THE ULTRA-VIOLET ABSORPTION SPECTRA OF SOME HALOGEN COMPOUNDS IN VARIOUS SOLVENTS.

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by

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CONTENTS.

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I. INTRODUCTION.

The modern theory regards the atom as made up of
a positively charged nucleus surrounded by a shell of
electrons, the number of electrons being equal to the
positive charge on the nucleus. These electrons are
supposed to exist in certain definite orbits or energy
states, and energy may be absorbed or emitted as one
quantum of monochromatic light when an electron passes
from one state to another: the difference of the
energies of the atom in the initial and final states
is equal to the energy of the radiation absorbed or
emitted.

For each electron there is a state of minimum
energy known as the "ground state", and if the atom
collides sufficiently violently with another atom
(as at high temperatures) it may have one of its
outer electrons raised to one of the states of higher
energy, and the energy that the electron gives out
in returning from this excited state to the ground
state appears as monochromatic light. The light from
a glowing gas or vapour is the sum of millions of
such processes in the separate atoms.

Certain energy states will be more favoured than
others, and some transitions will be frequent and
others improbable. To each such transition corres-
ponds/

corresponds a spectrum line, the intensity of which
will depend on the above probabilities.

All spectra fall into two main classes: emission
spectra and absorption spectra. Emission spectra can
be excited in a number of ways (e.g. by violent col-
lision). Absorption spectra are usually obtained by
passing the light from a source of continuous spec-
trum through a cell containing the gas or liquid under
investigation and examining the spectrum of the emerg-
ing light. From the bright continuous background of
colour certain radiations are then missing - having
been absorbed - and these constitute the absorption
spectrum of the substance. The absorption spectrum
of a substance is not necessarily the exact reverse
of its emission spectrum, because chiefly those lines
occur in the absorption spectrum which correspond to
a transition from the ground state to some state of
higher energy; in the emission spectrum however there
can occur lines corresponding to a transition from
one excited state to another.

Unlike the atom, which from a spectroscopic stand-
point can only possess electronic energy, a molecule
can have three kinds: electronic energy, vibrational
energy (of the nuclei) and rotational energy. To each
of these types of energy the quantum conditions must
be applied. If only changes in the rotation energy
take place, the radiation appears in the far infra-red
(at/

(at wave-lengths in the neighbourhood of 100μ).
If rotational and vibrational changes take place to-
gether, the magnitude of the latter raises the fre-
quency of the emitted light into the near infra-red
region. If an electronic change occurs simultaneously
with these, the spectrum will be emitted in the visible
or **u. v.** region. In a molecule of a substance in
the gaseous state, to a first approximation, we may
regard these energies as independent and write down
the frequency of any band line as the sum of the con-
tributions from these three separate sources. Thus:

$E = E_c + E_v + E_r$ (1) where the order of magni-
tude is $E_c > E_v > E_r$

When the energy supplied to the molecule corres-
ponds to wavelengths in the far infra-red the quanta
of energy are not large enough to change the electronic
or vibrational energy states but are only large enough
to change the rotational energy states and so the
spectrum of the substance consists of a series of
lines the wavelengths of which correspond to the
energy differences of the various rotational states
of the molecule.

If however the energy supplied is of wavelengths
in the near infra-red the quanta are large enough to
affect the vibrational energy states. In this case
a series of bands (instead of single lines) is ob-
tained, each of which is made up of a group of lines;
this/

this is due to the fact that rotational energy changes occur at the same time as the vibrational energy changes. If E is the energy supplied to the molecule then for each line

$$E = E_v + E_r$$ where E_v is the energy of a vibrational change and E_r is the energy of a rotational change, then for a definite value of E_v there will be series of values of E corresponding to different values of E_r , so that for each value of E_v possible to the molecule there will appear in the spectrum a band of lines each of which corresponds to a different value of E_r .

Wave-lengths in the visible and u.v. regions correspond to energy quanta large enough to produce changes in the electronic energy states; to each electronic energy change there corresponds a series of vibrational energy changes and to each vibrational energy change a series of rotational energy changes and the energy E supplied is given by equation (1). So that the spectrum of a substance in this region consists of a series of bands (each due to an electronic energy change) each made up of a series of smaller bands (due to vibrational energy changes), each of which, in its turn, is made up of a series of lines (due to rotational energy changes).

The foregoing remarks apply to the spectra of substances in the gaseous state. It is found that at constant temperature with increasing pressure of foreign/

foreign inert gas the rotational fine structure dis-
appears and the vibrational bands gradually broaden and
finally overlap and just appear as a series of maxima
in the electronic band. For the symmetrical broaden-
ing of the rotational lines on the addition of an
inert gas at high pressure to an absorbing molecular
vapour at low partial pressure the Lorentz collision-
damping hypothesis gives a good explanation up to a
pressure of 10 atmospheres foreign gas.   For still
higher pressure of foreign gas there is a strong in-
crease in the broadening, which as well as the shift
in the edge of the band, and the increase in energy
absorbed and the final appearance of new bands are
due to effects other than the collision effect. These
effects show analogies to the Stark effect although
we cannot make definite assertions as to their nature.

The u. v. absorption spectrum of a substance
dissolved in a chemically inert solvent consists of
a series of maxima which in general show no fine
structure. Teves (1) suggests that this non-appearance
of fine structure may be explained by assuming that
the solvent acts in part, as an inert gas at high
pressure. But the problem involves much more than
this because it is found that the absorption spectrum
of a substance varies to a greater or less degree with
the solvent; and the phenomenon of liquefaction is
itself a result of intermolecular forces.

The/

The first attempt to systematise the observed variation of an absorption spectrum of a solution with change of solvent was due to Kundt who propounded the rule which states "that the absorption band of a substance is shifted towards the red the greater is the index of refraction of the solvent in which the substance is dissolved".

In 1912 in a paper entitled "A Theory of Fluorescence" Baly and Krulla (2) brought forward the theory that every elementary atom possesses both primary and secondary valencies; in a compound formed by virtue of the primary valencies only the secondary valencies are unsatisfied, so that every atom is the centre of a field of force the nature and strength of which depends on the nature of the secondary valencies, and whose lines of force radiate in every direction. On the atoms coming together to form a molecule the fields of force condense together with the liberation of free energy, and a closed system of force lines is obtained and the free affinities of the atoms constituting the molecule will be considerably reduced; the whole of the free energy will only disappear when there is perfect equality between those of opposite types within the molecule. Where there is not perfect equality a "residual affinity" exists. These "condensed systems" may be unlocked by the absorption/

absorption of light, the light does work against the chemical forces which tend to produce the closed systems, and only those rays are absorbed which suit the particular system. In solutions the residual affinity of the solvent comes into play and this field of force will tend to penetrate the closed force field of the solute molecules, with the result that it will be partly or completely opened, and the amount of opening depends on the relation between the affinities of the solvent and solute and on their relative masses. The greater the difference in affinity the more will the closed system of the solute be opened, so that Kundt's rule should read "that the absorption band of a substance is shifted towards the red the greater the relative and residual affinity of the solvent." *

This theory of Baly and Krulla contains the nucleus of the modern theory of association. The theory of the absorption of light by dissolved sub-stances is very complicated because we have to con-sider the solute molecules each surrounded by a large number of solvent molecules. According to the theory of Fajans & Joos (3) if the solvent molecules are polar/

* In modern quantitative work on the absorption of light by solutions it is usual to plot the log of the extinction coefficient (which is a function of the ratio $\frac{I}{I_0}$) against the wave-length, and a curve with one or more maxima is obtained.

polar i.e. if the "centres of gravity" of the posi-
tive and negative charges of the molecule do not
coincide they will exert a "deforming" influence on
the shell of electrons of the solute molecules which
they surround, the electrons being drawn towards the
positive part of the solvent molecule and repelled by
the negative part. It is very probable that the
energy states of the deformed molecule are not the
same as those of the undeformed molecule, so that a
difference is to be expected between the spectrum of
a substance in the gaseous state and in solution in
a polar solvent. (3) It might be expected that the
amount that the solute molecule is deformed will
depend on the strength of the dipole of the solvent,
and in many cases in practice a parallelism is found
between the change in absorption (as compared with
the gaseous state) and the dipole of the solvent.
In non-polar solvents, such as hexane, the absorption
spectrum is very similar to that in the gaseous state,
so that in general the absorption in hexane is taken
as that of the normal undeformed molecule, and is used
as a standard for comparison of the spectra of the
same substance in other solvents.

Scheibe (4) finds that the measured shift of an
absorption maximum on change of solvent is not a
simple function of the dipole of the solvent molecule,
because the measured dipole is made up of constituent
parts/

parts which are screened by non-charged groups; the
measured dipole just gives the distance apart of the
centres of gravity of the positive and negative charges.
The effect of a dipole field on a neighbouring mole-
cule depends on the possibility of approach, and for
equal charges this can be quite different because of
different screening groups.

Scheibe divides the effect of a change of solvent
on the absorption spectrum of a dissolved substance
into two parts:- (1) the change in height of the
band and (2) the displacement of the centre of the
band. He attributes these effects to two distinct
processes.

Each molecule absorbs the frequency corresponding
to the difference in energy between the original and
final energy states of its electrons. This energy
difference can vary from molecule to molecule in the
solution because of (1) variation in the inner states
of the molecules (e.g. rotation, vibration of atoms
and groups) or (2) change in the value of the field
strength of the neighbouring molecules by change in
their distance from the absorbing molecule. The
strength of absorption at a given wavelength is
determined by the number of molecules with the corres-
ponding energy difference in its two states.   In
liquid and dissolved substances at ordinary tempera-
tures within certain limits there is a continuous
variation/

variation in this energy difference. The absorption curve is an image of the frequency of occurrence of the different states for a dissolved substance and varies from solvent to solvent. This effect does not radically alter the shape of the curve, rather it only shows itself in variation of the position of the curve as measured by the position of the maximum absorption, i.e. by the energy difference which appears most often. By changing the field due to the solvent we can change the energy difference of the solute electron states so that the place of maximum absorption changes although the total area of the curve i.e. the total number of molecules absorbing remains the same; this shift is purely due to the effect of the neighbouring molecules i.e. to solvation. In complicated organic molecules there may be an equilibrium between two tautomeric forms and the solvent may affect this equilibrium and therefore change the height of the curve.   There are indications that two forms may exist in other molecules where ordinary conceptions of valency do not permit it. The pure solvent effect gives the shift in the position of the maximum, and the fall in the height is a result of the solvent effect on this equilibrium.

According to the quantum theory the height of the band gives a measure of the frequency of the absorption process, and a change in height can occur in/

in different ways according to the structure of the
molecule. Scheibe (as described above) ascribes the
change in the position of the band to compound forma-
tion between the solvent and solute, the variation
being dependent on the dipole characters of the sol-
vent and solute. If the chromophore group of the
solution is positively charged the negative parts of
the solvent dipoles are in its vicinity, so that the
electron "spring" is made more difficult, i.e. re-
quires more energy and the whole electron band shifts
towards the ultra violet. If on the other hand, the
chromophore group is negative the positive parts of
the dipole are surrounding it, the electron spring
is facilitated and the whole band shifts towards the
red.

Wolf in 1929 in a paper on Dipole moments,
Association and U.V. Absorption (5) developed a formula
connecting the refractive index of a solution with
the special vibrational frequencies of its constituent
absorbing groups. But this formula only holds if no
new forces are set up in the solution i.e. both sol-
ute and solvent are non-polar. If the solvent has
a permanent dipole it will deform the electron shell
of the solute and both the position and height of the
absorption band will be changed. The polarisability
of a molecule is a measure of the ease with which its
electron shell can be deformed, and so the change in
absorption/

absorption due to one particular group in a molecule
by the introduction of another can be taken as a meas-
ure of the deforming power of the second group.

Wolf also emphasises the fact that if the solute
possesses a dipole it will have a deforming effect on
the electron shells of the solvent molecules. Owing
to the small number of solute molecules compared with
the number of solvent molecules this effect may be
neglected if the solvent is polar; but this is not
always possible in the case of a polar solute and a
non-polar solvent.   Fuchs & Donle (6) assert that
it is possible to divide non-polar solvents into two
groups, those with small, and those with large dis-
turbing effect. The former group contains the satur-
ated aliphatic and alicyclic hydrocarbons (e.g. hexane,
cyclohexane, decalin) , i.e. compounds having no polar
groups and low polarisability.   The second group, of
non-polar solvents with a large influence on the solute,
is composed of substances which contain polar groups
whose influence is, however balanced out by symmetry,
e.g. CCl_4 CS_2 , dioxane, $Cl\!-\!\!\bigcirc\!\!-\!Cl$, $\underset{Cl}{\overset{Cl}{>}}C=C\underset{Cl}{\overset{Cl}{<}}$
These substances are all easily polarised, so that
in the presence of a polar solute a dipole is induced
in the solvent molecule which then acts as a polar
solvent.

Another theory discusses the shift of absorption
spectra in terms of energies of solvation rather than
of/

of deformed orbits.　In heteropolar compounds it is
quite understandable that association should take
place between the solute molecules, and it has also
been shown to occur to some extent in non-polar hydro-
carbons such as diphenyl and phenanthrene in solution.
From this fact Berger (7) deduces that the permanent
dipole in a molecule is not the only factor entering
into association.　Association of a dissolved sub-
stance is the resultant of two attractive forces
(1) the mutual attraction between the dissolved mole-
cules, and (2) the attraction between the solute and
solvent molecules, and Berger develops formulae for
these attractions depending on the polarisabilities
of the molecules.　Briegleb (8) (9) has shown that
not only the mean polarisability but also the aniso-
tropy of the polarisability is of importance in assoc-
iation.

So that for all substances in solution we may
assume association between the solute and solvent
molecules to a greater or less degree; and this assoc-
iation alters in some way the potential energies of
the ground and excited states, which are intimately
bound up with change in absorption of light.　This
is discussed by Iredale and Mills (10) who point out
that the association need not always be of the same
type.　One form may have a greater difference in
potential energy between the ground and excited states
compared/

compared with the normal molecule, and another form
may have associated molecules with a smaller differ-
ence in potential energy between the ground and ex-
cited states (again referred to the normal molecule).
There is also the possibility that the difference in
the potential energies of the ground and excited states
is the same for the associate as for the normal mole-
cule.   These three types may be represented diagram-
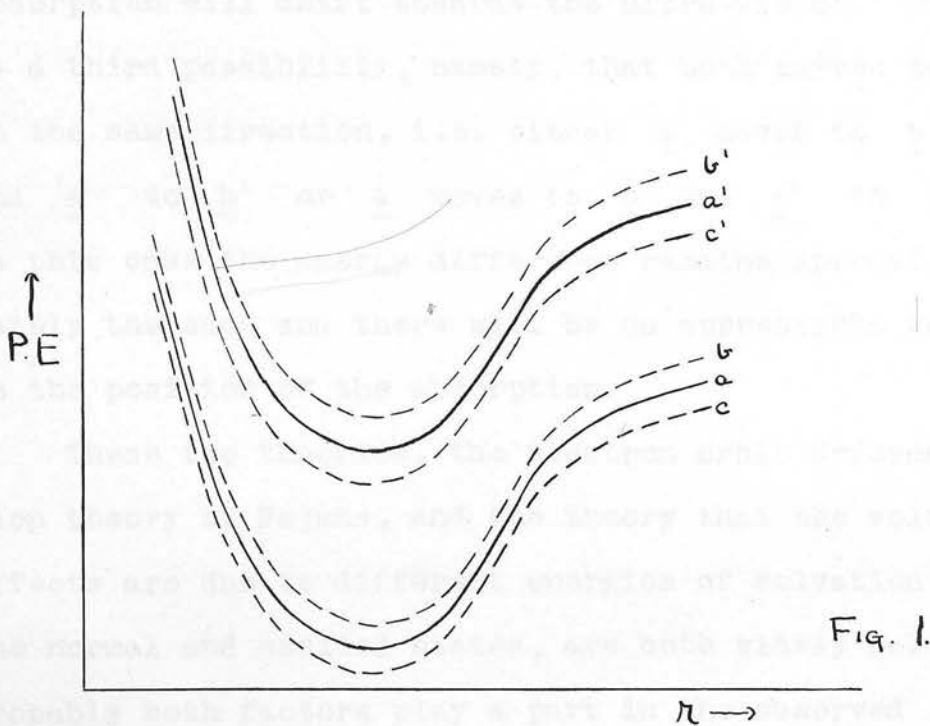matically as follows:-

FIG. 1.

The curves a and a'   represent the potential energy
curves for the normal molecule in the ground and ex-
cited states. On dissolving the substance in a solvent
the energies of both states will be altered (due to
solvation) and the curves will move either up or down

but/

but   r for the equilibrium positions will not alter appreciably. They may or may not move in the same direction. If $\underline{a}$ move to $\underline{b}$ and $\underline{a}'$ to $\underline{c}'$ the difference in the energies of the ground and excited states will be less for this form than for the normal molecule, and less energy will be required to excite the molecule, so the absorption will move towards the red. If on the other hand $\underline{a}$ move to $\underline{c}$ and $\underline{a}'$ to $\underline{b}'$ the energy difference will increase, more energy will be required to excite the molecule and the absorption will shift towards the ultra-violet. There is a third possibility, namely, that both curves move in the same direction, i.e. either $\underline{a}$ moves to $\underline{b}$ and $\underline{a}'$ to $\underline{b}'$ or $\underline{a}$ moves to $\underline{c}$ and $\underline{a}'$ to $\underline{c}'$. In this case the energy difference remains approximately the same and there will be no appreciable shift in the position of the absorption.

These two theories, the electron orbit deformation theory of Fajans, and the theory that the solvent effects are due to different energies of solvation in the normal and excited states, are both widely held. Probably both factors play a part in the observed shifts of the absorption bands.

The exact shape of the curves a b c a' b' c' depends on the forces controlling the internal vibrations of the molecule in the normal and excited states, and these forces will be altered by the influence which the/

the solvent introduces. In general one could expect
the effect of non-polar solvents to be slight, the
effect of solvents containing strong but symmetrical
polar groups to be observable, and for strongly polar
solvents quite considerable.   Their study will in-
volve accurate determination of the shapes of absorp-
tion curves as well as of the position of the maximum,
and perhaps, attention to the effect of temperature
on the shape of the curves. Towards the end of the
discussion of the results obtained in the work des-
cribed in this essay, a tentative explanation of the
effect of the solvents is advanced on the basis of
the second of the two theories mentioned above.

II. METHODS OF MEASUREMENT.

1. GENERAL REMARKS.

It is well known that when light passes
through a medium a certain amount is absorbed. There
are two principal laws which govern the amount of
light which is absorbed. Lambert's law states that
the proportion of light absorbed by a substance is
independent of the intensity of the incident light.
This law appears to be rigidly true in all experiments
which have been made. (Except in such cases as the
intensity of the light is sufficient to produce
measureable changes in the stationary concentration of
the absorbing molecule (59)). Bunsen and Roscoe
assumed only Lambert's law in their definition of
"extinction coefficient":- "Let I_0 be the intensity
of the incident light which enters the medium, I
the intensity remaining after its subsequent passage
through a path length d , and $\frac{1}{\alpha}$ the path length,
passage through which reduces the light intensity to
$\frac{1}{10}$ th ; then

$I = I_0 \, 10^{-\alpha d}$ where α , a constant depend-
ing on the medium, is called by us the 'extinction
coefficient'. d is to be taken in centimetres."

The Bunsen - Roscoe extinction coefficient is,
then, the reciprocal of the thickness which is neces-
sary/

necessary to weaken the light to $\frac{1}{10}$ th of its in-
cident value.

Beer's law states that if an absorbing substance
is dissolved in a non-absorbing liquid its absorption
of a beam of homogeneous light depends on the number
of molecules of the absorbing substance which the
beam of light passes through, that is, on the concen-
tration of the solution.   If I_0 is the intensity
of the light entering the liquid, I that after passing
ing through d cm of the liquid, and c the concen-
tration, Beer's law can be expressed $I = I_0 \alpha^{-dc}$
Here α is a constant of the liquid and is obviously
the ratio of the transmitted to the incident light
for unit thickness and concentration. We can write
this is another way.   If α_0 is the extinction co-
efficient of a solution for unit thickness and con-
centration, then Beer's law says that $I = I_0 . 10^{-d\alpha_0 c}$
In other words the extinction coefficient, for a given
wave-length, of a solution of concentration "c" is
c times that of the same solution of unit concentra-
tion.

Beer's law has been checked again and again and
holds in many instances for dilute solutions with
great exactness (11).When, as is very frequently the
case, departures occur they indicate an alteration of
the absorbing molecules, or the formation of fresh
molecular aggregates, as a result of the alteration
of/

of concentrations. At small concentrations the absorbing molecules will not be able to influence one another to any appreciable extent, but as the concentration increases and they approach close to one another polarisation and association effects will appear. Halban and Ebert (see above) find deviation from Beer's law for the NO_3^- ion at concentrations greater than $\angle$ *about 0.1 molar* and according to Weigert (12) the complex ions $Cr_2O_7^=$, $CrO_4^=$, MnO_4^-, $PtCl_6^=$ etc. show similar deviation at high concentrations. If the extinction coefficient of a crystal of known thickness and density be measured and then, successively, the extinction coefficients of solutions of the same substance with different concentrations, it is found that the extinction coefficient increases with dilution from the minimum value given by the solid to a maximum. It would seem that the relation between the maximum extinction coefficient K in a given solvent, and the extinction coefficient k at the concentration c in that solvent is given by

$$\frac{k}{K} = 1 - e^{-\frac{\alpha}{c}}$$

where α is a constant characteristic of the solvent. For small values of c the right hand side of this equation approximates to 1 so that k = K i.e. Beer's law holds for dilute solutions. In all the solutions measured in this work the concentrations of the absorbing substances were small and in the region of/

of complete validity of Beer's law, so that any change
in an absorption curve with concentration is assumed
to be evidence for a corresponding change in the nature
and concentration of the absorbing substance or sub-
stances present.

When the term "absorption spectrum" is used in a
quantitative sense there is meant the curve showing
the variation of the "extinction coefficient" with
the wave-length (or frequency) where the extinction
coefficient is defined by the Beer-Lambert laws for
the absorption of light by an absorbing medium

$$I = I_o e^{-\varepsilon c d}$$

$$or \quad \log \frac{I_o}{I} = \varepsilon c d$$

Here I_0 is the intensity of the beam of monochron-
atic light.

I is the intensity of the same beam after passing
through a length d of the absorbing medium.

c is the concentration of the absorbing substance

ε is the extinction coefficient.

In practice, d is expressed in centimetres, c in
mols per litre, and the more convenient $\log_{10}$ are
used instead of $\log_e$. This gives a different
absolute value of the absorption coefficient, in this
case denoted by K where K = 0.4343 ε . Hence
the determination of an "absorption spectrum" involves
the measurement of values of K corresponding to a
number/

number of different wave-lengths spaced at small inter-
vals.   It is usual in plotting the absorption curve
to employ log K instead of K as, since the values
of K measured may range from 10^{-1} to 10^{5} in this
way features of the curve occurring at widely differ-
ent values of K are more equally brought out.

The older methods of measuring absorption spectra
were carried out with the help of a Baly tube, and a
spectroscope or spectrograph. The light source was
one which gave either a continuous and uniform spec-
trum, or a line spectrum in which the lines are very
close together and evenly distributed throughout every
region of the spectrum to be explored. The method of
making observations was as follows: the cell was
filled with a solution of known concentration and
placed in front of the slit of the spectroscope.
The wave-length readings were then taken at both edges
of the band or bands.   The strength of the solution
was then diminished to about $\frac{1}{2}$ or $\frac{1}{3}$ of the original
concentration and the new readings of the edges of the
bands were taken. The process was repeated until the
dilution was such as to cause but a single very narrow
band; the mean of the readings for this narrow band gave
the position of the "Maximum Absorption" or the "head".
of the band.   The experimental data were plotted in
the form of curves the abscissae being wave-lengths or
frequencies/

frequencies and the ordinates logarithms of equivalent thicknesses. This method was very laborious and did not give very dependable results.

Actually to measure K , the extinction coefficient, it would theoretically be simplest to pass a beam of light of known wave-length and known intensity through a known thickness of a known concentration of the absorbing substance and to measure the intensity of the emergent beam. This is the method used by V. Halban and Siedentopf (13) (14) who used a mono-chromator and a photo-electric cell and reached an accuracy of 0.1%. But if K is to be measured for a large number of different wave-lengths the method becomes exceedingly slow and laborious and a photo-graphic method is enormously more convenient.

The later and more systematic methods of absorption spectroscopy depend on spectrophotometry i.e. on the science of measuring the intensity of the light of each wave-length in the various regions of the spectrum. Just as with ordinary photometry, the method is one of comparison by the method of rendering the known and unknown equal. In spectroscopy the standard rays are derived from the same source as are the unknown because one cannot rely on getting from two similar sources two identically equal spectra or on the one source remaining constant from second to second.

Hence/

Hence in most spectrophotometers a pencil of light from any suitable source is divided into two equal parts, one to pass directly into the spectroscope to function as a standard, and the other to suffer change by its passage through the given medium; the amount of change at any point can then be determined by reference to the respective standard.
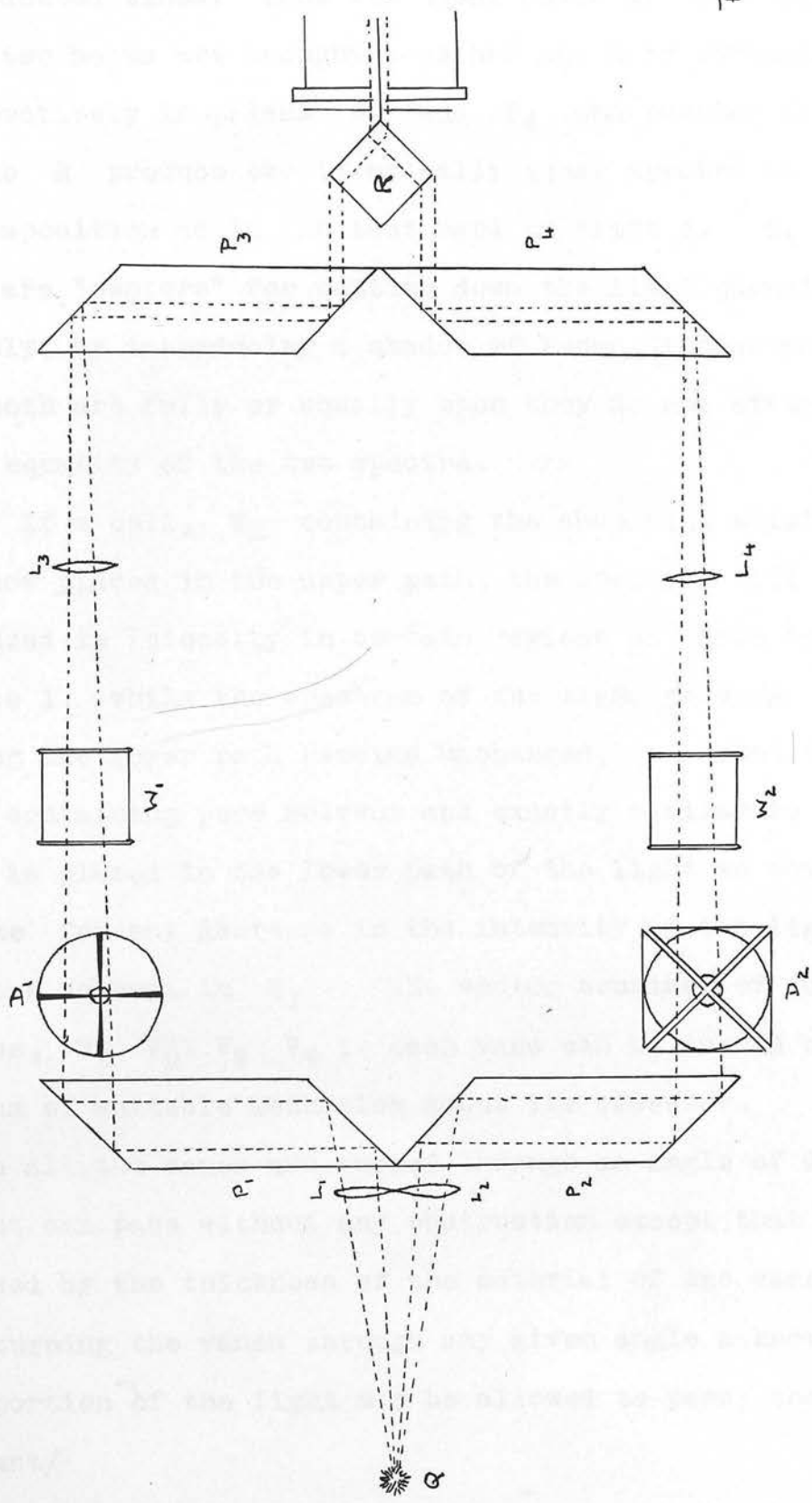
The first accurate method of spectrophotometry was devised by Vierordt in 1873 who may be regarded as a pioneer in applying measurements of absorption spectra to chemical problems.

Different methods have been used by various investigators for cutting down the intensity of the comparison beam. Houston (15) and Schaeffer (16) used two similar light sources and varied the intensity of the illumination from one by altering its position; Winther (17) used a calibrated blackened gauze for the reduction of intensity; V. Henri (18) used two equal sources and varied the time of exposure to one. The objection to these methods are all fairly obvious.

But the three most important methods for rapid measuring of the extinction coefficient over a series of wavelengths making use of the comparison of an unknown with a known intensity are: (1) the Judd Lewis sector photometer method   (2) the Hilger rotating sector photometer   (3) the Echelon cell.

In the Judd Lewis sector photometer method beams of light/

light from Q [Fig. 2] is reflected at the first
prism P_1 and at the fourth prism P_4 and gives
the dotted lines. Thus we have [illegible] [illegible]
The two beams are [illegible] at [illegible] and [illegible]
respectively in [illegible] [illegible] L_3 and [illegible] [illegible]
where a [illegible] of [illegible] will give [illegible]
juxtaposition of [illegible]. When [illegible] S_1 and S_2
S_2 are [illegible] the [illegible] the [illegible] respec-
tively [illegible] [illegible] and [illegible] [illegible]
if both are full, or nearly when they [illegible] are [illegible]
the equality of the two spectra.

If [illegible] W_1 [illegible] the [illegible] is [illegible]
be now [illegible] in the upper part, the [illegible] [illegible] is
reduced in intensity in certain [illegible] as [illegible] in
[illegible] [illegible] while the [illegible] of the [illegible] is [illegible]
almost [illegible] [illegible] is [illegible] unchanged.
W_2 [illegible] the pure [illegible] and quietly [illegible] [illegible]
W_1 is [illegible] in the [illegible] part of the [illegible] [illegible]
make [illegible] difference in the intensity [illegible] [illegible]
of [illegible] [illegible] in [illegible]. The whole amount of [illegible]
range [illegible] from S_1 S_2 is [illegible] each time and [illegible] [illegible] by
exact [illegible] [illegible] [illegible] [illegible] [illegible]
when all [illegible] [illegible] [illegible] [illegible] angle of 90°
light, [illegible] [illegible] without the [illegible] except that
caused by the [illegible] [illegible] material of the [illegible].
By turning the [illegible] through any given angle a given
proportion of the light can be allowed to pass, and
amount [illegible]

Fig. 2.

light from Q (Fig. 2) are reflected at the faces in prism P_1 and at the faces in prism P_2 as shown by the dotted lines. Thus two equal beams are produced. The two beams are brought together again by reflection respectively in prisms P_3 and P_4 and passing through rhomb R produce two identically equal spectra in juxtaposition as in the test band in Plate 1. D_1 and D_2 are "sectors" for cutting down the light quantita- tively, by introducing a shadow of known dimensions, if both are fully or equally open they do not affect the equality of the two spectra.

If a cell, W_1 containing the absorbing solution be now placed in the upper path, the spectrum will be reduced in intensity in certain regions as shown in plate 1. while the spectrum of the light passing along the lower path remains unchanged; a second cell W_2 containing pure solvent and exactly similar to W_1 is placed in the lower path of the light to compen- :sate for any decrease in the intensity of the light by the solvent in W_1 . The sector consists of four vanes, V_1 V_2 V_3 V_4 ; each vane can be turned by means of suitable mechanism about its bisector. When all the vanes are turned through an angle of 90° light can pass without any obstruction except that caused by the thickness of the material of the vanes. By turning the vanes through any given angle a known proportion of the light may be allowed to pass; the amount/

PLATE I.

amount of rotation of the vanes is measured by a pointer.

In working the photometer the vanes are arranged in the upper path so that the maximum light can pass, so that in that path the light is only cut down by the absorbing substance in the cell W_1 .   In the lower path the light is cut down by a known amount by adjusting the vanes; a series of exposures is taken, each corresponding to a different setting of the vanes in the lower path, and by an examination of the pairs of spectra obtained we can pick out the wavelengths at which the light is cut down equally by the solution and by the vanes (the latter "cutting down" being known).

Provided that the mechanism for reducing the light intensity is accurate, a method which involves only the comparison of equal intensities obtained by identical exposures cannot have theoretical errors. (Except when the intermittent nature of the illumination makes a difference, which seldom happens.) The only difficulty encountered with the Judd Lewis photometer is that the mechanism for reducing the light intensity involves somewhat elaborate correc- tions which are only valid if the mounting in the workshop has been accurately carried out.

In the Hilger rotating sector spectrograph the principle is similar to that in the Judd Lewis spectro- graph/

spectrograph in that light from a single source is divided into two beams, one of which passes through the absorbing solution, and the other passes through the pure solvent and is then cut down by a known amount by mechanical means. The two beams eventually produce a pair of spectrum photographs in close juxtaposition, one of which is of reduced density throughout its whole length, the other - that which has passed through the material under test - being more dense than the first in certain parts and less so in others, there being certain wave-lengths where the two densities are equal. In this case the light is cut down in the comparison beam by means of a rotating sector the aperture of which can be varied. The beam passing through the absorbing solution also passes through a rotating sector of fixed opening. This is necessary so that both beams falling on the plate may be of an intermittent nature.

In both the Judd Lewis and Hilger Spectrographs the length of absorbing liquid is varied by using cells of different lengths.

Schwarzschild (19) found that when the product of intensity of illumination into time of exposure (It) is constant the density or blackening of a photographic plate was not necessarily constant. His experience is summarised in the equation

$$\frac{I_1}{I_2} = \left(\frac{t_1}{t_2}\right)^n \qquad \text{(where } n \text{ is a constant.)}$$

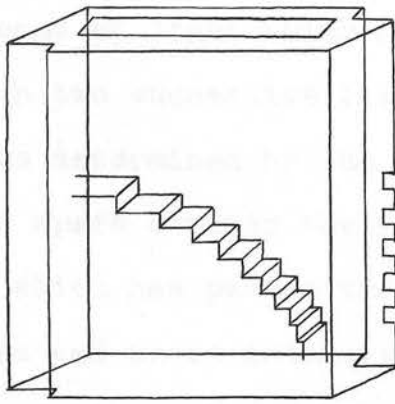for constant density of the finished photographic
plate.

The significance of this Schwarzschild constant
is obvious in all measurements of extinction coefficients
by photographic methods, especially when a rotating
sector is employed.

Howe and Gibson (20) stated that "within the
limits of experimental error, and under the conditions
obtaining in the use of the Hilger sector photometer,
the index n may be taken as unity". This statement
was later confirmed by Gibson, McNicholas, Tyndall,
Frehafer and Matthewson (21). The same conclusion
was reached by Scheibe, May and Fischer (22).
Baly, Morton, and Riding, (23) in a survey of the
various methods of measuring the extinction coefficient
of a substance come to the conclusion that "the sector
photometer and the Judd Lewis sector spectrophotometer
are both reliable instruments, and they give concordant
results within a range of experimental error rarely
if ever exceeding $\pm$ 2%".

The latest device, an echelon cell, to study the
absorption spectrum of a liquid was described by
F. Twyman in a paper read before the Physical Society
on 21st October 1932. Fig. 3. The ten steps in the
echelon determine the thickness of the layer of the
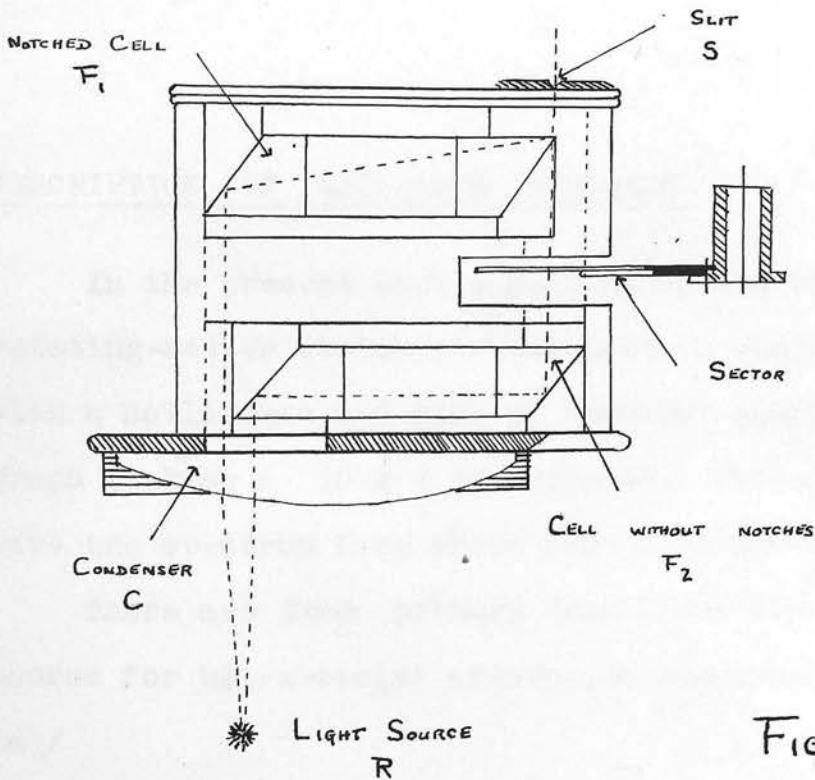liquid to be examined. There are five notches along
the/

the edge of the reflecting the slit. Part of which is reflected onto the end of the steps reaches the beaker [illegible] through the mirror [illegible]. The light which can also be deviated by [illegible]. Through [illegible] in the figure [illegible] so that only the light which has passed through a given thickness of [illegible] by a rotating sectors. The whole arrangement is shown in Fig. [illegible]. In order to [illegible] bright the whole cell shown in front of [illegible] and the steps seen in Fig. 3. [illegible] solution and the [illegible] to reduce [illegible] grouped in one expansion. Its [illegible] from [illegible]. (1) No solution should not [illegible] by ultraviolet [illegible] and (2) [illegible] and [illegible] convenient range of dispersion.

NOTCHED CELL   CELL WITHOUT NOTCHES

FIG. 3.

FIG. 4.

the edge of the cell against the slit, from each of
which is reflected onto the slit of the spectrograph
two beams of light which have passed respectively
through two successive layers of liquid whose thicknes-
ses are determined by the echelon.   Through the ad-
jacent space between the notches passes a beam of
light which has passed through a control cell without
notches and whose intensity is reduced by known amount
by a rotating sector. The whole arrangement is shown
in Fig. 4.   The echelon being only 2 cm. in total
height the whole cell stands in front of the slit,
and the whole twenty bands (i.e. ten through the
echelon and ten through the control cell.) are photo-
graphed in one exposure. Its special value is two-
fold: (1) in studying liquids subject to rapid change
by ultra-violet radiation, and (2) as a speedy and
convenient means of experiment.

2. DESCRIPTION OF APPARATUS EMPLOYED.

In the present work a Bellingham and Stanley
rotating-sector photometer was used in conjunction
with a Bellingham and Stanley "medium" quartz spectro-
graph (taking a 10 x 4 inch plate). This combination
gave the spectrum from about 180 $m\mu$ to the red.

There are four primary conditions for a light
source for ultra-violet absorption spectrophotography.

(a)/

(a) The source should be as free from fluctuations as possible, (b) it should have a high intrinsic brightness, (c) it should yield a spectrum as nearly continuous as possible, (d) it should be a point source. In the present case an iron spark 2-3 mm. in length was used in series with a second spark gap and in parallel with a condenser of about 0.025 microfarad. capacity. The spark was worked by a transformer on the 230 volt A.C. supply, giving about 6000 volts across the secondary. As the cells of the photometer were mounted on convergent axes, the spark had to be at the intersection of these; a latitude in its position of a few mm. each way was allowable. When the spark was in the correct position, the fact that the two cells had identical "entrance pupils" determined that two exactly equal beams should be produced. The electrodes had one end sharpened to a wedge and this edge was placed so as to be colinear with the optical axis of the spectrophotometer. Then any wandering of the discharge will only take place along this axis and will have no ill effect upon the results.

The photometer had two sectors, one with fixed and one with variable opening; the latter read directly in terms of $\log \frac{I_0}{I}$, giving values of this quantity from 0 to 2. A range of cell sizes of 0.1 to 4.0 cm. was available - cells with screw-on quartz ends for 1.0, 2.0 and 4.0 cm., and glass distance-pieces with/

with quartz end-plates for 0.1, 0.2 and 0.4 cm. These thicknesses in the latter case were not quite accurate, but measurement with a micrometer enabled a corrected value of $\log d$ to be fixed. It was found not advisable to use values of $\log \frac{I_o}{I}$ less than about 0.30 as then the two spectra of the pair were of such nearly equal intensity in the region of no absorption, that it was very difficult to fix the point of equal blackening. The exposures did not, of course, need to be timed accurately. Before each set of exposures, an approximate calculation showed the correct value of d to use with the concentration in question. Each sector-opening corresponds to a certain value of $\log Kcd$ according to the relation

$$\log \frac{I_o}{I} = Kcd \quad \therefore \quad \log K = \log(\log \frac{I_o}{I}) - \log c - \log d .$$

Hence a table was drawn up, giving the values of $\log Kcd$ for each sector-opening and also $\log Kc$ for each combination of opening and size of cell. Hence $\log K$ by the above equation. The sector-openings used were chosen so as to give values of $\log K$ differing by about 0.1.

Ilford "Thin-film Half-tone" plates were used for wave-lengths less than 400 $m\mu$ and were very satisfactory on account of their high contrast; but as they were most insensitive to longer wave-lengths, "Zenith Super-Sensitive" (650 H & D) plates were used for this region. The finished plates were examined/

examined with a magnifying glass in order to determine
the points of equal blackening for each pair of spectra.
The wave-lengths were fixed by comparison with an en-
larged photograph of the iron spark spectrum with the
wave-lengths of the lines marked.   Each plate was
examined twice at least, with an interval of time in
between, and it was also found advantageous to re-
verse the plate between examinations; when this led
to two different points being chosen, a mean position
was taken.

3. PREPARATION   OF   MATERIALS.

Sn I_4 .   This was prepared by the method of
McDermott.   12 grammes tin ("British Chemical Stan-
dard" 99.98% pure granulated) and 50 grammes A.R.
iodine were refluxed in 75 grammes carbon tetrachloride
(free of chlorine, HCl and sulphur) until the violet
colour of the iodine vapour was gone. The stannic
iodide was filtered off when cool and twice recrystal-
lised from carbon tetrachloride. Melting point 142.5°
C. (uncorrected).

Sn Br_4 . Prepared by the method of Lorenz (25).
Tin was placed in a distilling flask, closed at the
top with a cork fitted with a separating funnel drawn
out/

out to a capillary point; the funnel was filled with
bromine, which was added to the tin so slowly that the
temperature remained at 35 - 59° and the side-tube did
not become filled with bromine vapour.   When the
greater portion of the tin had disappeared the con-
tents of the flask were distilled; the first few drops
contained bromine but that which subsequently passed
over was pure stannic bromide. Boiling Point   =
200°C. (uncorrected).

   Sn Br$_2$.   By the method of Butler and Hamilton for
the preparation of zinc chloride. (26)

      Pure dry tin (30 gms.) was placed in a flask with
sodium-dried redistilled ether (100 cc.).
Pure dry H Br (Erdmann "Anleitung zur Darstellung
chemische Praparate" prepared by dropping redistilled
bromine onto pure sodium-dried benzene) was passed
into the flask until the tin had completely dissolved.
The clear liquid separated into two layers.   The flask
was warmed on a water bath and ether and excess H Br
distilled in vacuo, further heating in vacuo yielded
the pure product.

   Sn Cl$_4$.   The product supplied by Hopkin and
Williams was purified by redistillation over tin in
an all glass distilling apparatus.

   C$_2$I$_2$.   By the method of Dehn (27) (J.A.C.S. 33.
1598) Acetylene was passed into a solution of KI   in
water, into which was dropped a solution of Na OCl
(prepared/

(prepared by passing Cl_2 into an aqueous solution of NaOH) until all the KI was used up, i.e. until the KI lost its power of giving a brown colouration with NaOCl. The C_2I_2 formed as a white flocculent precipitate, this was filtered off, washed thoroughly with water, dissolved in low boiling ligroin, dried over $CaCl_2$ and decanted off and allowed to crystalise. Very fine white crystals with a melting point of 80°C. were obtained.

C_2I_4 . By the method of Datta and Prosad (28) Nitrogen iodide was first obtained as a black precipitate by adding strong ammonia to a KI solution of iodine. It was washed thoroughly with water by decantation, placed under water, and acetylene slowly passed in with shaking from time to time. At first the greenish yellow supernatant liquid began to decolourise, on shaking the colour reappeared due to the dissolution of some nitrogen iodide which was again decolourised in a similar way. The reaction became more rapid as the reaction proceeded. Crystals began to appear which gradually increased until the whole of the nitrogen iodide was converted into a mass of dirty white fine crystals which on the further action of the gas turned orange-yellow. The substance was recrystallised from ether, when small light yellow needle-shaped crystals with a melting point of 185°C were obtained.

CHI/

CHI = CHI. By the method of Biltz (29)

Acetylene was passed slowly into a flask containing 100 gms. finely ground iodine, covered with 200 gms. EtOH for five days. The acetylene was slowly absorbed, and white needle-like crystals formed. The contents of the flask were poured into water, the excess iodine removed with NaOH , the crystals filtered off, washed and recrystallised twice from EtOH. White needles with a melting point of $73^{\circ}C$ were obtained.

$\underline{CH_2I - CH_2I}$. By the method of Semenow (30)

A paste of iodine in EtOH was saturated with ethylene with constant shaking and with repeated addition of iodine. The iodine solution was decanted from the crystalline mass formed; the latter was washed with cold EtOH and purified (31) by two recrystallisations from ether, free iodine being removed by shaking up the ethereal solution with a solution of NaOH. Melting point $81 - 82^{\circ}C$. It was found that if left exposed to the atmosphere the crystals slowly gave off iodine, but this decomposition was prevented if the substance was kept in an atmosphere of ethylene.

$\underline{CH_2I_2}$. By the method of Auger (32) 1 gm.-mol. weight of CHI_3 was mixed with an excess of trisodium-arsenite (obtained by dissolving 1 gm. mol. weight of As_2O_3 in 6 gm.-mol. weights of a 33% caustic soda solution/

solution) and the mixture steam-distilled. The CH_2I_2 formed as a straw-coloured oily liquid and was purified by a vacuum distillation. The CH_2I_2 decomposed readily with the formation of free iodine. Such decompositions are known to be catalysed by free iodine and it was found that in the presence of a little mercury the CH_2I_2 was quite stable.

Hexane. The "specially purified for spectroscopy" product of the B.D.H. was used.

Carbon Tetrachloride. The ordinary sulphur-free A.R. tetrachloride was found to be sufficiently transparent not to require further purification.

Ethyl Acetate. The A.R. product in this case also needed no further purification.

Ethyl Alcohol. A very large number of different methods for purifying this substance have been given. As it was desired here to obtain a product with the greatest transparency in the ultra-violet, the method of Castille and Henri (33) which was specially designed to give a product suitable in this respect, seemed to be the most promising. After some experiment the following modification of the above method was adopted. Ordinary absolute alcohol was refluxed for 3 - 4 hours with 2 gms. iodine per litre. 30 - 35 gms. calcium (to remove the iodine and water simultaneously) were then added, and the refluxing continued for a day. The alcohol was then distilled off/

off, while a current of air dried by passage through
a 5 foot tube filled with $CaCl_2$ was passed through
it in order to remove any traces of ammonia. The first
product was rejected, in case it contained ammonia,
and the distillation was stopped when about two-thirds
had come over. The alcohol so obtained showed the
following transmission:-

In a 4 cm. layer to 230 mμ

In a 1 mm. " " 215 mμ

(Exposure: just sufficient to record to about 208 mμ
in air). The spectrum down to the limit of trans-
mission of the apparatus could easily be photographed
through the alcohol using increased exposures

Methyl Alcohol.

"Absolute" $MeOH$ ($\frac{1}{2}$ - 1% H_2O) reacts actively
with magnesium (10 gms. / litre) and is quite de-
hydrated. The reaction proceeds of itself and the
$MeOH$ boils. When the Mg has disappeared, the $MeOH$
is refluxed gently for several hours and then dis-
tilled in a stream of dry air, the first portion of
the distillate being rejected. (34)

Acetonitrile. A.R. acetonitrile was dehydrated over
phosphorus pentoxide for several days and redistilled
(35).

The solutions were prepared by dissolving a
weighed amount of the substance in the solvent, with
subsequent/

subsequent dilution of necessary.   The concentra-
tions used in calculating log K were simply based on
the weight of substance dissolved.

III. EXPERIMENTAL.

1. STANNIC HALIDES.

Previous workers (60) had found that a solution of stannic iodide in ethyl alcohol gave an absorption curve very similar to that of a solution of iodine in ethyl alcohol. This seemed to support Scheibe's view that absorptions of this type are determined only by the halogen atom present (36). It was the original aim of this research to find out if this similarity held for other solvents.

For solvents such as hexane, which have very small dipoles, the deformation of the electron system of the dissolved molecule is very slight, so that the absorption of a substance dissolved in hexane may be taken as closely approximating to that of the non-deformed unsolvated molecule. For this reason hexane was the first solvent used in this research.

A solution of iodine in hexane is purple and has an absorption curve similar to that of iodine vapour (Graph 1, curve 1).   Stannic iodide in hexane gives a yellow solution with an absorption curve similar to that of iodine in ethyl alcohol (Graph 1, curve 2), but it was found that this solution did not obey Beer's Law, and on standing the colour slowly changed to brown and later to purple, and a white deposit formed. This solid was filtered off, washed thoroughly with/

with hexane, and on examination was found to contain tin but no iodine. This pointed to the stannic iodide having decomposed with the formation of free iodine; to test this the purple solution was shaken up with finely divided metallic silver, the solution became colourless and a yellow deposit (which proved to be silver iodide) formed on the surface of the silver.

Means were than sought by which to prevent the decomposition of the stannic iodide, and it was found that if allowed to stand over finely-divided metallic tin the solution did not darken on standing although a white deposit gradually formed. This solution gave an absorption curve (Graph 2, curve 4) which obeyed Beer's Law within the limits used.

A solution of iodine in hexane was then shaken up with finely-divided tin, and it was observed that the colour gradually changed from violet through brown to pale yellow; the final solution gave the same curve as that of stannic iodide in hexane over tin (Graph 2, curve 4) if in calculating the concentration of iodine the molecule is taken as I_4, and obeyed Beer's Law. Tin and iodine combine directly with the formation of stannic iodide, so this curve may be taken as the true curve for stannic iodide in hexane.

It seemed probable that the observed similarity between the curves for stannic iodide and iodine in ethyl/

ethyl alcohol was due to the slow decomposition of the
stannic iodide with the liberation of free iodine, so
a solution of stannic iodide in ethyl alcohol was made
up and allowed to stand over metallic tin. This solu-
tion was pale yellow and gave a curve (Graph 2, curve
3) quite different from that of iodine in ethyl alcohol
(Graph 1, curve 1) and obeyed Beer's Law. Stannic
iodide in ethyl alcohol with no metallic tin present
had an absorption curve which changed on standing
(Graph 2, curves 1 and 2). Ethyl alcohol was allowed
to stand over tin for a month but no absorption was
observed. A solution of iodine in ethyl alcohol was
shaken up with metallic tin and the colour gradually
changed from dark brown to pale yellow; the resulting
solution gave the same curve as that of stannic iodide
in ethyl alcohol if in calculating the concentration
of iodine the molecule is taken as I_4 (Graph 2, curve
3); this solution also obeyed Beer's Law. This
curve may be taken as the true curve for stannic iodide
in ethyl alcohol.

Similarly stannic iodide in methyl alcohol in
the presence of metallic tin gave a curve (Graph 2,
curve 5) quite different from that of iodine in methyl
alcohol without tin (Graph 1, curve 3), but the same
as that for iodine in methyl alcohol over tin.

A solution of stannic iodide in acetonitrile over
tin/

tin decomposed too rapidly under the action of the
ultra-violet light for any curve to be obtained.

As the curves for stannic iodide in ethyl alcohol
and in hexane are so different a series of solutions
of stannic iodide in hexane containing varying amounts
of ethyl alcohol over metallic tin was examined in an
attempt to trace the transition from one curve to the
other.   With small amounts of ethyl alcohol (.0318
and .09 molar) the curve differed very little from
that of stannic iodide in hexane over tin (Graph 3,
curves 1 and 2).   But with increasing amount of
alcohol (Graph 3, curves 3-6) the short-wave maximum
rose and shifted towards the red, while the long-wave
maximum fell and shifted towards the ultra-violet, the
curve gradually flattening out until at length both
maxima practically disappeared. All the curves passed
through the same point (within the limits of experi-
mental error) at about λ = 343 mμ and log K = 3.66.

A solution of stannic bromide in hexane (which
is colourless) was examined and it was found that, even
in the presence of metallic tin, the absorption altered
with time (Graph 4, curves 1-3).   The maximum wave-
length did not change but log K_{max} gradually decreased.

The absorption of stannic bromide in methyl alco-
hol over tin also changed with time (Graph 5, curves
1, 2, 4).   Both in the case of hexane and methyl
alcohol/

alcohol a white deposit formed when the solution was allowed to stand, but the solution itself remained colourless. Stannous bromide in methyl alcohol has a curve (Graph 5, curve 3.) similar to that of stannic bromide in methyl alcohol but further towards the ultra-violet. Stannous bromide is insoluble in hexane.

In order to complete the series a solution of stannic chloride in hexane was examined. As with even a trace of moisture stannic chloride reacts rapidly to form stannic hydroxide, the following method was used:- Some stannic chloride was distilled into some hexane in an all glass distilling apparatus, the cloudy solution so obtained was filtered and the filtrate analysed for stannic tin (37); in the analysis a known volume of the hexane solution was added to 250 cc. of water containing the equivalent of 50 cc. of concentrated hydrochloric acid, and the solution boiled for some time to drive off the hexane. The solution was then reduced by heating with lead shot (38) in an atmosphere of carbon dioxide, when the solution has cooled it was titrated with standard iodine using starch as indicator. Two concordant results were obtained. This standard solution of stannic chloride was then diluted to the correct con-centrations as required. As the absorption was well over into the ultra-violet a copper spark was used as the source of ultra-violet light, and the plates used were/

were "Zenith Super-Sensitive" (650 H & D) sensitised with oil, and long exposures were given. Hexane was the only solvent possible because stannic chloride was found to react rapidly with the others (Graph 4. curve 4.).

It was intended to have measured the absorption spectrum of stannic iodide in acetonitrile (this was later found to be impossible owing to the instability of the solution) and as a preliminary, a solution of iodine in acetonitrile was examined. The absorption of this solution changed with time, and a series of curves were obtained (Graph 6). Similar results were obtained by Ley and Engelhardt (39) for iodine in ethyl alcohol.

All the tin solutions were kept under a blackened bell-jar as they tended to decompose if exposed to bright sunlight; for the same reason, as short ex- posures as possible were used and the solution in the cell was changed before each exposure.

2. CARBON - IODINE COMPOUNDS.

Previous Work.

Crymble, Stewart and Wright (31) meas- ured the absorption spectra of $C_2H_2I_2$ and CH_2I_2 in ethyl alcohol, and from these results in conjunction with/

with results from similar work with CHI_3 , KI_3 , C_2H_5I and I_2 put forward a theory to account for the absorption (This theory is discussed later in this essay).

Macbeth and Stewart (40) examined the absorption of C_2I_2 , $C_2H_2I_2$ and $C_2H_4I_2$ and put forward an explanation of their results on the basis of the change produced in the absorptive power of the iodine atoms by the introduction of double and triple bonds into the $C_2H_4I_2$ molecule.

Massol and Faucon (41) studied the absorption of CH_2I_2 in the course of a work undertaken with a view to correlating the absorption of the iodine derivatives of methane with that of iodine.

None of these authors measured the absorption coefficients of the substances and their work was not of a strictly quantitative nature. In view of the small amount of work which has been done on these com-pounds it was thought that a systematic study of the absorption curves of the series C_2I_2 C_2I_4 $C_2H_2I_2$ $C_2H_4I_2$ and CH_2I_2 in various solvents might yield interesting results.

48

PRELIMINARY EXPERIMENTS.

The white crystals of C_2I_2 were found to be easily soluble in hexane, ethyl alcohol, methyl alcohol and acetonitrile, but it was observed that the solution became coloured (hexane solution became violet, and the others brown) if they were left exposed to bright sunlight or ultra-violet light. It was thought that perhaps it was only the far ultra-violet light that was causing the decomposition, so various filters were tried. It was finally found that a thin sheet of vita-glass (transmitting to $\lambda = 275$ mμ for a 5 secs. exposure) placed between the source of ultra-violet light and the solution prevented the decomposition of the latter; the same was found to hold good for all the other iodine compounds of carbon studied, so it was decided to use this filter during the measurement of their absorptions; this was found to be quite satisfactory and gave reproduceable results.

TABLE./

SOLUTIONS MEASURED.

| No. | Solute | Solvent | Conc. in Mols. per litre | | Graph. | Curve. |
			I.	II.		
1.	C_2I_2	Hexane	.000642	.00642	8	1.
2.		CCl_4	.00641	.0320	8	2.
3.		Ethyl acetate	.00642	.0321	8	3.
4.		EtOH	.00642	.0321	8	4.
5.		MeOH	.00642	.0321	8	4.
6.		CH_3CN	.00642	.0321	8	4.
7.	C_2I_4	Hexane	.000642	.000321	7	1.
8.		CCl_4	.001002	.000334	7	2.
9.		Ethyl acetate	.001062	.000334	7	3.
10.		EtOH	.000668	.000334	7	4.
11.		MeOH	.001068	.000356	7	4.
12.		CH_3CN	.000975	.000670	7	5.
13.	$C_2H_2I_2$	Hexane	.001670	.00835	9	1.
14.		CCl_4	.001674	.00837	9	2.
15.		Ethyl acetate	.001697	.008486	9	3.
16.		EtOH	.001670	.00835	9	3.
17.		MeOH	.001677	.008387	9	3.
18.		CH CN	.001683	.008414	9	4.

50

SOLUTIONS MEASURED. (Contd.)

No.	Solute	Solvent	Conc. in Mols. per Litre		Graph.	Curve.
			I.	II.		
19.	$C_2H_4I_2$	Hexane	.008301	.001660	10	1.
20.		CCl_4	.008171	.001634	10	2.
21.		Ethyl acetate	.008171	.001634	10	1.
22.		EtOH	.008130	.001626	10	1.
23.		MeOH	.008215	.001643	10	3.
24.		CH_3CN	.008228	.001645	10	4.
25.	CH_2I_2	Hexane	.005546	.001109	11	1.
26.		CCl_4	.005224	.001045	11	1.
27.		Ethyl acetate	.004286	.001200	11	2.
28.		EtOH	.005952	.001190	11	2.
29.		MeOH	.005662	.001132	11	2.
30.		CH_3CN	.004349	.001230	11	3.

In the case of CH_2I_2 a small amount of mercury was
placed in the cells during the exposures as this was
found to act as a negative catalyst in the decompos-
ition of CH_2I_2 .

DESCRIPTION OF CURVES.

C_2I_4.

C_2I_4 in hexane has an absorption curve with two maxima (1) at $\lambda = 332$ mμ and (2) at $\lambda =$ approximately 290 mμ. There is a shallow minimum between these two maxima. The curve then rises steeply into the ultra-violet.

The values for log K at the two maxima are (1) 2.94 and (2) 3.08.

The curve changes with change in solvent, and with increasing polarity of solvent the two maxima appear to move together, until with ethyl alcohol only one appears, and with acetonitrile there is no definite maximum at all.

C_2I_2.

The solution in hexane has a curve rising fairly steeply to about $\lambda = 334$ mμ (log K = 1.75) where the curve flattens out until about $\lambda = 304$ mμ (log K = 2.0) and then rises steeply to log K = 2.64 where the first part of a maximum is obtained at $\lambda = 273$ mμ. The whole of the maximum could not be measured because it was beyond the region of transmission of the vita-glass.

The solution in CCl$_4$ gave the same curve as that in hexane except at the flattened-out part of the curve where a shift towards the red is observed.

The/

The curve for ethyl acetate is further to the ultra-violet than that for hexane and the region of inflexion is less apparent; Ethyl alcohol, methyl alcohol and acetonitrile all give the same curve which is further to the ultra-violet than the ethyl acetate curve and the region of inflexion is still less pronounced.

$C_2H_2I_2$.

All the curves (except that for CH_3CN) just consist of a branch rising fairly steeply towards the ultra-violet.   In the case of hexane there is a change in direction at $\lambda = 307$ mμ (log $K = 2.1$) this is not apparent in the polar solvents, but appears in CCl_4 at $\lambda = 305$ mμ (log $K = 2.15$).

The curve for CH_3CN flattens out from $\lambda = 330$ mμ (log $K = 1.27$) to $\lambda = 370$ mμ (log $K = 1.1$) and then falls off into the visible.

The curves for EtOH MeOH and ethyl acetate are coincident and further to the ultra-violet than the curve for hexane.

The curve for CCl_4 shows a shift towards the red compared with hexane.

$C_2H_4I_2$.

There are only four distinct curves for this the substance, the curves for ethyl acetate, EtOH and hexane being coincident. They each consist of

a/

a single branch rising steeply towards the ultra-violet.

CCl_4 shows a shift towards the red compared with the position for hexane, while the curves for MeOH and CH_3CN are further towards the ultra-violet (again compared with hexane) the shift for CH_3CN being greater than that for MeOH.

CH_2I_2.

The curve in hexane rises steeply to a maximum at $\lambda = 297$ mμ (log K = 3.14) and then falls away again towards the ultra-violet. The curve for CCl_4 is coincident with that for hexane.

The curves for ethyl acetate, EtOH and MeOH are coincident (MeOH diverges on the lower part of the long-wave branch) and show a maximum at $\lambda = 293$ mμ (log K = 3.11)

The Acetonitrile curve is still further to the ultra-violet $\lambda_{max} = 291$ mμ (log K = 3.04)

Beer's Law was found to hold for all the solutions of all the curves measured.

IV. DISCUSSION.

1. INTRODUCTION.

Lowry and Sass (42) hold that the absorption due to the bond C - X where X is a halogen atom might be shifted towards the red as a result of the weakening of the C - X bond under the influence of contiguous negative atoms. In order to obtain experimental proof of this theory they examined the series of compounds CH_3I CH_2I_2 CHI_3 CI_4 . The last of the series was found to be too unstable to examine.

They showed that the absorption shifts towards the red in passing from CH_3I to CH_2I_2 to $CH I_3$ at which point two maxima appear.   They state from the general form and position of the curves that they are dealing with the same band throughout, and that although the second and third iodine atoms may re-inforce and develop the band they are not needed to initiate it.

Massol and Faucon (41) had studied the same series and compared the absorption spectra in ethyl alcohol with that of iodine in the same solvent and in the case of CHI_3 observed two bands which they said corres-ponded to two of the iodine bands. They had hoped to find a correspondence between the bands of all the compounds/

compounds and one or other of the iodine bands but
this was found to be impossible with CH_2I_2 and CH_3I.
CI_4 gave an absorption very similar to that of iodine,
but we now see that this was probably due to the de-
composition of CI_4 with the formation of free iodine.

Crymble Stewart and Wright (31) attribute the
methylene iodide band to the juxtaposition of two
atoms of iodine in the same molecule, i.e. they sug-
gest that $I - \overset{|}{C} - I$ gives the same band as $I - I$
but that $I - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - I$ behaves like $- \overset{\backslash}{\underset{/}{C}} - I$.

Lowry and Sass (42) show that there is a great
similarity between the curves for CHI_3 and for KI_3
(i.e. iodine in a solution of potassium iodide
(Fig. 5.), but find that this is not accounted for
by the formulae commonly assigned to these compounds,
and state that it appears to be beyond the scope of
our present theories of valency. They tentatively
put forward the suggestion that it may be due to the
presence of three contiguous atoms of iodine in the
space models of the two compounds; they picture both
molecules as dominated by a cluster or ring of three
contiguous iodine atoms, just as (according to W.L.
Bragg's determination) the crystal structures of most
of the oxysalts and of many of the metallic oxides are
dominated by clusters of contiguous oxygen atoms,
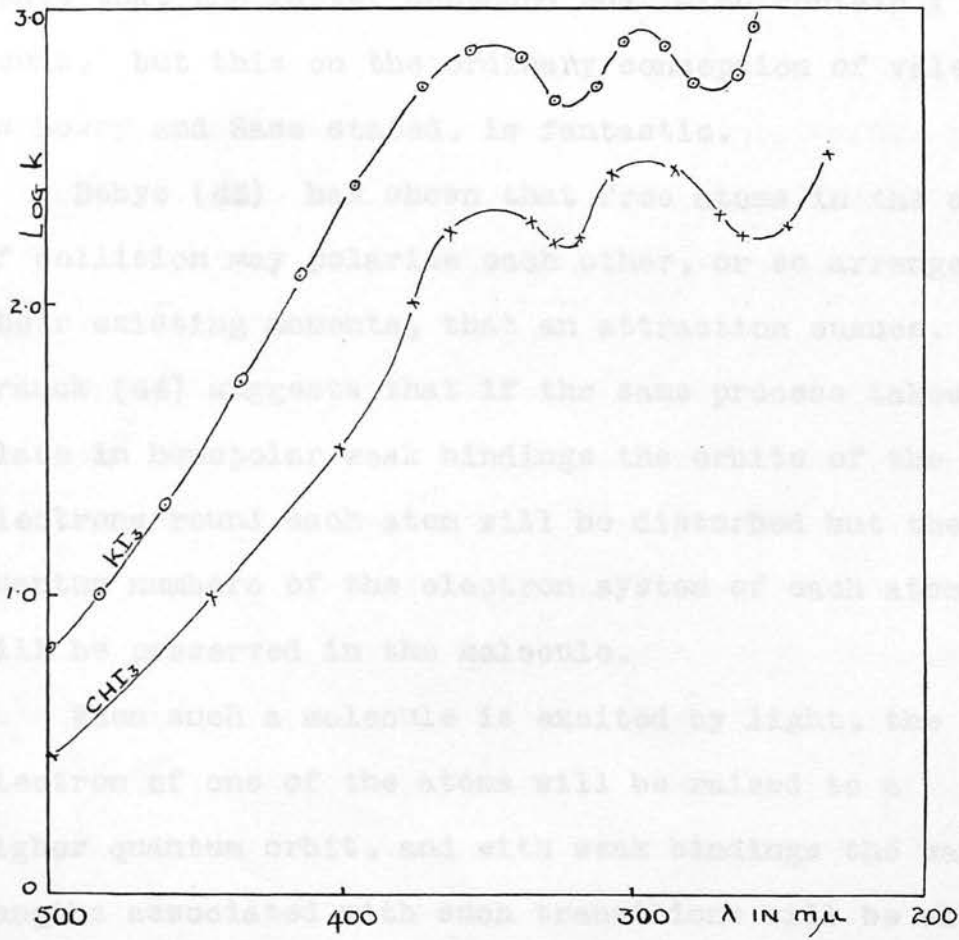leaving the co-ordinating atom to occupy a mere cavity
between/

Fig. 5.

between the oxygens. The colour of KI_3 is always attributed to the negative ion I_3^- which (like iodine itself) can only contain I - I bonds, so that the similarity in the spectra of KI_3 and CHI_3 suggests that the latter compound must also contain I - I bonds, but this on the ordinary conception of valency, as Lowry and Sass stated, is fantastic.

Debye (43) has shown that free atoms in the act of collision may polarise each other, or so arrange their existing moments, that an attraction ensues. Franck (44) suggests that if the same process takes place in homopolar weak bindings the orbits of the electrons round each atom will be disturbed but the quantum numbers of the electron system of each atom will be preserved in the molecule.

When such a molecule is excited by light, the electron of one of the atoms will be raised to a higher quantum orbit, and with weak bindings the wavelengths associated with such transitions will be almost identical with those absorbed by the free atoms.

The work of Mecke (45) on the absorption spectrum of gaseous iodine has shown the I - I binding to be of this type. So that the absorption spectrum of iodine is that of two iodine atoms held together by attractive forces but each retaining their own electronic orbits although in a deformed state.

In/

In the case of solutions of iodine Getman (46)
(J.A.C.S. 50 2883) who measured the absorption co-
efficients of iodine through the visible spectrum in
a series of carefully purified solvents showed that
the solutions may be divided into two distinct groups
as follows:-

(a) solns. in n-hexane, benzene, toluene, carbon di-
sulphide, carbon tetrachloride, and chloroform which
are violet with   absorption maxima ranging from
520 mμ to   540 mμ .

(b) Solutions in ethyl alcohol, isopropyl alcohol,
acetone, acetophenone, and pyridine which are brown
with absorption maxima ranging from 460 mμ to 480 mμ .
The first group of solvents he calls "saturated com-
pounds" while the second group "unsaturated compounds".
He finds that the maximum intensity of absorption is
found with the "saturated" solvents and is practically
constant throughout the group, while in the second
group of "unsaturated" solvents the intensity of
absorption varies appreciably from solvent to solvent
and is in every case less than with "saturated" sol-
vents. Also the solutions tend to undergo a change,
with corresponding change in absorption, on standing.
Getman concludes that "the colour and stability of
iodine solutions on exposure to ultra-violet radiation
appear to be more or less dependent upon the degree
of/

of "saturation" of the solvent."   It is not very clear what Getman implies by an "unsaturated" solvent.

Ley and Engelhardt (47) after studying the change in the absorption of solutions of iodine with time, adopt the view of Beckmann that in the brown solution there is an equilibrium between the iodine and a solvation product.

$$I_2 + mS = (I_2 S_m)$$
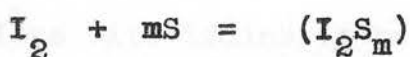
This view is supported by Waentig   whose work proves a connection between the shift in the absorption and the heat of solution.

de Boer and Custers (48) measured the absorption of iodine adsorbed on calcium fluoride at different degrees of saturation of the surface. They found that at small degrees of saturation the absorption curve shows two decided maxima at 283 mμ and 342 mμ ; if more molecules are adsorbed the curve becomes less definite and the maxima (especially the long-wave one) are shifted towards the visible.   They observe that there is a marked similarity between the spectrum for KI$_3$ and the spectrum of adsorbed iodine on calcium fluoride.

In discussing their results de Boer and Custers employ the formula

$$h\nu = \Delta E + Q_A - Q_A'$$

where ν is the frequency of the light absorbed, ΔE the energy difference of the excited and unexcited molecule/

molecule A' in the free gaseous state, Q_A is the
energy of binding in the unexcited state, and $Q'_{A'}$
is the energy of binding in the excited state.
So they state that the position of the absorption will
depend on $(Q_A - Q'_{A'})$ and this quantity will vary
with the state of the iodine.

But in the case of the solvents which give brown
solutions with iodine it has been shown that compound
formation occurs between the solute and solvent, (the
compound with pyridine has been actually isolated) so
that the energy of binding of the solvate should also
be taken into account i.e.

$$h\nu = \Delta E + Q_A - Q'_{A'} + S_A - S'_{A'}$$

where S_A and $S'_{A'}$ are the energies of solvation of
the excited and unexcited molecules. The fact that
the pyridine compound has been isolated shows that, in
some cases at any rate the S terms are of the same
order as the Q terms and therefore cannot be neglected.
The equation now contains so many variables that it is
impossible to predict from it the shift in absorption
with change in solvent.

Chatelet (49) states that the absorption curves
for brown solutions of iodine only seem compatible
with the hypothesis of the combination of iodine with
solvent.

Getman's two groups of solvents may therefore be
defined/

defined as follows:-(1) "saturated" solvents are those
which have little effect on the strength of binding
of the dissolved iodine molecule, i.e. in which Q_A
$Q'_{A'}$ in the above equation and S_A and $S'_{A'}$ are
negligible so that the absorption of the solution
approximates to that of free gaseous iodine; and
(2) "unsaturated" solvents which enter into a type of
combination with the iodine molecule and thus affect
the strength of the binding of the latter.

The iodine derivates of methane are all fairly
unstable and decompose under the action of light with
the formation of free iodine. This indicates that the
homopolar $-\overset{|}{\underset{|}{C}} - I$ binding is a weak one. Thus it
may be anticipated that it comes into the same cate-
gory as the I - I linkage in the iodine molecule,
i.e. consists of a carbon atom and an iodine atom held
together by attractive forces, each retaining its own
electronic orbits though in a deformed state.
If we consider the space formula of CHI_3 we see that
it consists of three iodine atoms held by attractive
forces to a - CH radical. The attraction between
the carbon and iodine atoms is
represented by the ordinary valency
bonds directed out from the carbon
at the centre of the tetrahedron to
the three iodine atoms at the vertices. But as these
iodine atoms are only held to the carbon by weak forces
and/
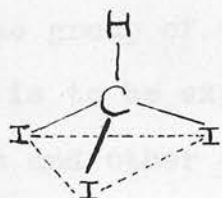
and each retains its own electronic orbits although
in a deformed state, it is probable that the iodine
atoms will exert similar attractive forces on each
other, i.e. the molecule will approximate to a ring
of three I - I bonds held by attractive forces to
a CH group. KI_3 is always considered to be made
up of a K^+ ion and an I_3^- ion, so this compound also
contains a group of three $\overset{iodine}{\wedge}$ atoms held by attractive
forces, so that this may help to explain the similarity
in the absorption spectra of the two compounds.

When we consider the space formula of carbon
tetraiodide we see that the molecule consists of a
carbon atom at the centre of a regular tetrahedron
with an iodine atom at each of the vertices, so that,
by reasoning similar to that employed in the case of
CHI_3 , we can imagine the C atom surrounded by a
shell of deformed I - I linkages;   thus the spec-
trum of carbon tetraiodide might approximate to the
spectrum of iodine.

Carbon tetraiodide is found to be too unstable
to be convenient to work with.   However, tin is in the
same group of the Periodic System as carbon, so that
it is to be expected that the type of linkage between
tin and other elements is similar to the type of link-
ages between carbon and the same elements.   On this
basis the Sn - I linkage may be considered as a weak
homopolar/

homopolar binding, this is supported by the fact that
stannic iodide decomposes fairly easily under the
action of light with the formation of free iodine.

2. STANNIC HALIDES.

(a) Stannic Iodide in Hexane.

Hexane is a practically non-polar sol-
vent, so that its molecules have little or no modify-
ing effect on the absorption of the molecules of sub-
stances dissolved in it. Hence the molecules of
stannic iodide are merely dissolved in the hexane and
not solvated (i.e. not associated with solvent mole-
cules) to any appreciable extent, and the absorption
curve in hexane is that for stannic iodide in the
normal unsolvated state.   This curve shows two maxima
(1) at λ = 365 mμ and (2) at λ = 285 mμ .
Thus the spectrum of stannic iodide very closely re-
sembles the spectrum of iodine in solvents with which
it gives a brown solution, i.e. with solvents in which
the iodine molecule is combined with solvent molecules.
This is an interesting analogy when we consider that
on the above theory the stannic iodide molecule is
pictured as a shell of deformed I - I linkages
held together by a tatravalent tin atom; while in
iodine in brown solutions, the I - I linkages will be
deformed by the solute - solvent forces.

(b)/

(b)   Stannic Iodide in Ethyl Alcohol.

In the case of the solution of stannic
iodide in ethyl alcohol, the condition of the stannic
iodide molecule is greatly altered by strong associa-
tion with the solvent, and now the association com-
plex is unable to absorb radiation at λ = 365 mμ
as no maximum appears at that wave-length on the
curve for stannic iodide in ethyl alcohol. The ability
to absorb radiation is a question of resonance, and
the natural frequencies of the association complex do
not respond to λ = 365 mμ .

Stannic Iodide in Methyl Alcohol.

This curve shows neither of the two max-
ima of the curve of stannic iodide in hexane. Methyl
alcohol is a more highly polar solvent than ethyl
alcohol, so that the degree of solvation of the dis-
solved stannic iodide molecules is even greater and
the distribution of the radiation absorbed by them
differs from that when ethyl alcohol is the solvent so
that a different absorption curve would be expected,
and the results obtained fulfil this expectation.

(c)   Stannic iodide in hexane and ethyl alcohol.

When increasing amounts of ethyl alcohol
are added to the hexane used as solvent, the dissolved
stannic iodide molecules gradually become solvated.
The curves all pass through one point so that an
equilibrium/

equilibrium exists between the two states of stannic
iodide (solvated and unsolvated) in the solution (51).
Only the unsolvated molecule absorbs to any great ex-
tent at λ = 365 mμ ;   on the addition of ethyl alco-
hol some of the stannic iodide molecules become sol-
vated, so that there are fewer in the state capable
of absorbing the radiation at λ = 365 mμ and the
value of log K at that point falls. The degree of
solvation can be calculated as follows:-

Let α = degree of solvation

"   c = total molar concentration of stannic iodide.

$\therefore$ conc. of solvated molecules = α c

"   "   unsolvated   "   =   (1 - α) c

Let K_m = measured absorption coefficient at λ = 365 mμ

" K_1 = absorption coefficient for unsolvated SnI_4

            at λ = 365 mμ

" K_2 = absorption coefficient for solvated SnI_4

            at λ = 365 mμ

(K_1 and K_2 are obtained from the curves for stannic
iodide in hexane and in ethyl alcohol respectively).

$$K_m c = K_2 \alpha c + K_1 c (1 - \alpha)$$
$$K_m = K_2 \alpha + K_1 (1 - \alpha)$$

This equation gives α for each concentration of ethyl
alcohol. If α is plotted against the concentration of
ethyl alcohol a smooth curve is obtained (Fig. 5A).

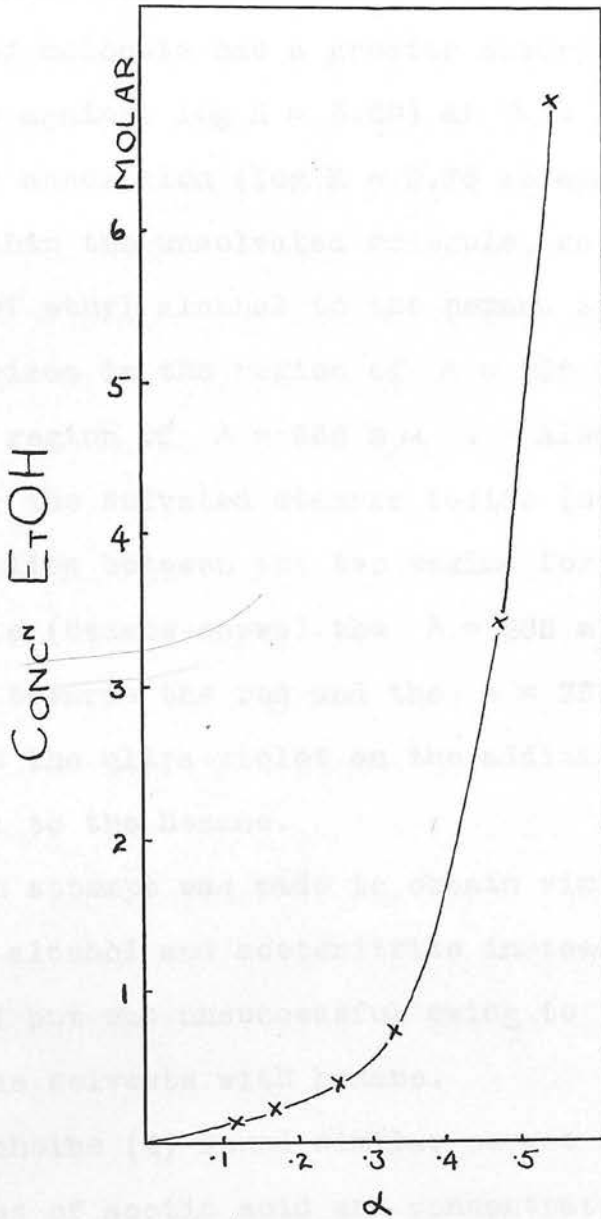The curve for stannic iodide in ethyl alcohol
and/

Fig. 5A.

and hexane is the resultant of the curves for stannic iodide in ethyl alcohol and in hexane; on increasing the amount of ethyl alcohol, more and more stannic iodide molecules become solvated and the ethyl alcohol curve gradually predominates. At λ = 285 mμ the solvated molecule has a greater absorption (log K = 3.67 as against log K = 3.60) at λ = 365 mμ a much smaller absorption (log K = 2.76 as against log K = 3.90) than the unsolvated molecule, so that on addition of ethyl alcohol to the hexane solution the curve rises in the region of λ = 285 mμ and falls in the region of λ = 365 mμ . Also as the maximum for the solvated stannic iodide (ethyl alcohol curve) lies between the two maxima for the unsolvated molecule (hexane curve) the λ = 285 mμ maximum shifts towards the red and the λ = 365 mμ maximum towards the ultra-violet on the addition of ethyl alcohol to the hexane.

An attempt was made to obtain similar series with methyl alcohol and acetonitrile instead of ethyl alcohol but was unsuccessful owing to the immiscibility of these solvents with hexane.

Scheibe (4) found similar curves for phoron in mixtures of acetic acid and concentrated sulphuric acid and explains his results by assuming that there are two states of phoron, one stable in concentrated sulphuric acid and the other in acetic acid.

(d)/

(d)   Stannic Bromide.

Stannic bromide can be pictured as having a molecule similarly constituted to that of SnI_4 but with the iodine atoms replaced by bromine atoms, so that the tin atom is surrounded by a shell of deformed Br - Br linkages, and the spectrum of stannic bromide might, on these grounds, be similar to that of bromine in one of Getman's "unsaturated" solvents.   Owing to the fact that the bromine atom is smaller than the iodine atom it will have a greater deforming effect on the electronic orbits of the tin orbit, so that the bond between the tin and bromine in $SnBr_4$ will be stronger than the bond between tin and iodine in SnI_4 ;   hence the absorption of Sn - Br bond will approximate less closely to that of a bromine atom in a deformed bromine molecule; therefore there will probably be less similarity between the curves for $Sn\ Br_4$ and Br_2 than between the curves for SnI_4 and I_2.   In practice it was found that $Sn\ Br_4$ in hexane gave a single maximum at $\lambda = 239\ m\mu$, while Bovis (50) for a solution of bromine in ethyl alcohol found a single maximum at $\lambda = 264\ m\mu$.   Thus there is found to be a certain similarity between the two curves, but it is less than in the case of iodine.

(e)/

(e)   Comparison of Behaviour of the Curves for Stannic
   Iodide and Stannic Bromide.

        Stannic iodide and stannic bromide being
very similar compounds it might have been expected that
their absorption curves would behave in a similar man-
ner under the same influence, but we see from the
above results that this is not the case. Solutions of
stannic iodide standing over metallic tin are stable
and obey Beer's Law, while if no tin is present the
solution gradually turns brown. On the other hand,
solutions of stannic bromide remain colourless but
their absorption changes with time whether metallic
tin is present or not. In the case of both halides a
white deposit forms slowly.

        The stannic halides are fairly readily hydrolysed
by water (52) and the following explanation of the
above observations is based on this fact.

        The solvent, however carefully dried, absorbs
moisture from the air whenever the stopper of the
flask is removed, and from the surfaces of the various
vessels used. These traces of moisture gradually
hydrolyse the stannic halide with the eventual forma-
tion of stannic hydroxide which appears as the white
deposit observed. Probably various oxyhalides are
formed as intermediate products during the hydrolysis,
but they in their turn are hydrolysed until finally
stannic/

stannic hydroxide is reached. The complete reaction may
be represented by the equation

$$SnX_4 + 4H_2O = Sn(OH)_4 + 4HX$$
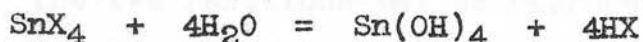
In the case of stannic iodide the hydrogen iodide
liberated is unstable (especially in sunlight) (53)
and readily forms free iodine which produces the brown
colouration of the solution; iodine, however, reacts
with metallic tin with the formation of stannic iodide,
so that, in the presence of tin, the iodine is taken
up as soon as it is formed, and the concentration of
stannic iodide in the solution remains constant, and
the equivalent of the tin that goes into solution as
stannic iodide is deposited as stannic hydroxide.

Hydrogen bromide, on the other hand, does not
readily decompose with the formation of free bromine
so the solution remains colourless, but hydrogen
bromide reacts with metallic tin to form stannous
bromide. Thus in solutions of stannic bromide the
concentration of stannic bromide gradually decreases,
and that of stannous bromide increases (in solvents
in which it is soluble) as the hydrolysis proceeds,
so that the maximum on the curve for stannic bromide
gradually falls. Stannous bromide is insoluble in
hexane but soluble in methyl alcohol so that with the
former solvent there is no shift of the maximum wave-
length, but with the latter solvent the curve gradually
moves/

moves towards that for stannous bromide, i.e. towards the ultra-violet.

The two reactions may be represented diagrammatically thus:-

$$SnI_4 \xrightarrow{\;H_2O\;} Sn(OH)_4 \;+\; HI$$

$$Sn$$

$$I_2$$

$$SnBr_4 \xrightarrow{\;H_2O\;} Sn(OH)_4 \;+\; HBr$$

$$Sn$$

$$SnBr_2$$
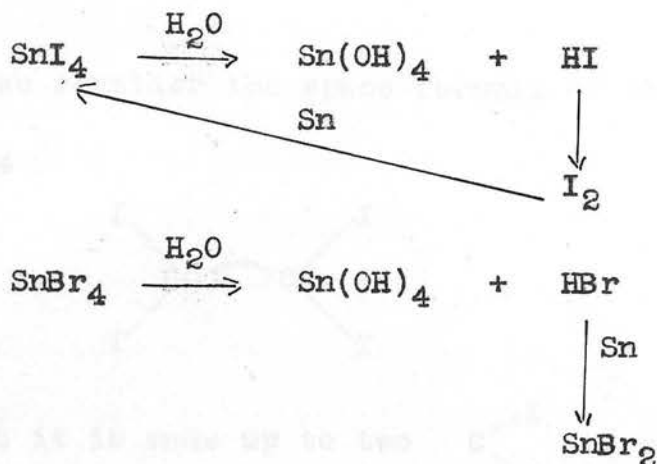
(f) <u>Stannic Chloride in Hexane.</u>

Such a small proportion this curve was measurable with the apparatus employed, that it is almost impossible to discuss its position except in relation to the curves for stannic iodide and stannic bromide, for on the theory that the absorption of the stannic halides is mainly due to the absorption of deformed halogen atoms it is interesting to note that the absorptions of the series Sn I_4 SnBr$_4$ and Sn Cl$_4$ changes in a manner similar to the change in absorption in the series I_2 Br$_2$ and Cl$_2$.

3./

3. SOME IODINE DERIVATIVES OF CARBON.

(a)   The effect of change in molecular structure.

C_2I_4.

When we consider the space formula of the com-
pound C_2I_4
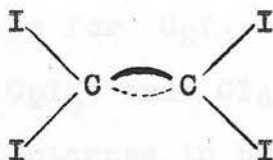
we see that it is made up to two $C{<}^I_I$ groups held
together by a double bond; so that it   consists of two
regular tetrahedra with one edge (and two vertices)
in common.   The other two vertices in each case are
occupied by iodine atoms.   On the Baeyer strain theory
there will be a change in the angle between the valen-
cies which join the carbon atoms, i.e. they will be
brought closer together than they are in such com-
pounds as CH_4.   But the angles between the valencies
joining the iodine atoms to the carbons will not be
appreciably altered from that in CI_4, so that the
distance between the iodine atoms approximates to that
between the iodine atoms in CI_4 or CHI_3 .

The resemblance of the CHI_3 and KI_3 spectra,
discussed earlier, led to the suggestion that the
C - I bond is a weak one, sufficiently so as to per-
mit/

permit us to consider the CHI_3 and KI_3 spectra as
arising from the iodine atoms in the I_3 group.
In C_2I_4 we have again weak $C - I$ bonds, and two
pairs of two adjacent iodine atoms. In CI_4 the
carbon is completely surrounded by $I - I$ linkages,
but this is not the case in either CHI_3 or C_2I_4 so
it would be more reasonable to look for a similarity
between the curves for C_2I_4 and CHI_3 than between
the curves for C_2I_4 and CI_4 . (In all cases the
curves of the substances in hexane, i.e. the curves
for the substances in the normal unsolvated states
are under consideration; solvation effects will be
examined later.) In fulfilment of this expectation
it was found in practice that the curve for C_2I_4 is
very similar to that for CHI_3 .

C_2I_2

There are two possibilities in the space model
of C_2I_2 . (1) in which the iodine atoms are on
the same side of the carbon linkage
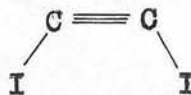
and (2) in which the iodine atoms are on different
sides of the carbon linkages
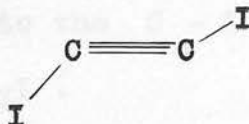
But C_2I_2 has been shown (54) xxxxxxxxxxxx to have
a dipole moment of 0.33 so that formula (1) is the
more probable. In this molecule the iodine atoms are
further/

further apart than they are in C_2I_4 so that the
attractive forces between the iodine atoms will be
much less but there will still be some attraction.
Owing to the decrease in the attraction between the
iodine atoms the attraction between the carbon and
iodine atoms will be more apparent. Also owing to
the fact that there is only one I - I "bond" in
the C_2I_2 molecule (compared with four in C_2I_4) it
would be expected that the intensity of absorption
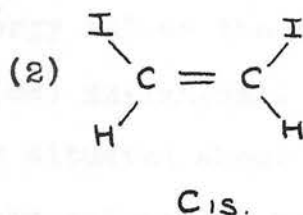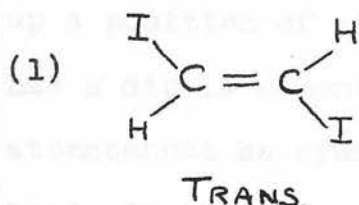would be decreased.

This is supported by the curve obtained experi-
mentally for C_2I_2 . The inflexion stretching from
approximately $\lambda = 335$ mμ to $\lambda = 300$ mμ corres-
ponds to the region of absorption in C_2I_4 which was
attributed to the I - I bonds. The value of log K
(which on the quantum theory is a measure of the fre-
quency of the occurrence of the absorption process)
is only 1.9 at the inflexion on the C_2I_2 curve
compared with an average value of log K = 3.0 for
the same on the C_2I_4 curve.

The maximum to which the C_2I_2 curve rises at
$\lambda = 270$m$\mu$is probably that due to the C - I linkage
which appears at $\lambda = 250$mμin CH_3I .

$C_2H_2I_2$.

$C_2H_2I_2$ can exist in two isomeric forms, one
solid and one liquid. The two possible formulae
are/

are

(1) [structural formula: trans form of C₂H₂I₂ with I and H on C=C]

TRANS.

(2) [structural formula: cis form of C₂H₂I₂ with I and H on C=C]

CIS.

The trans-form has been shown as would be expected,
to have zero dipole moment (55) xxxxxxxxxx and a
dipole moment of .75 has been found for the cis-
form (56) xxxxxxxxxx.   By the preparation of fumaric
and maleic acids from the two forms Keiser (57)
(Am: Chem: Jour. 48 518) decided that the solid
variety had the trans-form and the liquid variety
the cis-form.   When either form is heated to 146°C
for several hours an equilibrium between the forms is
established. In the present work the solid form (i.e.
the non-polar form) was prepared.

In the trans-form the iodine atoms are on oppos-
ite sides of the molecule so that there will be only
a slight absorption due to an I - I "bond" but in-
stead it will be almost all due to the C - I bonds.
In accordance with this the curve for $C_2H_2I_2$ consists
of a branch rising towards the ultra-violet; this is
probably the absorption due to the C - I bonds.
Just about λ = 307 mμ there is an inflexion in the
curve which may be caused by the I - I "bond".

$C_2H_4I_2$

There is only one possible formula for this
compound because of the free rotation of the atoms/

atoms round the bonds. The atoms will tend to take
up a position of minimum energy but as the molecule
has a dipole moment of 1.3 (58) xxxxxxxxxx the iodine
atoms cannot be symmetrically situated about the C - C
bond; in that case some slight attraction between the
iodine atoms will exist; in agreement with this it
is found that although the main absorption consists of
a branch rising towards the ultra-violet (presumably
due to the C - I linkages) there is a kink in the
curve at λ = 307 mμ which is in the region of ab-
sorption attributed to the I - I "bond".

CH_2I_2

        In the CH_2I_2 molecule where the iodine and
hydrogen atoms are at the vertices of a tetrahedron
at the centre of which is the carbon atom, the iodine
atoms are bound to be adjacent to each other in space,
so that there must be some interaction between them,
and one would expect it to be of the same order of
magnitude as in CHI_3.   It is rather difficult to
deduce any agreement with this from the experimental
curve owing to the fact that the maximum attributed
to the C - I linkage has moved so far towards the
visible compared with its position in CH_3I (to λ = 297 mμ
in fact) that it overlaps into the region attributed
to the I - I linkage.   However it may be noted that
a change in the direction of the curve occurs at

   λ = 354 mμ while the first maximum of the I - I

"bond"/

"bond" in C_2I_4 occurs at $\lambda = 330$ mμ .

The shift of the C - I maximum from its position at $\lambda = 250$ mμ in CH_3I to $\lambda = 297$ mμ in CH_2I_2 is due according to Lowry and Sass to the weakening of the C - I bond by the other iodine atom in the molecule.

(b) The Solvent Effect.

When an absorbing substance is dissolved in a solvent the electrons of the absorbing group will be under the influence of the dipole (if any) of the solvent. But as the field of a dipole falls off very rapidly with distance the effect of the solvent dipole is negligible compared with that of the dipole of the chromophore group; and any deformation of the electron system of the absorbing group caused by the polar solvent will be small compared with the potential energy changes in the solute molecule due to the form-ation of solvation complexes and may, therefore, be neglected in a consideration of the effect of change of solvent on the absorption of the solute.

Let η = the excitation energy of the molecule when not influenced by solvent.

There are several cases to be considered:-

1. A polar molecule dissolved in a non-polar unpolar-isable solvent e.g. hexane.

In/

In this case there will be no electrostatic interaction
with the solvent.

Let the solvation energy in the unexcited state
be W , this energy is due to van der Waal's type
of forces, and represents the energy required to re-
move the molecule from its solvation shell.

When the molecule is excited the solvation energy
will change to $W + \Delta W$. It will be assumed that
the solvation energy is altered to approximately the
same extent ΔW in all the cases discussed, this
assumption is permissible because in each case dis-
cussed here we are dealing with the same chromophore.

Fig
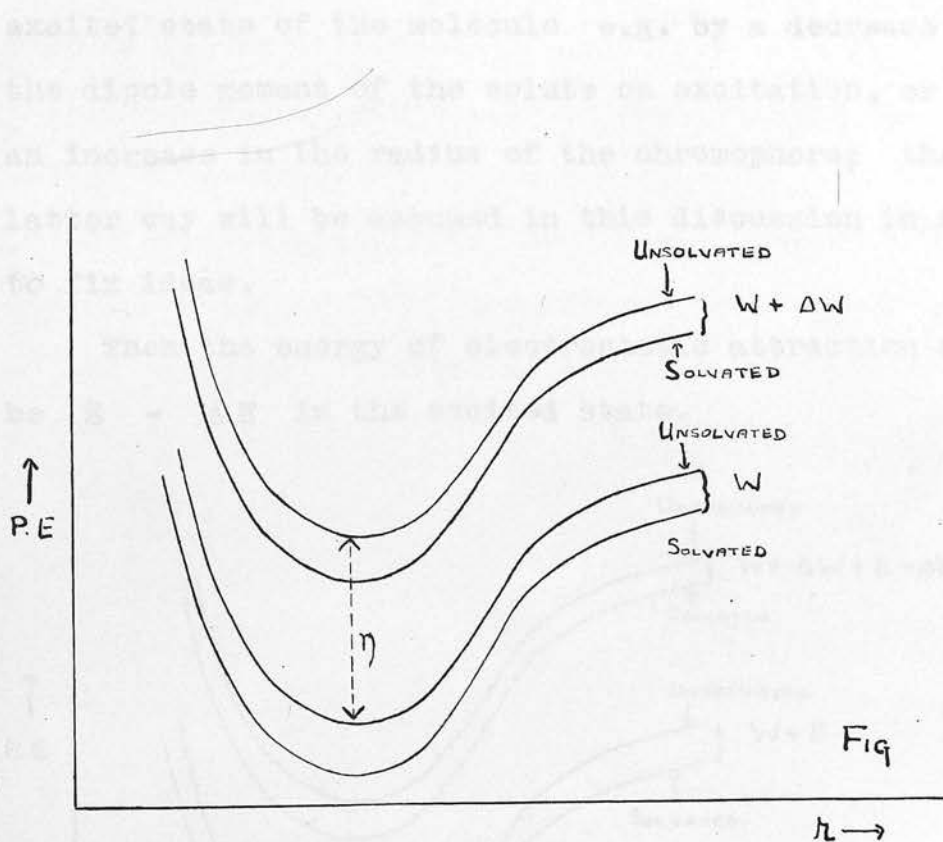
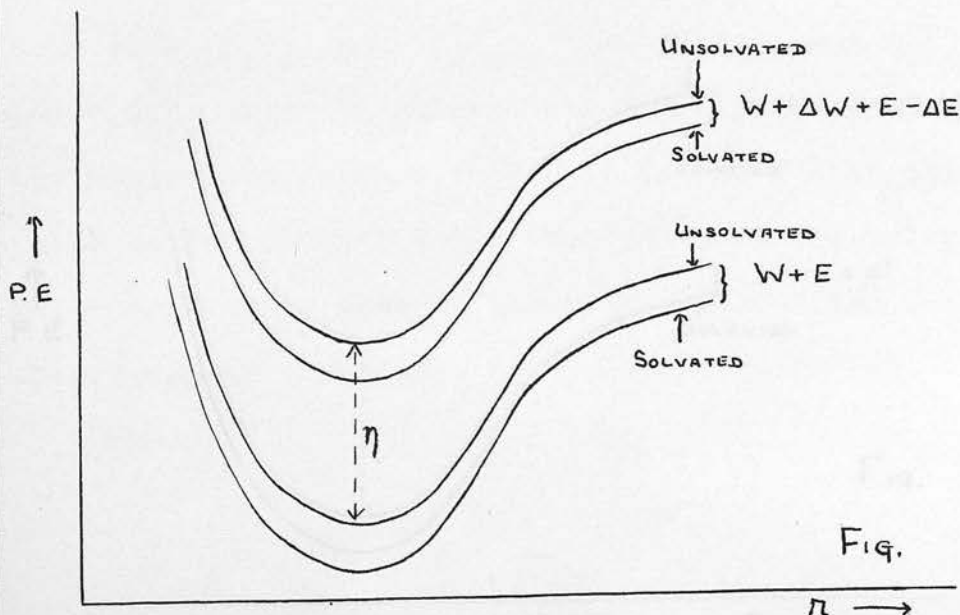Energy of light absorbed by solvated molecule
on being excited $= \eta - \Delta W$

Wave-length of absorbed light $= \dfrac{hc}{\eta - \Delta W}$ ----- (1)

(2) A polar molecule dissolved in a polar but un-
    polarisable solvent such as EtOH.

In the unexcited state the energy of solvation is W
as before; added to this is the energy E of electro-
static attraction between the dipoles of the solute
and of the solvent.

In the excited state the solvation energy becomes
W + ΔW. The electrostatic energy may be decreased
in several ways in passing from the unexcited to the
excited state of the molecule e.g. by a decrease in
the dipole moment of the solute on excitation, or by
an increase in the radius of the chromophore; the
latter way will be assumed in this discussion in order
to fix ideas.

Then the energy of electrostatic attraction will
be E - ΔE in the excited state.

UNSOLVATED
} W + ΔW + E - ΔE
SOLVATED

UNSOLVATED
} W + E
SOLVATED

P.E

η

Fig.

$n \longrightarrow$

Energy of light required to excite solvated mole-
$$\text{cule} = \eta \quad - \quad \Delta W \quad + \quad \Delta E$$

Wave-length of absorbed light $= \dfrac{hc}{\eta - \Delta W + \Delta E}$ (2).

This is less than (1) so that a shift in absorption
towards the ultra-violet would be expected.

(3)   A polar molecule dissolved in a non-polar but
       polarisable solvent e.g. CCl_4.

In the unexcited state the solvation energy is   W.
The solute molecule being polar will induce a dipole
in the solvent molecules. To withdraw the solute
molecule from the solvent, energy   W - H   must be
exerted where   H   is the energy required to create the
dipoles in the solvent.

Putting in the electrostatic attraction term E' the
energy of solution is $W - H + E'$.

In the excited state both the H and E' terms will be
diminished due to the increased radius of the molecule,
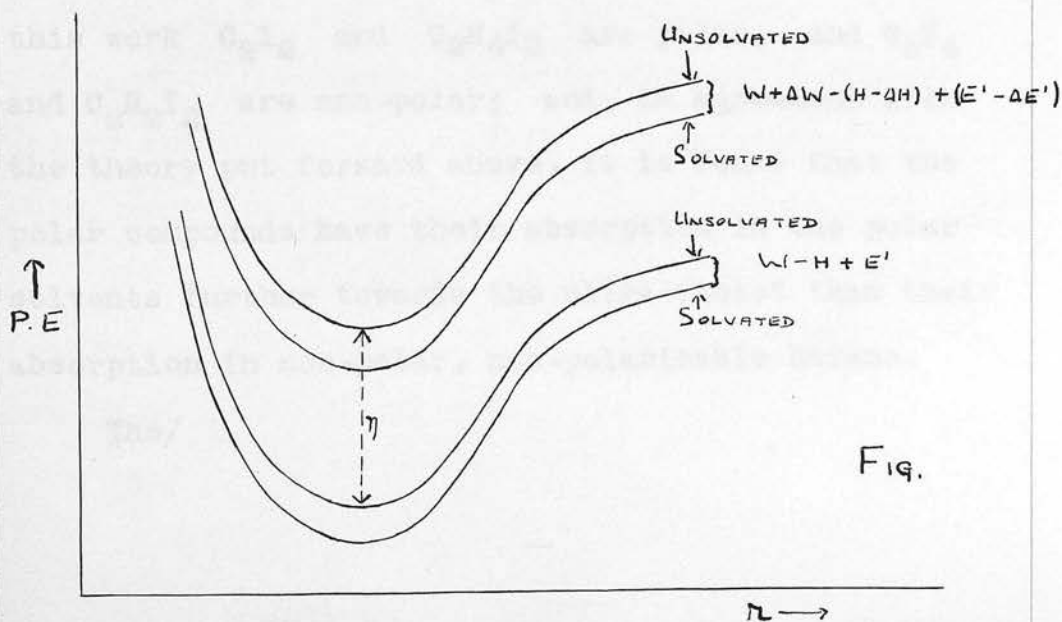so the energy of solution is now $W + \Delta W - (H - \Delta H)$
$+ (E' - \Delta E')$.

Fig.

Energy of light required to excite molecule in sol-
vated state $= \eta - \Delta W - \Delta H + \Delta E'$

Wave-length of absorbed light $= \dfrac{hc}{\eta - \Delta W - \Delta H + \Delta E'}$ (3).

where $\Delta E'$ must be less than ΔH.
The value of the wave-length of the absorbed light in
this case is greater than in (1) so that the absorp-
tion should shift towards the red.

It may be mentioned that for this case, the pres-
ent theory is in agreement with Kundt's Rule. This
rule is no longer regarded as having general validity,
but Scheibe has found also that polar solutes in non-
polar polarisable solvents have their absorption
curves shifted towards the red.

(4) A non-polar molecule in a non-polar solvent

whether the latter is polarisable or not. This
is really the same as case 1. because there will be
no electrostatic interaction between the solute and
solvent.

In the series of carbon compounds examined in
this work C_2I_2 and $C_2H_4I_2$ are polar, and C_2I_4
and $C_2H_2I_2$ are non-polar; and, in agreement with
the theory put forward above, it is found that the
polar compounds have their absorption in the polar
solvents further towards the ultra-violet than their
absorption in non-polar, non-polarisable hexane.

The/

The non-polar compounds here investigated also show a shift towards the ultra-violet in their absorption spectra, when dissolved in polar solvents. These non-polar compounds consist, however, in each case of a set of polar bonds arranged symmetrically so as to have no resultant moment. In a polar solvent, each bond will probably interact with the electrostatic field of the solvent molecule nearest to it, so that the case will approximate to that of a polar solute and a polar solvent.

The effect in CCl_4 (non-polar but polarisable) is not however the same as for a polar solute, for even if each bond interacts with its adjacent solvent molecule, the effect will be symmetrical throughout the whole solvation complex; i.e. the solvent will on the whole be unaffected. The observed coincidence of the curves of compounds of this type in hexane and CCl_4 is in agreement with this.

C_2I_2 $C_2H_2I_2$ and $C_2H_4I_2$ all show a shift in absorption towards the red in CCl_4 as compared with hexane. C_2I_2 and $C_2H_4I_2$ are both polar and so the results for these compounds support the above theory which predicts a shift towards the red under such conditions.

The $C_2H_2I_2$ used was the trans-form, which is non-polar. The reason for the observed shift to the red in CCl_4 is not evident.

The/

The polarity of CH_2I_2 does not seem to have been investigated.

C_2I_4 is non-polar but it seems impossible to draw any conclusions from the results obtained as the variation in the curves is not regular and other effects seem to enter in.

In general there does not appear to be any strict parallelism between the polarity of the solvent and the amount of shift of the absorption.   The reason for this is probably the occurrence of specific solute - solvent effects as distinct from general effects.

SUMMARY.

The absorption spectra of SnI_4 , $SnBr_4$, $SnCl_4$, $SnBr_2$, C_2I_4 , C_2I_2 , $C_2H_2I_2$, $C_2H_4I_2$, and CH_2I_2 have been measured in various solvents. It is shown that results of previous workers for SnI_4 have been subject to errors due to decomposition of the compound. This decomposition was prevented in the curves obtained in this work. The decomposition could not be stopped in the case of $SnBr_4$ and a hypothesis is put to explain this difference in the behaviour of SnI_4 and $SnBr_4$.

The spectra of the iodine compounds are discussed on the basis of the theory that in compounds containing several iodine atoms and weak X - I bonds part of the absorption is due to interaction between the iodine atoms.

The effect of change of solvent on the absorption of the carbon compounds was studied and a tentative explanation put forward.

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