Zeleny

The Spectrum of the Sodium Salt of

Octochlorquinhydrone

and its

Generators

A Thesis

Submitted to the

Faculty of the Graduate School

of the

University of Minnesota

by

Minerva Morse

In partial fulfillment of the requirements

for the degree of

Master of Science

June

1920

THE SPECTRUM OF THE SODIUM SALT OF
OCTOCHLORQUINHYDRONE AND ITS GENERATORS.

INTRODUCTION

The cause of color in organic compounds has long been a subject of discussion. Physicists have shown that light is a form of electro-magnetic energy transmitted through the ether in some form of wave motion. They have shown also that when white light falls on a body, some of the light may be reflected, some transmitted, and some absorbed within the body, the amount of each depending upon the nature of the body. The absorption of some of the light energy is the immediate cause of color, for only that which is not absorbed will be reflected or transmitted. The light that strikes the eye will have lost some of that energy which made the total appear white, and the effect will be that of color. The problem now consists in determining the reason why energy corresponding to waves of different lengths is absorbed in a colored substance. A discussion here will have to be extended to include absorption in the ultra violet, since absorption both in the visible and ultra violet range of the spectrum seems to be due to the same cause.

ISORROPESIS THEORY

One of the first[1] explanations of absorption by

[1] J.Chem.Soc. 39, 153 (1881); 95, 52 (1909).

solutions was given by Hartley in 1881. He said that there must
be some vibrations of particles in the solution synchronous with
certain of the light waves. Just as sound waves, striking against
a string that has the same natural period of vibration, set it
vibrating, so certain of the light waves would act upon these
particles in solution, setting them into vibration if they were
not already vibrating, or increasing the amplitude of their
vibrations. Their energy would be given to the vibrating
particles, and as a result they would be absorbed. Hartley
attributed general absorption to the translatory movement of the
molecular, and selective absorption to vibrations of certain atoms.
The next problem consisted in determining what vibrations of atoms
were possible. Baly and Desch[2] attributed the vibrations to a
dynamic equilibrium between keto and enol forms, basing their
arguments on the fact that substances containing the group
$-CH_2-CO-$ as a rule show only general absorption, while their salts
in solution show strong selective absorption in the ultra violet.
For instance, the absorption spectrum of acetoacetic ester,
$CH_3-\overset{O}{C}-\overset{H_2}{C}-\overset{O}{C}-OC_2H_5$, showed only general absorption, while that of
its sodium salt, which is believed to have the structural formula
$CH_3 - \overset{\overset{Na}{|}}{\underset{C}{C}} = \overset{\overset{H}{|}}{\underset{C}{C}} - \overset{O}{\underset{C}{C}} - OC_2H_5$, showed selective absorption. The same
was true of acetyl succinic ester, $CH_3-\overset{O}{\underset{|}{C}}-\overset{H}{\underset{|}{C}}-COOC_2H_5$, and its sodium
$H-\underset{\overset{|}{H}}{C}-COOC_2H_5$
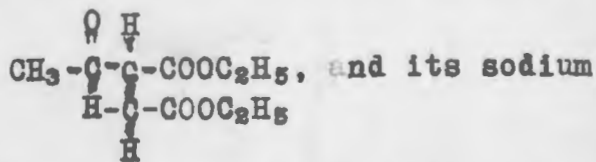
salt. In every case the salt was supposed to exist in the enol form
and this suggested that enolic structure was the cause of selective

[2] J.Chem.Soc. 85, 1029(1904); 87, 766(1905).

absorption.   It had already been proven that the hydroxyl group and the ethylene linking did not cause selective absorption, for the absorption spectrum of many aliphatic alcohols and unsaturated hydrocarbons showed only general absorption.   This proved that the selective absorption was not due to the enolic structure of the salt, and suggested that it might have been caused by the oscillation of the hydrogen or metallic atom between keto and enol forms. Baly and Desch found that the absorption spectrum of acetyl acetone did not differ much from those of its aluminium and thorium salts. All showed strong selective absorption.   According to the conception that absorption was caused by a vibration of the labile hydrogen or metallic atom back and forth between keto and enol forms, this result was unreasonable.   It was inconceivable that the heavy thorium atom could vibrate as fast as the light hydrogen atom. They concluded that the real cause of absorption was not an atom shift, but a valence or electron shift.

        This theory was further borne out by the discovery of Baly and Stewart[3] that compounds containing the -CO-CO- group, in which no atom shift is possible, show selective absorption, often in the visible range.   In such cases a valence shift from keto to peroxide form was suggested.   They applied the same reasoning to quinones, and explained their yellow color by absorption due to the oscillation of valences between the quinone and peroxide form.

$$-\overset{O}{\underset{}{\overset{\|}{C}}}-\overset{O}{\underset{}{\overset{\|}{C}}}- \rightleftharpoons -\overset{O-O}{\underset{}{\overset{|}{C}}=\overset{|}{C}}-$$
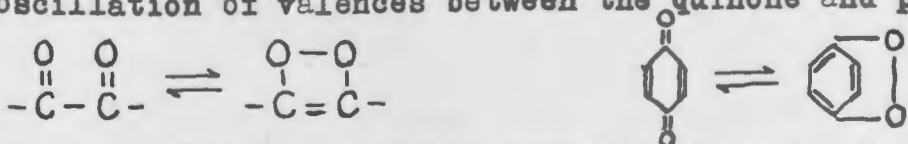
At this time they proposed the term "isorropesis" to indicate the possible vibration of "residual affinities" between two isomeric

3
 J.Chem.Soc. 89, 489, 502(1906)

structures.

Baly, Edwards and Stewart[4] then explained benzene absorption in the ultra violet by showing how the benzene ring might pulsate between two displaced forms, ⬡ and ▭ , and how in this process seven different makes and breaks in residual affinities might occur. This would account for the seven absorption bands of benzene.

FORCE FIELD THEORY.

In 1912 Baly[5] brought forth a different theory to account for light absorption, known as the force field theory. According to him the formation of hydrates and double salts is due to the secondary valences which all atoms possess to a greater or less extent. Since molecules are made up of atoms, each of which is the center of a force field, the fields of force will mutually affect one another and all or most of them will condense or close, as do the lines of force of a horseshoe magnet when an iron bar is laid across its ends. That amount of affinity left uncompensated after the maximum condensation between the various force fields has occurred is called "residual affinity." Opening of the force fields may be brought about by the application of free energy. Light waves of definite length might supply this energy, opening up the closed fields of force, and thus transferring their energy to the force fields, or in other words, being selectively absorbed. In some cases light does not supply enough energy to open up the closed systems of a pure substance,

[4] J.Chem.Soc. 89, 514(1906).

[5] J.Chem.Soc. 101, 1469, 1475 (1912).

but will act on a substance when in solution.   In such cases
a solvent with strong residual affinity will start the opening
process and set up an equilibrium between the closed and more
open systems, while the absorption of light waves shifts the
equilibrium still further toward the more open phase.   This
theory explains the catalytic effect of light, since absorption
of light causes the force field to open up, thus increasing the
amount of residual affinity, and this in turn increasing the
reactivity of the molecules.

QUINHYDRONE THEORY.

A special case of the isorropesis theory, known as the
quinhydrone theory, grew out of an attempt to explain the cause
of "deep color."   It has long been known that if equal
molecular quantities of yellow quinone and colorless hydroquinone
are dissolved in alcohol and the two solutions mixed, a deep
olive green precipitate of quinhydrone will result.   The exact
relationship between the two compounds is uncertain, but they
are usually recognized as forming an addition compound, and,
in writing their structural formulae, dotted lines from the
carbonyl oxygen of the quinone to the hydroxyl of the hydroquinone,
since both of these show strong residual affinities, indicate
some force of attraction between the two.   There are many
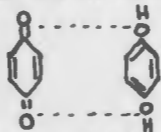
similar quinhydrones known, and all are deeply colored substances
derived from weakly colored quinones and colorless hydroquinones.
The striking feature in them is the presence of a chromophore
in the quinone and an auxochrome, hydroxyl or amino group, in the

hydroquinone.   Thus the two factors which, occurring together in one molecule, produce deep color in dye stuffs, here produced deep color although the two are apparently in two different molecules. In 1907 Baeyer[6], in a study of aniline dyes, found that at least two amino groups in the para position were necessary for "deep color," and that in the case of diamino triphenyl carbinol it did not matter which amidated benzene ring passed into the quinoid form when treated with an acid.   This suggested that the quinoid form of one ring passed into the quinoid form of the other ring, and meant that there was a continual oscillation of valences back and forth, so that at one moment one benzene ring would be quinoid and the other benzenoid, while at the next moment the condition would be just reversed.   Baeyer prepared the following formulae to
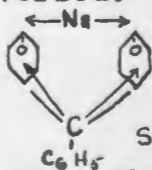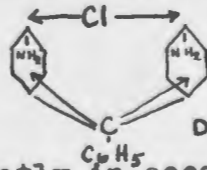
Sodium Benzaurin   Döbner's Violet

illustrate this theory.   It is strictly in accord with Baly's theory of isorropesis, since it suggests a dynamic condition in which the two valences are continually vibrating back and forth between the two nuclei.

Willstätter and Piccard[7] saw an analogy between the theory of aniline dyes as proposed by Baeyer, and the action of the quinhydrones.   They applied the same theory of isorropesis to the quinhydrones and suggested an oscillation of valences back and forth between the two molecules in such a way that one molecule would not be wholly quinoid, but at one moment quinoid and the next moment

[6] Ann. 354, 163(1907).

[7] Ber. 41, 1463(1908).

benzenoid.   The following equation represents the final stages
of such an equilibrium:
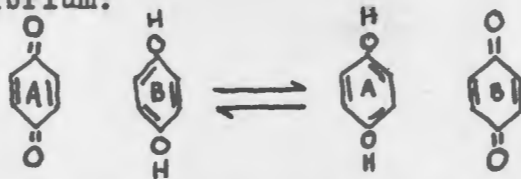
In almost every case of deep color such a quinhydrone oscillation
between two or more nuclei, either in the same molecule, or
in different molecules seems possible.   The quinhydrone theory
has been employed to explain the deepening of color produced by the
presence of an auxochrome.

The question arises as to whether there is any relation
between Baly's theory and the quinhydrone theory.   Can the
quinhydrone formation be explained by Baly's theory as well as by
the isorropesis theory?   Hydroquinone contains the two hydroxyl
groups which have strong residual affinity.   When present in the
same solution, the hydroxyl groups would have the same or probably
a greater effect than the solvent in opening up the force fields
around the quinone, so that those light waves would be absorbed
which produce the effect of deep color.   Such an explanation
would not necessitate the benzenoid ring changing to the quinoid
form and back again.   It was in an effort to clear up the relation
between quinone and hydroquinone in the quinhydrone that the
present work was undertaken.   It was hoped that a comparison
of the absorption spectrum of the sodium salt of octochlorquin-
hydrone with those of its components would give some clue as to its
nature.

TYPES OF QUINHYDRONE.

It is well, before discussing the special bearing that

this paper has on the question, to briefly review quinhydrone
formation in general.   The first quinhydrones known were those
formed from quinone and hydroquinone and their simple derivatives.
The next step was to recognize the Würster salts as quinhydrones.[8]
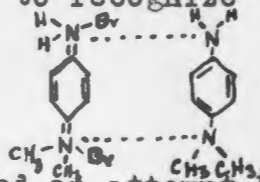
Würster's Red

After this followed an attempt by Knorr and Schlenk[9] to prepare the
free quinhydronelike base, in which the imine and amine groups
replace the carbonyl and hydroxyl.   They found that when equivalent
amounts of yellow quinonediimine and colorless p-phenylenediamine
in ether solution were mixed, the solution turned red, but they
were unable to purify the mass which separated when the solvent
was evaporated off in vacuo.   When they used benzidene instead of
p-phenylenediamine, a dark red, crystalline addition product
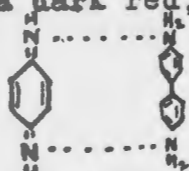
precipitated out of the ether solution.   Schlenk and Knorr secured
beautiful, shiny, bronze crystals from a benzene solution of
chloranil and tetramethyl p-phenylenediamine, and deep blue crystals
from mixing saturated ether solutions of quinone and p-phenylene-
diamine.   The peculiar point about the last quinhydrone is that
analysis showed its components present in the ratio of 5:2 instead
of 1:1, as in the others.

        It was formerly believed that one molecule of quinone
unites with two molecules of a monovalent or one molecule of a

[8] Ber.41, 1463 (1908).

[9] Ann. 368, 277(1909).

divalent phenol, but in 1909 Meyer[10] showed that this does not hold because, aside from the case just mentioned, he was successful in preparing quinhydrones with either one or two molecules of the phenol. Siegmund[11] had already prepared a compound of quinone with two molecules of pyrocatechol, a divalent phenol. Meyer prepared an orange quinhydrone from quinone and one molecule of a chlorphenol, a dark phenoquinone with two molecules of the chlorphenol, a dark red quinhydrone with one molecule of *-naphthol, and a dark brown phenoquinone with two molecules of the latter.

Schlenk and Knorr also attempted to make a quinhydrone from quinone and the dimethyl ether of hydroquinone. The two when heated in a tube on a water bath, without the medium of a solution, united and turned dark red. On cooling and solidifying, the color disappeared. This seems to indicate the existence of a quinhydrone, unstable or dissociated at ordinary temperatures, which does not contain a labile atom which might vibrate back and forth between two molecules. Pfeiffer[12] succeeded in making a similar, stable compound out of chloranil and p,p[1]-diethoxydinaphth-oxystilbene. This mixture gave a dark green melt which, on cooling, remained a dark solid. A hot benzene solution of the two, on cooling slowly, gave black crystals with a blue luster, which dissolved in benzene with a green color. Analysis showed that they consisted of one molecule of chloranil and two molecules of the diethoxydinaphthoxystilbene.

[1]Ber. 42, 1149(1909).

[11]J.pr. Chem. II, 83, 553(1911).

[12]Ann. 404, 1(1914).

Another fact which must be taken into account in formulating a theory as to quinhydrone formation is that quinone forms very dark, garnet-red, crystals of quinhydrone with resorcin,[13] a compound which could hardly shift into the quinoid form, since no meta-quinones are known.

Still another type of quinhydronelike compounds is that formed by the action of aromatic compounds upon quinones. Pfeiffer[14] found that solutions of quinone in molten stilbene, naphthalene, and anthracene are deep orange in color, but on cooling turn back to the yellow color of the quinone. The same was true of chloranil with these substances. He also found that color reactions of this kind take place in solution. For example, a mixture of chloranil and naphthalene gives an orange chloroform solution, but on evaporation the color of the chloranil returns. He also succeeded in obtaining an orange red, crystalline substance by dissolving chloranil in durol, $C_6H_2(CH_3)_4$.

ABSORPTION SPECTRA OF QUINHYDRONE.

Some work has already been done on the comparison of the absorption spectra of quinhydrone with those of their constituents. Hartley and Leonard[15] in 1909 photographed the absorption spectra of solutions of benzoquinone in ether, hydroquinone in water and their quinhydrone in alcohol, and recorded their results in a diagram of dilution curves as shown in Fig.1. A comparison of the curves seemed to show that the union of the

[13] Ber.12, 1978(1879).

[14] Ann.404, 1(1914).

[15] J.Chem.Soc. 95, 34(1909).

OSCILLATION FREQUENCIES

1000   1500   2000   2500   3000   3500   4000   4500   5000
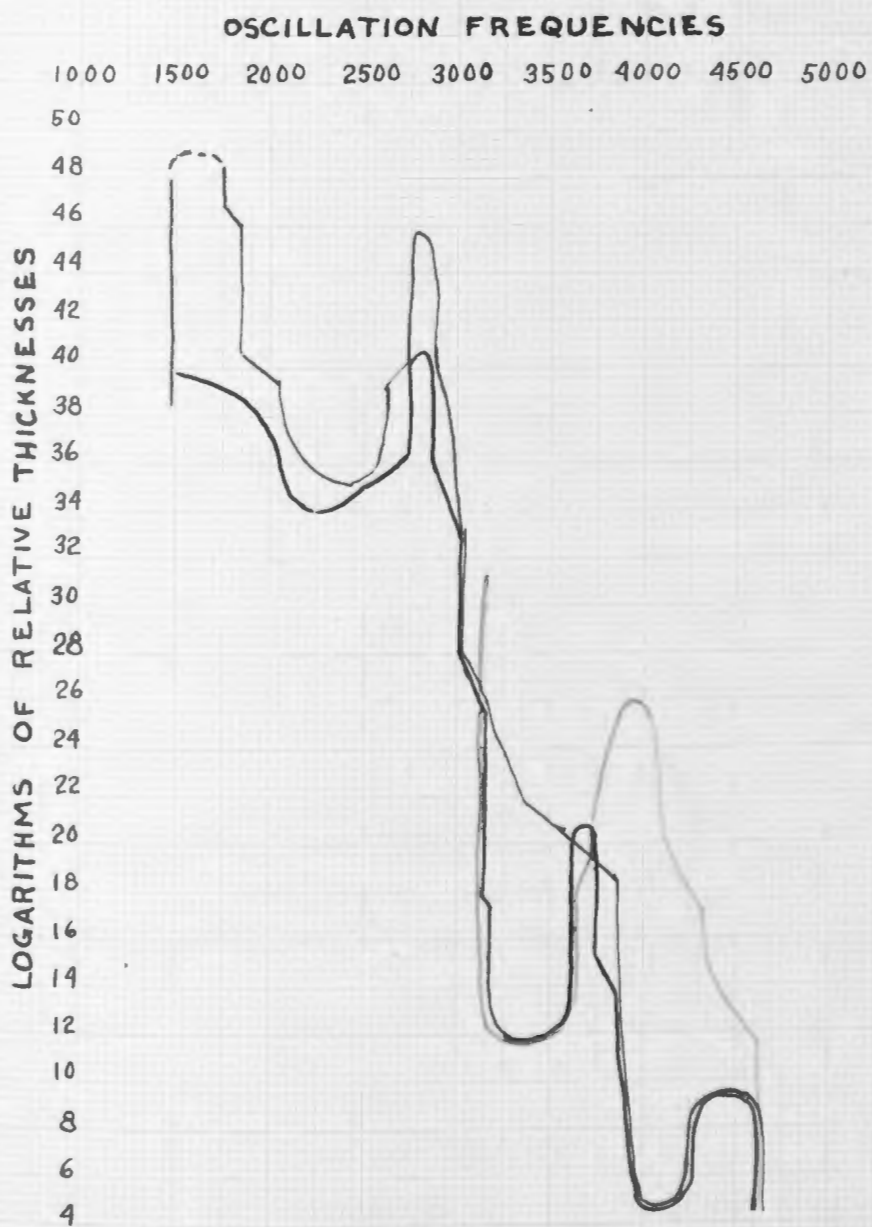

FIG.1

——————— P-BENZOQUINONE IN ETHER

—————— QUINHYDRONE IN ALCOHOL

←————— HYDROQUINONE IN WATER

two molecules was not of a very firm nature, because the curve
of the quinhydrone exhibited the absorption curves of each of
the constituents almost as completely as if the photographs of the
two substances had been superposed upon each other.   However,
the bands were shifted slightly toward the red, and in the visible
range were quite altered.   They concluded from this slight
evidence that quinhydrone does not undergo dissociation in
alcohol.

Pratt and Gibbs[16] in 1913 tried the same experiment
using two equivalents of phenol instead of one equivalent of
hydroquinone, and represented their results as in Fig. 2.   They
found that in the case of phenolquinone the alcoholic solutions
of .01 and .001 molar concentrations gave curves which were not
continuous with the curve for a .1 molar solution, nor with each
other, and explained this as due to the increased dissociation
into components in the weaker solutions.   To cut down dissociation
they increased the concentration of phenol, one of the components,
by photographing the absorption spectrum of quinone in eight
equivalents of phenol, and in pure phenol.   With phenol used as
a solvent, the dissociation would be at a minimum.   This gave
a curve for phenolquinone which exhibited merely a step-off,
where the curve of benzoquinone shows a well marked band. Lifschitz[17]
in 1915 repeated the experiment with the quinhydrone and obtained
slightly different curves as shown in Fig. 3.   The important
point to be noticed here is that the curves of the quinhydrone
in the various concentrations are not continuous, and again seem

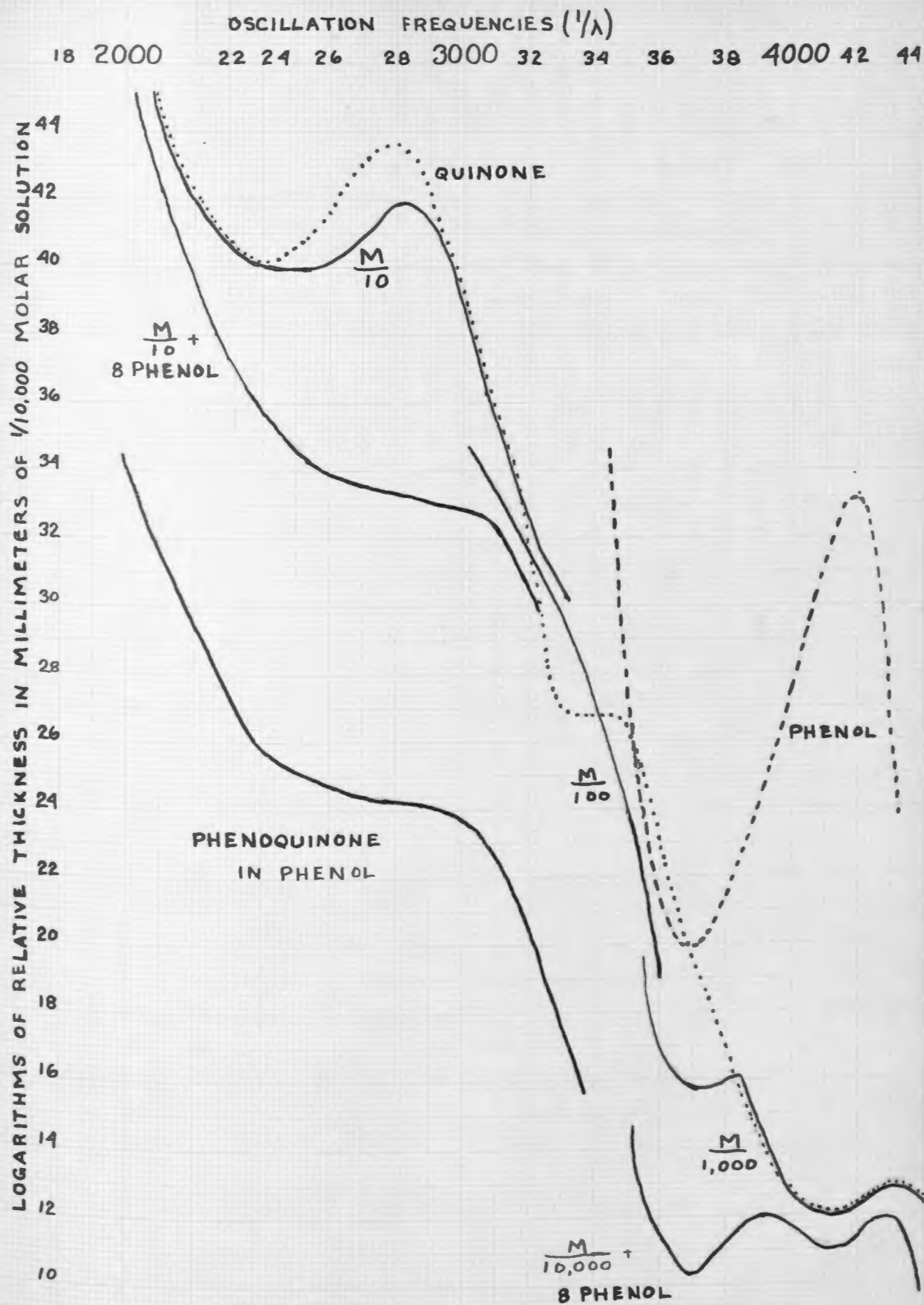[16] Phillipine J.Sci. A, 8, 51(1913).

[17] Ber. 48,1130(1915).

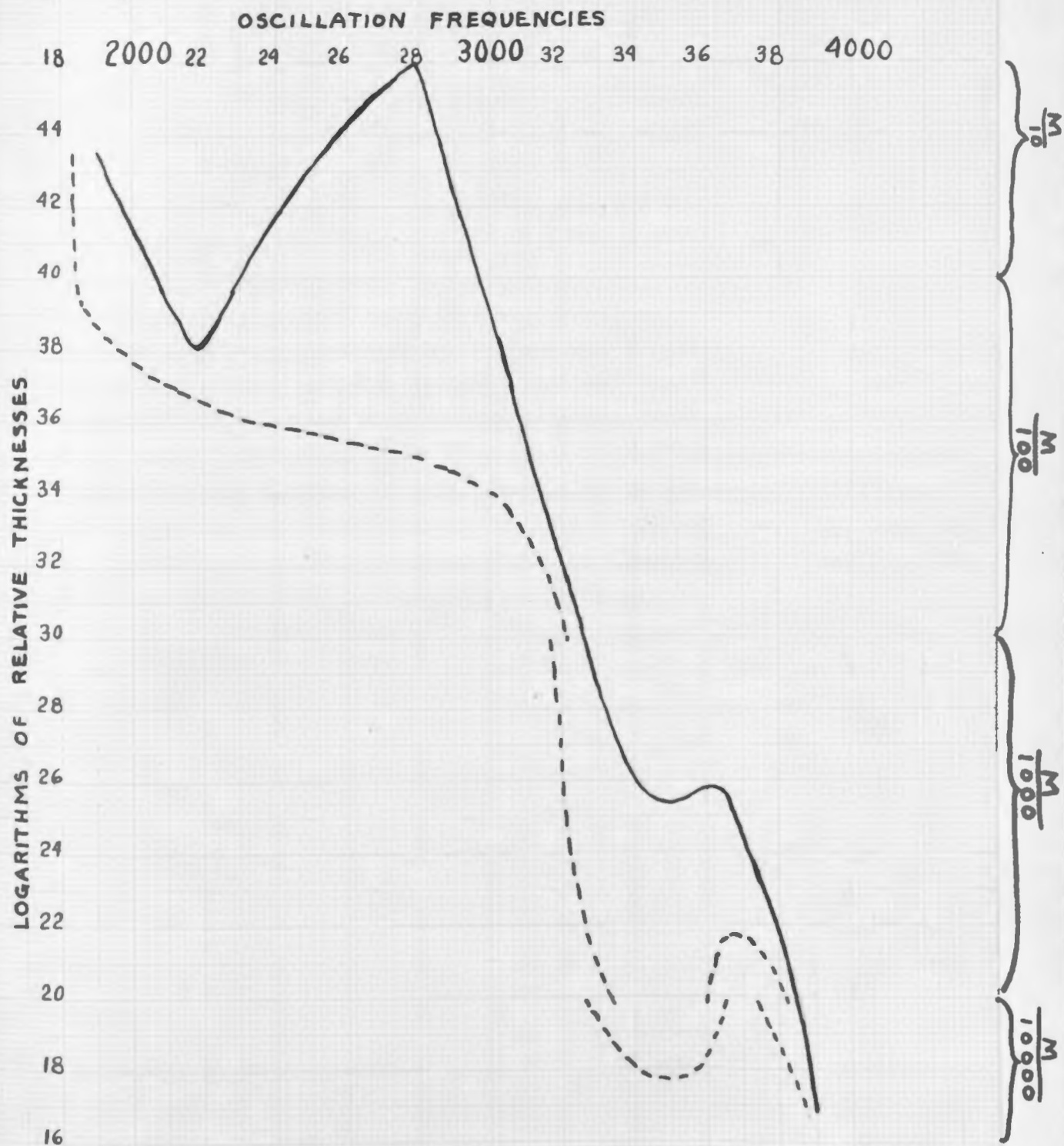FIG. 2   FULL CURVES = PHENOQUINONE

FIG.3

——————— QUINONE IN ALCOHOL
- - - - - QUINHYDRONE IN ALCOHOL

to point to increased dissociation in the dilute solutions.

Hantzch [18] repeated the experiment, using increasing concentrations of hydroquinone to a given concentration of quinone, in an effort to cut down dissociation.   The curves obtained, as shown in Fig. 4, indicate an increasing persistence of the quinone band in the visible region, and an increasing tendency of the band toward general absorption, somewhat similar to the curve of quinone in phenol.   These results seem to show that the quinhydrones and phenoquinones in solution are considerably dissociated, and that the comparison of their absorption spectra with those of their components is not successful in showing the relation between the two in the quinhydrone.   This conclusion is confirmed by the results of Torrey and Hardenbergh [19] in connection with molecular weight determinations of phenoquinone and quinhydrone by the freezing- and boiling-point methods.   Their determinations show that both phenoquinone and quinhydrone are highly dissociated in benzene, and that the addition of either component reduces the amount of dissociation.   About the same time Biltris [20] obtained the same results for ether solutions.

Lifschitz [21] then compared the absorption spectrum curves of chloranil, hexamethyl benzene, and their quinhydrone which appeared to be more stable in solution, and found that the curve of the quinhydrone was quite different from those of its components. We were not able to get a copy of Lifschitz's original article,

[18]Ber.42, 511 (1916).
[19]Am.Chem.J. 33, 167(1905).
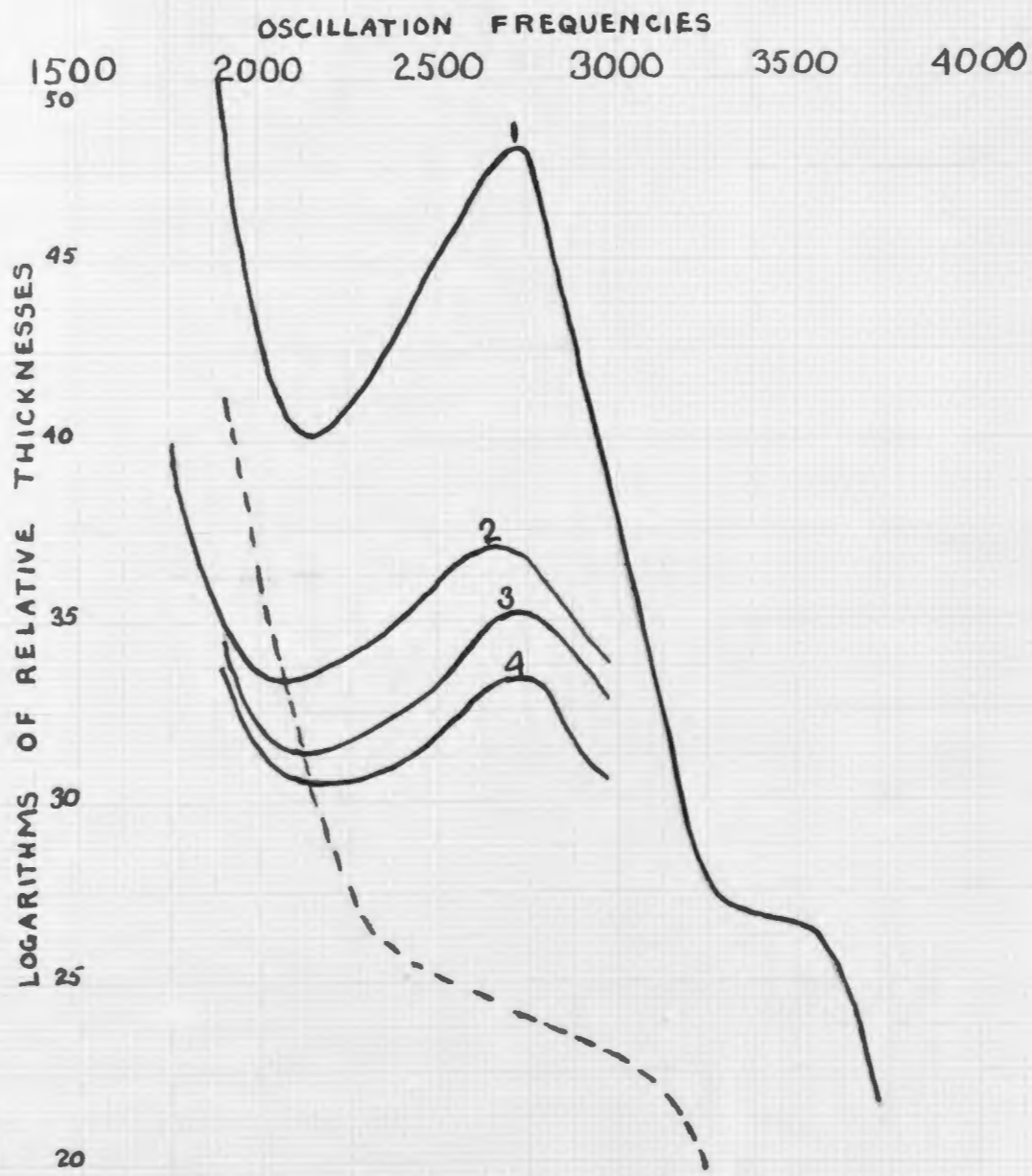[20]Acad.Roy.d.Belgique. III, 32, 300; 35, 60
[21]J.Chem.Soc.,110 A., 823(1916).

OSCILLATION FREQUENCIES

FIG. 4

——— 1. QUINONE IN ALCOHOL

——— 2. $n/100$-QUINONE $+1n$- HYDROQUINONE IN ALCOHOL

——— 3. "   " $+2n$-   "   "   "

——— 4. "   " $+3n$-   "   "   "

— — — QUINONE IN PHENOL + LITTLE CHLOROFORM

and so cannot reproduce the curve here. We have undertaken to compare the absorption curves of the sodium salt of octochlorquin- hydrone with that of its components in the hope that this substance would show less dissociation, and that its absorption spectrum would represent more nearly that of the pure substance.

OCTOCHLORQUINHYDRONE.

Ling and Baker,[22] in an attempt to make chlorinated quinhydrones, succeeded in making the di- and tetra-chlor deriva- tives easily, the hexa-chlor with difficulty, and the octo-chlor not at all. It was then decided that increasing the number of negative groups in the quinoid nucleus reduced the reactivity or residual affinity of the carbonyl groups, so that, when four chlorine atoms were introduced into the ring, the resulting molecule had lost all power to form quinhydrones. This theory is borne out by the fact that octoiodoquinhydrone, containing the less megative iodine atoms, has been made.[23] It was also apparently confirmed by Richter[24] when he discovered that it was possible to make a quinhydrone from the mono-nitroquinone, but not from the di-nitroquinone. In 1912 Torrey and Hunter[25] found that chloranil when dissolved in cold, absolutely dry acetone and treated with a cold, saturated solution of anhydrous sodium iodide immediately gave a dark, blue-green precipitate which, when analyzed, proved to be the sodium salt of octochlorquinhydrone. This suggested that the non-formation of the octochlorquinhydrone

[22]J.Chem.Soc. 63, 1314(1893).
[23]Ber. 45, 871(1915).
[24]Ber. 46, 3434(1913).
[25]J.Am.Chem.Soc. 34, 702 (1912).

was not due so much to the decreased reactivity of quinone as to the change in solubility of the quinhydrone and its components. In the case of the fairly soluble mono- and di-chlor quinones and their corresponding hydroquinones, a concentration could be secured larg enough to reach the solubility product of their quinhydrones, but the chloranil and tetrachlorhydroquinone are so insoluble that it is impossible to reach the solubility product of the octochlorquinhydrone. Its sodium salt, however, is much more insoluble and will precipitate out.

EFFECT OF CHLORINE SUBSTITUENTS ON QUINONE RING.

One point to be considered in studying the quinhydrone of chloranil is the different state of the quinone ring in quinone and chloranil. Kehrmann[26] showed that when the hydrogen atoms of benzoquinone are replaced, one at a time, by methyl radicals or by halogen atoms, a change takes place in the reactivity of the carbonyl groups. His conclusions were based on the oxime formation of substituted quinones. Mono-substituted quinones, when teated with hydroxylamine, first form a monoxime and, on further treatment, a dioxime. Para or 2.5 disubstituted quinones form dioximes, while meta or 2.6 disubstituted quinones only form a monoxime. Tri-substituted quionones form monoximes only, while tetra-substituted quinones form no oxime.

Baly and Stewart[27] took photographs of the absorption spectra of benzo-quinone and its mono-, di-, and tri-chlor derivatives and found that the isorropic band gradually diminished until it vanished into general absorption, while the persistence

[26] Ber. 21, 3315; J.pf.Chem. II,32,399(1889);40,257(1889).
[27] J.Chem.Soc. 89, 618(1906).

of the benzenoid band gradually increased.   This seemed to mean
a decrease in the quinoid character of the quinone and an increase
in its benzenoid character.   If the quinone is in a continual state
of oscillation between quinoid and peroxide forms, as is assumed
in the theory of isorropesis, then the equilibrium is shifted
over toward the peroxide form by the influenėe of substituent groups.
Evidently the chloranil should be still more peroxide in its
behavious, and this should show up in its absorption spectrum.
This change in nature should have some influence on its quinhydrone
formation.

COLOR DEEPENING EFFECT OF METALS.

The effect of introducing the metal sodium into the
quinhydrone molecule, as is done in the case of the sodium salt
of tetrachlor quinhydrone, offers a further complication in the
problem.   If a metal is introduced into a colorless substance which
shows an absorption spectrum in the ultra violet, that band is
shifted toward the red end of the spectrum.   For example, the
absorption spectra of phenol[28] and hydroquinone,[29] in the presence
of one or more equivalents of sodium, differ quite considerably
from the absorption spectra of the pure substances.   The band
becomes shallower, is shifted slightly toward the red, and a
shallow band in the benzene region makes its appearance.   In the
case of phenol, and the same reasoning might be applied to hydro-
quinone, this is explained[28] by assuming that the phenol band is
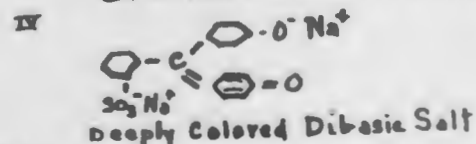due to a keto-enol tautomerism between the form usually written and
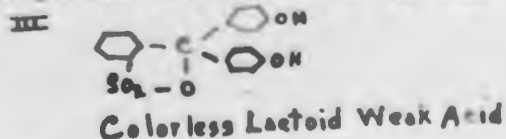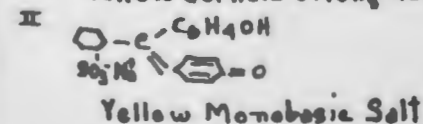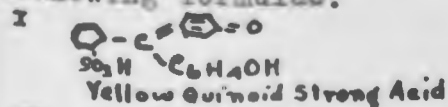
[28]Phillipine J. Sci. A, 8, 33(1913).
[29]J.Chem.Soc., 87, 1353(1905).

a quinoid form, $C_6H_5OH \rightleftharpoons C_6H_4O \cdot H_2$, and that the presence of the sodium shifts the equilibrium back toward the enol or benzenoid form.

The general effect of introducing a metal atom into a substance already colored is to deepen the intensity of the color. For example, phenolquinone has a beautiful, red, crystalline structure, but its sodium salt, made by mixing a quinone solution with two equivalents of sodiumphenylate, is a dark blue, amorphous powder[30] when dried in vacuo. When dried in air it has a bronze tinge which may be a surface color, similar to that of dye stuffs, or due to some decomposition product, since the powder is very hygroscopic and decomposes readily in the presence of water. The same color deepening in the presence of metallic ions takes place in the phenolphthalein indicators, according to Acree.[31] In the case of phenolsulfonphthalein he found the color in the presence of small amounts of alkali is light yellow, and remains so until seventy-five per cent of an alkali equivalent is added. When ninety-five per cent of an equivalent is reached, the indicator turns dark red. He explained this color effect by assuming that, of the two replaceable hydrogen atoms, the hydrogen of the SO_3H group is replaced first by sodium, and the hydrogen of the hydroxyl later. He showed the various steps in the reaction by the following formulae:

I — Yellow Quinoid Strong Acid

II — Yellow Monobasic Salt

III — Colorless Lactoid Weak Acid

IV — Deeply Colored Dibasic Salt

[30] Am.Chem.J. 18, 14 (1896).
[31] J.Am.Chem.Soc. 40, 1092 (1918).

In such a condition, quinoid and phenol groups in the same
molecule correspond to a phenoquinone, but are only capable of
producing a light yellow color.   When the sodium atom replaces
the hydrogen atom of the phenol, then the deep red color appears.

The same color deepening effect should be expected in
the case of the quinhydrones.   This relation cannot be proved,
because the sodium salt of quinhydrone has never been made, and
the sodium salt of octochlorquinhydrone has no corresponding
quinhydrone with which it can be compared.

The fact that the sodium salt of octochlorquinhydrone
is stable, while the free acid compound is not, may give some clue
as to the action of the sodium in deepening the color of the pheno-
quinones and related compounds.   The free acid, hydroquinone or
phenol, is very slightly dissociated, while the corresponding salt
should be highly ionized.   This just mean that the great number
of free sodium ions exerts a much greater effect than the com-
paratively few hydrogen ions in holding the two unlike molecules
together.   At the same time the sodium ions would either increase
the amount of isorropesis between the quinone and phenol or
hydroquinone, or open up further the force fields of the quinone,
depending upon which theory best explains the facts.

EXPERIMENTAL

TETRACHLORHYDROQUINONE.

Tetrachlorhydroquinone was obtained by reducing a commercial chloranil which contained trichlorquinone as an impurity. The impure chloranil was dissolved in hot acetone saturated with sulphur dioxide. Distilled water was then added, producing a light yellow precipitate of chloranil, which soon disappeared under the reducing action of the sulphurous acid. Tetrachlorhydroquinone was formed, but was soluble in the mixture of acetone and water. The acetone was distilled off, and the tetrachlorhydroquinone fell out as a white crystalline precipitate. The trichlorhydroquinone remained in solution in the hot water. The precipitate was filtered off and recrystallised from glacial acetic acid. The crystals contained glacial acetic acid of crystallization which was soon lost on standing in air. The fine white powder remaining melted at 232°, the correct temperature.

CHLORANIL.

Part of this pure tetrachlorhydroquinone was oxidized back to tetrachlorquinone by boiling gently for two hours with concentrated nitric acid. The mixture was then diluted with water, the yellow tetrachlorquinone filtered off, washed free from nitric acid and recrystallised from glacial acetic acid. The crystals melted in a sealed tube at 286°C. The pure chloranil melts at 290°C. All attempts to get crystals with a higher melting point failed, but, according to Graebe,[32] a product that

[32] Ann. 283, 19.

melts between 280° and 290°C. should be considered pure chloranil, since a very small amount of the trichlorquinone lowers the melting point considerably.
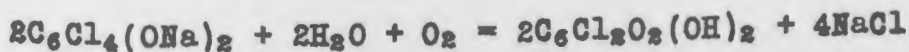
SODIUM SALT OF OCTOCHLORHYDROQUINONE.

The sodium salt of octochlorquinhydrone was made according to the method previously described. Cold, saturated, absolutely dry acetone solutions of chloranil and sodium iodide were mixed. A dark blue-green precipitate appeared immediately. This was filtered off, washed with dry acetone until the washings gave no test for free iodine, and dried in a desiccator.
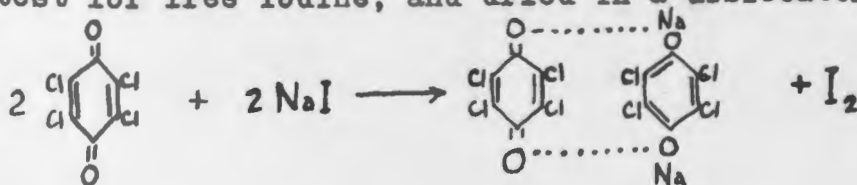
SODIUM SALT OF TETRACHLORHYDROQUINONE.

Attempts were made to prepare the sodium salt of the tetrachlorhydroquinone. Graebe[33] tried to make the corresponding potassium salt by dissolving tetrachlorhydroquinone in potassium hydroxide solution, but since the substance was eadily soluble in water and alcohol, and was quickly decomposed, he was unable to obtain it in a pure condition. The solution was clear at first, but quickly turned reddish-brown if exposed to the air. On standing, crystals of chloranilic acid separated out. We found the same true of the sodium salt.

$$2C_6Cl_4(ONa)_2 + 2H_2O + O_2 = 2C_6Cl_2O_2(OH)_2 + 4NaCl$$

We thought that by dissolving the tetrachlorhydroquinone in an absolute alcohol solution containing two equivalents of sodium ethylate we might obtain a solution of the sodium salt which would be stable long enough to be photographed. Experiment sho wed

[33] Ann.146, 19 (1868).

that the solution started to turn brown just as soon as the tetrachlorhydroquinone came in contact with the sodium ethylate. The color continually deepened at the surface, showing that decomposition was due to the action of the air. This probably oxidized the tetrachlorhydroquinone to chloranil, which in turn reacted with sodium ethylate to form the diethyl ether of chloranilic acid. Since it was impossible, in taking photographs of the absorption spectra, to use a cell for the solution which did not expose it to the air, this plan had to be abandoned.

DIETHYL ETHER OF TETRACHLORHYDROQUINONE.

The diethyl ether was prepared according to the method of Graebe[34] by heating tetrachlorhydroquinone with two equivalents of sodium ethylate, and a little more than two equivalents of ethyl iodide in a concentrated alcohol solution for three hours. The flask containing the mixture was connected with a reflux condenser and heated on an oil bath kept at a temperature of about 140°C. The excess ethyl iodide and alcohol were removed by evaporation, and the potassium iodide was dissolved out with water. A thick dark mass was left, out of which impure crystals of the diethyl ether were secured by sublimation. When recrystallized twice out of alcohol, white, needle-shaped crystals were formed which showed a melting point of 110°C., which did not change on recrystallizing again.

TETRACHLORHYDROQUINONE DIACETATE.

The diacetate was made by heating the tetrachlorhydroquinone with a little more than the calculated amount of acetic

[34] Ann. 146, 19 (1868).

anhydride for about three hours on a water bath.   White, needle-
shaped cyrstals separated out.   These were filtered, washed, and
recrystallized twice from hot alcohol.   They showed a melting
point of 242°C., which was not changed by further crystallization.

DICHLORODIETHOXYQUINONE.

Dichlorodiethoxyquinone was prepared according to the
method of Kehrman [35] by letting a one per cent alcoholic solution
containing two equivalents of sodium fall drop by drop, with
constant shaking, on to some finely powdered chloranil moistened
with alcohol.   The solution turned red and the chloranil dis-
appeared.   One half its volume of boiling water was added, the
solution cooled, and the granite red precipitate, which separated
out, filtered.   The precipitate was crystallized three times
out of alcohol.   The crystals melted at 96°C.

SOLVENTS.

Absolute alcohol and chloroform were purified before
using them as solvent media in determining the absorption spectra
of the various substances.   The chloroform was washed several
times with a dilute sodium hydroxide solution to remove traces
of hydrochloric acid, chlorine, or phosgene, separated from the
solution in a dropping funnel, dried over calcium chloride, and
finally distilled.   The absolute alcohol was refluxed several times
over lime and sodium hydroxide to remove traces of water and
aldehyde, and then distilled.

METHOD OF PHOTOGRAPHING ABSORPTION SPECTRUM.

The photographs were taken by means of a Hilger quartz

[35] J.pr.Chem. II, 40, 367 (1889).

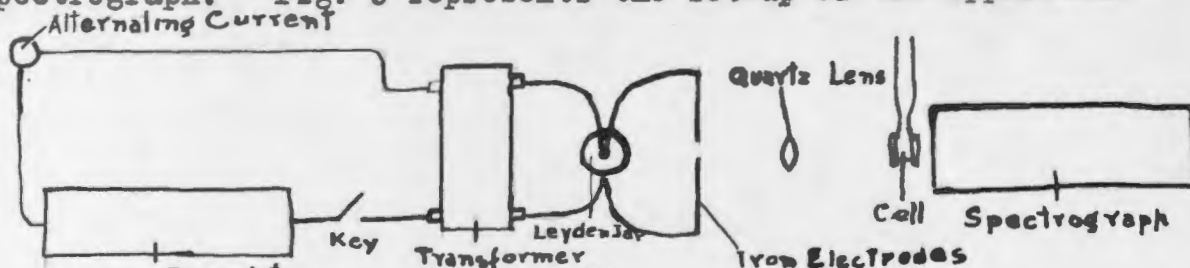spectrograph.   Fig. 5 represents the set-up of the apparatus.

FIG. 5

An iron spark was used as the source of light; since it consists

of such a continuous series of lines, it is fairly easy to locate

where absorption takes place.   It has one disadvantage; that is,

that its lines are not of the same intensity.   This means that

at the edges of the absorption band, bright lines show up faintly

where faint lines would be completely absorbed, and prevents

an accurate determination of the limits of the band.   The rays

of light from the iron spark, before entering the spectrograph,

pass through a quartz lens which brought the rays to a focus on

the slit of the spectrograph, and then through a cell containing

a solution of the substance whose absorption spectrum was to be

determined.   This cell was devised by G. H. Woollett and A. G.

Mayers.   It was made with two parallel faces of quartz, one

centimeter apart, and was connected to the

lower end of a burette which was fitted with

a side outlet and stop-cock as shown in the

diagram in Fig. 6.   The solution was diluted

with one half its volume of solvent each time

after an exposure was made, so that a series

of photographs was made on each plate, each

one representing the absorption spectrum of

FIG.6

a solution with two-thirds the concentration of the one just above

it.

METHOD OF REPRESENTING RESULTS.

For the purpose of comparison, graphs of the various absorption curves are given. Along the abscissae are plotted oscillation frequencies, the reciprocals of the wave-lengths, and along the ordinates, logarithms of relative layer thicknesses. This method was devised by Hartley in 1879 and has been in use ever since. Investigators have usually used a cell in which the thickness of the layer of absorbing solution could be varied. Our cell has the advantage that the thickness of the layer of solvent can be kept constant, thus avoiding the possible intro-duction of bands due to the solvent alone. At the same time our relative dilution can be converted over to relative layer thicknesses according to Beer's law, which says that the absorbing power of a solution is proportional to its concentration and to the thickness of the layer through which the light passes. Thus, a given solution one centimeter thick would have its absorbing power trebled, no matter whether the layer is made three times as thick, or the concentration of the solution trebled while the thickness of the layer is kept constant. In order to measure the wave length at the edge of each absorption band, the distance of the edge from the line in the iron spark spectrum at $\frac{1}{\lambda}$ 1979 was measured, and referred to a dispersion curve in which oscillation frequencies could be read off immediately. This graph was made by plotting the known oscillation frequencies of the lines in the cadmium spark spectrum as abscissae, their distances from the line at $\frac{1}{\lambda}$ 1966 as ordinates, and drawing a smooth curve through these points. It was found that the iron

line at $'/\lambda$ 1979 was so close to the cadmium line at $'/\lambda$ 1966 on
this dispersion curve that distances on the iron spark spectrum,
measured from $'/\lambda$ 1966 and referred to the curve, would give
oscillation frequencies that agree within experimental errors
with the true wave lengths.   The difficulty of determining
the exact point at which absorption begins introduces the biggest
source of error.

TERMS.

It might be well, also, to define certain terms that
will be used often.   The head of a band is the lowest point of
the curve.   The persistence of a band refers to the depth of the
band.   A band is very persistent if it shows up through a great
amount of dilution.   The symbol λ stands for wave length and
$'/\lambda$ for the reciprocal of the wave length, which is proportional
to the oscillation frequency, and is commonly called "oscillation
frequency."

ABSORPTION SPECTRUM OF CHLORANIL.

The absorption of chloranil, dissolved in chloroform,
is shown in Figs. 7 and 9.   There are two bands.   One is very
shallow, heading at about $'/\lambda$ 2700, and extending slightly into
the visible range of the spectrum.   The other band, heading at
about $'/\lambda$ 3420 is very persistent.

ABSORPTION SPECTRUM OF DICHLORDIETHOXYQUINONE.

The alcohol solution of dichlordiethoxyquinone gave a
somewhat similar absorption spectrum, as shown in Figs. 8 and 10.
Again there are two bands, one a very shallow, broad band in the
visible range, heading at about $'/\lambda$ 2380, and the other, a very
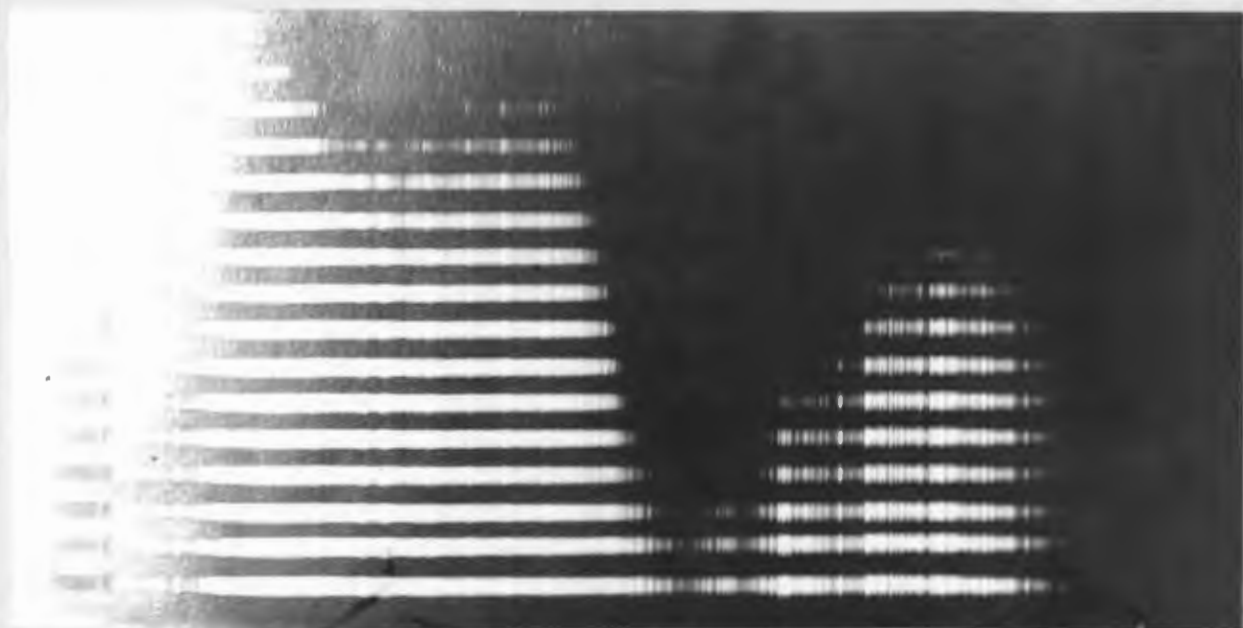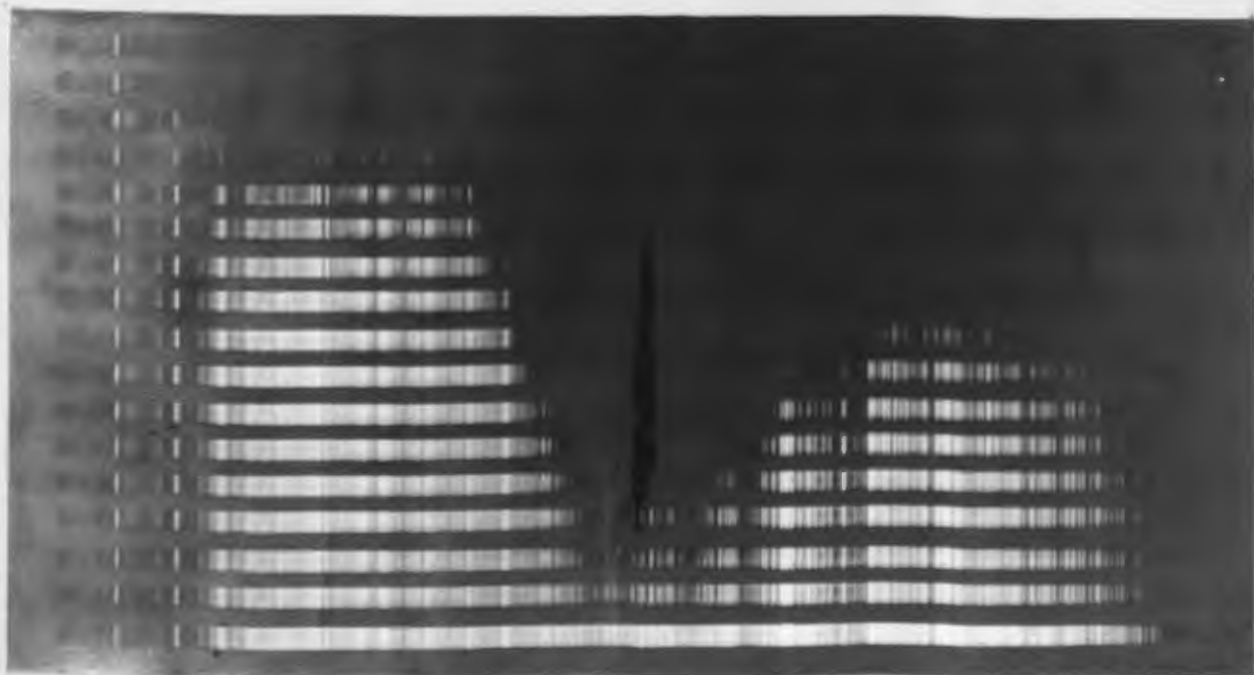
FIG.7   CHLORANIL IN CHLOROFORM
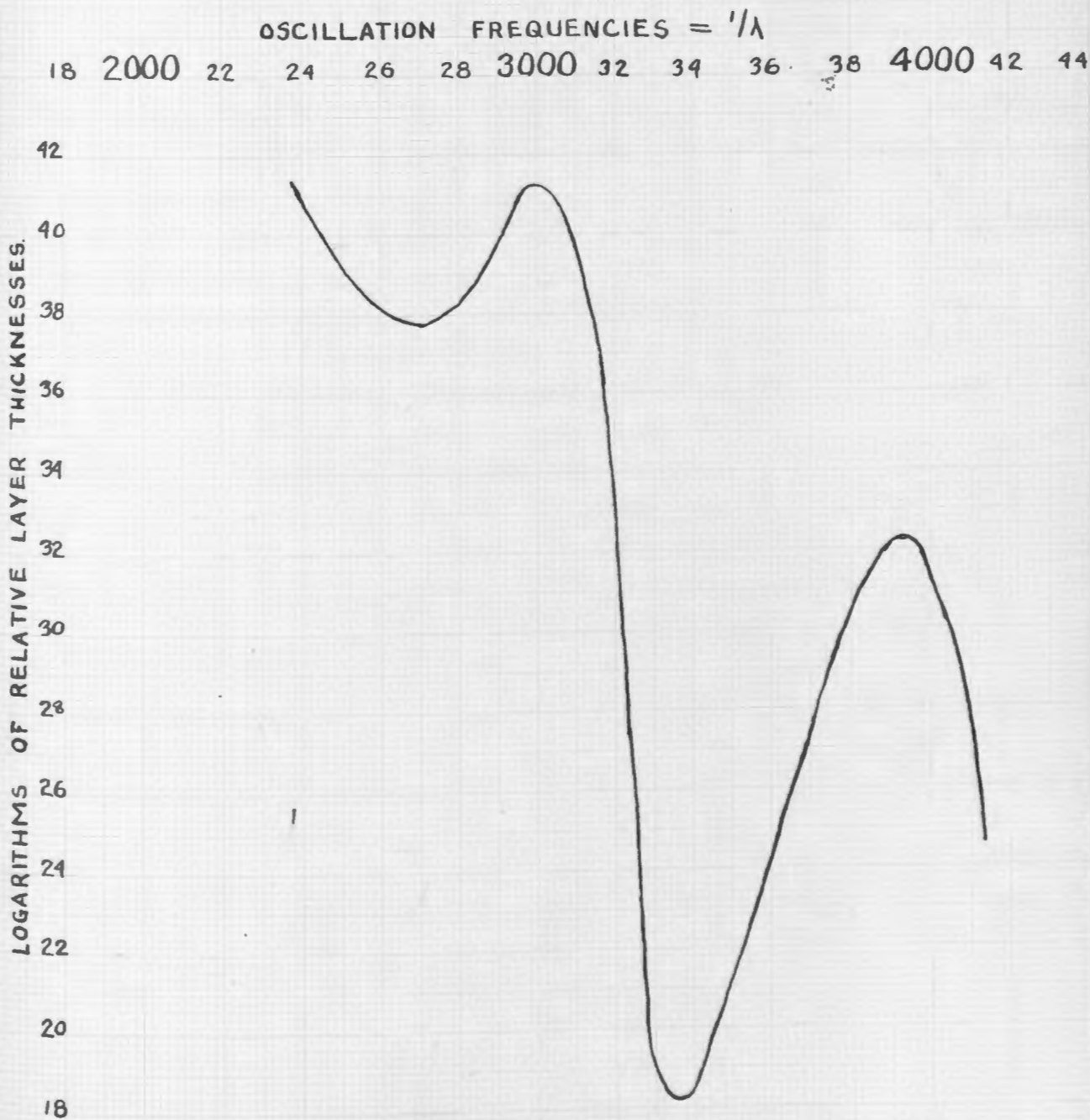

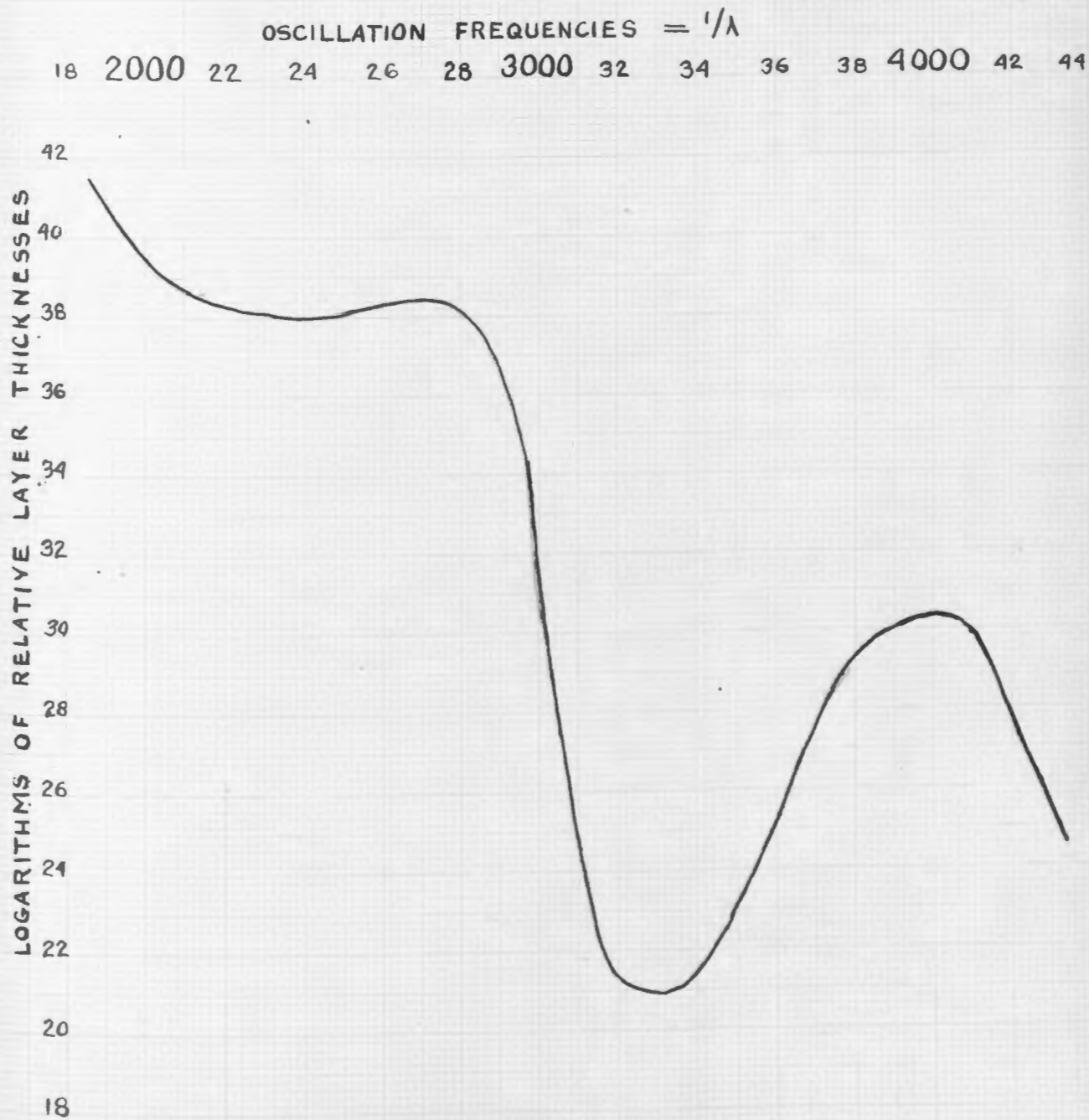FIG.8   DICHLORDIETHOXYQUINONE IN ALCOHOL

FIG. 9   CHLORANIL IN CHLOROFORM.

FIG. IO DICHLORODIETHOXYQUINONE IN ALCOHOL

persistent band in the ultra violet at about $1/\lambda$ 3300.

ABSORPTION SPECTRUM OF TETRACHLORHYDROQUINONE AND ITS DERIVATIVES.

Figs. 11 and 13 show the absorption of tetrachlorhydro-
quinone dissolved in chloroform.   There is one fairly persistent
band at about $1/\lambda$ 3260.   The diethyl ether of tetrachlorhydroquinone
in alcohol shows a corresponding band as is illustrated in Figs.
12 and 14.   This band is farther toward the ultra violet end of
the spectrum at $1/\lambda$ 3430 and is less persistent.   The chloroform
solution of tetrachlorhydronequinone diacetate gave a similar
band as shown is Figs. 15 and 17.   This band is at $1/\lambda$ 3510,
still farther to the right, and much less persistent.

It was impossible, as was explained before, to determine
the absorption spectrum of the sodium derivative of tetrachlor-
hydroquinone, because of its unstable nature in the presence of
air.   Reasoning by its analogy to phenol and hydroquinone, the
substitution of sodium for hydrogen should shift the band of the
tetrachlorhydroquinohe a little farther toward the visible spectrum
and make it shallower.   It might also introduce a shallow band
in the benzene region.   These possible effects must be taken
into account before comparing the absorption spectrum of the
sodium salt of octochlorquinhydrone with those of chloranil and
tetrachlorhydroquinone.

ABSORPTION SPECTRUM OF THE SODIUM SALT OF OCTOCHLORQUINHYDRONE.

The instability of the green, water solution prevented
the taking of its absorption spectrum.   A photograph of the
absorption spectrum of the red, alcohol solution was taken.
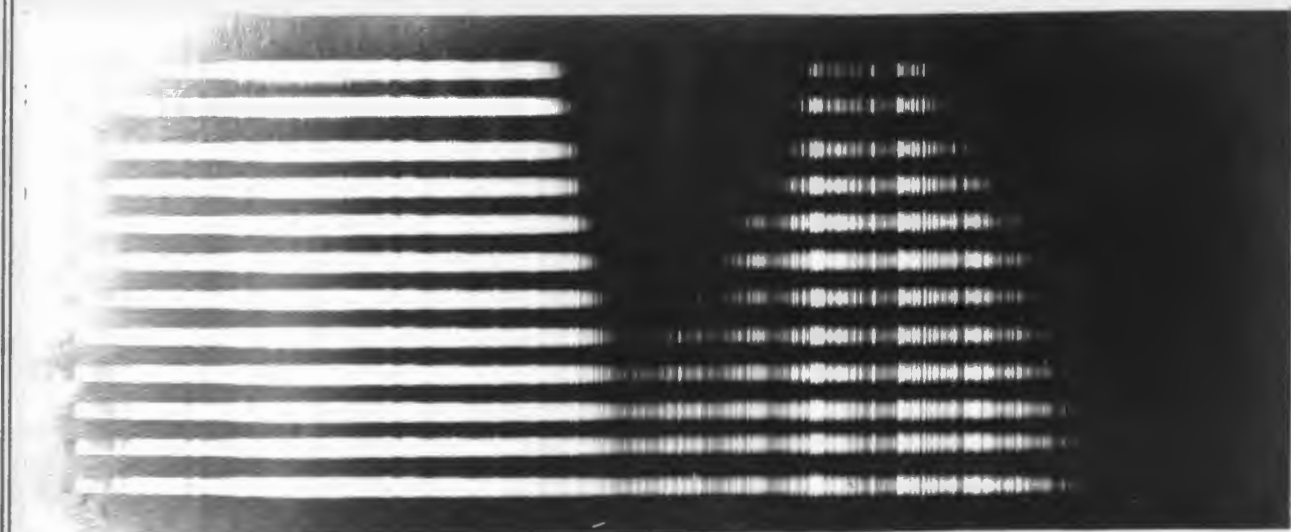
FIG.II TETRACHLORHYDROQUINONE IN CHLOROFORM

FIG.12 DIETHYL ETHER OF TETRACHLORHYDROQUINONE
IN ALCOHOL

OSCILLATION FREQUENCIES = $^1/\lambda$

FIG. 13   TETRACHLORHYDROQUINONE

IN CHLOROFORM

OSCILLATION FREQUENCIES = $1/\lambda$
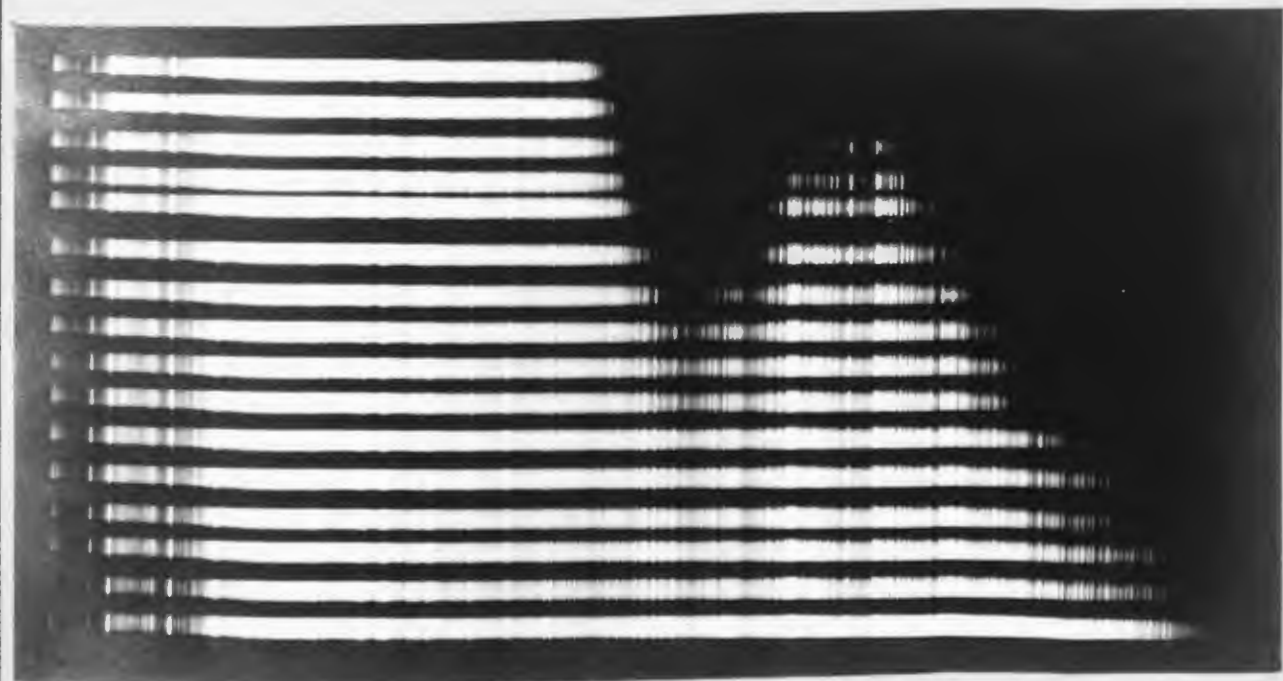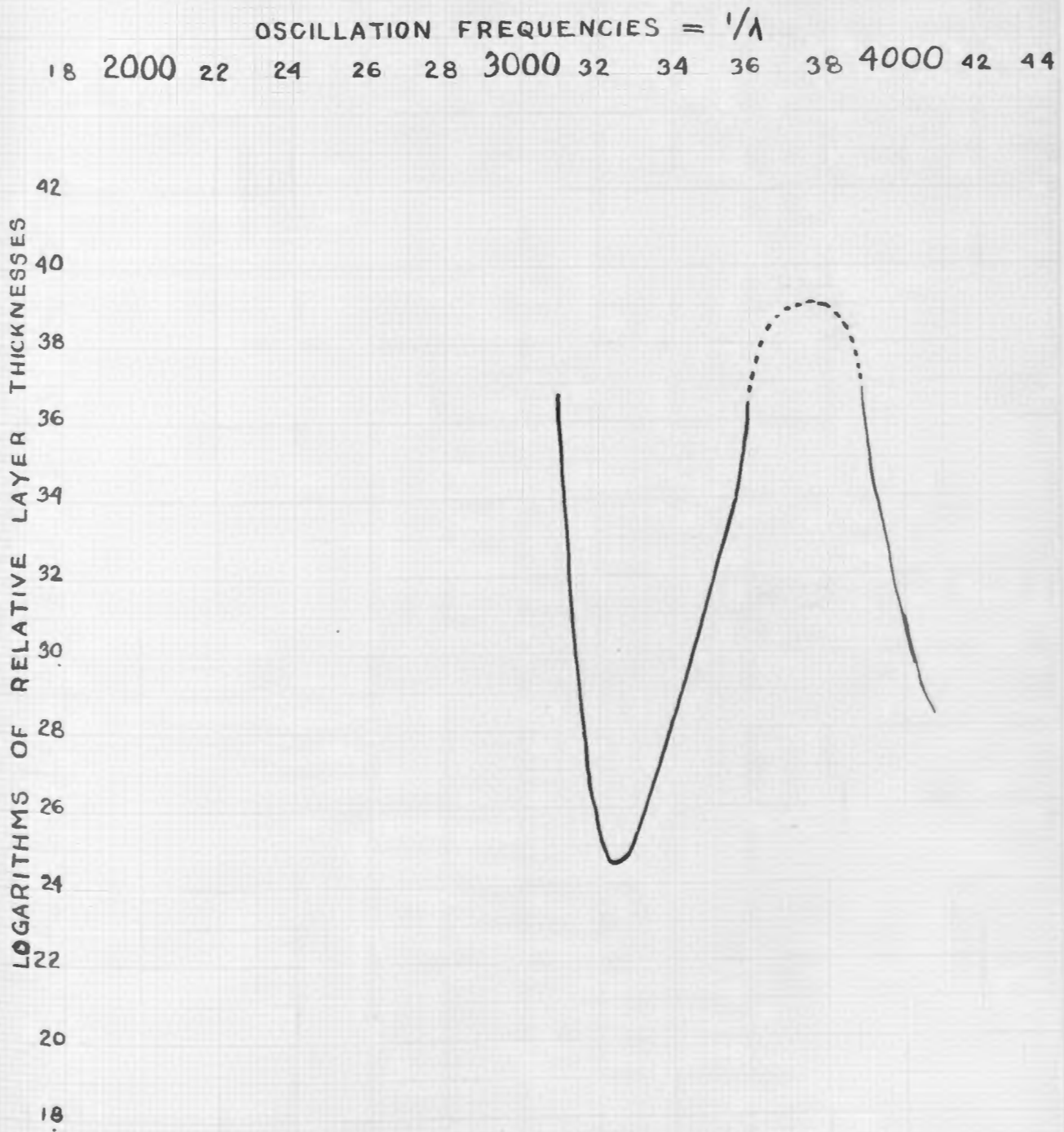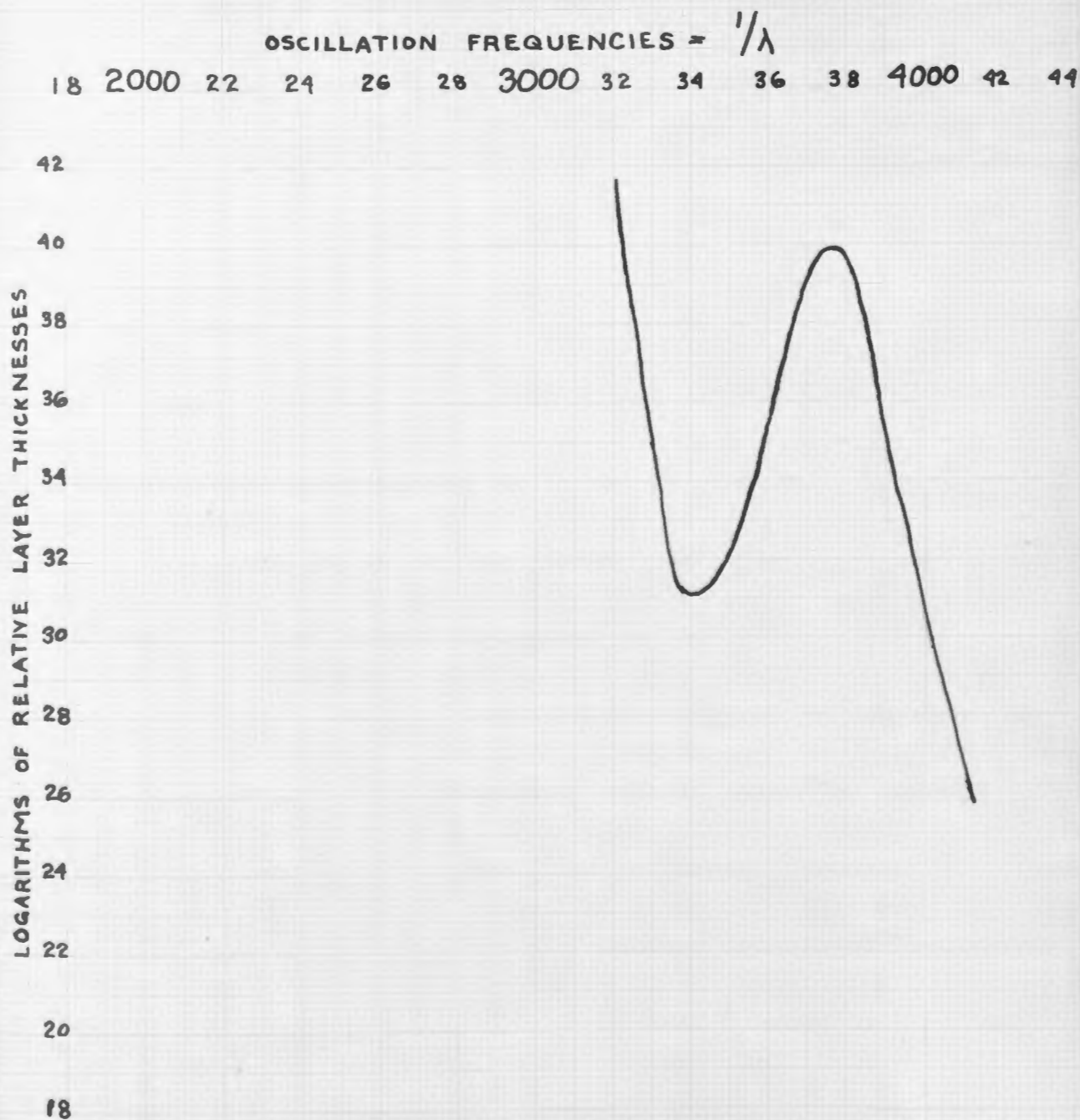
FIG.14   DIETHYL ETHER OF TETRACHLORHYDROQUINONE
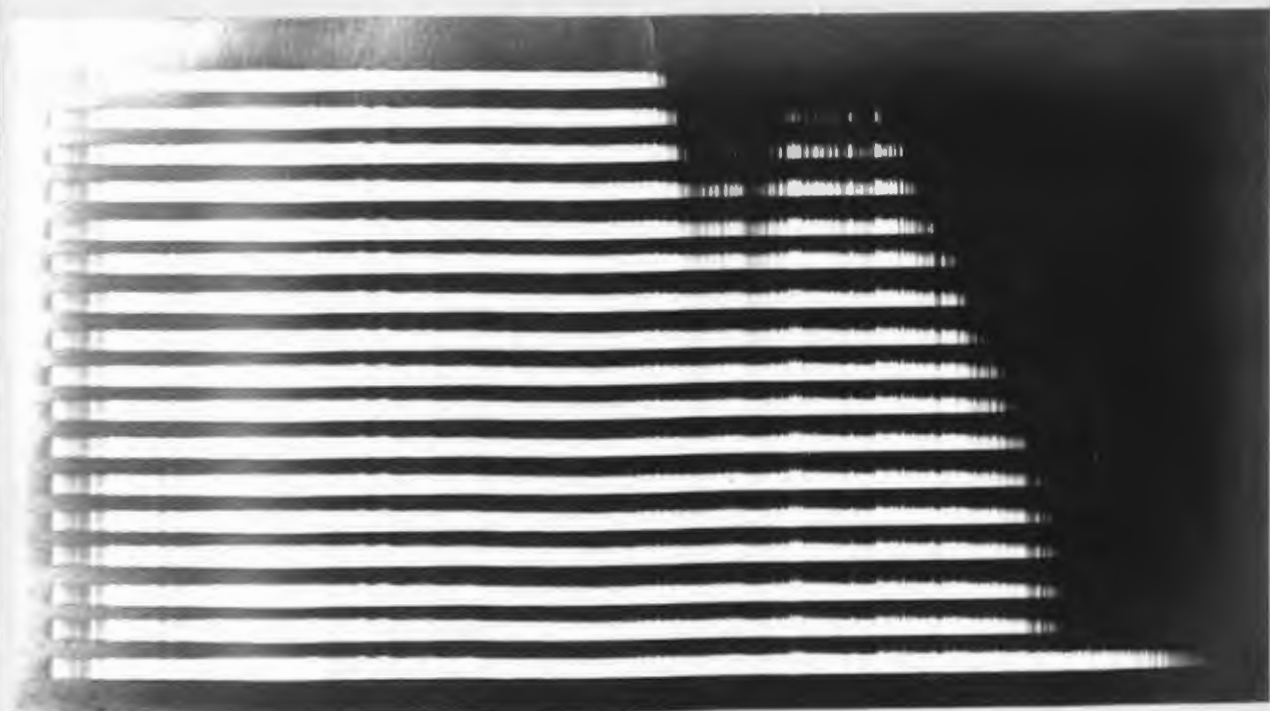
IN ALCOHOL

FIG.15 TETRACHLORHYDROQUINONE DIACETATE
IN CHLOROFORM

FIG.16 SODIUM SALT OF OCTOCHLORQUINHYDRONE
IN ALCOHOL
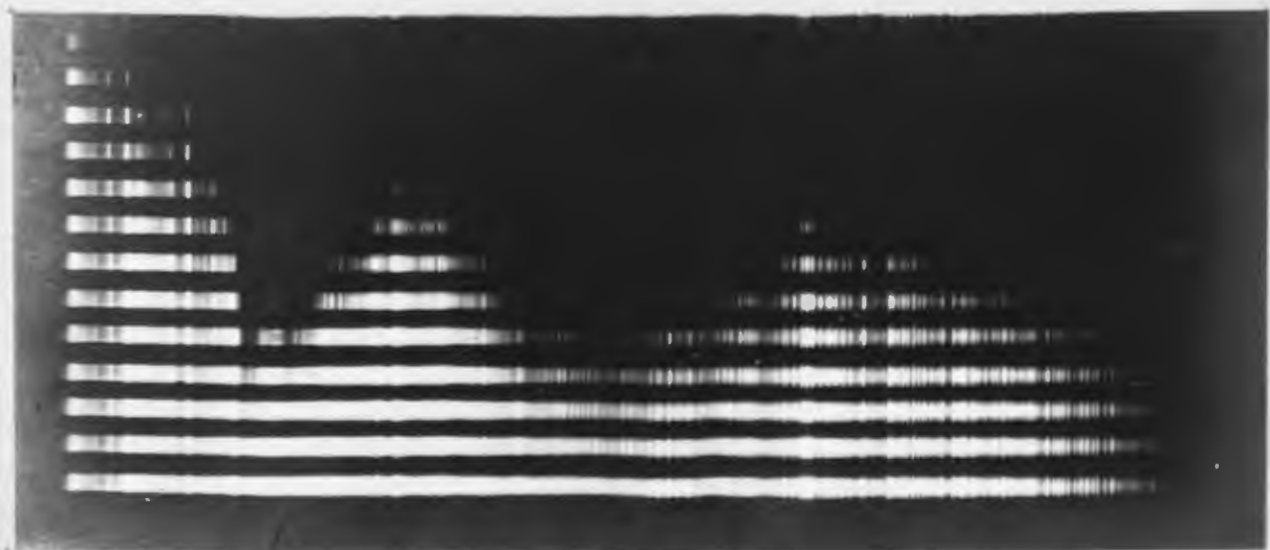
OSCILLATION FREQUENCIES = $^1/\lambda$
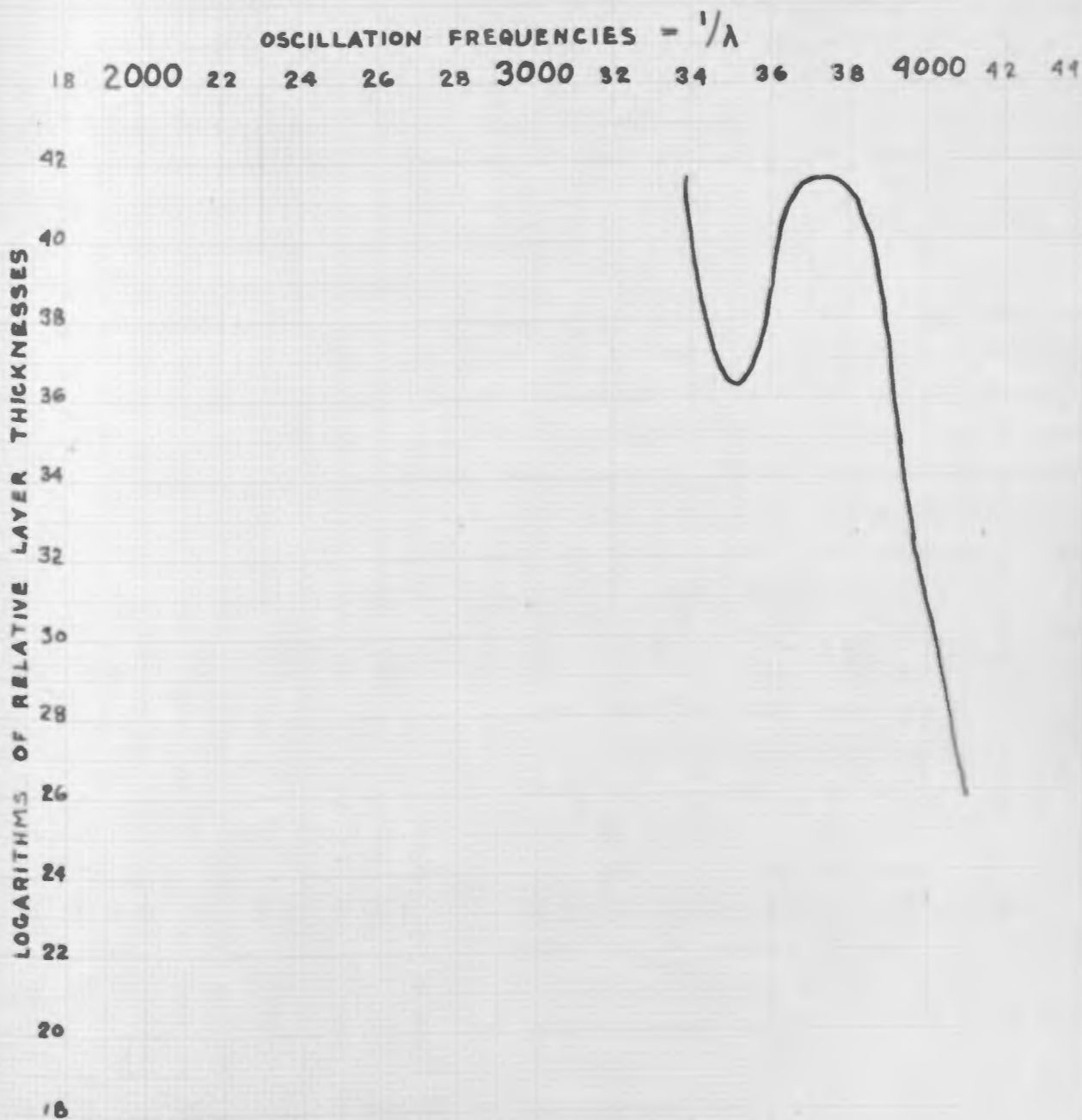
FIG. 17 TETRACHLORHYDROQUINONE DIACETATE

IN CHLOROFORM

OSCILLATION FREQUENCIES = $^1/\lambda$

18 2000 22 24 26 28 3000 32 34 36 38 4000 42 44

LOGARITHMS OF RELATIVE LAYER THICKNESSES

42 40 38 36 34 32 30 28 26 24 22 20 18
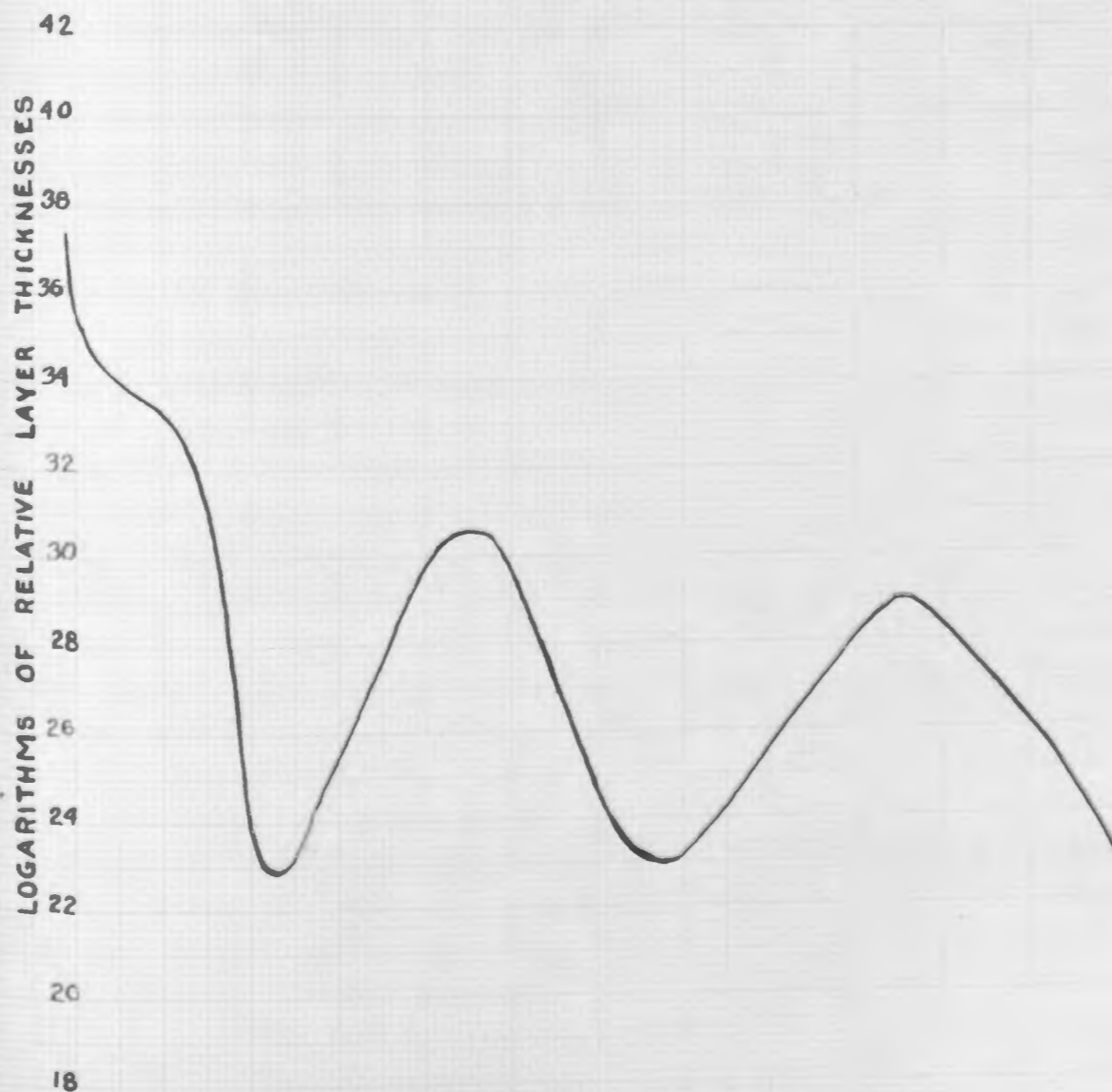
FIG.18 SODIUM SALT OF OCTOCHLORQUINHYDRONE

IN ALCOHOL

The results are shown in Figs. 16 and 18. The most concentrated solution shows general absorption of everything except the extreme red end of the spectrum. On increasing the dilution, the general absorption decreases in extent, and is suddenly cut off by a persistent band heading at $1/\lambda$ 2280 in the visible range. There is another band in the ultra violet with its head at $1/\lambda$ 3180 which is very broad and rather persistent.

ABSORPTION OF A MIXTURE OF CHLORANIL AND TETRACHLORHYDROQUINONE.

A photograph of the absorption spectrum of a mixture of equivalent amounts of chloranil and tetrachlorhydroquinone in chloroform was taken to prove that when the two components are not closely bound together, the absorption spectrum of the mixture will be a summation of the curves of the two substances. Figs. 19 and 20 show this supposition to be correct. There is one band heading at $1/\lambda$ 3420 corresponding to the band of chloranil. The left edge of the band is shifted farther toward the visible range, corresponding to the edge of the tetrachlorhydroquinone band, but at $1/\lambda$ 3260 there is a shift toward the ultra violet, indicating the end of the tetrachlorhydroquinone band. It was unfortunate that the chloranil was not soluble enough in alcohol, nor the tetrachlorhydroquinone in chloroform, to get a more concentrated solution of the two. In order to get equivalent amounts of each, the solution had to be so dilute that the chloranil band at $1/\lambda$ 2710 was cut out entirely.

DISCUSSION.

In order to get at the meaning of the chloranil bands, they must be compared with the bands shown by benzoquinone and

FIG.19 MIXTURE OF CHLORANIL

AND TETRACHLORHYDROQUINONE

IN CHLOROFORM

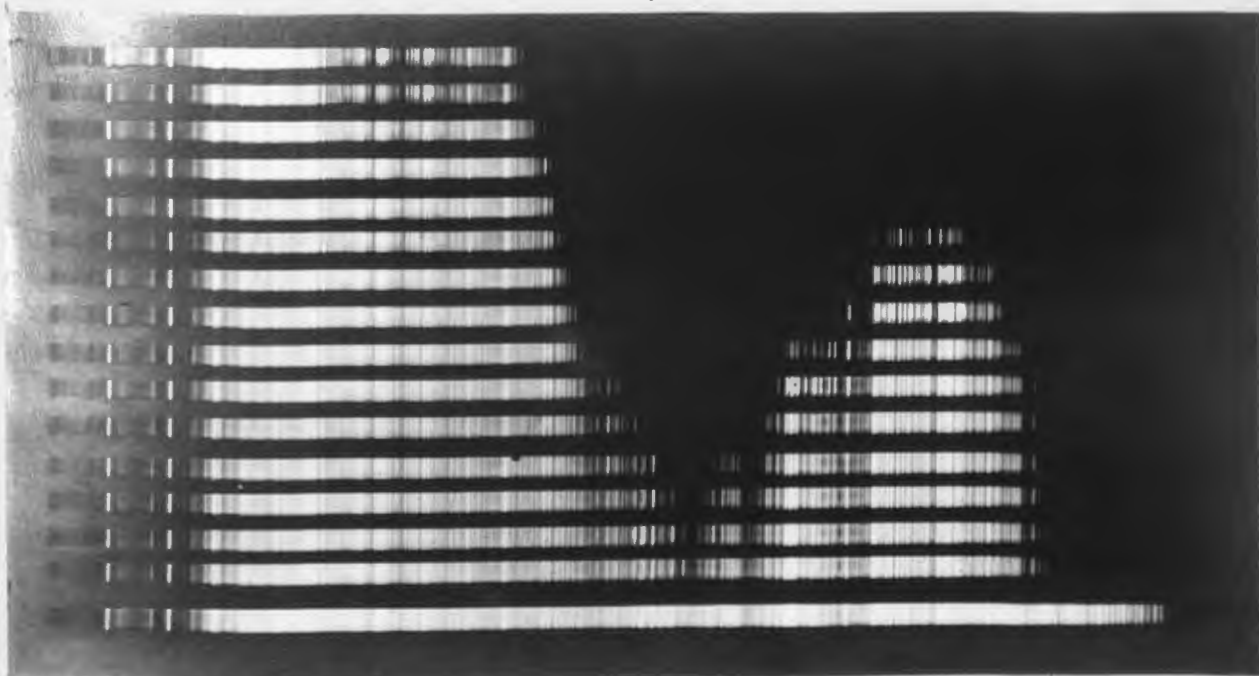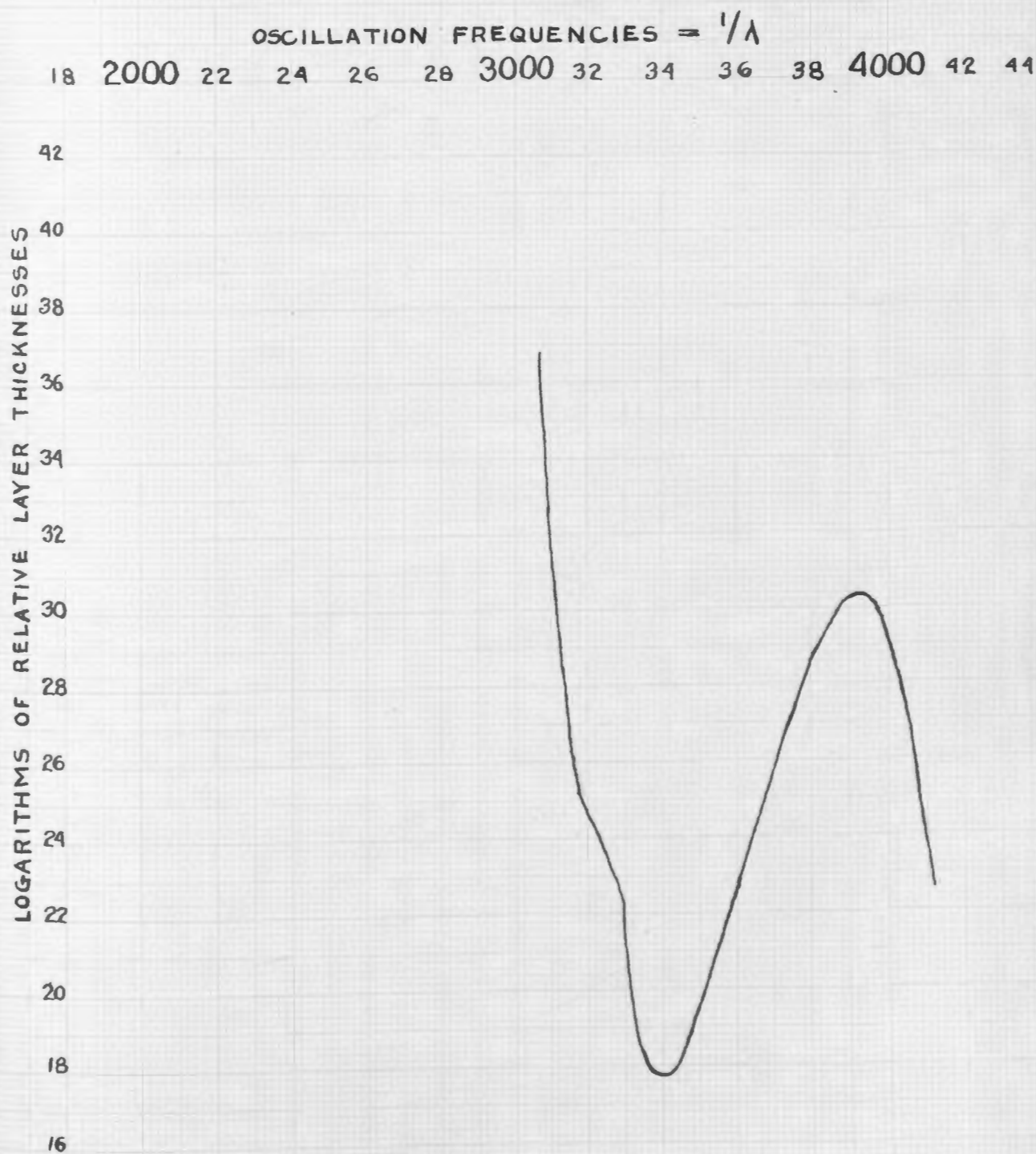FIG.20 EQUIVALENT AMOUNTS OF CHLORANIL AND
TETRACHLORHYDROQUINONE IN CHLOROFORM

its mono-, di-, and tri-chlor derivatives.   These curves are
reproduced from an article by Baly and Stewart[36] in Fig. 21.
Benzoquinone in alcohol, according to Hartley and Leonard,[37]
shows a rather shallow band in the visible range at $^1/_\lambda$ 2150,
an incipient band at $^1/_\lambda$ 3400, and, upon extreme dilution, another
shallow band at $^1/_\lambda$ 4000.

Hartley and Leonard showed that the incipient band
at $^1/_\lambda$ 3400 became a mere step-off when the pure quinone was
dissolved in ether, while it became more pronounced in water.
They also showed that this band occupied the same position as
the hydroquinone band, and accordingly attributed it to a reduction
of some of the quinone into hydroquinone, this reaction being
very slight in alcohol, quite decided in water, and not occurring
at all in ether.   Baly and Stewart[38] had previously explained this
band, according to the force field theory, as due to the effect
of a solvent of strong residual affinity.

The band at $^1/_\lambda$ 2150 was explained by Baly and Stewart[39]
as due to an isorropesis between the quinoid form and a peroxide form.

The band at $^1/_\lambda$ 4000 was supposed to be due to benzene
vibrations[40] of the ring while in the peroxide form.   The latter
band occupies approximately the same position in the spectrum
as the benzene band.

[36] J.Chem. Soc. 89, 507, 622 (1906).
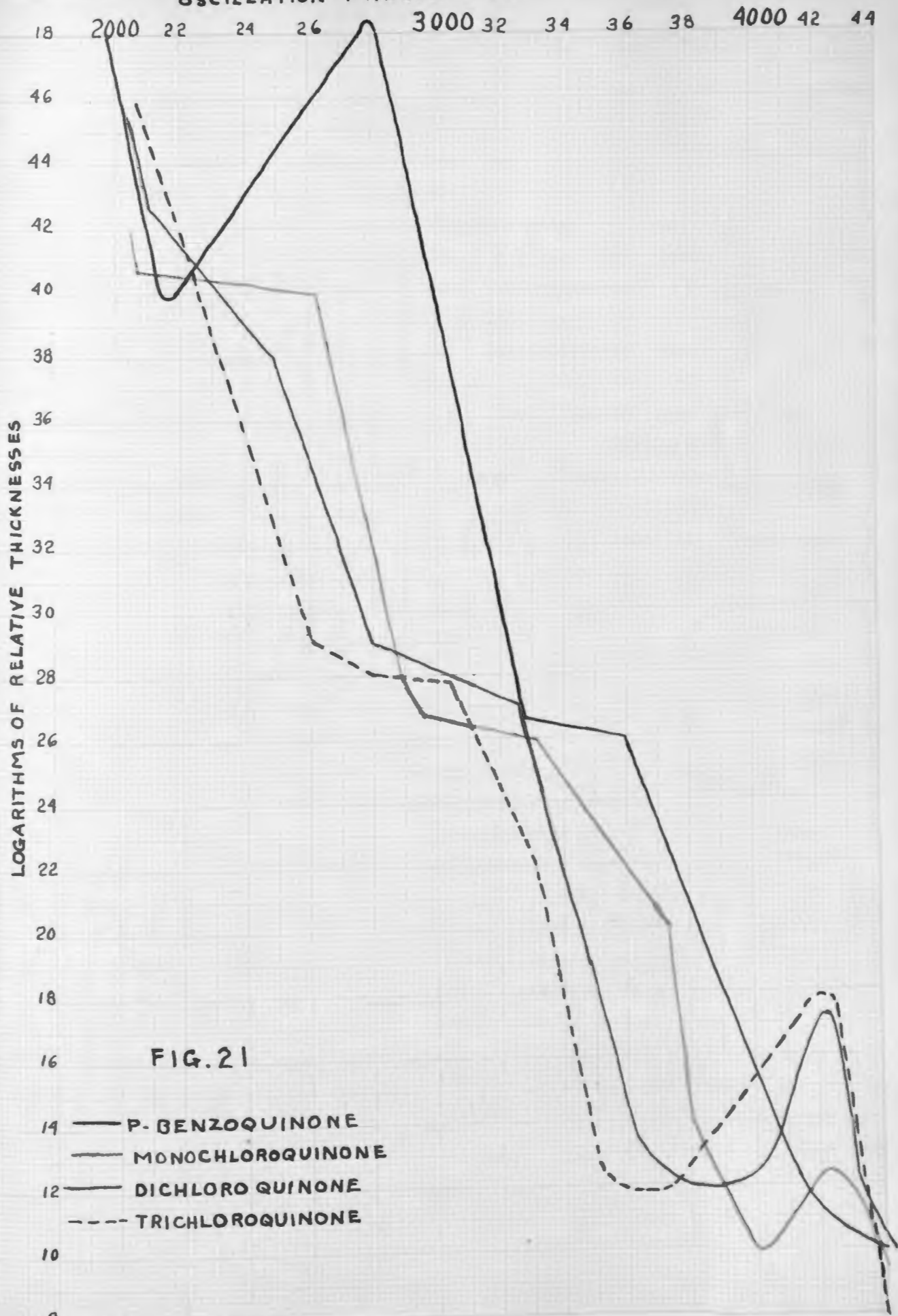[37] J.Chem. Soc. 95, 43, (1909).
[38] J.Chem.Soc. 89, 506 (1906)
[39] Ibid.
[40] Ibid.

FIG. 21

OSCILLATION FREQUENCIES

LOGARITHMS OF RELATIVE THICKNESSES

—— P·BENZOQUINONE
—— MONOCHLOROQUINONE
—— DICHLOROQUINONE
--- TRICHLOROQUINONE

A glance at Fig. 21 shows that, as chlorine atoms are introduced into the ring, the shallow "isorropic" band gradually disappears, the incipient band and the "benzenoid" band are shifted toward the red end of the spectrum, and the "benzenoid" band becomes increasingly persistent. If these tendencies are carried over to the tetrachlorquinone, it would appear that the shallow band at $1/\lambda$ 2700 corresponded to the incipient band, and the persistent band at $1/\lambda$ 3420 to the "benzenoid" band of the other chlorine derivatives of quinone. On account of the insolubility of the chloranil it was impossible to continue the curve far enough into the visible range to determine whether the disappearance of the "isorropic" band was complete, but analogy to the other chlorine derivatives indicates that it would be.

Kehrman[41] showed that by introducing chlorine or alkyl radicals into the quinoid ring the character of the carbonyl oxygen was altered, as was manifested by the decreasing tendency toward oxime formation. This was at first explained by the theory of steric hindrance. The vibrations of groups in the ortho position to the carbonyl group were supposed to create such a condition that the hydroxylamine group could not get close enough to react. Baly and Stewart[42], as was mentioned in the introduction, attempted to substitute for this theory the idea of a change in the equilibrium between the quinoid and benzenoid character of the ring. If the quinone band at $1/\lambda$ 2150 was due to the vibration of electrons back and forth between quinoid and benzenoid structures, then it was entirely probable that the

41 Ber.21, 3315 (1888); J.pr.Chem. II,39,399(1889);40,257(1889)
42 J.Chem.Soc. 89, 618 (1906).

introduction of other groups into the ring would affect this equilibrium.   They showed by means of absorption spectra of the mono-, di-, and tri-chlor quinones, that the "isorropic" band practically disappeared and the "benzenoid" band became increasingly persistent.   This confirmed their belief that as chlorine atoms are substituted into the ring the quinone loses its quinoid characteristics and becomes more and more peroxide in form and behaviour.   The absorption spectrum of chloranil confirms this theory.   The peroxide nature of chloranil is further borne out by the close resemblance of its "benzenoid" band to the band of tetrachlorhydroquinone.   Although the chloranil band appears in weaker concentrations, the head of its band is fairly close to that of the tetrachlorhydroquinone, and their curves have about the same general outline and persistence.

The chloranil band at $^1/\lambda$ 2700 introduces another problem.   It appears to correspond with the incipient band of quinone and its other chlor derivatives, but in this case it can hardly be attributed to the reduction of some of the quinone to the hydroquinone by solvent action, since its position is not at all that of the tetrachlorhydroquinone band.   Baly offers a more satisfactory explanation when he accounts for this band in quinone as due to the action of the residual affinities of the solvent upon the force fields of the quinone molecules.   If the chloranil is more peroxide in structure, it ought to be in a condition that would be more affected by the residual affinities of a solvent.   As a result, it would show a more prominent band in its absorption spectrum, and this is the case.

The absorption spectrum of tetrachlorhydroquinone must be compared with those of some of its derivatives and with that of hydroquinone itself. The absorption curve of hydroquinone is reproduced in Fig. 1 from an article by Hartley and Leonard.[43] It is very similar to the curve of tetrachlorhydroquinone except for a shift in its position. The hydroquinone band heads at $1/\lambda$ 3410 while the tetrachlorhydroquinone band heads at $1/\lambda$ 3260. The substitution of four chlorine atoms seems to have exerted its effect in pulling the band toward the visible end of the spectrum because of their increased weight. The absorption band of hydroquinone is similar to those of phenol and pyrocatechol. These bands were explained by Gibbs and Pratt[44], after a study of the effect of the presence of sodium ions on their absorption spectra, by assuming a tautomeric equilibrium between a quinoid and a benzenoid form. They base their arguments on the fact that in the presence of sodium ions the absorption curves became more shallow and another shallow band appeared in the benzene region. They argued that the band was approximately in a position where bands due to keto-enol vibrations usually occurred, and that if such a keto-enol equilibrium did exist, it would be shifted toward the enol form in the presence of sodium. This would mean that the band would be more shallow, since there would be fewer molecules shifting to the quinoid form, and a benzenoid band might appear, since more molecules would exist in the enol form.

43 J.Chem.Soc. 95,45 (1909).
44 Phillipine J.Sci. A, 8, 33 (1913).

The same reasoning might be applied to hydroquinone and tetrachlor-
hydroquinone. It falls down, however, when applied to their
alkyl and acetyl derivatives. The dimethyl ether of hydroquinone,
as shown by Baly and Ewbank,[45] has practically the same absorption
band as hydroquinone. Here the stable methyl group has replaced
the labile hydrogen atom and it is impossible to imagine the methyl
group shifting from one atom to another. The diethyl ether
of tetrachlorhydroquinone, as we have shown, has an absorption
band very similar to that of the tetrachlorhydroquinone, somewhat
less persistent, but shifted a little to the ultra violet. Here
again it seems unreasonable for the ethyl group to shift its
position. The diacetate of tetrachlorhydroquinone, in which the
labile hydrogen atom is replaced by the negative acetyl group,
gives an absorption band that is much less persistent, and still
farther to the right. Here there is still less chance for a
keto-enol tautomerism to exist, and an explanation must be sought
for the cause of the band other than from the theory of isorropesis.
Baly's force field theory again offers a more plausible explanation,
since it is reasonable to expect that the replacement of a
hydrogen atom by a more positive alkyl group, or by a more negative
acetyl group, would have an effect upon the condition of the force
fields.

Before discussing the conclusions that may be drawn
from a study of the absorption spectrum of the sodium salt of
octochlorquinhydrone, it is necessary to say a few words about the

[45] J.Chem.Soc. 87, 1353 (1905).

color of its alcohol solution. In the solid form it is a dark, blue=green powder. It dissolves in water with a green color, but the solution is very unstable, for a white precipitate soon appears on the surface of the solution, and the solution turns first brown, and then purple, the color of chloranilic acid. Its alcoholic solution has a greenish-brown color when dilute and a reddish-brown color when more concentrated. The salt is not soluble in other solvents. The question arises as to whether the color of the alcoholic solution is the color of the pure sodium salt of octochlorquinhydrone, the color of its dissociated components, or the color of a decomposition product.

If the salt dissociates, the solution should contain some chloranil and the sodium salt of tetrachlorhydroquinone. The chloranil is yellow, while the sodium salt of tetrachlorhydroquinone in alcoholic solution oxidizes in air and turns brown, the color deepening at the surface. Although the solution of the sodium salt of octochlorquinhydrone has a reddish-brown color, its color does not deepen at the surface where it is exposed to air. This leads to the belief that the red color is not due to the dissociated components. This belief is further borne out by the absorption spectrum of its alcoholic solution. If the salt dissociates, then as the dilution increases, the degree of dissociation will increase, and the absorption curve will approach more nearly to a summation of the curves of the two components. This is clearly not the case. The absorption band of the salt shows very little similarity to those of its components, even if we imagine the tetrachlorhydroquinone curve converted into

that of its sodium salt as has been suggested.   The band in the
ultra violet at $'/\lambda$ 3180 compares slightly with the band of
chloranil at $'/\lambda$ 3410 andthat of tetrachlorhydroquinone at $'/\lambda$ 3260,
but is placed farther to the left, is much broader and more
shallow than either band, and is less persistent than that of
chloranil.   On the other hand, the mixture of equivalent amounts
of chloranil and tetrachlorhydroquinone gives an absorption
band that corresponds almost exactly to a summation of the two
curves.   There does not seem to be any positive evidence for
the dissociation of the sodium salt of octochlorquinhydrone.

Another reasonable explanation of the red color of the
alcohol solution is that it might be due to a decomposition product.
Chloranil in the presence of sodium ethylate and alcohol is
converted into the diethyl ether of chloranilic acid.   This
ether exists in the form of granite-red crystals and dissolves
very readily in alcohol with a reddish-brown color.   This seems
to be the most probable decomposition product of the sodium salt
of octochlorquinhydrone since, if the salt did dissociate, the
sodium salt of tetrachlorhydroquinone might react with the alcohol
to form some sodium ethylate, which in turn would convert the
chloranil into the diethyl ether of chloranilic acid.   Some of
the diethyl ether of chloranilic acid, or dichlordiethoxyquinone,
was prepared and a photograph of its absorption spectrum taken,
in order to determine whether its presence would show up in the
absorption spectrum of the sodium salt of octochlorquinhydrone.
It is evident from a comparison of their photographs that if the
dichlordiethoxyquinone is present in the solution at all, it is
not there in large ehough quantites to show up.   The bands in the

absorption spectrum of the sodium salt of octochlorquinhydrone
are not similar to those of dichlordiethoxyquinone, and must be
due to some other cause.   There is a possibility that the sodium
salt of tetrachlorhydroquinone itself might combine with the
chloranil in a similar way, at the same time liberating sodium
chloride.   If such a reaction did occur, the solution ought to
give a test for free chlorides.   To determine this, a fresh,
alcohol solution of the sodium salt of octochlorquinhydrone was
made up, and part of it treated immediately with a drop of silver
nitrate solution.   A dark grey, finely granulated precipitate
came down immediately, probably the silver salt of octochlorquin-
hydrone.   The solution was tested in a similar manner every
fifteen minutes for an interval of two hours with the same result.
At the end of nine hours, a curdy, white precipitate of silver
chloride appeared when one drop of silver nitrate was added.
When an excess of silver nitrate was used another grey precipitate
came down.   After standing over night a drop of silver nitrate
brought down a fairly heavy white precipitate of silver chloride,
while an excess again turned the precipitate grey.   These results
indicate that there is some decomposition taking place in the
alcoholic solution, but it is of such a slow nature that if the
photograph is taken as soon as the solution is made up, it will
show only the absorption spectrum of the pure substance.

Since decomposition and dissociation seem improbable,
it must be assumed that the red color of the alcoholic solution
is the color of the pure salt in alcohol.   The reason for this
change in color must be left in doubt, although various suggestions
to account for it might be made.   The green color of the solid

might be a surface color, similar to that of fuchsine and other dyes which appear green in the solid form, but red in solution. This seems to be true in the case of a similar substance, ordinary quinhydrone.   Quinhydrone in the solid form has an olive green, metallic luster.   It dissolves in cold alcohol with a yellow color, but in a hot concentrated alcohol solution appears reddish-brown.   It has been shown by Torrey and Hardenbergh, and Biltris[46] that the light yellow solution consists almost entirely of the dissociated components, quinone and hydroquinone, but the hot, concentrated solution contains much undissociated quinone. The red color, therefore, seems to be the color of the quinhydrone in solution, while the green is characteristic of the solid phase. The color effects might be a phenomenon due to associations of the molecules.   Both water and alcohol as a rule are non-associating solvents, but in a few cases a substance will associate to a greater degree in water than in alcohol, while in other cases the reverse is true.   For example, benzoic acid[47] in water shows a molecular weight of 240, while in ethyl alcohol it is only 125.   On the other hand, a good many organic salts, such as diethyl ammonium chloride, and tetraethyl ammonium iodide, show a higher degree of association in alcohol than in water.   For instance, triethyl ammonium iodide[48] whose calculated molecular weight is 227 gives an observed molecular weight of 272.6-250.2 in ethyl alcohol, while in water it is only 144-103.1; and

[46]Loc. cit.
[47]W.E.S.Turner, Molecular association, p. 43.
[48]Ibid, pp. 158, 159.

quinoline ethiodide, whose calculated molecular weight is 285, shows an observed molecular weight of 225.8-155.5 in water, but 560.4-291.2 in ethyl alcohol. This might mean that the sodium salt of octochlorquinhydrone is more associated in alcohol and that the red color is due to associated molecules. The change in color with different solvents might also be explained by Baly's force field theory. Alcohol might open up the force fields around the molecules of salt less than water could, thus causing the absorption of energy from different light waves. Whatever may be the cause of this difference in color between solid and solution, it is not of prime importance in this discussion. We are interested primarily in the comparison of the absorption spectrum of the solution of the sodium salt of octochlorquinhydrone with that of solutions of chloranil and tetrachlorhydroquinone.

The absorption spectrum of the alcoholic solution of the sodium salt of octochlorquinhydrone appears to be an entirely different curve from what would be expected of a summation of the two curves of its components. Fig. 21 shows the relative positions of the curves of chloranil, tetrachlorhydro- quinone, and the sodium salt of octochlorquinhydrone, while Fig. 22 shows the same for the curves of chloranil, tetrachlorhydro- quinone, and a mixture of equivalent amounts of chloranil and tetrachlorhydroquinone. The latter comparison shows that the curves of chloranil and tetrachlorhydroquinone, obtained from their separate solutions, when superposed upon each other, give a resultant curve which is almost exactly that which is obtained from a mixture of the two in the same solution. In comparing
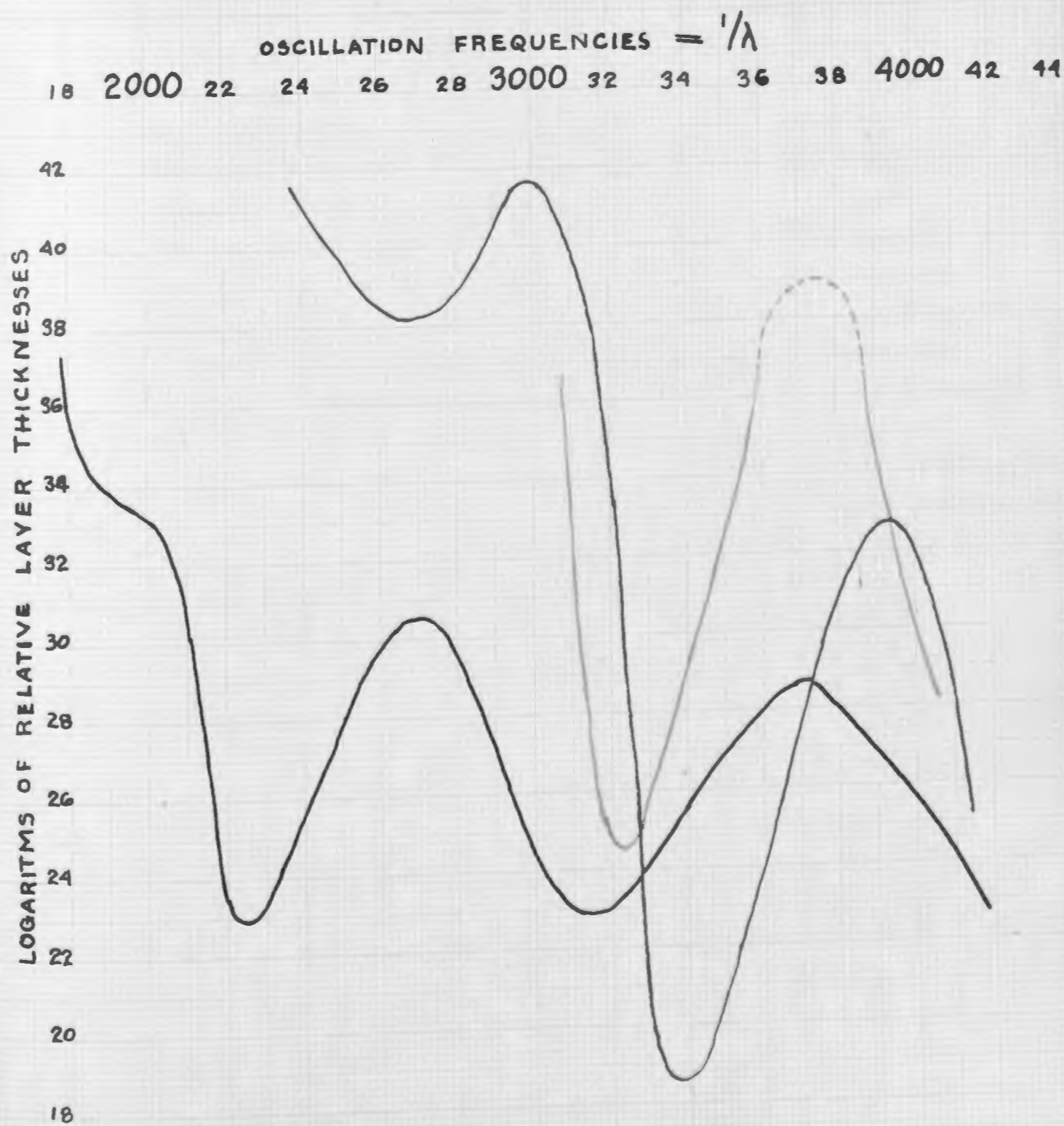
FIG. 21

—— CHLORANIL

—— TETRACHLORHYDROQUINONE

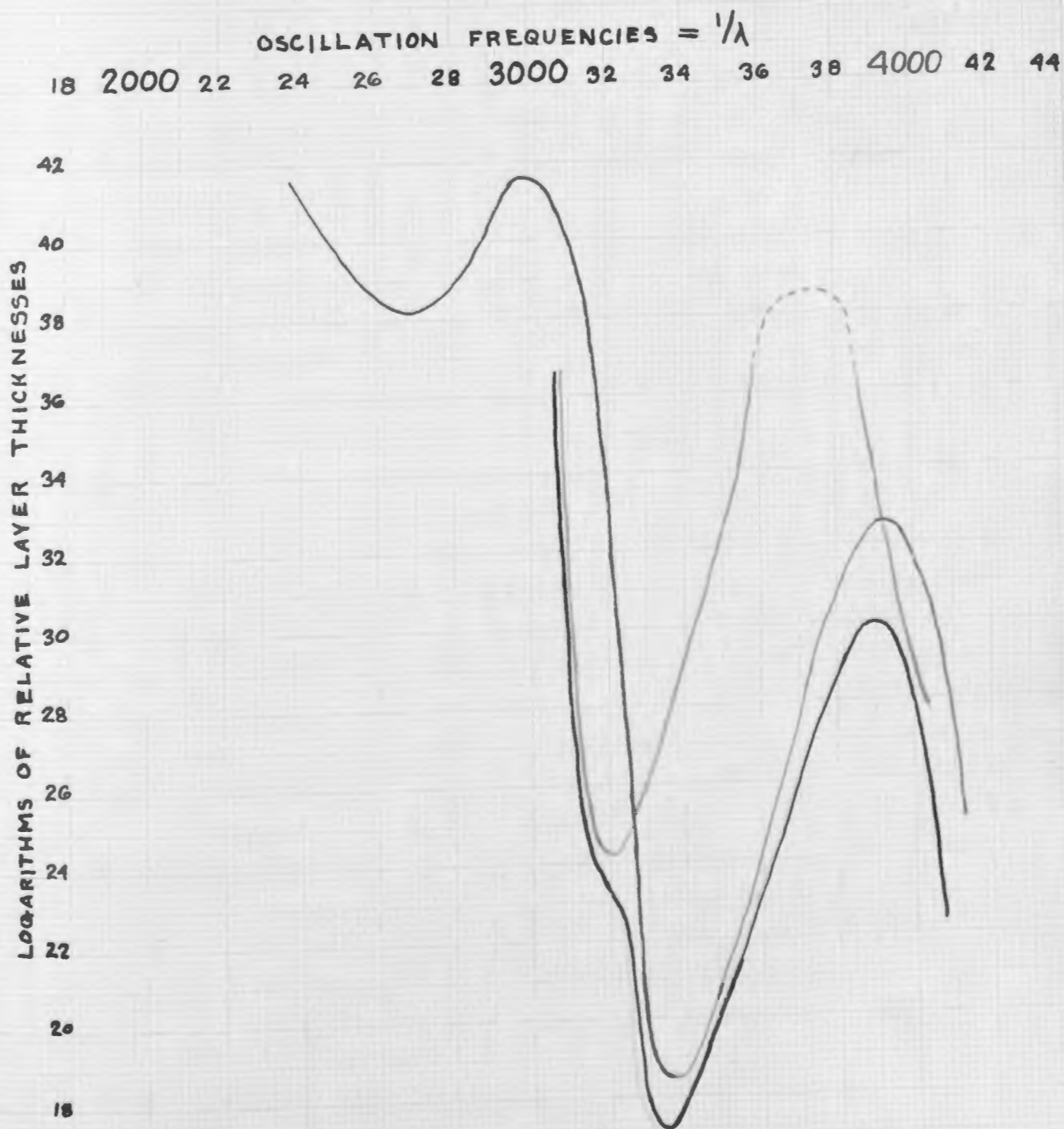—— SODIUM SALT OF OCTOCHLORQUINHYDRONE

OSCILLATION FREQUENCIES = $1/\lambda$

FIG. 22

CHLORANIL

TETRACHLORHYDROQUINONE

MIXTURE OF EQUIVALENT AMOUNTS OF CHLORANIL
AND TETRACHLORHYDROQUINONE

the curve of the sodium salt of octochlorquinhydrone with those
of its components, it must be remembered that its components
are really chloranil and the sodium salt of tetrachlorhydroquinone,
and that the latter could not be made because of the ease with
which it oxidized.   Instead of comparing the curve of the
sodium salt of octochlorquinhydrone with those of chloranil and
tetrachlorhydroquinone, it must be compared with those of chloranil
and the imaginary curve of the sodium salt of tetrachlorhydro-
quinone.   As was mentioned before, this curve, if analogous to the
curve of the sodium salt of hydroquinone, would show a much less
persistent band than that of tetrachlorhydroquinone, shifted
farther toward the visible spectrum.   If so, the band of the
sodium salt of octrochlorquinhydrone at $1/\lambda$ 3180 might correspond
rather closely to that of the sodium salt of tetrachlorhydroquinone,
since it, too, is much less persistent than the curve of tetra-
chlorhydroquinone, and is situated farther toward the visible
range.   On the other hand, this band at $1/\lambda$ 3180 shows no sign
of the persistent chloranil band at $1/\lambda$ 3410 as it should if it
were a summation of the bands of its two components.   In the
visible range, the band of the sodium salt of octochlorquinhydrone
at $1/\lambda$ 2280 shows very plainly that the curve is not a summation
of the curves of its components, for the sodium salt of tetrachlor-
hydroquinone would have no band in the visible range, and the
band of chloranil at $1/\lambda$ 2710, although it extends slightly into
the visible range, is cut out long before the dilution is reached
at which this band of the octochlorquinhydrone salt appears.

The band of the sodium salt of octochlorquinhydrone at
$1/\lambda$ 3180, as was suggested in the preceding paragraph, is very

similar to what would be expected from the sodium salt of tetra-
chlorhydroquinone.   It is shifted slightly to the left of the
band of tetrachlorhydroquinone, is much less persistent, and much
broader.   It shows very little similarity to the corresponding
band of chloranil at $1/\lambda$ 3410 which is much more persistent and is
situated farther toward the ultra violet.   It would seem clear,
then, that the position of the band of the sodium salt of octo-
chlorquinhydrone in the ultra violet indicates that is is due to
benzene vibrations, modified by substituent groups.

The band of the sodium salt of octochlorquinhydrone
at $1/\lambda$ 2280 differs very much from any band in the curves of its
components.   It corresponds most closely to the shallow band of
chloranil at $1/\lambda$ 2700, but its resemblance to this band is extremely
slight.   The band at $1/\lambda$ 2280 is hidden by general absorption
at the concentration at which the chloranil band at $1/\lambda$ 2700
disappears, and it is not until the solution is made much more
dilute that this band appears at all.   It is also much more
persistent than the chloranil band, and is situated almost entirely
in the visible range, while the chloranil band extends only slightly
into the visible.   These facts seem to show that this band at
$1/\lambda$ 2280 is due to an entirely different cause from that of the
chloranil band.   Its similarity to the persistent bands of dye
stuffs that are found in the visible spectrum indicates that its
absorption may be due to the same causes.

At the red end of the visible region, the absorption
spectrum of the sodium salt of octochlorquinhydrone shows a
shallow band which is suddenly cut off by the persistent band at

$'/\lambda$ 2280.   This shallow band resembles the band of chloranil
at $'/\lambda$ 2700 in shape and persistence, but is situated much farther
toward the red end of the spectrum.   It is a question whether
this is really a band at all.   It might be considered the
beginning of general absorption.   The great amount of general
absorption shown by the curve of the sodium salt of octochlorquin-
hydrone is a striking difference between this curve and those of
its components.   It covers the whole range of the spectrum until
a very dilute solution is used, and cuts out most of the field
in which the chloranil and tetrachlorhydroquinone bands appear.
This recalls the absorption spectrum of phenoquinone in the presence
of phenol as khown by Pratt and Gibbs which exhibited only general
absorption.

The two theories available for explaining the cause
of the light absorption are the isorropesis theory and the force
field theory.

Assuming the isorropesis theory, the presence of the band
at $'/\lambda$ 2280 in the visible spectrum, and its similarity to the
absorption bands of dyes suggests that the absorption band may be
caused by an oscillation of electrons or valences.   This was
the explanation given by Baeyer to the triphenolmethane dyes,
and applied by Willstatter and Piccard to the quinhydrones.
According to this theory, valence electrons would vibrate back and
forth between the quinoid and benzenoid molecules.   Just what
the isorropesis would be in the case of the sodium salt of octo-
chlorquinhydrone must be considered.   For ordinary quinhydrones
an oscillation such as is shown in the following figure was
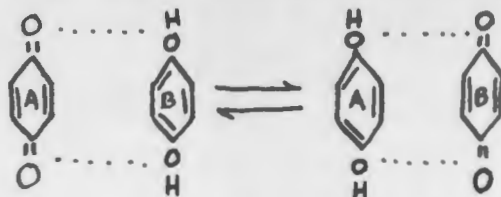
suggested. One difficulty in applying this oscillation to the sodium salt of octochlorquinhydrone is that, by a study of the absorption spectrum of chloranil, we have tried to prove that much of the chloranil is in the peroxide form. We must therefore assume an oscillation of valences between a peroxide form and the salt of hydroquinone. This would involve no such change in the structure of the benzene ring, as would occur in the case of the quinhydrone, when the ring changed from quinoid to benzenoid, and vice versa.

If an oscillation is assumed between the peroxide form and the hydroquinone form, an equilibrium between the two forms should exist. We should expect to see in the absorption spectrum, besides the isorropic band, the ultra violet bands of chloranil and the sodium salt of tetrachlorhydroquinone. It has been shown that the absorption curve of the sodium salt of octochlor-quinhydrone shows a band in the ultra violet which might correspond to the band of the sodium salt of octochlorquinhydrone, but which shows very little resemblance to the band of chloranil. This could mean either that the condition was such that the ring structure of the chloranil had changed its nature when it became a part of the sodium salt of octochlorquinhydrone, or that the amounts of chloranil and the sodium salt of tetrachlorhydroquinone were too small to show above the general absorption of the mixture. It seems probable that the two components have lost their original character.

the simplest application of the isorropesis theory to the sodium salt of octochlorquinhydrone might be such as is shown in the following diagram:

This equilibrium would involve an oscillation of the sodium valence from one molecule to the other, and it is possible that this oscillation would be the cause of the absorption band at $1/\lambda$ 2280. The chances are, however, that this is not the only reaction that taken place in solution. We could easily imagine that the valences of the two sodium ions of the molecule of the sodium salt of tetrachlorhydroquinone would not vibrate at the same time, or that the relative positions of that molecule and the chloranil molecule would not be such that both sodium atoms would have the same effect. In the former case, we could imagine one sodium ion leaving molecule B, breaking the bond between the oxygen atoms of the chloranil molecule and attaching itself to one of them. This would leave the valence of the other atom free. The free valence might react in several different ways. It might break the benzene bonds, and start an isorropesis between benzenoid and quinoid forms; it might break the bond between the oxygen and sodium atoms, either in the same molecule, or in the other molecule, and the simple oscillation of the sodium and oxygen valence electrons would continue; or it might attract the free oxygen valence from the other molecule to form a new compound, $Na O \bigcirc -O-O-\bigcirc O Na$, such a maze of possible oscillations
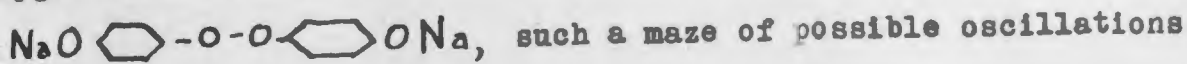
would be capable of producing all sorts of conditions which could absorb light, and the result would be a great amount of general absorption, as is actually the case.

Such arguments do not prove that the isorropesis theory holds. They only show that the isorropesis theory may be used to explain the bands which actually occur. To summarize, we would explain that according to the isorropesis theory the band at $'/\lambda$ 2280 would be due to some oscillation between the valence electrons of the sodium and oxygen atoms, the band at $'/\lambda$ 3180 would be due to the modified benzene vibrations of the ring structures, and the great amount of general absorption would be the result of various other vibrations caused by the unsymmetrical oscillations of the sodium valences.

It remains to be shown how Baly's force field theory might be used to explain the bands. According to this theory, each molecule is a complex of closed force fields which may be opened, either by light alone, or by the combined action of light with a solvent of strong, residual affinity. In the sodium salt of octochlorquinhydrone each component must be considered a source of closed force fields, upon which both the residual affinities of the solvent and the other component are acting. Composed as it is of two molecules, acting in some way on each other, there are many chances for closed systems of force fields to be opened. The chief difficulty consists in locating the exact force fields which do the absorbing. The two persistent bands indicate that there are two force fields somewhere within the complex molecule, which are opened up, either by light, or by light plus the mutual action of the two molecules upon each other.

A study of the two molecules helps us to pick out the
two force fields.   One ought to be centered around the oxygen atoms
of the two molecules, and the other around the unsaturated bonds
of the benzene ring structure.   According to Baly, the reactivity
of the molecule is dependent on the amount of residual affinity
which the molecule possesses.   The carbonyl groups of quinone
and the hydroxyl groups of hydroquinone are supposed to possess
a great amount of residual affinity, since they are capable of
reacting readily, and of forming addition products.   Quinone
forms a dioxime readily, but tetrachlorquinone does not form any
oxime.   This would indicate that the residual affinity of the
carbonyl group of chloranil is less than, or quite different
in character from, those of quinone.   We would imagine that the
force fields around the chloranil molecule are quite well closed,
but that in the presence of the sodium salt of tetrachlorhydroquinone
they are partially opened by its residual affinities.   The fact
that the free octochlorquinhydrone does not exist indicates that
there is not enough difference between the force fields around
the oxygen atoms of chloranil and tetrachlorhydroquinone for them
to react on each other.   When the hydrogen of the hydroxyl group
is replaced by sodium, a greater degree of reactivity results
toward the negative groups.   This will change the character of
the force fields in such a way that they can react on those of
chloranil.   With the partial opening of the force fields, a
condition is obtained which will absorb light, and the band at
$1/\lambda$ 2280 results.

Since the band at $1/\lambda$ 3180 corresponds fairly well with

the imaginary curve of the sodium salt of tetrachlorhydroquinone, we are led to believe it is due to somewhat similar causes. These would be attributed to the absorption of light in opening force fields around the benzene nucleus of either molecule. We might expect two bands in the ultra violet, to correspond to the two different nuclei, but they do not appear. This may mean that, because of the mutual action of one molecule upon the other, the force fields around both benzene nuclei are reduced to the same condition. The application of the two theories to the sodium salt of octochlorquinhydrone has shown that they correspond exactly. The isorropesis theory explained the band at $1/\lambda$ 2280 as due to an oscillation of valence electrons between the sodium atom and the chloranil and tetrachlorhydroquinone oxygen atoms, while the force field theory assumes an interaction between the force fields of the oxygen groups due to the influence of the sodium atom. If an isorropesis actually occurred, it would involve an interaction of force fields. At the same time, Baly's theory states that if the potential gradient between the two force fields is steep enough, there may be an interchange of electrons. In regard to the band at $1/\lambda$ 3180, both theories explain it as due to a modified benzene ring structure, but neither can prove definitely what is its cause.

It should be shown how the different colors of the sodium of octochlorquinhydrone in water and alcohol apply to the two theories. According to Baly, the difference in color would be due to the different amounts of opening of the force fields. The difference in the degree of opening might be due to two causes. It might be purely a solvent effect, since water, having a greater amount of residual affinity than alcohol, might open up another force field

or increase the amount of opening of the force fields around the oxygen groups. The more reasonable explanation is that the sodium salt of tetrachlorhydroquinone is much more highly ionised in water than in alcohol. This increased ionization would probably increase the residual affinities of the sodium ions and open up still farther the force fields around the oxygen atoms. This color change in water and alcohol could be explained in a similar way by the isorropesis thoery. The increased ionization of the sodium salt of tetrachlorhydroquinone would increase the amount, and probably the speed, of the isorropesis, and this would necessitate the absorption of different wave lengths of light.

Baly's force field theory then leads to the same conclusion as the isorropesis theory. They both explain the deep color of the sodium salt of octochlorquinhydrone by some interaction between the two molecules which generate it. The two theories use different terms to express what this interaction is. The isorropesis theory assumes a vibration of electrons between the molecules, while the force field theory requires an interaction of force fields which may possibly result in an exchange of electrons. Both theories, however, involve an electro-magnetic disturbance between the molecules which is capable of absorbing some of the electro-magnetic waves of light.

In conclusion, we may say that we have proven by comparison of the absorption spectrum of the sodium salt of octrochlorquinhydrone with those of its components that the salt is not a mixture of its components, nor are the molecules of the components unchanged. The absorption spectrum of the sodium salt is entirely different from those of either components, especially in the visible spectrum.

In this region a new persistent band is introduced, while in the ultra violet the band is considerably modified.   This indicates that, whatever the relation between the molecules in the sodium salt may be, a real difference in their light absorbing properties exists.

Both the isorropesis theory and Baly's force field theory are capable of explaining the relation between the molecules in the sodium salt, one by a vibration of electrons between them, the other by a mutual interaction of their force fields.   No conclusion, therefore, can be drawn as to which theory holds better.

We can decide, however, that there is much interaction in the molecule, of a kind that cannot be represented by a single, static formula.