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EUROPEAN SCIENTIFIC NOTES

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SPECIFIC HEAT OF SOLID HYDROGEN

Dr. R. W. Hill (Oxford University) has recently completed measurements of the specific heat of solid hydrogen down to about 1°K and has observed a λ -point, which has been correlated with an orientation of the molecular rotations in the orthohydrogen component. The measurements were made with the hydrogen in a small calorimeter immersed in a liquid helium bath, the temperature of which was maintained by pumping the helium.

In the first set of experiments, the specific heats of various samples with different ortho-concentrations were determined over the range 12° to 2°K, the latter being the lowest temperature which could be reached because of the heat generation in the sample from the ortho-para conversion. The results are shown in Fig. 1, where the curve for 0.5 per cent ortho-concentration is

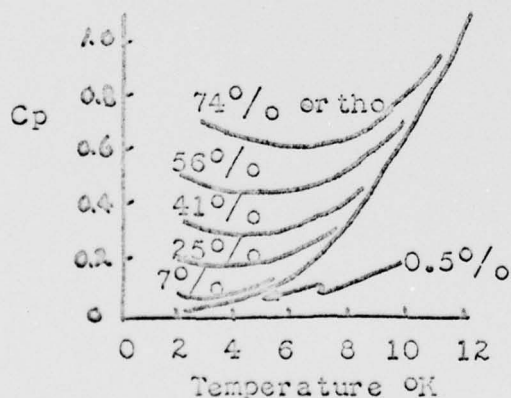


Fig. 1. Specific Heat of Solid H₂ for Various Ortho-Concentrations.

in agreement with what one would expect for pure para-hydrogen, showing the behavior of a system of weakly interacting particles. These results corroborate earlier measurements of the specific heat of hydrogen in this region, but they are more accurate and in addition clearly show the effect of varying the ortho-concentration. The anomalous part of the specific heat is found to be proportional to the square of the concentration of the ortho-component, a fact which suggests that it is the ortho-ortho interactions which are important here.

With an improved design of the equipment, Hill was able to extend the measurements to lower temperatures, although because of the heat generated by the ortho-para conversion, the lowest temperature reached with normal hydrogen (75 per cent ortho) was 1.5°K. In this set of experiments the temperature of the hydrogen specimen was followed as a function of time during warm-up, and it was assumed that there was a constant source of heat to the specimen, namely the ortho-para conversion heat. No other heat was supplied to the specimen. The specific heats of two samples, i.e., 66 per cent ortho and 74 per cent, are plotted in Fig. 2 for the range 1° to 2°K; it is seen that both curves show a λ -point, the position of which (T_c) is dependent on ortho-concentration. By integrating the specific heat curve from the lowest measured temperature up to about 1.2°K, it is found that the anomalous specific heat contributes an entropy just slightly less than $R \log 3$ per mole, which is the entropy one would expect from an orientation of the molecular rotations in the solid.

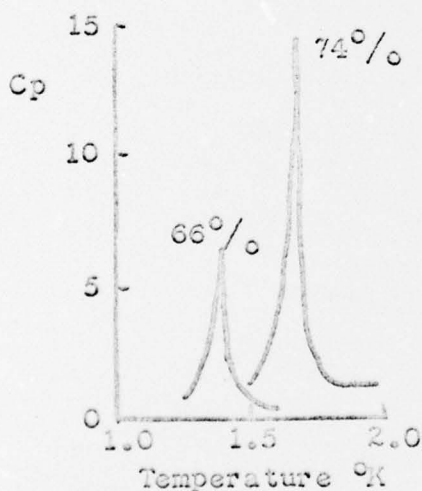


Fig. 2.
Specific Heat of Solid
 H_2 in cal. deg⁻¹ mole⁻¹
for two ortho-concentrations.

Other possible causes of the observed specific heat anomaly were investigated. The intermolecular forces in the solid and the forces tending to align nuclear spins are too small to have a direct effect. If the effect were due to mixing, there should be a maximum in the anomaly for 50-50 ortho-para mixtures, which is not observed.

The interpretation of the specific heat anomaly as an orientation of the molecular rotations of the ortho-component is in accord with the measurements of nuclear magnetic resonance in solid hydrogen by Hatton and Rollin and by Reif and Purcell. The latter authors (Phys. Rev. 91, 631 (1953)) have explained the observed line shape in the resonance as arising from the magnetic dipole interaction of the two protons in the hydrogen molecule, provided one also takes into consideration the effect of the crystalline potential which lifts the rotational degeneracy of the ortho-molecules in the solid. In particular, the $J = 1$ state of the ortho-molecules is broken up into two sublevels, $\bar{m}_J = 0$, $\bar{m}_J = \pm 1$, which differ in energy by $V = (2/5)A$, where $W = -AP_2^0(\cos\theta)$ is the approximate crystalline potential. Here P_2^0 is a spherical harmonic. The orientation of the molecular rotations is thus equivalent to the orthohydrogen going into its lowest, $\bar{m}_J = 0$, state.

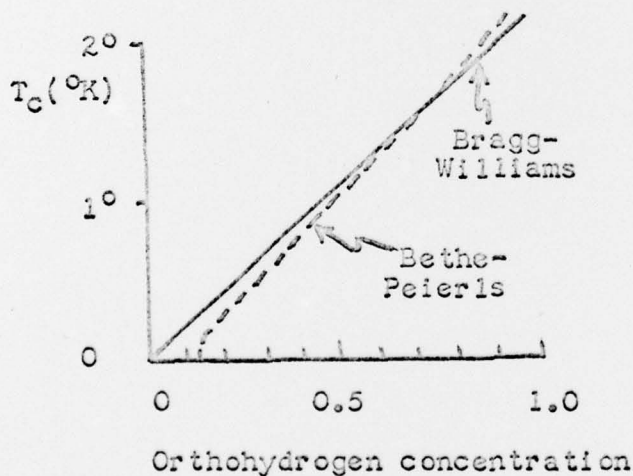


Fig. 3.
Calculations by Tomita of T_c as a function of ortho-concentration.

Rotational Sublevel Splitting in Solid Hydrogen

Dr. K. Tomita (Oxford) has calculated the level splitting, V , of the $J = 1$ state, which is equivalent to determining the crystalline potential, on the basis of various models. From the spin-lattice relaxation time expressed as a function of the mean life of a molecular orientational configuration, Tomita has obtained $V \approx 3^\circ$ to 4°K . From a calculation of the intermolecular forces including overlap forces, quadrupole-quadrupole forces, induced dipole-dipole forces, and induced dipole-quadrupole forces and from an analysis of the width of the resonance, he has obtained $V = 4.08^\circ$ and 4.10°K respectively. Finally he calculated the concentration dependence of the λ -point (T_c), and obtained therefrom $V = 4.02^\circ\text{K}$. For this last calculation, Tomita used an order-disorder treatment in which the magnitude of the axial symmetric field in the crystal is proportional to the concentration of orthohydrogen present. The resulting dependence of T_c on ortho-concentration is shown in Fig. 3. In all of Tomita's calculations, it was assumed that the crystal structure of solid hydrogen is hexagonal-close-packed, such as has been determined for solid parahydrogen.

THE SCATTERING OF FAST MUONS BY LEAD

Mr. I. B. McDiarmid of the University of Manchester has used an 18-inch cloud chamber to investigate the scattering of fast μ -mesons in six lead plates each of 2 cm thickness and placed in the cloud chamber which was operated underground at a depth of 26 meters water equivalent. The momentum distribution of the μ -mesons was determined from multiple scattering, and the μ -mesons were then separated into groups. A stereoscopic camera subtending an angle of 15° was used, but in measuring the angles of deflection the plane-projected angle was observed. The noise level of the chamber had a standard deviation of $1\frac{1}{2}$ degree. The first figure gives McDiarmid's results for the group of mesons of average energy 1000 Mev and a spread in energy of ± 500 Mev which made 1508 traversals of a 2 cm lead plate. The probability of a scattering greater than the angle θ is plotted as a function of the angle θ . The theoretical curve labelled "point nucleus" is drawn in both magnitude and angular dependence from the theory of Moliere as re-presented by

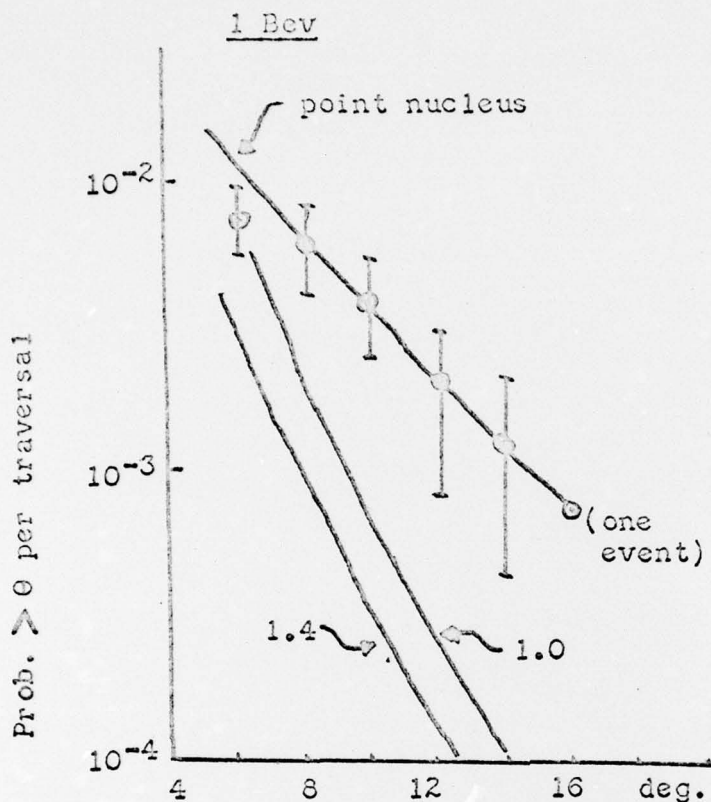


Fig. 1. Projected Angle θ

Bethe (Phys. Rev. 89, 1256 (1953)). The multiple scattering correction is important only for the lowest angle in this figure. The other curves are plotted from the theory of Olbert (Phys. Rev. 87, 319 (1952)) which takes into account the finite size of the nucleus and correspond to nuclear radii of $1.4 \times 10^{-13} A^{1/3}$ and $1.0 \times 10^{-13} A^{1/3}$ cm.

The results are even more striking for the high energy group where the energy distribution of the μ -mesons for this process lies between 3 and 4 Bev. In this case 18,000 traversals of the 2 cm plates have been observed and the second figure shows the actual number of deviations observed greater than θ as a function of θ .

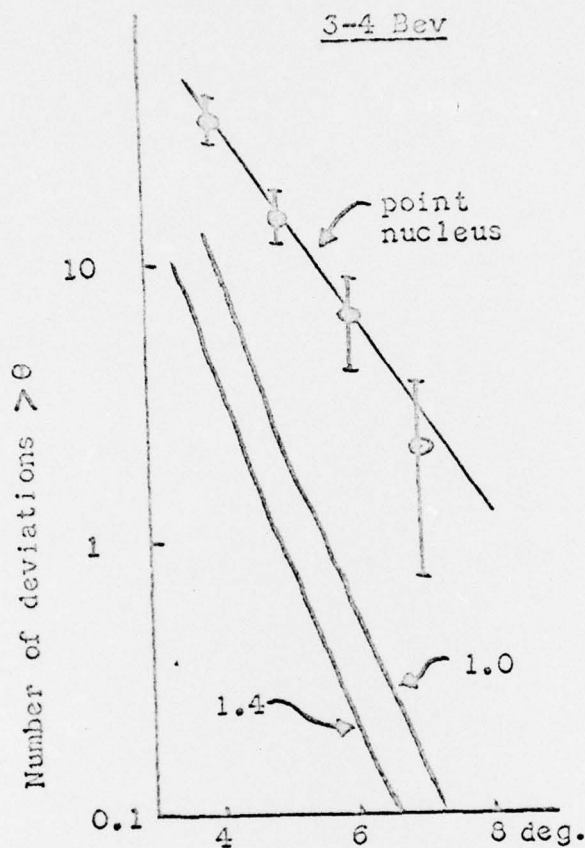


Fig. 2.

Projected Angle θ

Here again the agreement with the predictions of the point nucleus is well within experimental error. It is to be noted that the wavelength of these mesons is quite small compared to the nuclear radius and that presumably the nuclear interaction is negligible.

NUCLEAR INTERACTION OF K MESONS

One of the interesting points about the characteristics of K mesons as observed in photographic emulsions has been their apparent lack of interaction with nuclei (see, for example, Proceedings of the Cosmic Ray Conference at Bagnères, July 1953). Cloud chamber evidence indicates that positively

and negatively charged V-particles occur in approximately equal numbers. The particles appear to be directly created in nuclear interactions and therefore one would expect them to be strongly interacting and produce nuclear disintegrations when brought to rest in solids (at least the negatively charged ones). Very few such disintegrations have been found although extensive searches have been made.

Mr. J. V. Major of the University of Manchester has observed two events in photographic emulsions which appear to represent the nuclear interaction of K^- mesons. The particles definitely appear to be slowing down as the disintegration is approached. The first particle has a range of 1616 microns and an apparent mass of 1500 ± 600 according to the method of Menon and 830 ± 90 referred to a typical proton by the method of gap counting and range. Its secondaries are as follows:

Particle	Range	$p\beta$ (Mev/c)	g^*	Identification	K.E.
a	7	96 ± 15	$1.16 \pm .04$	π or μ	55 ± 10 Mev
b			black	p, d or α	> 15 Mev

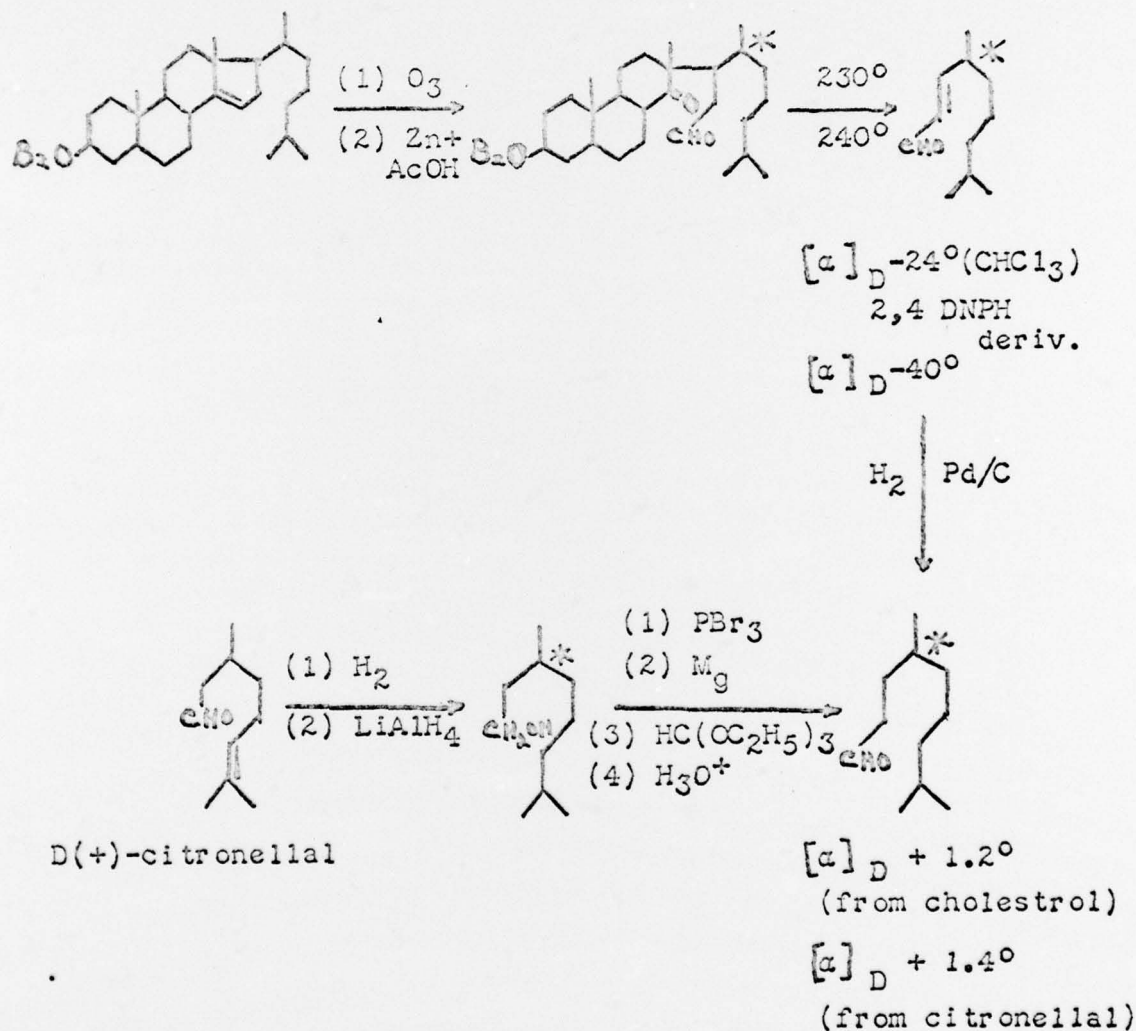
The second particle has a range of 1560 microns and an apparent mass of 1240 ± 400 according to the method of Goldsack and 1030 ± 300 by photometric measurement. The ionizing disintegration products are two protons and an alpha particle with a total kinetic energy of about 20 Mev.

ABSOLUTE CONFIGURATION OF THE STEROIDS

A group under the immediate supervision of Dr. O. Jeger at the Federal Institute of Technology in Zurich has succeeded in relating cholesterol to D(+)-glyceraldehyde by an ingenious series of degradations. Since the relative configuration of the various asymmetric centers in the important steroids, including cholesterol, is known (for an excellent review and critical discussion of the stereochemistry of the steroids see chapter 10 by Dr. R. B. Turner in "Natural Products Related to Phenanthrene", Fieser and Fieser, 3rd ed., Reinhold Publishing Corporation, N.Y. (1949)), this constitutes a complete determination of the

stereochemistry of the steroids related to the arbitrary standard D(+)-glyceraldehyde. The absolute configuration of D(+)-glyceraldehyde has been settled by the work of J. M. Bijvoet (*Nature* 168, 271 (1950)), who determined directly the absolute configuration of sodium rubidium tartrate by X-ray methods; therefore the absolute stereochemistry of the steroids is now established.

The starting point in the degradation sequence carried out by Jeger was Δ^{14} cholesteryl benzoate. After disruption of the D-ring by ozonization, the side-



chain and carbons 15, 16 and 17 were eliminated at 230°-240°C by a reverse Michael reaction. The same degradation had been reported previously, but Jeger's group made the rather surprising discovery that the eliminated unsaturated aldehyde fragment possessed considerable optical activity. Hydrogenation over palladium on charcoal leads to a saturated aldehyde with definite but low optical activity, which proved to be identical to a sample prepared independently from D(+)-citronellal. Since the asymmetric center in D(+)-citronellal has been related to D(+)-glyceraldehyde the proof of configuration at C₂₀ of the original cholesterol derivative is complete. The reaction sequence is outlined in the accompanying diagram. D(+)-citronellal was hydrogenated to the corresponding saturated aldehyde, which was further reduced to the carbinol by lithium aluminum hydride. Homologation was accomplished by conversion through the bromide to the Grignard reagent, which was treated with ethyl orthoformate.

It is expected that knowledge of the absolute configuration at each of the asymmetric centers in the steroid nucleus will be helpful in working out possible biological relationships among the terpenes, steroids and simpler carbon precursors.

AGARD COMBUSTION COLLOQUIUM

A Colloquium on Combustion, organized by AGARD (Advisory Group for Aeronautical Research and Development) and held at Cambridge, England, December 7 - 11, 1953, embraced the following subjects: laminar flame propagation, turbulent combustion, solid and liquid propellants, and technical combustion problems. The Colloquium ended with a round table discussion on fundamental aspects of the problem. Prof. T. von Karman, Chairman of AGARD, was chiefly responsible for the organization of the meeting and presided over the Colloquium as a whole; all NATO countries were represented by scientists active in the field, the largest delegation from abroad being that from the United States. The complete proceedings of the Colloquium will be published in a book available to interested scientists at no charge through their national representative in AGARD; in the United States distribution of these proceedings will be handled by the National Advisory Council for Aeronautics, Washington, D. C. A few of the conclusions will be briefly summarized below, while

a somewhat more detailed account of the meeting constitutes Technical Report ONRL-11-54.

The current status of the theory of the laminar flame appears to be that the thermal flame theory of a simple reaction neglecting diffusion is well understood. The contributions of von Karman and Penner, based on the earlier work of Hirschfelder, treat the case of a simple reaction with diffusion satisfactorily and make some progress towards the problem of multiple reactions. In most practical flames, however, branched chain reactions occur and none of the theories developed so far take satisfactory account of these. It seems clear, as was pointed out by Dr. Marjorie Evans (Stanford), that little further progress can be made until studies of high speed flame kinetics provide more positive knowledge of reaction mechanisms and reaction rates.

The contributions and discussion on turbulent combustion indicate the need for strict distinction between two types of flame turbulence: if the unburnt gas itself is turbulent, this will affect its physical properties so as to increase the flame speed, while turbulence may also be created by the flame itself.

Combustion of Solid Propellants

An interesting variety of problems was discussed in the session devoted to solid and liquid propellants. Drs. G. K. Adams and L. A. Wiseman (ERDE, Waltham Abbey, England) showed that the combustion of the simpler, liquid nitric esters provides correlations between rate of burning, chemical structure, and heat of explosion. In the field of solid propellants, a deeper understanding of solid phase reactions is an obvious need to enable us to draw useful conclusions concerning the improvement of solid propellants. The temperature of the burning surface was one of the chief topics of interest and several investigators quoted temperatures of the order of 800°C - 1000°C on the surface of a burning solid; these are considerably higher than those preferred by most investigators in the past. Prof. A. R. Ubbelohde (Belfast) raised a fundamental question regarding this point: in many cases it is open to doubt whether or not the burning surface corresponds to a liquid or a solid phase.

Recently developed experimental techniques which promise valuable new information on solid propellant

combustion are the reflection electron microscope and rapid infrared spectroscopy using a pneumatic detector. Dr. J. W. Menter, working in Dr. F. P. Bowden's laboratory (Cambridge) developed a simple reflection electron microscope which avoids the necessity of the replica technique and thus permits the continuous observation of changes occurring on solid surfaces (see ESN 8, 36 (1954)). Prof. B. L. Crawford (Minnesota) described briefly the infrared spectrograph with which it is hoped to observe the intermediate species occurring in the chemical reactions in solid propellant flames. The instrument is not as rapid as some others currently in use; the use of a pneumatic detector, however, permits study of a much larger region in the infrared than is possible with photoconductive cells.

A KINETIC STUDY OF THE EXCHANGE BETWEEN BLOOD AND BRAIN
COMPARED WITH EXCHANGE BETWEEN BLOOD AND AQUEOUS HUMOR

Dr. H. Davson, Medical Research Council, Department of Physiology, University College, London, has compared in a given rabbit the rates of penetration of a number of substances from blood to aqueous humor and from blood to the cerebro-spinal fluid (c.s.f.). For very slowly penetrating substances, such as raffinose and p-amino-hippurate, the rates of penetration differ by a factor of at least 20, the amounts penetrating the c.s.f. being barely measurable; as the rate of penetration increases, the discrepancy becomes smaller and eventually changes sign, in the sense that penetration into the c.s.f. is the more rapid.

Thus with creatine, which penetrates the aqueous humor some 3 times more rapidly than raffinose, the ratio of the rates of penetration into the aqueous and the c.s.f. is 5; with Na^{24} it is approximately 2; with thiourea it is 1.3; with methyl thiourea it is approximately unity; while with ethyl thiourea, propyl thiourea and ethyl alcohol it is 0.65, 0.65 and 0.16 respectively. The behavior of glucose is exceptional in that it penetrates the aqueous humor approximately as rapidly as ethyl thiourea, but penetrates the c.s.f. at only about one third this rate. When penetration into the brain tissue is compared with penetration into the c.s.f., it is found that Na^{24} approaches equilibrium with the cerebral interstitial fluid (chloride-space) at almost exactly the same rate as with the c.s.f.

With all the other substances studied (creatinine and the thioureas) the concentration in the cerebral interstitial fluid is consistently higher than in the c.s.f., and the times required for complete equilibration between total brain water (excluding c.s.f.) and blood plasma are very much shorter than for equilibration between c.s.f. and plasma; e.g. with methyl thiourea equilibration with brain water occurs between 60 and 120 min, whereas equilibration with c.s.f. requires over 4 hr. With these substances, therefore, the cerebral interstitial fluid may act as an intermediary between blood and c.s.f., so that the direct process of penetration from blood to c.s.f. in the choroid plexuses and the subarachnoid spaces may be augmented by a penetration from the cerebral tissue. It is possible that this circumstance could account for the change in the aqueous/c.s.f. rate-ratio as the rate of penetration increases.

The penetration of Na^{24} into the c.s.f. follows the simple kinetics previously described for the aqueous humor, the value of the rate constant, derived from experiments on sixty-eight animals and extending in duration from 15 - 300 min, was 0.0046 min^{-1} , compared with a value of 0.0084 min^{-1} for the aqueous humor. The steady-state distribution ratio between plasma and c.s.f. is approximately unity, whence it may be deduced that the maximum rate of turnover of c.s.f. is 0.46 per cent per min, i.e., rather more than half the value that may be computed from similar parameters describing penetration into the aqueous humor of the same animals. The rate of turnover of c.s.f. may, however, be considerably less than the maximum value indicated above.

HISTAMINE LIBERATION AND LYMPHAGOGUE ACTION

Prof. W.D.M. Paton of the University College Hospital Medical School, London, has recently conducted experiments to determine whether extracts of lobster, crayfish, and mussels can release histamine, and whether known histamine liberators are lymphagogues. R. Heidenhain (Pflug. Arch. ges. Physiol. 49, 209-300 (1891)) described a variety of substances including extracts of these three animals as "lymphagogues of the first order".

Alcoholic extracts of the muscle of lobsters, crayfish, and mussels were prepared by Heidenhain's method. It was found that when the extracts were injected into the cat's isolated perfused skin they released

histamine (assayed on the guinea-pig ileum) in amounts corresponding to about 50 µg histamine per gram of flesh. From these data it was calculated that a whole lobster might thus release 5-10 mg of histamine.

In cats anaesthetized with chloralose, in which the thoracic duct was cannulated for lymph-collection, the intravenous injection of propamidine, D-tubocurarine or morphine, for example, caused an increase in the rate of flow of lymph from the duct up to twenty-fold. With successive injections of the same dose, the lymphagogue action waned. It was concluded that the lymphagogue action of these substances, as well as some of the known effects of over-indulgence in crustacean delicacies, rests on their ability to release histamine from the tissues.

EFFECT OF SUCCESS OR FAILURE ON PERSONALITY

A book entitled "Tache, Reussite et Echec, Theorie de la Conduite Humaine" ("Task, Success and Failure - A Theory of Human Behavior") by J. Nuttin, Professor of Psychology, University of Louvain, has just been published by Publications Universitaires de Louvain, Standard-Boekhandel N.V., Belgium. In this book Prof. Nuttin is concerned primarily with the problem of how failure or success in a given situation influences the personality as well as the behavior of the one who acts. Nuttin attempts to show, among other things, how success and failure influence the conception that man has of himself (self-concept), by examining the personality factors which affect and distort the perception of success and failure. Nuttin draws upon the findings of both clinical and experimental psychology. Many of the author's own experiments on human learning are described and the results are used in the development of a new interpretation of the laws of effect and reinforcement. Nuttin proposes a theory of learning which represents a compromise between the cognitive theory of Tolman and the reinforcement theories of Thorndike and Hull.

CONFERENCE ON OXIDATION

A Joint Conference of the Institution of Chemical Engineers (London) and the Chemical Engineering Group of the Society of Chemical Industry (London) with the Royal

Institution of Engineers of the Netherlands (Chemical Engineering Group) and the Royal Netherlands Chemical Society (Section for Chemical Technology) will be held at The Hague on May 6 - 7, 1954. The Conference will deal with Oxidation Processes and will include reports of current research from various university and industrial laboratories in Great Britain, the Netherlands and Germany. The Pergamon Press of London plan to publish the full Proceedings of the Conference shortly afterwards.

FOURTH WORLD PETROLEUM CONGRESS

The permanent Council of the World Petroleum Congress has decided to hold the fourth such Congress in Rome on 6 - 15 June, 1955. Further information regarding the organization, agenda, etc., of this Congress is available from the General Organizing Committee, Fourth World Petroleum Congress, Via Tevere 20, Rome, Italy.

CONFERENCE ON DISLOCATIONS IN CRYSTALS

A two-day Conference on the Mechanical Effects of Dislocations in Crystals will be held at the University of Birmingham on 19 - 20 July 1954. It will follow and be complementary to the Bristol Conference which will consider chemical aspects of dislocations in crystals. The Conference has been organized by the Department of Metallurgy at Birmingham and is under the chairmanship of Prof. A. H. Cottrell.

BRITISH ABSTRACTS OF MEDICAL SCIENCES

For the past sixteen years, Section AIII of British Abstracts, published under the direction of the Bureau of Abstracts, has covered physiological, biochemical, and medical publications. Section AIII will be replaced in 1954 by a new journal to be published under the auspices of the Anatomical, Biochemical, Endocrinological, Pathological, Pharmacological, and Physiological Societies. The publication will be entitled British Abstracts of Medical Sciences.

Commencing in January 1954, there will be twelve monthly issues, eleven of which will contain

abstracts, the December number containing an author and subject index for the year.


As hitherto, abstracts will cover all significant papers in anatomy, biochemistry, experimental biology, experimental medicine, microbiology, pathology, pharmacology, and physiology.

TECHNICAL REPORTS OF ONRL

The following reports have been forwarded to ONR, Washington. Copies may be obtained by addressing requests to the Commanding Officer, Office of Naval Research Branch Office, Navy No. 100, c/o Fleet Post Office, New York, N. Y.

- ONRL-4-54 "Organic Chemical Research at the University of Cambridge" by J. C. Sheehan
- ONRL-5-54 "Fluid Mechanics Institutes at Gottingen and Hannover" by W. D. Hayes
- ONRL-7-54 "Research on Polyacetylenes at the University of Manchester" by J. C. Sheehan
- ONRL-9-54 "The Absolute Configuration of Steroids" by J. C. Sheehan

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