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CONTENTS

The professional chemist or physicist must not only be capable of conducting an investigation in a competent and thorough manner but must also be able to report the results of his work clearly, accurately and briefly. It is not always easy to write succinctly and well on technical subject, even when one thoroughly understands his material. Anyone acquainted with modern scientific literature knows that poor presentation often adds greatly to the effect needed to read this literature intelligently.

Most scientists have at one time or another taken courses in English composition; however it seems that many do not apply this formal training to the preparation of their reports. Proficiency in technical writing comes only through practice, but if practice is not carefully supervised it is of little value. Improvement in writing will result only if each piece of work produced is subjected to thorough and intelligent criticism and revised accordingly.

We feel that student publications such as this journal offer an excellent opportunity for undergraduates to be-

come familiar with the techniques of expressing scientific concepts in a readable manner. Each of the articles in this issue has been carefully examined and repeatedly revised to insure clarity and accuracy. How well we have succeeded in this is for our readers to judge.

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ABSORPTION OF MICROWAVE ENERGY BY OZONE IN THE ATMOSPHERE*

by FRANCIS J. JACKSON '54

The development of radar and the consequent need for a source of powerful centimeter waves has resulted in widespread investigation of microwave phenomena. The microwave region is that portion of the electromagnetic spectrum which lies between the conventional radio-frequency and the far infra-red region. In the study of these microwave frequencies, some phenomena are observed which are of little consequence elsewhere, e.g. the absorption of electromagnetic radiation by the excitation of gas molecules present in the atmosphere.

Transitions between various molecular energy levels are the main causes of absorption in the microwave domain. A comparatively large number of high intensity absorption lines appear in the millimeter region of the spectrum of molecules possessing an electric dipole moment, such as H_2O, CO_2, and O_3. This absorption is a result of the interaction of the absorbing gas with the electromagnetic field. No absorption of this energy due to nitrogen occurs, since nitrogen does not possess an electric dipole. There is a weak but measurable absorption due to oxygen, since this atom possesses a magnetic dipole. However, the magnetic dipole intensity is weaker than the usual electric dipole interaction intensity by a factor of about 100.

In order to predict the positions of the various absorption lines in the spectrum, it is necessary to calculate the rotational energy levels of an absorbing gas molecule and the transitions which occur between them. Once the positions of these lines have been determined, their intensities may be calculated.

Molecules are generally divided into types, such as linear rotors, symmetric tops, asymmetric tops, etc., depending upon the relative position of the nuclei.

One of the major absorbers of microwave energy is ozone, which exists in a layer high up in the atmosphere. The ozone molecule has a structure similar to that of the water molecule, as is shown in the figure below.[1]

Fig. 1

The Ozone Molecule
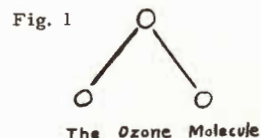
Structure	Isosceles triangle
Bond lengths	1.278 ± 0.003 Å
Bond angle	$116^{o}49' \pm 30'$
Electric dipole moment	0.53 ± 0.02 debye
Principle moments of inertia (g-cm)	$I_a = 7.8749 \times 10^{-40}$ $I_b = 62.844 \times 10^{-40}$ $I_c = 70.888 \times 10^{-40}$

It is classified as an asymmetric rotor, since its three principle moments of inertia are all unequal; that is, $I_a \neq I_b \neq I_c$. Thus it is distinguished from the two limiting cases of the symmetric rotor, namely, prolate and oblate. In the prolate symmetric rotor, $I_a < I_b = I_c$, and in the oblate symmetric rotor $I_a > I_b = I_c$.

The mathematical methods required for solving the quantum mechanical equation of the symmetric rotor are complex. A solution of the wave equation for the symmetric

*This article was written in connection with a research program under the direction of Dr. Edwin K. Gora.

rotor leads to the expression for the characteristic energy values:

$$(1) \quad E_{J,K} = \frac{h^2}{8\pi^2 I_b} J(J+1) + \frac{h^2}{8\pi^2}\left(\frac{1}{I_a} - \frac{1}{I_b}\right)K^2 ,$$

J is used here to designate the principle quantum number and may assume values $J = 0, 1, 2, 3, \ldots$. K is a quantum number which is used to denote the sub-levels, and may take on vaules $K = 0, \pm1, \pm2, \pm3, \ldots$. For every value of J, there will be $2J+1$ sub-levels, since the values of K will run from $-J$ to J.

The calculations for the asymmetric rotor are more involved. The expression for the characteristic energies may be given as:

$$(2) \quad E_{J_\tau} = \frac{A+C}{2} J(J+1) + \frac{A-C}{2} E^J_\tau (\mathcal{K})$$

where: $\quad A = \dfrac{h}{8\pi^2 I_a} \quad\quad B = \dfrac{h}{8\pi^2 I_b} \quad\quad C = \dfrac{h}{8\pi^2 I_c}$.

τ is a psuedo-quantum number used to denote the particular sub-level. A complete discussion of the significance of the factor $E^J_\tau(\mathcal{K})$ as well as a comprehensive mathematical treatment is given in the papers of King, Hainer and Cross.[2] Briefly, the $E^J_\tau(\mathcal{K})$ values are eigenvalues of a complex matrix of the order $2J+1$. These characteristic values have been tabulated (Reference 2) from $J=0$ to $J=12$. A parameter of asymmetry,

$$(3) \quad \mathcal{K} = \frac{2\ B-A-C}{A-C}$$

is then defined. It is this parameter which determines the classification of molecules with regard to their nuclear arrangments. For the limiting prolate symmetric rotor, $(A > B = C)$, $\mathcal{K} = -1$; whereas $\mathcal{K} = 0$ for the perfect asymmetric rotor $(A \neq B \neq C)$ and $\mathcal{K} = +1$ for the oblate-symmetric rotor. $(A < B = C)$.

For the ozone molecule, the value $\mathcal{K} = -0.968$. The ozone molecule approaches the limiting case of the prolate symmetric rotor. This fact allows the use of certain approximation methods which simplify the calculations of the $E^J_\tau (\mathcal{K})$ characteristic values. One of these methods is based on the series expansion:

$$(4) \quad E^J_\tau (\delta) = a_0 + a_1\delta + a_2\delta^2 + a_3\delta^3 \text{ -----}$$

in terms of the asymmetry parameter $\delta = \mathcal{K}+1$. Values of $a_0, a_1, a_2,$ and a_3, up to $J = 12$ are also tabulated in reference 2.[2] For values higher than 12, these coefficients can be computed by fairly simple mathematical methods. In the case of ozone, it will probably be necessary to go as high as $J = 50$ to obtain all the transitions in the microwave domain.

This series expansion gives comparatively good results for low values of J and high values of τ . Unfortunately the accuracy of this method decreases with increasing values of J and high negative values of τ . These are the particular energy levels needed for calculations in the microwave region.

A second method of approximation is based on the use of Mathieu's differential equation. The applicability of this method has been investigated by Golden,[3] and it seems this method will give the more accurate results for high negative values of τ .

The possibility of predicting the position and structure of absorption lines by theoretical methods is of particular interest in the millimeter domain, where labora-

tory experiments are, as yet, almost impossible to perform. However, since the effects of atmospheric absorption of millimeter waves are of considerable importance for the development of radar and other microwave techniques, investigations in this region are being carried on.

References:
1) Trambarulo, R., et al., J. Chem. Phys., 21, 851 (1953)
2) King, G.W., Hainer, R.W., Cross, P.C., ibid. 11 27 (1943)
   Hainer, R.W., Thesis, Brown University, (1947)
3) Golden, S., J. Chem. Phys. 16, 78, (1948)

RADIATION CHEMISTRY

Richard H. Marcil, '53   B. S.

Radiation chemistry is the chemistry of a system which is subjected to irradiation from some source. Concentrated beams of alpha and beta particles, protons, deuterons, gamma rays, X-rays, etc., when directed into a chemical system may produce unexpected reactions.
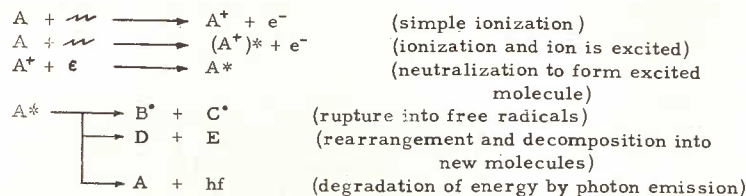
All of these irradiations except X-rays and gamma rays can be treated as mechanical collisions in their interactions with matter. The two exceptions are analogous to photochemical interaction with matter. In mechanical collision, a high energy particle gives up some of its momentum when it collides or interacts with another particle. If the target is a large organic molecule there are two things which may happen with each high energy interaction: either the molecule may be excited only: or excitation may lead to ionization. In a particle collision with a complicated organic molecule, the results depend upon the part of the molecule hit. The incident particle may strike a point within the molecule and transfer enough excitation energy to break a bond and cause ionization. However, if the molecule can dissipate that energy throughout its structure through various modes of vibration, there will be no local ionization but rather a completely excited molecule. This molecule may the return to its original state by emitting a photon or by colliding with other molecules which are poorer in energy.

Absorption of an incident beam of radiation is measured by comparing the beam current before and after passing through the absorbing material. As the thickness of absorbent is increased it is noticed that the absorption deviates more and more from Beer's absorption law. The reasons for this are: first, the material scatters some of the beam, and second, as the particles collide and lose energy, the energy of the beam is decreased. It is also true of radiation that the density of interaction increases rapidly as the radiation approches thermal energies.

A term which is often used in the discussion of irradiation is the capture cross section. This is a type of probability which has the units of an area. The capture cross section is a measure of the probability that a particle will be captured by a target. The capture cross section for neutrons run from 10^{-20} cm^2 to 10^{-32} cm^2 , so whimsical physicists defined 10^{-36} cm^2 as a Barn which should be relatively easy to hit.

Let us consider a few reactions which are often encountered in radiation chemistry. But first we must adopt a new symbol which is $\sim\!\!\!\sim$ and is read "under

high energy particle irradiation."

$$A + \text{\textasciitilde} \longrightarrow A^+ + e^- \quad \text{(simple ionization)}$$
$$A + \text{\textasciitilde} \longrightarrow (A^+)* + e^- \quad \text{(ionization and ion is excited)}$$
$$A^+ + e \longrightarrow A* \quad \text{(neutralization to form excited molecule)}$$
$$A* \longrightarrow B^\bullet + C^\bullet \quad \text{(rupture into free radicals)}$$
$$\longrightarrow D + E \quad \text{(rearrangement and decomposition into new molecules)}$$
$$\longrightarrow A + hf \quad \text{(degradation of energy by photon emission)}$$

A single or free electron has no geometric potential energy levels but it may exhibit excitation merely by displaying more kinetic energy. Any of the complex molecules or ions have electrons that exist in geometric potential energy levels, and as a result of irradiation processes these particles may be transformed into an excited state depending on the process used. Stabilization of these excited particles usually comes by way of photon emission, thermal collision, fluorescence or phosphorescence.

In addition to the foregoing reactions, neutrons and heavy positively charged particles may knock a nucleus from its atom. In a sense this is a wholesale ionization of the atom because the electrons are no longer held in their orbits. Hence they become free electrons with their tangential velocities slightly moderated by the nucleus in its exit. This nucleus goes around robbing other nuclei as well as reclaiming some of its former electrons. The net chemical result is that an extremely powerful agent has been migrating and causing unusual chemical reactions in restricted localities. In a manner similar to the nucleus knock out, there is the possibility that a neutron hit upon a target nucleus will dislodge it from the center of electronic charge forming a temporary dipole. This amounts to a form of excitation because the electrons each could emit a photon in returning to their proper orbit.

Let us now consider the interaction of an electron beam with a chemical system. The electron, because it is very light, loses a great deal of momentum with every collision or interaction with another particle's field. This interaction may be mechanical as in the case where the incident electron strikes an orbital electron of the target material. The incident particle would lose a great deal of its momentum while the orbital electron would become excited or even displaced, bringing about ionization. After a number of these collisions the incident electron would be thermalized and subject to capture by a positive ion or a neutral molecule. Most of these captures are exothermal, or at the most they require only a small amount of activation energy. These reactions can cause stable or metastable molecules or negative ions.

In analyzing the products formed by irradiation of a system, the yield of the product is usually expressed in terms of a G value which is the number of ions or molecules formed per 100 electron volts of beam current passed through the system. In giving the G values, mention is also made of the energy per irradiating ion or photon, because the energy per particle can be used to determine the rate of irradiation or the average beam intensity.

In considering the kinetics of electron capture, it is necessary to take into account the fact that the capture cross section is a function of the electron's energy, plus the fact that there is a distribution of electron energies even if they originally came from a narrow monoenergetic beam. These electrons quickly begin to lose energy and soon a Maxwellian distribution exists in the steady state of electron energies. Using reasonable assumptions, Magee & Burton were able to derive an equation which is essentially the Arrhenius equation.

SOAP AND DETERGENCY*

Francis E. Lussier

Detergency means cleansing power. The two types of substances which are useful because of their detergency are the soaps and the so called synthetic detergents.

The history of soap making probably began around 70 A.D. when an accidental spilling of animal fat on hot wood ashes produced the first soap. By the eighteenth century, soaps were produced by the direct reaction of alkalies with animal or vegetable fats and oils. Chevreul in 1811 showed that soaps produced in this manner consisted of sodium and potassium salts of long chain fatty acids.

Most commercial soaps are mixtures of salts of several fatty acids. Among the acids commonly found are the saturated acids, caproic ($C_6H_{12}O_2$), lauric ($C_{12}H_{24}O_2$), palmitic ($C_{16}H_{32}O_2$), and the unsaturated oleic ($C_{18}H_{34}O_2$) and linoleic ($C_{18}H_{32}O_2$) acids. Approximately forty percent of all the fats and oils used in the soap industry are of animal origin; the remainder are vegetable oils.

The soap molecule consists of a long hydrocarbon chain with a polar group at one end. The shape of the molecule can be pictured as similar to a wooden match with hydrocarbon chain as the "match stick" and the hydrophylic carboxylate groups as the "head".


Schematic Drawing of a Soap Molecule

The anion polar group tends to be soluble in water and pulls the hydrocarbon chain into solution along with it. Since the hydrocarbon end of a soap molecule is hydrophobic (water-fearing), it tends to remove itself from solution as much as possible. These opposing tendencies bring about a two-fold effect.

In the body of the solution the soap molecules cluster together in spherical formations known as micelles. The hydrocarbon portions of the soap molecules group together in the center away from the water while the polar ends of the molecule are located on the periphery of the sphere in contact with the water.

At the surface of a soap solution, and at any other interface, the soap molecules line up such that the hydrophobic fatty acid chains extend up and out of the solution while the ionic polar groups are oriented toward the aqueous solution and dip into its surface. This second effect brings about a greater concentration of soap molecules at the surface than in the body of the solution and thereby lowers the surface tension. Both micelle formation and the accumulation at the surface are effective in the role of soap as a cleansing agent.
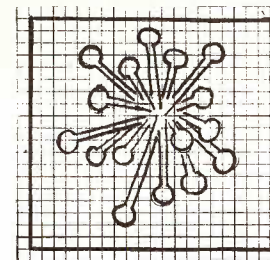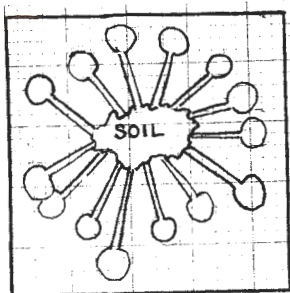

Micelle formation of soap molecules

This article was edited from a seminar delivered October 15, 1953.

The process of detergency or cleansing action on fabrics may be divided into three steps: first, the loosening of soil from the fabric; second, the stabilization of the displaced soil; and third, the removal of dispersed soil.

In order for a soap solution to remove soil from a fabric it must wet the fibers. The lowered surface tension of the soap solution increases its wetting power, and the nature of the hydrocarbon chain causes soap molecules to be held to the organic fiber more strongly than is the soil. The energy of the soil-fiber bond is reduced to such an extent that the soil is replaced by soap molecules and may be dispersed in solution by mechanical means such as agitation.

Soil particle entrapped in a micelle

Once dispersed, these minute soil particles constitute ideal nuclei for micelle formation. The soil particles are stabilized by the hydrophobic portion of the soap molecule arranging itself around the soil particle facing inward, while the hydrophylic end of the soap molecule faces towards the water such that it tends to solubilize the soil. Therefore a micelle is created in which the soil is isolated in the center of the sphere and thus stabilized. The charge on both the soil and fabric is negative in alkaline detergent solution due to micelle formation and absorption of soap anion on the fabric. The electrostatic repulsion between the emulsified soil and the fabric prevents redeposition.

The soil removal process used extensively in the laundering industry is one called "multiple suds". This process consists of a combination of foaming and mechanical agitation. In the first "suds" (washing), soil is removed up to a certain point and then the wash solution is dumped before the concentration of the soil and the time of its exposure to the fabric is sufficient to cause redeposition. A complete washing consists of a series of these "short suds" processes followed by a soapless rinsing. The foaming action of soap solutions, a consequence of their lowered surface tension, provides large surface areas on which soil particles already dispersed may be absorbed.

References: Adam, N.K. and Stevenson, D.G., Endeavour 12, 45, (1953)
               Galkowski, T.T., "Synthetic Detergents,Part I" (unpublished)
               McBain, J.W., "Colloid Science", Heath, N.Y., 1950
               Nivin, W.W., "Fundamentals of Detergency",Reinhold,N.Y.
                                                                (1950)

Radiation Chemistry   .... continued from page 6

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               Magee, J.L. and Burton M., J.A.C.S., 73, 523 (1951)
               Burton, M., J. Chem. Ed., 28, 404, (1951)

Blue Ribbon Boner

Vapor pressure — that point at which the surface tension is broken and the fumes come off as a gas. (P.C., May, 1954)
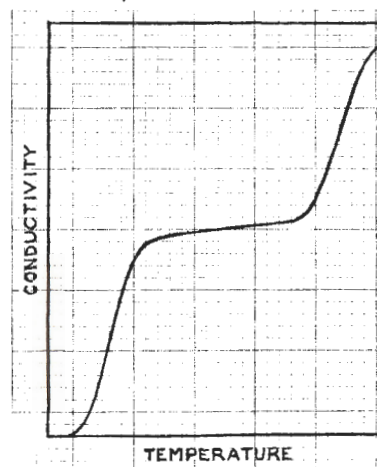
SEMICONDUCTORS AND CONTACT RECTIFIERS*

Walter G. Horbert

Semiconductors are solids having specific conductances lying between that of conductors and that of insulators. The conductivity values of common conductors and insulators are fairly constant over a wide range of conditions, while the conductivities of semiconductors vary greatly with thermal and chemical treatment. It is significant that simple substances which are good insulators follow the law of combining proportions very closely while semiconductors show considerable deviation from ideal stoichiometric proportions.

Deviation from stoichiometric proportions necessitates a disorder within the lattice of a crystalline substance. The two types of disorder most commonly found in semiconductors are the Frenkel and Schottky defects. The Frenkel defect occurs when atoms of the constituent present in excess occupy interstitial positions within the lattice. The Schottky defect occurs when lattice sites are left vacant due to a deficiency of one constituent.

An example of a semiconductor in which the Frenkel disorder predominates is zinc oxide. This substance becomes a semiconductor only after it has been heated strongly. In this process some oxygen is driven off, leaving an excess of zinc atoms at the surface of the crystal. These atoms diffuse into the crystal and occupy interstitial positions within the lattice. When excited, these zinc atoms ionize and produce current-carrying electrons. Because the current is carried by negative particles, this class of semiconductors is referred to as the N-Type. In addition, there are formed some zinc molecules which are ionized more easily than the zinc atoms. Therefore at very low temperatures all the atoms and molecules are unionized. As the temperature rises more and more of the molecules become ionized, causing a continual rise of conductivity up to the point where all the zinc molecules are ionized. As the temperature continues to rise, the conductivity remains constant until the zinc atoms begin to ionize. From this point the conductivity varies regularly with temperature until the zinc atoms are all ionized and the conductivity reaches a saturation value. In this region the conductivity is due mostly to the electrons from the zinc atoms as these are present in much greater numbers.

The second type of disorder within a crystal, the Schottky defect, is exemplified by cuprous oxide. In the formation of the semiconductor from cuprous oxide, oxygen is absorbed on the surface during ignition. Cuprous ions within the crystal are thought to acquire electrons (from neighboring oxygen ions) and migrate to the surface as neutral atoms. At the surface, the copper atoms react with absorbed oxygen to form a new layer of cuprous oxide. As a result of this migration, lattice sites within the crystal are vacated and "holes" are left in the electronic structure of the oxide ions. These "holes" are normally bound to the vacant sites but they may be freed by thermal energy and so travel throughout the crystal. Since the conductivity of substances such as cuprous oxide is due to those "holes", which may be considered as positive charges, this class of substances is referred to as

* Edited from a seminar given April 9, 1953.

the P-Type class of semiconductors. The conductivity of cuprous oxide varies with temperature much the same as that of zinc oxide in the range of proportional conductivity.

Since the semiconductivity of certain elements, such as selenium, cannot be attributed to deviation from stoichiometric proportions, these elements are referred to as intrinsic semiconductors. The conductivity of such monatomic semiconductors is sometimes due to free electrons produced by ionization of atoms at relatively high temperatures which occupy interstitial positions with the crystal. In the case of other monatomic semiconductors, foreign atoms are present within the crystal which give rise to conducting electrons or "holes" and thus to P- or N-Type semiconductivity. In commercial practice, the semiconductor material is prepared to a very high degree of purity and then "doped" in a controlled manner with chosen impurities.

Semiconductors are used in the rectification of alternating current in the form of a metal-semiconductor junction. When an N-Type semiconductor is placed in contact with a metal, current will flow when the semiconductor side of the junction is negative. When the semiconductor side becomes positive, current is prevented from flowing by the removal of the conducting electrons from the junction by electrostatic attraction. This creates a barrier which most electrons do not have sufficient energy to jump. In the case of P-Type semiconductors, the procedure is similar but the current flows in the opposite direction.

Semiconductors have already found many applications. Selenium rectifiers are in wide use in radio and television equipment. Other semiconductors are being studied with regard to their possible use as amplifiers or photoconductors and, depending upon their performance, will find extensive application in electronic equipment.

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The Spirit of Chemistry

The chemist who will make his mark
    Identifies solvents in the dark,
He needn't know what labels spell
    He knows the contents by the smell.

He'll raise a flask to nose so keen
    And promptly name the stuff benezene.
Next flash he'll whiff, and make a bet
    The contents held is carbon tet.

Third flask he'll inhale long and slow
    His face will take on radiant glow
'Tis strange the time he needs to recall
    The aroma of ethyl alcohol.

THE ELECTRON GAS THEORY OF THE ABSORPTION OF LIGHT BY ORGANIC DYES*

Joseph E. Earley '54

Several attempts have been made to correlate the molecular structure of organic dyes with their colors which are specified by the wavelengths and intensities of a small number of major bands in the dyes' absorption spectrum. The electron gas theory is a recently developed, quantum mechanical approach which gives quantitative results comparable to those obtained by earlier, more complex methods. The fundamental assumption of the electron gas theory is that each molecule of a conjugated organic compound contains free electrons similar to those considered to be present in metals. This assumption may be justified by a qualitative consideration of certain aspects of the theory of atomic and molecular orbitals.

The electronic configuration of the carbon atom in its ground state is represented by atomic orbital notation as $1s^2 2s^2 2p_x 2p_y$. This indicates that only two electrons are unpaired and hence capable of bond formation. It is, therefore, not a satisfactory representation of the tetravalent carbon atom found in the saturated hydrocarbons. The formation of four single covalent bonds requires the presence of four unpaired electrons in the carbon atom. The most reasonable way to obtain these electrons would be to split the pair of electrons occupying the 2s shell and to raise one of them to the $2p_z$ state, thus giving rise to the configuration $1s^2 2s2p_x 2p_y 2p_z$. However if this were the case, the four bonds formed would not all be equivalent, since the bonds formed by the three 2p electrons would have slightly different energies than the one formed by the 2s electron. Since chemical evidence shows the four bonds of carbon to be equivalent, it must be concluded that tetravalent carbon contains four unpaired electrons which occupy identical orbitals.

Neither of the 2s shell nor the 2p shell can contain four unpaired electrons. These electrons must occupy a shell which is neither 2s nor 2p but rather a shell of intermediate energy formed by the redistribution of the energy of the one 2s orbital and the three 2p orbitals. The four "hybrid" orbitals which result from this redistribution of energy are referred to as sp^3 orbitals, since one 2s and three 2p orbitals were involved in their formation. Mathematical treatment shows that the electrons contained in the $2sp^3$ shell tend to form four single bonds directed toward the vertices of a tetrahedron. Therefore, the representation $1s^2 (2sp^3)^4$ provides a valid explanation for the properties of the carbon atom in saturated hydrocarbons.

In conjugated compound the carbon atom does not form four single bonds directed towards the vertices of a tetrahedron. Still another representation must be devised to explain the properties of carbon in such compounds. If the redistribution of energy mentioned above were to involve not all three 2p orbitals but only two, the resulting configuration would be, $1s^2 2 (sp^2)^3 2p_z$, where $2(sp^2)$ represents a new type of hybridized orbital formed by the interaction of the single 2s orbital with the $2p_x$ and $2p_y$ orbitals. The $2p_z$, orbital is not involved. The properties of the $2sp^2$ shell are such that it can contain three unpaired electrons which tend to form three bonds symetrically distributed in a single plane which is perpendicular to the direction of the $2p_z$ orbital.

The molecular orbital theory considers conjugated compounds to contain carbon atoms in the $1s^2 2(sp^2)^3 2p_z$ state. In the benzene molecule, for instance, the three co-planar sp^2 orbitals of each carbon atom form bonds with the sp^2 orbitals of the two adjacent carbon atoms and with a hydrogen atom. The $2p_z$ orbitals are perpendicular to the carbon ring and their electrons are attracted by the nuclei of the carbon atoms of the ring but repelled by the electrons which form the C-C and C-H bonds. Under the influence of these forces the electrons of the $2p_z$ atomic orbitals form nonlocalized molecular orbitals, which extend the length of the conjugated system. These are designated π orbitals and the electrons occupying them are referred to individually as π electrons or free electrons. It is the π electrons, present in all conjugated and resonating compounds, that comprise the "electron gas" and are held responsible for the absorption of visible light by organic molecules.

The electron gas of the dye ion which is the resonance hybrid of the structures shown in Figure I, is composed of eight π electrons, one from each conjugated carbon atom and two from each nitrogen atom, an electron being lost in ionization. Each of these electrons is free to move the entire length of the conjugated chain.

The potential energy of an electron moving from one end of the conjugated chain to the other may be represented by a sine curve. The maxima of the curve would be located midway between each pair of atoms and the minima would be located at the points where the electron most closely approaches the atoms. (Fig. II a). At one bond length past the end of the conjugated chain, the potential rises very sharply and so confines the electron. A useful approximation is to consider the potential to be constant within the molecule and infinite at a distance of one bond length beyond the conjugate chain (Fig. II b). Each electron may them be considered to be a particle free to move in a one dimensional box within which the potential energy is constant.
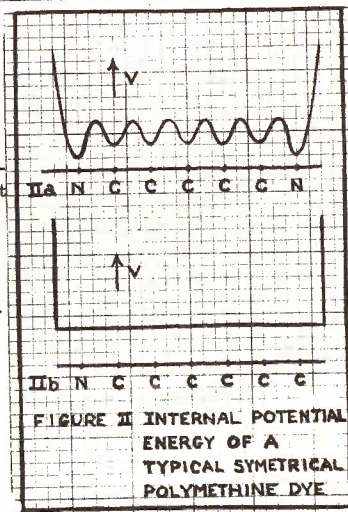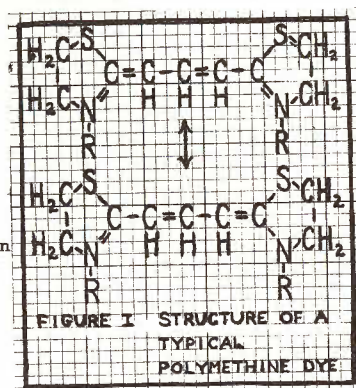
For such a particle, Pauling obtains the relation:

(1) $\oint p_x \, dx = \int_{-L}^{L} p_x \, dx = nh$

(2) $p_x = \dfrac{nh}{2L}$

L is the length of the potential energy box and p_x is the linear momentum of the electron. The kinetic energy of the electron is:

(3) $E_K = \frac{1}{2}mv^2 = \frac{1}{2m}(p_x)^2$ (4) $E_K = \dfrac{n^2 h^2}{2m \cdot 4L^2}$

FIGURE I   STRUCTURE OF A TYPICAL POLYMETHINE DYE

FIGURE II   INTERNAL POTENTIAL ENERGY OF A TYPICAL SYMETRICAL POLYMETHINE DYE

When light strikes a molecule, the most probable electronic transition (which is responsible for the principal absorption band) is the transition of an electron from the highest filled energy level to the lowest unfilled level. For a molecule having n π electrons this transition would be from the n/2 level to the $\left(\frac{n}{2}+1\right)$ level. The wavelength of maximum absorption of a dye with n electrons in a electron box of length L would then be:

5) $\lambda = \dfrac{hc}{\Delta E}$ 6) $\Delta E = E_{(n/2+1)} - E_{(\frac{n}{2})}$

7) $\Delta E = \dfrac{(n/2+1)^2 h^2}{8mL^2} - \dfrac{(n/2)^2 h^2}{8mL^2} = \dfrac{(n+1)^2 h^2}{8mL^2}$

8) $\lambda = \dfrac{8mL^2 c}{(n+1)h}$

All the bonds in the resonance hybrid represented in Fig. I are of approximately equal length, and the walls of the potential energy box are located one bond length past each terminal atom. Using Pauling's value for the length of such bonds (1.39 Å), we find the value of L to be 11.12 Å. Since the number of electrons is 8 and h, m, and c are known, the wave length of maximum absorption of the dye may be computed from equation (8). The result obtained, 4530 Å, is in good agreement with the observed value 4550 Å. The intensity of this band has been calculated through the use of the quantum mechanical transition probability.

In the case of those conjugated compounds which are not resonance hybrids involving interchange of double and single bonds, the approximation of constant potential energy within the electron gas is no longer useful. For example the structure shown in Figure IIIa contributes much more to the resting state of the octatetraene molecule than structures IIIb, IIIc and IIId combined. This condition implies inquality of bond lengths and hence the diagram of the potential energy is relatively complex (Figure IVa). A useful approximation is to consider the potential energy within this molecule to vary as a sine curve with amplitude V_0 (Figure IVb). The modified calculations which must be employed in this case yield the result

(9) $\lambda_1 = \left[\dfrac{V_0}{hc}\left(1 - \dfrac{1}{n}\right) + \dfrac{h}{8mc}\left(\dfrac{n+1}{L^2}\right) \right]^{-1}$

Once the value of the constant V_0 is obtained for one member of a series good results may be had for the remainder of the series. For the polyenes V_0 is taken as 2.00 e.v. and the value obtained for octatetraene is 3200 Å which may be compared with the observed value of 3020Å.

FIGURE III   RESONANCE STRUCTURES OF OCTATETRAENE

FIGURE IV   INTERNAL POTENTIAL ENERGY OF OCTATETRAENE
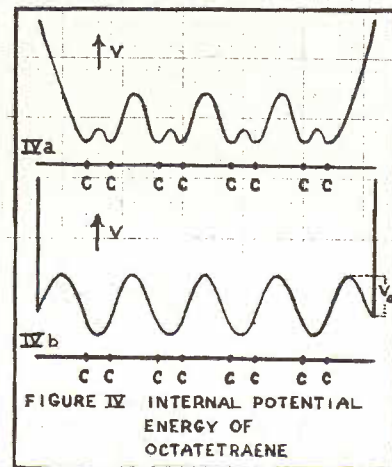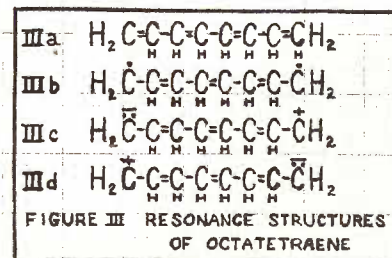
Certain modifications permit extension of this theory to cover most fairly simple organic dyes, including those having condensed rings and branched conjugate chains as well as those in which the bond distances may not be assumed to be uniform. Further refinement of the electron gas theory may produce much useful information regarding complex organic substances and also certain inorganic complexes.

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THE OSCILLOSCOPE
TRANSIT TIME ERRORS AT ULTRA HIGH FREQUENCIES*

Charles A. Richard, Jr.

If the wave reproduced on the screen of an oscilloscope is not identical in amplitude, shape, and frequency with that applied to the deflecting plates, the wave is distorted. When ultra high frequency voltages are applied to the deflecting plates, amplitude distortion results. This distortion is due to the finite time required for the electrons to traverse the deflecting plates (transit time).

The transit time is directly proportional to the length of the deflection plates, and inversely proportional to the horizontal velocity of the electron. The horizontal velocity of the electron expressed in terms of the accelerating anode potential is $V^2 = 2\frac{e}{m}V_a$ where e and m are the charge and rest mass of the electron and V_a the accelerating anode potential.

$$1) \qquad t = \frac{L}{V}$$

Now if an electron with a horizontal velocity V enters the deflecting plates to which there is applied a voltage $V\sin\omega t$, it will be accelerated along the   axis according to the equation:

$$2) \qquad \frac{d^2y}{dt^2} = \frac{e}{mS}V\sin\omega t$$

$$3) \qquad \frac{dy}{dt} = \int_t^{t+\frac{L}{V}} \frac{e}{mS}V\sin\omega t \, dt$$

where S is the distance between the vertical deflection plates. The velocity in the Y direction V_y is obtained by intergrating equation (2) once over the transit time, the limits being t, the time the electrons enter the deflecting field, and $t + \frac{L}{V}$, the time it leaves the field
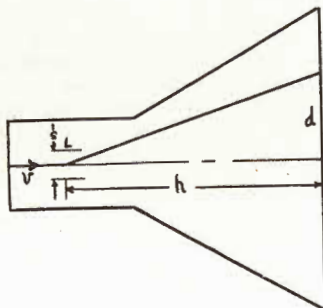
$$4) \qquad V_y = \frac{2e}{m\omega S}V\sin\frac{\omega L}{2V}\sin\omega T$$

T is equal to $t + \frac{L}{2V}$. If the deflection of the electron between the plates is small enough to be neglected, the deflection d at the screen will be given by

$$5) \qquad d = \frac{V_y}{V}h$$

where h is the distance from the center of the deflecting plates to the screen. When (4) is subsituted in (5) the result is

$$(6) \qquad d = \left[\frac{2eh}{mV\omega S}V\sin\frac{\omega L}{2V}\right]\sin\omega T$$

The deflection at the screen varies sinusoidally with time, and therefore if the voltage applied to the deflecting plates contains no harmonics there will be no distortion in frequency or shape. The amplitude of the deflection represented in equation (5) by the expression in brackets is dependent upon m, V, and ω.

Where the accelerating anode voltage does not exceed 30,000 volts it is not necessary to make relativity corrections for m and V. Above 30,000 volts these corrections should be considered. In this case m should be replaced by

$$(7) \qquad m = m_o\left(1 - \frac{V^2}{C^2}\right)^{-\frac{3}{2}}$$

and V by

$$(8.) \qquad V = c\left\{1 - \frac{1}{(1+\frac{eV_a}{m_oC^2})^{2/3}}\right\}^{1/2}$$

Using the expression $(m-m_o)c^2 = eV_a$ with equation (6), equation (7) can be derived. The vertical velocity V_y is in most all cases small enough so that relativity corrections do not apply to it.

Normally, if the period of the voltage applied to the deflecting plates is large compared with the transit time, the change in voltage during the time which an electron is between the plates is small and can be considered constant. Under these conditions the deflection d is proportional to the instantaneous voltage. For this to be true ω in equation (6) will have to be small compared with V. This will make the transit angle $\frac{\omega L}{2V}$ small, and for small angles $\frac{\omega L}{2V}$ is for all practical purposes equal to $\sin\frac{\omega L}{2V}$. Equation (5) will then reduce to

$$(9.) \qquad d' = \frac{ehL}{mV^2S}V\sin\omega T$$

* Edited from a seminar given February 25, 1954

which is the expression for static deflection. In order to correct for transit time errors the ratio d/d' can be plotted against frequency

$$(10.) \qquad \frac{d}{d'} = \frac{2V}{\omega L} \sin \frac{\omega L}{2V}$$

Since $\frac{L}{V}$ is equal to the transit time, the response of the oscilloscope, defined by the ratio of d to d', will vary as the ratio of the sine of half the transit angle to half the transit angle

$$(11.) \qquad \frac{d}{d'} = \frac{\sin \frac{\omega t'}{2}}{\frac{\omega t'}{2}}$$

Two things are evident from equation (10). The response of the oscilloscope will decrease with increasing frequency; and it will be zero for $\omega t' = 2n\pi$ where $n = 1, 2, 3$, etc. The usefulness of equation (10) is found in the fact that the frequency range of voltages for which an oscilloscope may be used to measure is greatly extended.

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Chemist At Work

My eyes droop low — my soul forlorn
    O why must day start with the morn?
I drop a beaker, watch it break,
    I set equipment, hands still shake.

Flames mumble softly in the hood,
    I pray this work will turn out good.
In seconds now, the proof will tell
    If my success will really gel.

The flame removed now from the pot,
    The liquid poured while boiling hot.
The test is passed, success is mine,
    This morning's coffee turned out fine.