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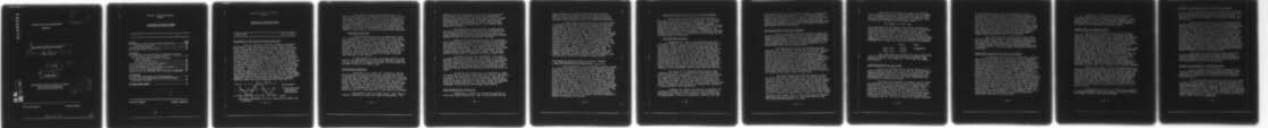
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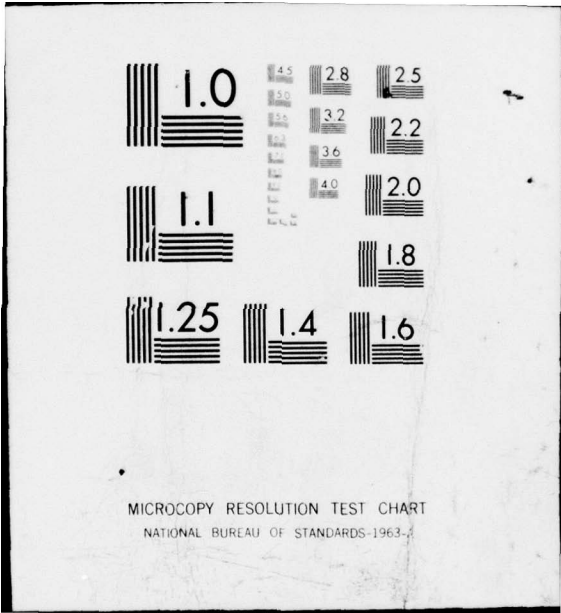
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EUROPEAN SCIENTIFIC NOTES

1951

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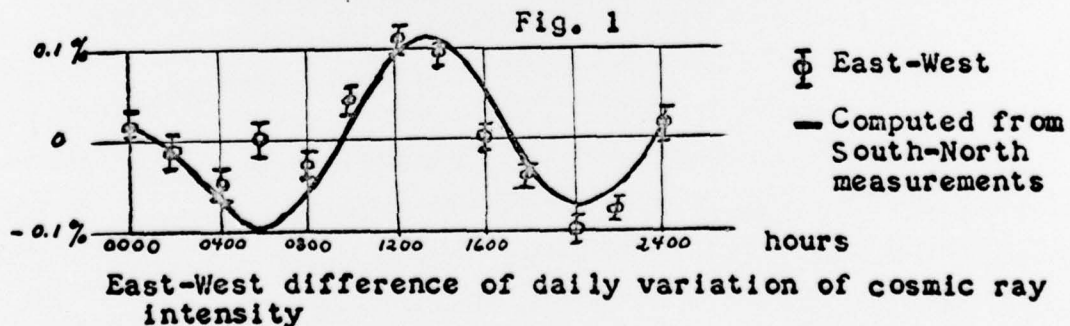
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ANISOTROPY OF THE PRIMARY COSMIC RADIATION

Drs. H. Elliott and D.W.N. Dolbear, Manchester University, have confirmed their former results (Proc. Phys. Soc. A, 62, 369 (1950)) on diurnal variation of the cosmic radiation at sea level by new data from shielded and unshielded cosmic ray telescopes. Their arrangement of two telescopes, inclined at 45° to the vertical, one pointing north, the other south, allows them to eliminate variations caused by atmospheric effects. They interpret the difference between the counting rates of the two telescopes to be a consequence of a non-isotropic distribution of the primary cosmic rays. This conclusion is strongly supported by measurements in which the same two telescopes are turned through 90° so as to point in the east and west direction. The same part of the sky is then scanned at successive times as the earth rotates, with a difference in time depending on the angle between the two telescopes. The hourly differences between the east and west telescopes, taken from data covering almost one year, are in very good agreement with the anticipated differences as computed from the north and south telescope data (see Fig. 1).



This lack of complete isotropy of the primary cosmic radiation is attributed to the solar streams which are assumed by some authors to cause geomagnetic disturbances and which are here assumed to be polarized in a solar magnetic field so as to provide acceleration or deceleration for cosmic ray particles traversing the stream. In support of this, Elliott and Dolbear have analyzed their data for magnetically disturbed days and found the amplitude of the daily variation much enhanced.

Variation with Time

From further analysis of the Manchester data, it is found that a small variation exists in the cosmic ray intensity as a function of sidereal time and this is confirmed by analysis of a large amount of ionization chamber data from Huancayo, Christchurch and Cheltenham. The sidereal daily variation thus found has an amplitude of about 0.02 percent with a time of maximum at about 0500 hr. This is opposite in phase to the variation expected on the basis of the Compton-Getting effect and therefore gives evidence against the origin of cosmic rays outside of our galaxy.

A full account of this work will appear in the Journal of Atmospheric and Terrestrial Physics, together with an account of atmospheric effects on the diurnal and seasonal variation of cosmic rays.

FLYING-SPOT MICROSCOPE

Professor J. Z. Young, Mr. F. Roberts, and Mr. David Causley at University College, London, have built a flying-spot microscope which they described very briefly in Nature 167, 231 (1951). The light source is a scanning raster on a "Flying-Spot Scanner Tube" built by E.M.I., Hayes, Middlesex. This is the type of tube commonly used in the flying-spot reproduction of movie films for television. This scanner tube (which has no manufacturer's number) is characterized by a rich blue and ultraviolet emission, and by a time-constant of less than 0.1 microsec.

The scanner tube is placed about a foot from an ordinary commercial microscope using no eye-piece. The

objective of the microscope images the scanning raster of the source on the object on the usual mechanical stage of the microscope. The light which passes through the microscope and the object is caught directly on a photomultiplier tube without the use of any condenser lens. The present photomultiplier is the VX5311 tube, also made by E.M.I.

The amplified signal from the photomultiplier tube is then displayed on a conventional television set. The present pictures contain 405 interlaced lines at a frame frequency of 50 cycles, using synchronizing signals picked up from the B.B.C. television stations.

Even in its present simple form, the apparatus gives outstanding results and one immediate application is for lecture demonstrations. It is planned to do routine counting of nerve fibres on the screen rather than from the customary photograph. The advantage of the instrument for this job is the large scale and brightness of the image, making a tedious task more simple. The flexible control of contrast is important to both of these uses.

The next plan for the instrument is to attach counting devices and modify the scan to see if it will be possible to do the counting of nerve fibres automatically. For this purpose, integration and pulse height discrimination of the electrical signal will be used and a study will be made of the possibility of distinguishing automatically among objects of different sizes in the field of view.

In the present instrument, no provision is made for matching the spectral characteristic of the combination of source and photo tube to the achromatic range of the objective. It is planned to use reflecting objectives as soon as suitable ones can be obtained. Among the problems which are being considered is the application of this technique to ultraviolet microscopy below 2000 Å.

LENS FLUCTUATIONS OF THE EYE

Professor A. Arnulf of l'Institut d'Optique in Paris has found recently that some of the failure of the

eye to achieve its theoretically maximum resolving power is due to fluctuations in the focal properties of the crystalline lens. Arnulf has demonstrated and measured these fluctuations by the following technique.

A very bright source of light is placed behind a pin-hole. This spot of light is watched steadily by a subject whose head is held rigidly with the aid of a mouth clamp. The retina of the eye is then examined through a half-silvered mirror, placed in the path of rays from the spot to the eye. The image of the spot of light is found to be a very tiny point, yellowish because of the color of the retina. When studied closely, this point is found not to remain stationary but to jitter slightly and at the same time to show rapidly-changing, randomly-oriented elongation. The fluctuations are estimated to be of about 1/10 of a diopter magnitude. The elongated images of the point tend to reach about $2\frac{1}{2}$ minutes of arc. Almost all the fluctuation takes the form of randomly-oriented elongation rather than symmetrical defocussing. Arnulf is studying this phenomena carefully to determine the manner in which it depends upon the physical condition of the observer and the extent to which it influences visual acuity.

THE MOLECULAR ORBITAL THEORY OF CHEMICAL VALENCY AND THE NATURE OF THE LIQUID STATE

The fundamentals of the molecular orbital theory of chemical valency were developed by Professor Lennard-Jones and his collaborators in a series of papers in the Proceedings of the Royal Society (1949, 1950). Several results of general importance have emerged. The spatial distribution of lone pair electrons in molecules such as water and ammonia was obtained and the part the electrons play in determining the equilibrium configuration of the molecules was evaluated. In contrast to previous treatments, it was shown that these electrons are concentrated on the side of the oxygen nucleus remote from the hydrogen atoms. Lone pair electrons thus make a very significant contribution to the dipole moment of such molecules. The theory suggests that in the equilibrium position the electronic structure of water can be described approximately by two sets of two equivalent orbitals pointing in nearly tetrahedral directions.

Molecular Association due to Lone Pair Electrons

The results summarized above were applied by Mr. J. A. Pople and Professor Lennard-Jones to a study of molecular association phenomena in liquids. If the lone pair electrons are distributed in localized regions, they will form regions of negative charge which can attract positively charged systems in their neighborhood. One, or usually two positive systems, may be attracted to this charged region of the water molecule. Considering hydrogen bonding in this manner, it can be seen to be primarily due to electrostatic attraction.

The Structure of Water

Extending this work, a detailed and very satisfactory theory of the water structure was developed by Mr. Pople. This is based essentially on a careful consideration of the flexible nature of hydrogen bonds between water molecules and of the effect of the bending of such bonds on the structure of the system. The primary difference between ice and liquid water according to this view is that in ice, due to the rigid long range order, adjoining hydrogen bonds can only bend in a cooperative manner, whereas once the long range order is broken down by thermal vibration and fusion has taken place the individual hydrogen bonds become independent of one another. Due to this increased freedom of the individual hydrogen bonds in water, unoccupied regions may become occupied, leading to the well-known volume diminution upon melting.

The value of the hydrogen bond bending force constant used leads to a frequency of the order of 200 cm^{-1} , which appears reasonable. To a first approximation, the distortion of the bonds in water was found to be of the order of $26-30^\circ$. The radial distribution functions were also evaluated and the importance of hydrogen bond distortions on the contributions of the second, third, etc., shells of molecules was found to be temperature dependent in good agreement with experiment.

Finally, the theory was applied to estimate the dielectric constant of liquid water. Good quantitative agreement was obtained with experiment over a wide range of temperature. This good agreement, together with the

very high value of the dielectric constant, is additional evidence for the correctness of the tetrahedral coordination on which this theory is based. Using the electrostatic model developed for the hydrogen bonds in this theory, the energy of the hydrogen bond was estimated from fundamental constants to be about 6 Kcal.mole⁻¹, again in good agreement with experiment.

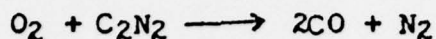
THE DISSOCIATION ENERGY OF NITROGEN

Dr. A. G. Gaydon, Imperial College, London, has recently discussed the current status of the dissociation energy of nitrogen. Spectroscopic evidence coupled with recent thermochemical results obtained on cyanogen flames very strongly favors the value of 9.76 electron volts for the dissociation energy of the nitrogen molecule to its constituent atoms in the ground state.

The dissociation energy of nitrogen has been uncertain for some years. During the last decade the two favored values have been 9.76 e.v. and 7.35 e.v. These values are known very precisely from predissociation spectra and the difficulty of choosing between them is due to the difficulty of deciding the level of excitation of the dissociated atoms. In reviewing the evidence, Dr. Gaydon discussed the Birge-Sponer extrapolation of the first absorption system of the singlet ground state, three predissociations and thermochemical results. The Birge-Sponer extrapolation leads to a value of 9.76 e.v. Since the extrapolation extends only from about 6.3 e.v. this would have to be a very anomalous case if it were to be fitted to the lower value of 7.35 e.v.

The three predissociations are known to occur at 12.14, 9.76 and at about 9.8 e.v. The first one of these is that in the C³π upper level of the strong second positive system. The second one is that in the B³π upper level of the first positive bands, while the third one has recently been discovered by Herzberg as a very weak band which occurs in the A¹π_g level. While in the first analysis these predissociations could be best interpreted as leading to a value of 7.35 e.v., Dr. Gaydon has already given an alternative explanation in terms of a 5Σ⁺_g level leading to the higher value. This level might be responsible for the predissociation of B³π and also of A¹π_g (cf. Dissociation Energies, p. 157).

Very strong independent evidence has recently been obtained by Dr. Leo Brewer (Berkeley) and Mr. Thomas in Dr. Gaydon's laboratory supporting the value of 9.76. They have determined the temperature in a cyanogen flame in which the following reaction takes place:



The temperature of the flame in the region immediately above the cone was determined by means of the vibrational intensity distribution of the cyanogen bands and was found to be $4800 \pm 300^\circ\text{K}$. The high energy evolved in this flame reaction goes largely into the specific heat terms of the components and calculating the expected flame temperature on the basis of the two possible dissociation energies for nitrogen the following results are obtained:

	$T_{\text{calc.}}$	$T_{\text{obs.}}$
D(N ₂) 9.76	4850°K	4800±300°K
D(N ₂) 7.35	4350°K	

The value recently obtained for the dissociation energy of the N-N bond in hydrazine also supports the value of 9.76 e.v. for D(N₂) (cf. Proc. Roy. Soc. A198, 267 (1949)).

OXYGEN EXCHANGE WITH ZINC OXIDE

Mr. J. A. Barnard and Dr. E.R.S. Winter of Imperial College, London, have found that in the exchange of oxygen with zinc oxide two processes are operative. The one below about 500°C has an activation energy of about 35 Kcal.mole⁻¹ while the one above that temperature has practically no activation energy.

The mass spectrographic technique used to study the exchange of O¹⁸ with solid oxides was developed and described by Dr. Winter previously (cf. Faraday Society Discussion on Heterogeneous Catalysis, p. 231). The technique involves essentially the determination of the ratio of the oxygen isotopes as a function of time in a system in which solid oxide is kept at a constant temperature with a fixed pressure of the enriched oxygen gas in contact with it. The solid oxides are always degassed

at temperatures higher than the temperature of the measurements. The runs made after different degassing temperatures yielded different reaction velocities without any change in the observed activation energies. The results obtained on zinc oxide are qualitatively similar to those found for chromic oxide (cf. loc. cit.). In both cases, two activation energies are obtained of which the high one is ascribed to the desorption of oxygen from the oxide surface, while the essentially zero activation energy probably represents the true exchange reaction. This probably involves exchange between chemisorbed oxygen atoms and oxygen ions in the surface.

The temperature of the inflection point indicating change in activation energy depends inversely on the degassing temperature. It is planned to investigate the kinetics of oxygen adsorption and desorption to elucidate further the mechanism of these reactions. It is planned also to study the oxygen exchange on vanadium pentoxide.

ROTATIONAL ISOMERISM AND CRYSTAL STRUCTURE

Interesting observations on rotational isomerism and crystal structure have been made by Dr. N. Sheppard and J. K. Brown, Cambridge University, in the course of their systematic investigations of the infrared absorption spectra of liquid and solid α, ω -dihalogenated paraffins. When 1,3-diiodopropane is frozen rapidly, a number of bands disappear from the spectrum. This behavior is similar to that of numerous other compounds capable of existing in several rotational isomeric forms. This crystalline form, which probably consists of zigzag, trans chains, is not stable, however. Upon warming, it transforms spontaneously into the stable crystalline form, which can also be obtained by slow cooling of the liquid phase. The spectrum of this form contains essentially those absorption bands which were present in the liquid but disappeared upon rapid freezing. This suggests that this stable form contains the molecules in the other rotational isomeric form, i.e., in some bent modification. It is planned to study these crystals by means of X-ray crystallography. If confirmed, this is the only known case of rotational isomerism yielding two different crystalline modifications.

Crystalline 1,5-dichloropentane consists of the trans rotational isomers while crystals of the analogous bromo and iodo compounds again contain a bent, gauche isomer. In none of these cases, however, has it been possible so far to produce more than one spectroscopically distinguishable crystalline form.

QUANTUM YIELD IN PHOTOSYNTHESIS

Dr. Dean Burk, National Institute of Health, Bethesda, and Dr. Otto Warburg, of the Kaiser Wilhelm Institut fur Zellphysiologie, have found that the quantum yield for the conversion of carbon dioxide to oxygen in the process of photosynthesis has a value of one. This conclusion is reached from experiments in which *Chlorella* was illuminated intermittently and monochromatically with light of high intensity. The radiation was accomplished by the two-vessel method previously described. The exposure times were one minute, alternating with one minute of darkness. During irradiation, 1 mole of absorbed light quanta causes the absorption of 1 mole of carbon dioxide and the liberation of 0.8 to 1 mole of oxygen. In the dark, the reverse process occurs. This combustion process in which oxygen is converted to carbon dioxide is proportional to the light intensity in the light period. The two reactions are thus mutually dependent on each other and together form a cyclic process.

Thus, in the light, 1 mole of carbon dioxide is obtained per mole of absorbed quanta, but $2/3$ of this gain is used in the combustion phase of the cyclic process so that the net gain amounts to only $1/3$ mole of carbon dioxide per mole of quanta. Through this cyclic mechanism the quanta of visible light accomplish a photochemical reaction that requires approximately three times the energy of a single light quantum. The results have been shown to be independent of wave-length by experiments in the blue (436m μ) and the red (644m μ), as well as in the green (546m μ).

A preliminary account of this work has appeared in *Naturwissenschaften* 37, 560 (1950), and further details will appear in *Zeit. fur Naturforschung*.

SYNTHESIS OF THE PENTOSES FROM GLYCOLLIC ALDEHYDE

Drs. J. K.N. Jones and L. Hough of the Chemistry Department, University of Bristol, have discussed recently the biosynthesis of monosaccharides, with particular emphasis on glycollic aldehyde as a precursor (Nature 167, 180 (1951)).

In this connection, Dr. Jones has been studying the in vitro synthesis of the pentoses by condensation of glycollic aldehyde with glyceraldehyde or dihydroxyacetone, and this work will form the basis of a series of papers to appear in the Journal of the Chemical Society. While the mixture, "Formose", obtained by boiling a solution of formaldehyde with calcium carbonate, was found by chromatographic examination to be a very complex mixture, the condensation of D-glyceraldehyde with glycollic aldehyde in alkaline medium at room temperature produces a relatively simple mixture from which all four aldopentoses have been isolated. The D-glyceraldehyde undergoes racemization in the alkaline medium with the result that the DL- as well as the D-sugars are formed; arabinose and xylose predominate. Dihydroxyacetone likewise undergoes condensation with glycollic aldehyde to yield the aldopentoses.

The sugars were identified by paper partition chromatography and separated on columns of cellulose. Further identification of DL-arabinose and DL-xylose was achieved through preparation of derivatives from which the crystalline sugars were regenerated.

MIRICIL D IN TREATMENT OF SCHISTOSOMIASIS

Dr. J. Newsome of the Bilharzia Research Unit of the Medical Research Council, Egypt, presented a paper recently at a meeting of the Royal Society of Tropical Medicine and Hygiene on the treatment of schistosomiasis with miricil D.

The thioxanthone derivative, miricil D, was shown to have a marked curative effect in patients infected with Schistosoma haematobium, but the action of this drug was less pronounced against S. mansoni. The pharmacologic side effects of miricil D were reduced by giving coated tablets. Discussions from the floor, however, indicated that clinical symptoms produced in patients in the Philippine Islands were severe enough to cause abandonment of the drug as a therapeutic agent against S. japonicum.

Tests in vitro on S. mansoni have shown that a maximum blood concentration of 4 to 5 mg. per ml. for 4 days is necessary to kill adult schistosomes. The salicylate of miricil D gives good absorption and high blood levels. Extraction of feces further indicated that the salicylate was better absorbed than the naphthoate. It appears that the naphthoate which has no taste and causes very slight symptoms may turn out to be adequate for mass treatment in those areas where bilharzia infections are not so severe as they are in Egypt.

A combination of three tests for cure was used for patients with haematobium or mansoni. These were by routine microscopy, improved urine examinations, and a rectal scraping technique.

IDENTIFICATION OF ANOPHELES BY SALIVARY GLAND CHROMOSOME PATTERNS

Early in 1947, Dr. Guido Frizzi of the Istituto di Zoologia e Genetica, Università di Pavia, Italy, reported considerable success in "mapping" salivary gland chromosome patterns in fourth instar anopheline larvae (Nature 160, 226 (1947)). Since that time, he has continued his investigations to determine whether comparative karyology might not provide an additional tool in the study and identification of geographic, ecologic, and physiologic variants within the genus Anopheles. Dr. Frizzi has completed studies on Anopheles maculipennis var. atroparvus and has made direct comparisons of the salivary gland patterns of elutus, typicus and messeae. It appears that his techniques, once the general patterns are recognized and identified, can be used to facilitate identification and control of malaria vectors in the maculipennis complex of anophelines in Europe.

In hybrids obtained from crosses with female typicus and male atroparvus, the salivary gland chromosomes show a heterozygous inversion in the III chromosome's "right" arm. The three chromosome pairs are incompletely paired and unpaired segments are more numerous and more extended. It would appear that the total or partial sterility of hybrids within the maculipennis species is correlated with chromosomal rearrangements.

Studies are planned to "map" and compare the patterns of representatives of the maculipennis stock known to occur in the United States.

PERSONAL NEWS ITEMS

The first Louis Rapkine Memorial Prize has been awarded to Dr. Gerald Oster. Dr. Oster is currently continuing his researches in biophysical chemistry at the Institut de Biologie Physico-chimique in Paris in the laboratories of Professor Wurmser.

Professor Georg Maria Schwab has accepted the chair of Physical Chemistry at the University of Munich. He has been director of the Physico-Chemical Institute at Pleacus, Greece, during the past 15 years and has recently returned to Munich.

At a recent Chemical Society meeting, it was announced that Professor C. K. Ingold is the recipient of the Longstaff medal for 1951.

The Walter Rosenheim Medal was awarded to Professor G. V. Raynor of the University of Birmingham, for his outstanding contributions in the field of physical metallurgy.

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