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Wide Band Voltage Tuning of Magnetrons

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In the usual method of operation of a magnetron, an electrical resonance of the anode structure is the primary element in determining the frequency of oscillation. As the anode voltage is increased, the rotational velocity of the space charge surrounding the cathode is increased, and power output is obtained when the rotating space charge synchronizes with the natural frequency of the anode.

It has now been found that high-frequency power may be produced with the space charge rotating nonsynchronously with respect to the natural frequency of the anode circuit if the anode circuit is heavily damped by resistive loading and if the electron emission from the cathode is partially restricted.

The frequency of the oscillation so produced is determined primarily by the rotational velocity of the space charge and is found to vary linearly with respect to anode voltage. Tuning ranges in excess of 2 to 1 in ratio have been demonstrated at power levels of approximately 100 w. Ranges in excess of 4 to 1 have been attained at lower powers. The effect has been checked over a wide range of power levels and is not foreseeably restricted to any particular frequency range.

The Properties of Pure Germanium

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Germanium is a tetravalent element located immediately below silicon in the periodic table and is physically and chemically very similar to silicon. Although most of the recent interest in germanium is concerned with its unique electrical characteristics, the element exhibits a number of other interesting properties. The coefficient of thermal expansion is unusually low, being 5.3×10^{-6}/deg C near room temperature. The element expands by a factor of 1.22 upon solidification at its mp of 940° C. Binary phase diagrams of germanium with nearly all other elements (silicon is known to be an exception) show very little solubility of these elements in solid germanium.

Germanium is regarded as a semiconductor in the sense that only a very small fraction of the electrons present can contribute to the flow of electricity. Free electrons may exist as the result of thermal agitation or because of the presence of donor impurities which add extra electrons or of acceptor impurities which remove bound electrons. In the latter case, the vacant electron site is free to move, and acts as a mobile positive charge, giving rise to what is called hole conduction. Germanium occupies an unusual place among semiconductors by virtue of the fact that the mobility of these free holes and electrons is an order of magnitude greater than that observed in other semiconductors.

In the absence of impurities, germanium has a resistivity of about 75 ohm cm at 20° C as the result of a few parts per billion of thermally excited holes and electrons. Donor or acceptor impurities when present in concentration greater than this cause a corresponding decrease in resistivity.

Donor and acceptor impurities fused to germanium act as sources of electrons and holes. Current flow between such contacts involves recombination and space-charge phenomena similar to those involved in gas discharges. The electrical characteristics of various combinations of donor and acceptor electrodes fused to germanium are discussed.

Intrinsic Conductivity of Germanium

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An experimental study has been made of the transition of the conduction properties of germanium from the impurity range to the intrinsic range. Among the properties studied were the variation of Hall coefficient and resistivity with magnetic field and the change of these characteristics with temperature, the variation of mobility figure ($10^8 R/\rho$) with temperature, and the evaluation of intrinsic conductivity and activation energy for a number of single crystals, both N- and P-type. For high resistivity P-type material, a large variation of Hall coefficient with magnetic field was found to occur. This leads to an actual reversal of Hall coefficient, with increasing magnetic field at temperatures close to the transition point. This effect has been explained qualitatively in terms of the difference in change of mobility of holes and electrons in a magnetic field. To explain the effects quantitatively, one must assume large inhomogeneities of resistance throughout the sample. Use of these effects for evaluation of homogeneity of germanium samples and application of the free electron theory of mixed conduction of electrons and holes to germanium are discussed.

Values for the intrinsic resistivity of various N- and P-single crystals ranged from 45 to 60 ohm cm; the activation energy ranged from 0.61 to 0.75, the most probable value being 0.72 ev. The magneto-resistance of germanium obeyed a T^{-3} law to a fair degree of accuracy. The ratio of electron to hole mobility was found to be about 1.50. Additional evidence was found that the "Hall mobility figure" for holes is about 3,000 cm^2/v sec, for electrons about 4,500 cm^2/v sec.

Boride Cathodes

J. M. Lafferty, *General Electric Research Laboratory*

The thermionic emission properties of the borides of the alkaline-earth and rare-earth metals and thorium have been investigated. These compounds all have the same formula MB_6 and the same crystal structure, consisting of a three-dimensional boron framework in whose interlattice spaces the metal atoms are embedded. The valence electrons of the metal atoms are not accepted by the B_6 complex, thus giving rise to the presence of free electrons, which impart a metallic character to these compounds. This, together with the strong bonds between the boron atoms in the framework, produces a series of compounds which have high electrical conductivities and high thermal and chemical stabilities—ideal properties for a cathode material. When this structure is heated to sufficiently high temperature, the metal atoms at the surface evaporate away. They are, however, immediately replaced by diffusion of metal atoms from the underlying cells. The boron framework does not evaporate but remains intact. This process gives a mechanism for constantly maintaining an active cathode surface. Thermionic emission measurements made on these materials show the rare-earth metal borides to be superior to the others. The highest emission was obtained from lanthanum boride. Its emission constants for the Dushman equation were $\Phi = 2.66$ v and $A = 29$ amps/cm^2/deg K^2. This is higher than the emission normally obtained from thoria. Lanthanum boride cathodes are especially useful in applications where high current densities are required. They are also suitable for high-voltage applications because they stand up well under positive ion bombardment. Since they are not affected by air or moisture, and activate easily, they have found wide use in experimental demountable systems.

Effects of Cathode Rays on Various Materials

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Work in this field was done in this laboratory as early as 1926. More recent work is being carried out at MIT and at the new Electronized Chemical Corporation.

An experimental cathode-ray unit in operation at the General Electric Research Laboratory is capable of delivering an ionization dose of 1 million equivalent r units in 7 sec at a distance of 10 cm from the tube window and at 800 kv (peak) energy. The unit is a modified 1-mev standard resonance transformer type x-ray machine, employing a sealed-off type cathode-ray tube.

A dose of 1 million r units has been found to be lethal to most molds and bacteria. The absorption of 10^6 r units produces a temperature rise of approximately 2°C/g of water absorbed, which low value makes this means of sterilization an attractive one, in particular for use in cases of temperature-sensitive materials.

Although it is possible to sterilize foodstuffs so that they can be stored without refrigeration, the sterilization dose in some cases is sufficient to produce undesirable changes in odor, taste, and color. Enzyme systems, both in the natural and isolated states, are deactivated by cathode rays. Chemical changes are produced in other materials irradiated with cathode rays. Plants from seeds irradiated with electrons produce flowers that show color mutations. The maximum survival dose was found to vary with the different varieties of seeds and over a range of approximately 5,000–100,000 r.

Neutron Production by a 50-Mev Betatron

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General Electric Research Laboratory

Research, therapy, and other applications of x-radiation of voltages above nuclear binding energies require evaluation of the neutron intensities associated with the x-ray beams. Measurements have been made of neutrons generated by the GE 50-mev biased betatron, using the 44-sec radioactivity induced by slow neutrons in rhodium as detector. Survey of areas adjacent to the unshielded betatron showed a moderate neutron background from passage of the x-ray beam through target and tube walls. With shielding, measurements were made of photoneutron generation in various elements. A 50-mev x-ray flux producing 1 r below ⅛ in. of the lead yielded, 1,860 Z^2 neutrons per mol; quanta of the order of 20 mev are chiefly responsible for the observed neutrons. The neutron energies average 2–5 mev. Some theoretical interpretations of the data are discussed. Relative shielding efficiency of various materials is considered. It is shown that, in therapeutic applications, the neutrons generated within a patient are the chief problem, but as they contribute a negligible fraction of the dose they do not constitute a limitation to high-voltage x-ray therapy.

Nonferromagnetic Synchrotron

James L. Lawson, *General Electric Research Laboratory*

A new type of synchrotron (electron accelerator) is described in which the required magnetic fields are produced by nonferromagnetic means. Current-carrying coils in an appropriate arrangement supply the (separate) fields for the betatron and synchrotron phases of operation. The betatron phase accelerates particles from the injection energy (about 80 kv) to about 2.5 million v where the particle velocity is nearly that of light. In this phase, acceleration takes place by means of the induced emf in the electron orbit path caused by the changing flux enclosed. In the ensuing synchrotron phase, acceleration is accomplished by means of the potentials obtained on r-f electrodes. In this operation, the electron is locked in its orbital path by the constant-frequency r-f source, and its ultimate energy is determined by the ultimate strength of the magnetic field at that orbit.

In the nonferromagnetic synchrotron at the Research Laboratory at General Electric, the peak electron energy is to be 300 million v, with a possible extension to considerably higher energies if operation at the design energy warrants the increase in power supply equipment.

This new method of synchrotron construction offers improvements in machine size for a given electron energy, in total stored magnetic energy for a given electron energy, and in the excellence of the magnetic field at the electron orbit.

Evidence for Exciton-induced Photoelectric Emission from F-Centers in Alkali Halides

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Alkali halides containing F-centers (electrons trapped in vacant negative ion lattice sites) exhibit photoelectric emission when irradiated with quanta of energy hν greater than about 2.5 ev. In the visible and near-ultraviolet (hν less than 5 ev), the photoelectrons arise from direct ionization of the F-centers by the incident quanta. The photoelectric yield is relatively small, of the order of magnitude 10^{-4} electron per incident quantum. For larger quantum energies lying in the first fundamental absorption band of the pure alkali halide, the process becomes more complex and the photoelectric yield rises by a factor as high as fifty. An attractive hypothesis is that the incident quanta produce excitons (coupled electrons and holes) which migrate through the crystal and eventually ionize F-centers. Thus, the incident energy is more effectively concentrated on the F-centers, and the photoelectric efficiency is accordingly increased. The behavior of the emission at 90° K indicates that excitons are destroyed at free surfaces.

The Attainment of Minimum Noise Figure in Ultra High Frequency Receivers

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This paper reviews briefly the advantages in the use of the noise figure concept for specifying receiver sensitivity performance. It then evaluates the basic types of radio frequency amplifiers in terms of their noise figure capabilities. As operating frequencies increase, such factors as transit-time loading and cathode-lead-inductance loading must be taken into consideration in determining noise figure capability. Although an optimum mismatch of the amplifier input and antenna circuits will produce a lower noise figure than for a matched input, this is not considered to be a practical, attainable operating condition in receivers designed to provide simple tuning over a wide frequency range. Information is presented to show the effects of various amounts of mismatch on noise figure. Vacuum tube characteristics of most importance to minimum noise figure attainment are discussed, and some representative performance data are given.

The Determination of the Molecular Structure of the Halogenosilanes by Microwave Spectroscopy

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Microwave spectroscopy is concerned with the detection and precise measurement of the absorption frequencies of microwave energy (1-cm wavelength) in gases. Such a procedure is analogous in principle to that employed in infrared and visible spectroscopy, except that it is done in a different region of the spectrum and so requires completely different techniques. A microwave spectroscope has several important advantages over those operating in the infrared and visible regions, viz., (1) the resolution is about 1,000 times better, and (2) absorption frequencies may be measured with the uncanny accuracy of 1 part in a million. These advantages permit the bond angles and lengths between atoms in a molecule to be determined to a much higher degree of accuracy than has been previously attainable from infrared and electron diffraction techniques. This paper includes a brief discussion of the experimental method and the manner of reducing the data to yield the molecular structures.

The halogenosilanes* are of interest to the General Electric Company because they represent basic starting materials for the silicone industry. They belong to a class of molecules, known as symmetric tops, whose molecular structure is completely specified by three parameters; viz., the Si-H distance (d_{SiH}), the Si-X distance ($d_{\mathrm{Si}X}$), and the bond angle ∠ H-Si-H. Table 1, where a comparison of the experimental accuracies obtainable from microwave and electron diffraction data is given, demonstrates the great possibilities of the method. The structural results obtained from the other members of this series of compounds are discussed.

TABLE 1

COMPARISON OF EXPERIMENTAL ERROR ON THE STRUCTURAL PARAMETERS OF $\mathrm{SiH_3Cl}$

	Microwave data	Electron diffraction data
$d_{\mathrm{Si-Cl}}$	2.048 ± .001 A	2.06–.05 A
$d_{\mathrm{Si-H}}$	1.50 ± .03 A	Yields no information
∠ H-Si-H	110° 57′ ± 1°	Yields no information

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* A halogenosilane is the generic name given to the series of monohalogen derivatives of silane having the formula SiH_3X, where X may be a fluorine, chlorine, bromine, or iodine atom.

Chronic Remote Nerve Stimulation Technique in Physiological Investigation

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and
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A method of stimulating any given nerve, and thereby any body organ that has a nerve supply, in an intact, unrestrained, unanesthetized animal for weeks or months at a time is described. The method utilizes radio waves and a buried receiving unit. The 1.25-in. diameter radio receiver is buried beneath the skin of laboratory animals. The receiver is connected by a lead wire to an electrode around any peripheral or autonomic nerve under investigation. The animals so prepared then live in an 8-ft diameter ''radio-field cage,'' where they can roam at will. The ''radio-field cage'' is essentially a circular antenna connected to a radio transmitter. By means of a square wave generator, the radio waves generated by the transmitter are so modulated that the receiving unit delivers to the nerve via the electrode, a d-c rectangular wave whose repetition rate, pulse width, and intensity can be controlled at will.

Such an investigative setup allows one to stimulate specific body organs—e.g., the stomach—in order to study the physiological effects of the nervous system on that organ. It also permits one to try to stimulate the emotional and nervous backgrounds that are such a prominent feature in clinical conditions like peptic ulcers of the stomach and in high blood pressure.

A brief résumé of attempts to reproduce clinical pathological states in laboratory animals is given.

Radiographic Gall-Bladder Contrast Agents

S. Archer, *Sterling-Winthrop Research Institute*

Several series of organic iodine compounds were prepared and tested for their ability to render the gall bladder opaque to x-rays. On the basis of the results an attempt is made to point out the structural features that are required for good visualization.

The Coxsackie Viruses

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In 1947 we discovered a group of viruses that seem to be common infections of man. Their existence had not been seriously suspected and, contrary to the traditional search for agents responsible for well-known diseases, we have in the present case discovered the agents before discovering the diseases they may cause.

The Coxsackie viruses are frequently associated with poliomyelitis and were discovered in the feces of poliomyelitis patients. They have since been found associated with poliomyelitis by many other workers in many parts of the world, but it is not clear whether they play an important role in poliomyelitis, with which quite different viruses are concerned. Moreover, there is equally good evidence of their association with another disease, epidemic pleurodynia, for which no causative agent has been established, and they have also been found under various other circumstances.

The Coxsackie viruses have unusual properties. Their tardy discovery is probably due to one of these characteristics, namely, that they may be experimentally propagated only in immature mice and hamsters. Such test animals had rarely been used. A second peculiar property is that although they cause paralysis in suckling mice they do so by destroying the skeletal muscles rather than the nerve cells. They are also uncommonly small, probably no larger than 10 $m\mu$. This is the size of poliomyelitis virus, and the two may be the smallest of the human pathogens.

Poliomyelitis and Coxsackie viruses are similar in other respects. Both are very durable. They are stable in glycerol for years. They are little affected by a wide range of pH. Both occur in the feces and frequently both may be found in the same fecal specimens. They are intimately associated in nature.

The association of Coxsackie viruses with poliomyelitis is our particular interest. It seems probable that the summer epidemics of poliomyelitis are actually mixed epidemics in which both viruses play a part. The Coxsackie viruses account for some of the illnesses. Perhaps the relationship is still more intimate and some cases are mixed infections. There is a natural tendency to oversimplify the etiology of infectious diseases. We do know that some are actually complex infections, that two different pathogens are required to cause illness. And it has been known for a dozen years that certain infectious diseases are rendered less severe by simultaneous infection with a second agent. Thus the association of the newly discovered Coxsackie viruses and the well-known poliomyelitis viruses raises a number of questions of considerable interest.

Quaternary Ammonium Salts as Antibacterial Agents

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Numerous quaternary ammonium salts belonging to the broad class of compounds termed surface-active agents have been described in the literature. Of these, many have been found to possess antibacterial activity.

A summary of some of the various chemical types that have found commercial application as germicides and sanitizing agents is given, and the relationships between chemical structure and antibacterial activity are pointed out.

Recently, a new series of aryloxyalkyl quaternary ammonium salts has been synthesized, and their antibacterial properties have been evaluated. A brief description of the synthesis and a comparison of the activity of some of the members of this series are given.

Two Antifungal Agents Produced by a Soil Actinomycete

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Two agents active against fungi have been obtained from a soil actinomycete. The one is extractable from the culture fluid and somewhat resembles actidione in chemical and biologic properties; the second is extractable with alcohols from the surface growth on liquid medium and differs from other antibiotics within our knowledge. The latter agent, tentatively designated fungicidin, is effective *in vitro* against a large number of nonpathogenic and pathogenic fungi, including *Candida albicans, Cryptococcus neoformans, Histoplasma capsulatum, Blastomyces dermatitidis, Coccidioides immitis, Paracoccidioides brasiliensis, Trichophyton rubrum* (*purpureum*), and *T. mentagrophytes* (*gypseum*). The agent has not shown activity in much higher concentrations against some of the common bacteria such as *Staphylococcus aureus, Salmonella paratyphi* B, *S. typhosa*, *Shigella paradysenteriae*, and *Bacterium coli.* Crude preparations of fungicidin, injected repeatedly in sublethal doses into mice infected with *C. neoformans*, prolong the life of the animals beyond that of the untreated controls.

Because of its unique *in vitro* properties, the therapeutic capacity of this antifungal substance (fungicidin) is under experimental investigation.

Ortho-Alkoxy Derivatives of Procaine as Local Anesthetics

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A new type of substitution in the nucleus of procaine has been studied in the Sterling-Winthrop Research Institute. We have synthesized and tested in this connection various series of ortho-substituted para-aminobenzoates and some of their analogs. Based upon laboratory results, certain of these compounds are more potent than tetracaine or dibucaine, the two most active local anesthetics in clinical usage at the present time.

In the present work the local anesthetic activity was studied by the sciatic nerve block method in guinea pigs, the irritancy was studied by intradermal injection in rabbits, and the toxicity (LD_{50}) was determined by intravenous injection in mice. These values were converted to "procaine ratios" by division of the threshold anesthetic concentration, the threshold irritant concentration, and the LD_{50} values for procaine by the corresponding values for the compounds under test.

The substitution of an ortho-hydroxy group in procaine brought about a substantial increase in activity, whereas the substitution of an ortho-methoxy group gave only a small increase in activity. However, as the size of the ortho-alkoxy group then increases further, the activity also increases rapidly. The ortho-hexyloxy compound, for example, is about 100 times as active as procaine. The toxicity of these compounds is roughly proportional to activity, and with the exception of the ortho-methoxy compound they appear to be less toxic than procaine on an activity basis.

The local irritation appears to be independent of activity or toxicity. The most active compounds show a very favorable activity/irritation ratio. Thus, the ortho-propoxy analog is about ten times as active as procaine and only twice as irritating.

Interaction of Beryllium with Enzymes

Friedrich W. Klemperer, ***Edward L. Trudeau Foundation***

Recent reports have indicated a high toxicity of beryllium to animals and man. Because beryllium exerts its toxic effect in very low concentrations, it appeared possible that this effect depended on inhibition of some enzyme by beryllium; therefore the effect of beryllium on a number of enzymes was studied. It was found that beryllium in concentrations as low as 10^{-6} M inhibited alkaline phosphatase. None of the other enzymes tested were inhibited by concentrations of 10^{-4} M or below. The enzymes studied were: acid phosphatase, adenosine triphosphatase, carboxylase, arginase, carbonic anhydrase, uricase, and aldolase. It was also found that beryllium had no influence on the oxygen uptake by tissue slices or on glycolysis by muscle extracts.

Maximum Oxygen Consumption for Work Periods of Six Minutes' Duration in Normal and Pathological Subjects

George W. Wright, ***Edward L. Trudeau Foundation***

The maximum ability of the human engine to expend energy at a sustained rate portrays the capacity of the human organism to perform as an integrated unit and provides a criterion whereby its excellence or impairment may be estimated. The human engine differs from man-made internal-combustion machines in that, although all the energy developed must ultimately be accounted for in terms of oxygen utilized in combustion, in the human being energy can for a limited time exceed the rate at which oxygen is being utilized. It is known that the maximum of sustained physical performance by man depends directly upon his ability to remove oxygen from the respired air during the actual work period. This ability in turn depends upon the integrity of the respiratory and circulatory systems and of the blood and active tissues.

The quantity of oxygen removed per minute from the respired air during the fifth and sixth minute of the most intense exertion tolerable for 6 minutes on the treadmill was measured in 41 normal men between the ages of 25 and 45. The data are as follows: the mean of oxygen expressed in l/min/sq m of body surface was 1.425 l (S.E. of 0.030 l) and a standard deviation of 0.185 l (S.E. = 0.020). The correlation coefficient between this function and age in years was −0.614 (S.E. = 0.097). The regression formula for this correlation is: Liters of oxygen/min/$M^2 = 1.855 - 10.41 \times$ age in years. The coefficient of variation for this formula is 12.5 percent. The wide variation between normal persons in this ability diminishes the sensitivity of this test and at the same time indicates the difficulty one faces in attempting to assay the normality of an individual. Study of this ability in persons suffering from pulmonary disease demonstrates that, although many have impairment of maximum ability to expend physical energy, others retain this ability to a degree comparable to normal persons in spite of evidence that a quite extensive anatomical abnormality exists.

The Significance and Prevalency of Subclinical Amebiasis

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The average incidence of infection with *Endamoeba histolytica* in the United States is not less than 13 percent. Clinical amebiasis and deaths have been reported from all parts of the nation, but very few "positive" cases come to the attention of physicians. In a recent survey of a presumably normal population sample of the Albany (N. Y.) area, the incidence of *E. histolytica* was 8.9 percent. Analysis of the records of 34 positive and 100 negative subjects shows that only 3 of the positive were without observed signs or symptoms referable to the gastrointestinal tract. Irregular bowel movements (more than 2 stools daily, intermittent diarrhea, alternate diarrhea and constipation, or chronic constipation), associated with abdominal tenderness, dominated the pattern in more than 70 percent. Among the control group, less than 10 percent presented any signs or symptoms referable to the gastrointestinal tract. The results of treatment and the importance of case finding in industrial organizations are discussed.

A Mechanism for the Origin of Cancer Foci

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It is suggested that a single cancer cell surrounded by normal tissue cannot initiate malignant growth, and that tumors appear at locations where for one reason or another a critical number of cancer cells are bunched together. The idea behind the critical-size concept is that individual cancer cells in normal tissue are bathed in normal chemistry, whereas a cancer cell surrounded by others of its kind is bathed in abnormal chemistry, where malignant growth no longer is inhibited.

The mutation theory of cancer has had difficulty in explaining the rapid rise in cancer incidence with age, for mutation rates should remain substantially constant with time. When the critical size concept is introduced, however, a constant rate of random mutation leads to the relationship $N \sim t^p$, where N is the number of cancers in a population, t is the age of the population, and p is the number of cells in a critical-size colony. This relationship, with $p \approx 6$, is followed very well for the over-all incidence of cancer in humans, and with $p \approx 4$ for mammary cancer in mice.

Experiments with carcinogenic materials support the critical-size hypothesis, as do observations concerning the location of metastases, and studies of the influences of cuts and burns. The main contributions of the critical-size viewpoint of cancer initiation are that it correlates and systematizes many previously unrelated facts, gives new life to the mutation theory of cancer, and raises new questions that might not otherwise have been asked.

Empirical Analysis of Viscosity Data

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and
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The equation generally used to interpret data obtained in variable head capillary type viscometers is the Wilberforce equation. This equation, which includes kinetic energy and end-effect corrections, can be rearranged to an equation in which apparent fluidity is linear in driving pressure. An additional term, also linear in pressure, is produced by drainage errors. A method is described for the experimental evaluation of these corrections.

Polystyrene, and polystyrene and polyvinylpyridine solutions exhibit a fluidity that varies linearly with pressure after the above corrections have been made. This residual variation is ascribed to distortion and/or orientation of the polymer molecule. Analysis of the data permits description of the shear dependence in terms of a single arbitrary constant k, the shear constant.

A General Equation for the Entropies of Aqueous Ions

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The experimental values for the entropies of the positive aqueous ions, 26 cases in all, including the ion types M^+, M^{+2}, M^{+3}, and M^{+4}, are in good agreement with the equation

$$S^0_{298.16} = 3/2\, R\ln \text{at.wt} - \frac{59Z}{r + 0.85} + 40,$$

where Z is the charge on the ion and r the ionic (crystal) radius. The entropy values, referred to $S_{H^+} = 0$, vary from -80 to $+35$, and r varies from 0.6 A to 1.4 A. In most cases the agreement between the experimental values and the values from the equation is within 2 entropy units. The experimental value for Ag^+, however, is about 8 units low. The equation implies that the radius of the ion in aqueous solution is proportional to the ionic crystal radius, and this probably is not true in the case of Ag^+, with which there is doubtless some bond formation by water.

The second term in the equation is essentially the entropy of hydration. Since the free energy of hydration, as given by the Born equation, is a function of Z^2/r, and the entropy is the temperature coefficient of the free energy, it is surprising that the entropy is a function of Z/r. This is a point of considerable theoretical interest and directs attention to the physical interpretation of the two quantities.

The Kinetics of the Thermal Decomposition of Diborane

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A number of hydrides of boron, compounds of the general formula B_xH_y, are known. Certain of these decompose or react readily at temperatures near 100° C; in such thermal reactions perhaps all boron hydrides play some role. Consequently, the thermal decomposition of any boron hydride presents an intricate problem in reaction kinetics, whose solution involves establishment of a complicated mechanism for the reaction. Diborane (B_2H_6) is a gaseous hydride of boron which undergoes rapid decomposition at 100° C and may be used as a starting material for preparation of other boron hydrides.

The kinetic studies of the thermal decomposition of diborane reported here are of three kinds. First, the rate of increase of total pressure has been measured as a function of temperature and initial pressure. Three conclusions are drawn from the results: the order of the rate-controlling step is 1.5; the reaction is homogeneous in glass; and the activation energy of the rate-controlling step is 27.4 ± 0.7 kcal/mole.

Second, the rate of formation of hydrogen has been measured. The results confirm the value 1.5 of the order, and indicate an activation energy of 25.5 ± 0.5 kcal/mole. The difference between activation energies is due to temperature effects on secondary reactions.

Third, the mass spectrometer has been used to follow the reaction; in this way the concentrations of several participant species were measured. It is concluded (1) that the order of the step controlling the rate of disappearance of diborane is 1.5, (2) that dihydropentaborane (B_5H_{11}) appears to be an intermediate in the formation of most other boranes from diborane, and (3) that the formation of pentaborane (B_5H_9) from dihydropentaborane is probably a simple first order step.

The reaction scheme proposed to account for these observations is:

$$B_2H_6 \rightleftharpoons 2BH_3$$
$$B_2H_6 + BH_3 \longrightarrow \text{Intermediate products}$$
$$\text{Intermediate products} + B_2H_6 \longrightarrow B_5H_{11} + H_2$$
$$B_5H_{11} \longrightarrow B_5H_9 + H_2$$
$$B_5H_{11} \longrightarrow \text{solids, } B_2H_6$$

Newer Curarelike Compounds

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The curarimimetic activity of a series of 2-mono- and 2,5-bis-dialkylaminoalkylaminobenzoquinones and their quaternary salts has been found to be related in the bis-series to the distance between basic nitrogen atoms and to the ionic bonding radius of the amine or ammonium groups. In the 2-mono-series, activity is related to the presence of a basic or cationic group at an optimum distance from an iminoquinone structure capable of bonding by chelation.

A New Class of Living Microchemical Reagents: The Chrysomonads

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Many important cell constituents cannot be measured except as they occur in essentially free condition. Cell constituents such as vitamins often occur bound up in large molecules and are unavailable in this form to microorganisms used for assay. Sometimes the metabolites are stable enough for chemical digestion to be useful, but frequently these methods are too drastic to be practical. Where animals can be used for assay purposes, susceptibility to this kind of chemical inactivation is usually not a handicap, since the animal's digestive enzymes may allow full utilization of bound metabolites. Microorganisms that ingest food as solid particles are an economical type of animal to use. In looking for new types of biochemically useful micro-animals, we were led to investigate the chrysomonads, a brown-pigmented group of algal flagellates, as a result of our observations that the photosynthetic flagellate *Euglena gracilis* requires vitamin B_{12}. Many chrysomonads, unlike *Euglena*, are known to feed on particulate matter such as bacteria. With the aid of information furnished by E. G. Pringsheim, two strains of *Ochromonas* were obtained in pure culture. They proved to require at least 3 amino acids, several known vitamins (including B_{12}), and several nucleic acid components (adenine, guanine, uracil) in addition to unidentified factors. Preliminary tests show that these flagellates have a definite ability to satisfy several of their requirements from high-molecular compounds; e.g., their purine and pyrimidine requirements are satisfied by intact nucleic acids as well as by the free bases. The question arises whether organisms with such impaired synthetic powers, although provided with plastids, can carry out a conventional photosynthesis.

Decomposition of Lauroyl Peroxide in Benzene and Diethyl Ether

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Benzoyl peroxide dissolved in an organic solvent undergoes thermal decomposition into free benzoate radicals as follows:

$$(C_6H_5COO)_2 \longrightarrow 2\ C_6H_5COO.$$

The work of Nozaki and Bartlett and of Cass showed that the rate of decomposition of benzoyl peroxide in solution varied greatly, depending upon the solvent. In order to explain the acceleration of rate in "fast" solvents (ethers, amines, alcohols, and phenols) the idea of "induced decomposition" of the peroxide was evolved. In induced decomposition, radicals derived from the solvent are believed to attack undecomposed benzoyl peroxide, forming a neutral molecule and a new peroxide-derived radical. A mechanism proposed for the induced decomposition in ethers involves the following steps (for diethyl ether):

$$(C_6H_5COO)_2 \xrightarrow{k_1} 2\,C_6H_5COO\cdot \qquad (1)$$

$$C_6H_5COO\cdot + C_2H_5OC_2H_5 \xrightarrow{k_2} C_6H_5COOH + C_2H_5O\underset{\cdot}{C}HCH_3 \qquad (2)$$

$$C_2H_5O\underset{\cdot}{C}HCH_3 + (C_6H_5COO)_2 \xrightarrow{k_3} C_6H_5COO\cdot + C_6H_5COOCH(CH_3)OC_2H_5 \qquad (3)$$

$$2\,C_2H_5O\underset{\cdot}{C}HCH_3 \xrightarrow{k_4} \text{termination*} \qquad (4)$$

* Other termination steps are possible.

Reactions (2) and (3) constitute a repeating chain mechanism. The isolation of the products shown in (2) and (3) in high yield gave support to the above mechanism.

Decomposition of lauroyl peroxide in benzene and diethyl ether. This work was undertaken to find out if lauroyl peroxide, an *aliphatic* diacyl peroxide, exhibited induced decomposition as does the aromatic diacyl peroxide, benzoyl peroxide. Lauroyl peroxide was found to decompose eight times as rapidly in diethyl ether, a typical fast solvent, as in benzene, a slow solvent. The products of reaction of lauroyl peroxide with diethyl ether were found to be carbon dioxide, hendecane, and the acylal, 1-ethoxyethyl laurate. The kinetics and products of reactions are believed to support the idea of an induced decomposition of lauroyl peroxide in diethyl ether.

Two points are of particular interest. First, the decomposition of lauroyl peroxide followed first order kinetics. This gives support to the idea of "retardation by aromatic products." Second, essentially no lauric acid was formed; i.e., decarboxylation of the intermediate laurate radical, $C_{11}H_{23}COO\cdot$, was practically complete. This indicates a difference in stability between the aromatic and aliphatic radicals.

Peroxides of this type are used industrially as initiators for vinyl polymerization.

Preliminary Studies on the Solubility of Iron in Liquid Sodium

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Preliminary measurements of the solubility of iron in liquid sodium have been made over the range 231°–483° C, by heating Na in an iron vessel in an argon atmosphere and sampling the fluid at temperature. The sodium obtained in this way was dissolved in alcohol, and the iron content measured spectrophotometrically using the α, α'-dipyridyl color reaction.

The equilibrium solubility data on 33 samples can be fitted, by the method of least squares, to the linear equation

$$S_T^{\circ} = -1.47 + 0.030\,T$$

where S_T° is the equilibrium solubility in parts per million by weight at a temperature T degrees C. The probable error in the measurements is ±1.7 ppm. From this equation, the solubility is 1.5 ppm at 100° C, and 13.5 ppm at 500° C. The heat of solution of Fe in Na, computed from the temperature coefficient of solubility, is 2496 ± 385 cal/mole (±15 percent).

These results are compared with the data on the solubility of Fe in Hg. The data are analyzed from the point of view of solution theory, and it is found that (1) in both the Fe-Hg and the Fe-Na systems the activity coefficients of iron are large and positive, and (2) the entropy of mixing of Fe with each of the two liquids is greater than that computed by the ideal solution laws, and is approximately the same in Hg and Na.

Synthetic Speech: A Study of the Auditory Perception of Complex Sounds

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Research on the perception of complex patterns of sound in general, and of the sounds of speech in particular, is greatly facilitated by a device that converts spectrographic displays into sound. The displays from which the sounds are produced may be either photographic copies of spectrograms of actual sounds or wholly synthetic "spectrograms" drawn by hand. This provides a very flexible arrangement for altering the sound in frequency, intensity, or time; and of course one can by listening tests determine how these alterations affect the perception. The method is a convenient one since the sounds can be manipulated conceptually and experimentally as relatively simple visual patterns. The audio-visual transformation implied in this procedure is discussed, and illustrated with sound recordings. Also, research applications of the equipment and techniques to studies in the perception of speech are presented.

Radiography in Corrosion Studies

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The annual cost of corrosion is so great that it is desirable to explore every promising technique for the investigation of corrosion processes. Among the most feared of these processes is pitting, which—being a form of localized attack—is well suited to investigation by methods such as radiography that depend upon the absorption of x-rays.

To illustrate the value of these methods, the pitting of three kinds of stainless steel in ferric chloride solution at room temperature has been studied. Radiographs have been obtained that show how pitting varies with the kind of steel and with the degree of cold deformation. Furthermore, it has been possible to demonstrate that the direction of attack can be profoundly influenced by gravitational forces and by the occurrence of crevices. Although the radiographs largely confirm past experience, they provide much detailed evidence that might escape visual observation, as a comparison with corresponding photographs will show. Finally, it has been possible to measure the rate of pit growth on specimens continuously immersed, an important fact because removal of the specimen from ferric chloride solution can stop altogether the growth of particular pits. The technique employed could be used to measure, in favorable cases, the rate of pitting in closed systems.

The Limiting Negative Pressure of Acetic Acid and Benzene in Relation to Temperature

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The limiting negative pressure of water is markedly influenced by temperature, dropping rapidly as the freezing point is approached. Is this a characteristic of other liquids?

The limiting negative pressure curve of dry benzene vs. temperature resembles that of water in this respect. The graph rises sharply from the mp of benzene (5.5° C) to a rather flat-topped maximum of about -150 bars. Donaghue, Vollrath, and Gerjouy obtained one reading of -159 bars for benzene in a sealed tube with a residual gas pressure of only 7×10^{-5} mm Hg. The maximum negative pressure of benzene is thus seen to be far below that of water (-275 bars).

Glacial acetic acid, on the other hand, shows only a slight increase in the limiting negative pressure between the mp (16.6° C) and the maximum value observed, -285 bars at 22.5° C. This is slightly higher than the maximum observed for water. Acetic acid, however, exhibits a minimum value of 28° C and a second (lower) maximum near 40° C.

The centrifugal method previously described was used throughout these measurements. To reduce the evaporation of the volatile liquids, the open ends of the legs of the capillary tube were brought back near the spin axis. Evacuated sealed tubes were also used.

Mechanism of Nonlinear Luminescence in Sulfide Phosphors

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The light emitted by a phosphor is in most cases proportional to the intensity of the ultraviolet excitation. However, quite a different effect is observed in zinc-cadmium sulfide phosphors. Constant efficiency is approached at extremely weak intensities, and a much higher constant efficiency is reached at moderate intensity. In the intervening intensity range the emitted light increases much more rapidly than the ultraviolet excitation. In an extreme case, the emission increases as the 3.5 power of the excitation.

The observed results may be interpreted quantitatively by a detailed model of the impurity centers responsible for luminescence and of the centers responsible for quenching the luminescence, as well as of the electron traps present in the phosphor. Two energy states of the activator or luminescent center—silver for example—need to be considered, namely, the ground state and the excited, or metastable, state. An excited electron either may be thermally activated to the conduction band or it may return to the ground state by the emission process. The quenching, or "killer," centers—cobalt for example—have a normally unoccupied energy state which can capture electrons from the conduction band and which can then be emptied by hole conduction in the filled band. The traps have their usual function of catching conduction electrons, holding them and then releasing them again as a result of thermal activation. By considering all these factors together, a quantitative explanation has been given for the experimental results. This has made it possible to calculate energy values of some of the states and to compare these results with other data.

Dependence of Luminescent Efficiency on Activator Concentration

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The amount of light emitted from impurity-activated luminescent solids for a given energy input generally increases with impurity concentration at low concentrations, passes through a maximum, and then decreases more or less gradually at higher concentrations. The optimum activator concentration depends on the constitution of the phosphor, the temperature, and the type of excitation energy.

The present work generalizes a previously published analysis of efficiency vs. activator concentration to include the effects of temperature and of different types of excitation energy—cathode rays, x-rays, and short- and long-wave ultraviolet. Data on a variety of inorganic phosphors are successfully correlated by the theory.

The important physical concepts involved in the formulation are as follows: (1) Incident energy can be absorbed by (*a*) exciton formation, (*b*) excitation of electrons to the conduction band, and (*c*) excitation to excited impurity levels. The relative contribution of each mechanism depends on the type of excitation. (2) Only activators not near other activators are luminescence centers. Activators situated near other activators tend to lose their energy by a radiationless process which is favored by smaller distance between activators and by higher temperature. (3) Capture of the energy, made available by one or more of the three primary mechanisms by radiative activators, competes with capture by nonluminescent activators and other nonluminescent impurities included in the host lattice to an extent dependent on the concentration of each and the facility, determined by the capture cross section, with which each one captures this energy. The concentrations and cross sections that lead to the capture of the greatest fraction of incident energy by radiative activators result in the phosphor of highest efficiency.

All the parameters considered above can be correlated with experimental results or with the physical properties of the phosphor constituents.

The Effect of Large Cortical Lesions on Learned Behavior in Monkeys

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The behavior of 4 normal monkeys and 8 monkeys with large cortical lesions was studied over a period of 5 years. The operated monkeys were first subjected to large unilateral lesions, with sparing of the motor and first somatic areas. Subsequently, these animals were divided into two groups, one with large lesions in the frontal association areas and the other with large lesions in the posterior association areas. An evaluation of the differential effects of these two bilateral lesions is the primary concern of this paper.

The animals with large bilateral lesions of the frontal areas showed severe loss when tested on delayed reaction tests, although complete loss of this function was not demonstrated in any subject. Little or no loss was found on a series of tests of visual discrimination learning. The subjects with large lesions in the posterior association areas showed severe deficit on all of a series of tests of visual discrimination but showed little or no loss on delayed-response performances. Both groups of operated monkeys were inferior to the normal animals on the oddity problem, a complex learning test.

The findings indicate that delayed reaction behavior and visual discrimination behavior have foci and gradients of representation in different cortical areas. The quantitative nature of the deficits suggests that these intellectual functions are not represented exclusively in the frontal or posterior association areas. The extreme persistence of the deficits implies a stability of representation for these cortical areas that argues against recovery by vicarious functioning.

An Absolute Theory of Solid-State Luminescence

Ferd E. Williams, *General Electric Research Laboratory*

Previous interpretations of solid-state luminescent phenomena have been qualitative or phenomenological. The quantitative calculation from first principles of the properties of a simple phosphor would be a significant theoretical advance. This has been accomplished for the absorption and emission spectra of thallium-activated potassium chloride.

It is first recognized that the luminescence of this phosphor is confined to transitions within the monovalent thallium ion and that the bonding of the crystal is largely ionic. After calculating the radial charge densities of the free thallium ion in the ground and excited states by the Hartree self-consistent field method for the outershell electrons, and the Fermi-Thomas method for the core, the polarizabilities, ionic radii, and compressibilities of these ions are deduced. The thallium ion in its various electronic states is substituted in dilute concentration for the potassium in potassium chloride, and the change in total energy of the system is calculated as a function of the thallium nearest chlorine ion distance, with the condition that the remainder of the lattice rearranges to minimize the total energy. Madelung, exchange repulsion, van der Waals, polarization, and coulomb overlap interactions are included. The absorption spectrum is then computed by recognizing that the various atomic configurations of the system in the ground state have probabilities in accord with a Boltzmann function, and that the probability of a particular transition energy is determined by the probability of the configuration that results in that transition energy. The emission spectrum is similarly determined from a Boltzmann distribution of configurations characteristic of the excited state.

The absorption and emission spectra are computed at various temperatures, and the peak positions and half-widths are found to be in satisfactory agreement with experiment. In addition, new insight is obtained on the detailed mechanism of solid-state luminescence.

Recent Contributions to New York Archeology

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In 1944, on the basis of much previous field and laboratory research, the writer published a sequence, description, and analysis of the earlier aboriginal cultures of New York State. This covered 13 different cultural groups, all preceding the Iroquois in time, as known from excavations on some 70 Indian habitation and burial sites in the New York area (including Pennsylvania, New Jersey, New England, and lower Ontario). Continued work in this area on another series of sites by the writer and others since 1944 has amply confirmed the sequence of occupations and, furthermore, has contributed greatly to an understanding of the fine relationships and continuities among certain cultures. This has largely been achieved by the first systematic analysis of pottery typology for the area.

One of the results of this study has been a new hypothesis concerning the origin of Iroquois culture, previously derived by migration from an ultimate Ohio Valley source. It now seems more probable that the most recent cultures, ascribed to Iroquoian-speaking tribes, developed in large part out of previous cultures in the same area.

The more detailed picture of prehistoric events in New

York State, and the eastern United States in general, emerging from the aforementioned researches, has very recently been given a sounder chronological perspective through the radioactive carbon studies of Libby and Arnold, of the University of Chicago. The dates they have derived from charcoal samples, taken from hearths on archaic period sites in New York during the course of our excavations, indicate an antiquity for the earliest occupation of more than 5,000 years of elapsed time. Other equally startling dates have been obtained.

[*To be concluded October 20, 1950*]

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Technical Papers

Effectiveness of Cortisone Administered Orally[1]

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Since the report by Hench and his associates (*1*) that cortisone (Kendall's Compound E) has great antirheumatic properties, much research has been conducted to learn (1) how this hormone effects its results, and (2) how cortisone might be used with the greatest practical value as a therapeutic agent. In the latter category there have been studies to determine whether cortisone is effective when administered in ways other than intramuscularly, as it was used originally. Scarcity of the hormone has limited research but recently, through the kindness of its medical director, James Carlisle, Merck & Co., Inc., has supplied us with a small quantity of tablets (each 100 mg) of cortisone for clinical trial.

This preparation of cortisone has been tested in 4 patients with rheumatoid arthritis. The dose commonly employed for intramuscular injection was used orally, namely, 300 mg the first day, 200 mg the second, and 100 mg daily thereafter. In 2 patients the dose was increased to 200 mg daily, following a few days of 100-mg dosage.

In all patients cortisone taken in tablet form effected impovement in the rheumatic disease. In 2 patients cortisone tablets were given for only 10 days; the patients improved significantly from the 2nd day of treatment and relapsed promptly after cessation of the drug. The 3rd and 4th patients received tablets of cortisone for longer periods, 20 and 19 days, respectively. In each of these patients there was excellent clinical effect; the arthritic condition improved promptly and progressively, erythrocyte sedimentation rate was reduced to nearly normal, and general systemic improvement was gratifying. The 3rd patient previously had received cortisone intramuscularly during 2 periods of 23 and 20 days, and ACTH for 1 period of 14 days. In all respects the clinical effects of orally administered cortisone were comparable to those of this hormone given parenterally, and to ACTH. The 4th patient had prompt improvement during the first 3 days that cortisone was administered orally, then worsened somewhat. Consequently, the dose was increased to 100 mg twice daily and was continued at this level for the last 11 days it was administered. With the larger dose, improvement again progressed until there was nearly complete clinical arrestment of the arthritis. Subsequently, when this patient received cortisone intramuscularly in dosage similar to that employed orally, clinical response was comparable to that effected by cortisone taken orally. Both the 3rd and 4th patients volunteered preference for the tablets, because they considered the effects to be smoother than when the hormone was injected.

These observations clearly indicate that cortisone is effective when administered orally. This knowledge is indeed gratifying, especially in anticipation of practical therapy, for in patients with a chronic illness, such as rheumatoid arthritis, prolonged use of any drug should be facilitated by an effective oral preparation. At the same time *abuse* of tablets of such a potent hormone must be avoided.

Further studies of oral use of cortisone will be conducted as soon as supplies will allow.

Reference

1. Hench, P. S., *et al. Proc. Staff Meet. Mayo Clinic*, 1949, **24**, 181.

Cytological Changes in Human Hypophyses after Cortisone and ACTH Treatment

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Following injections of cortisone in patients with various diseases, microscopical changes have been noted in the anterior hypophyses at post-mortem examination. The relevant data concerning age, principal disease, total

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