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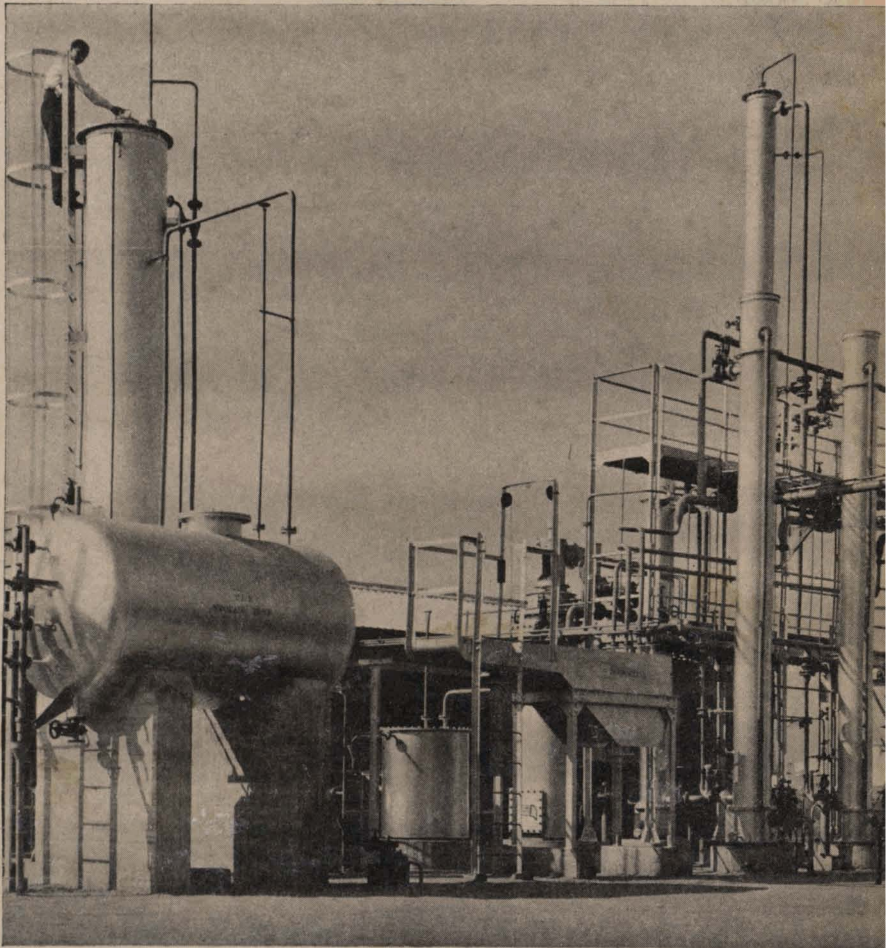

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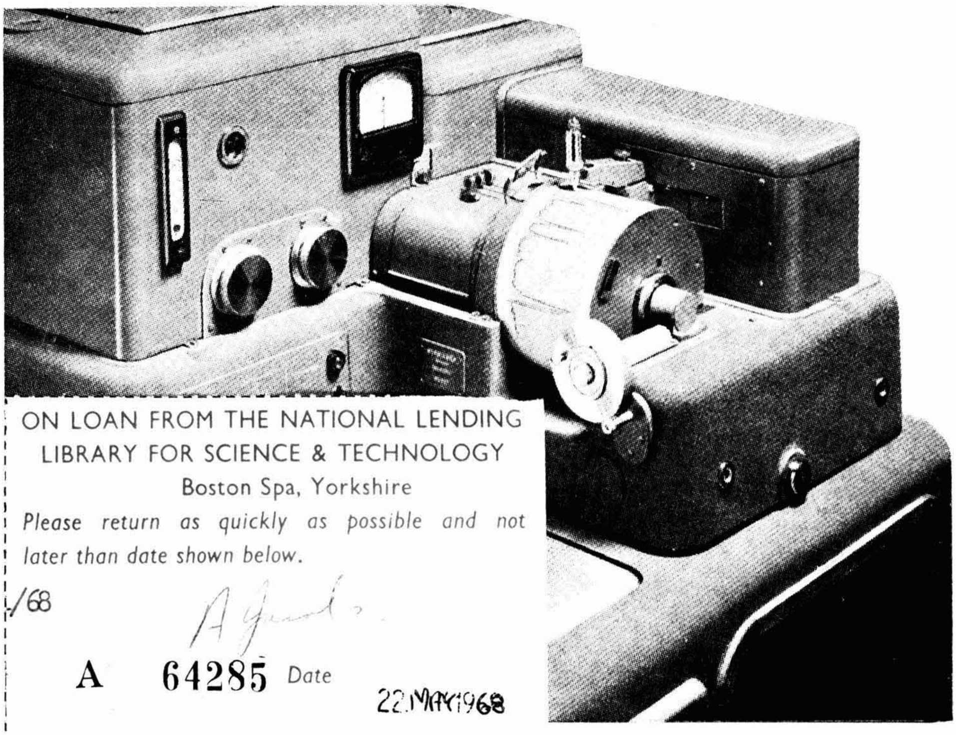

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Journal of
Scientific & Industrial Research

Vol. 17A, No. 2, FEBRUARY 1958

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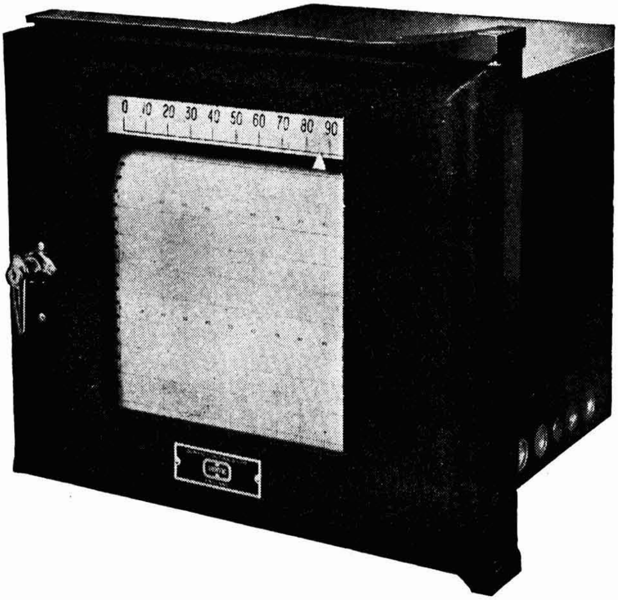

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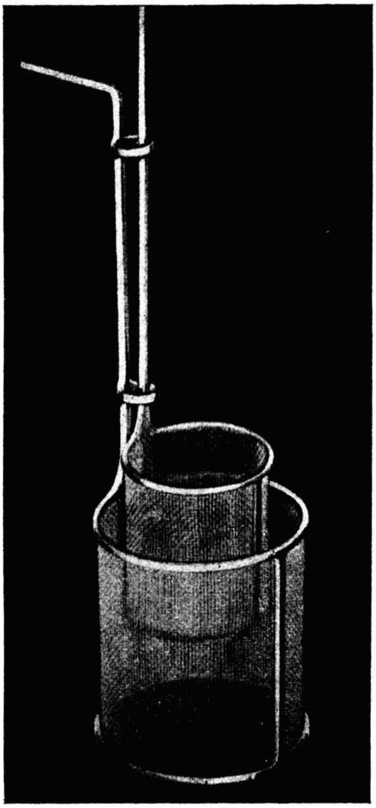

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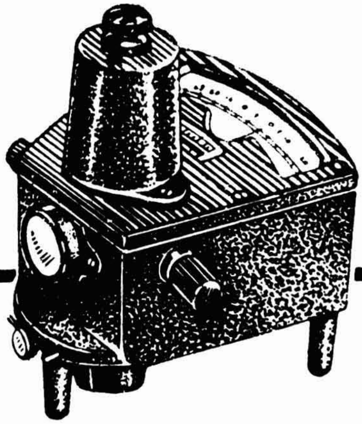

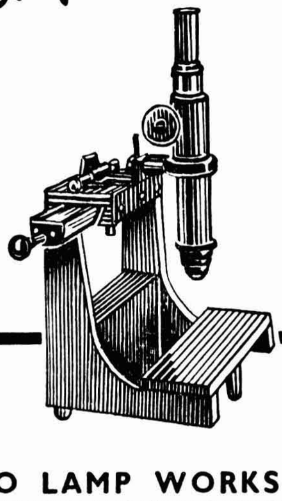

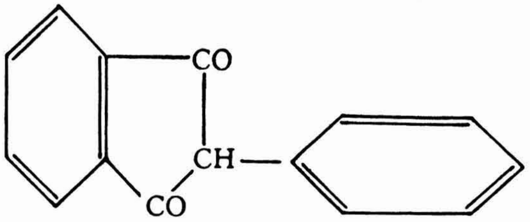
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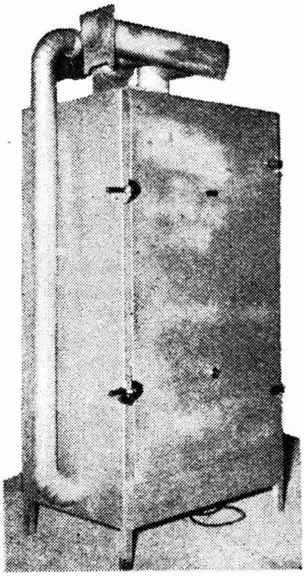

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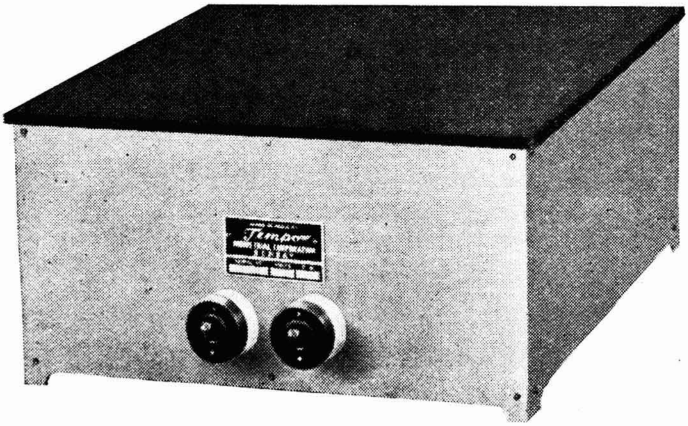

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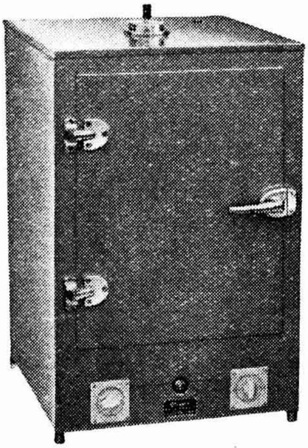

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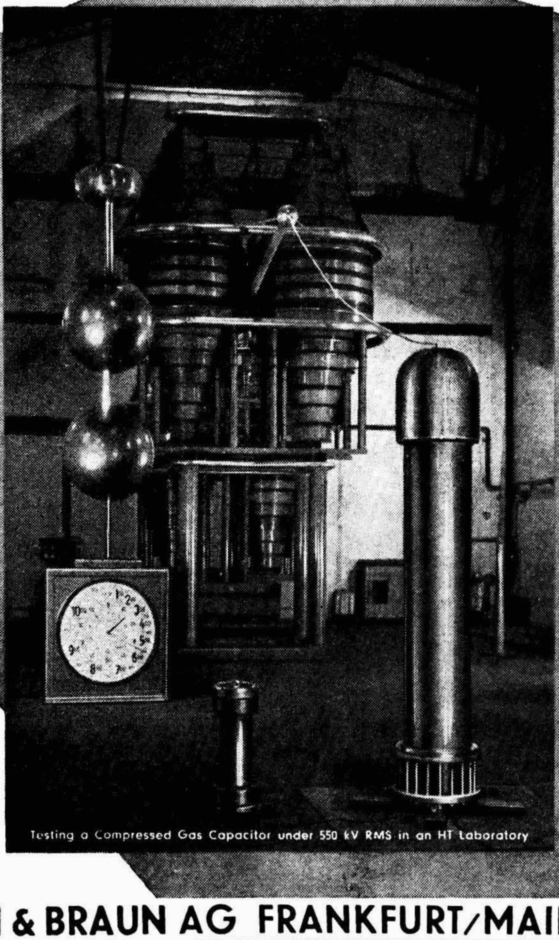

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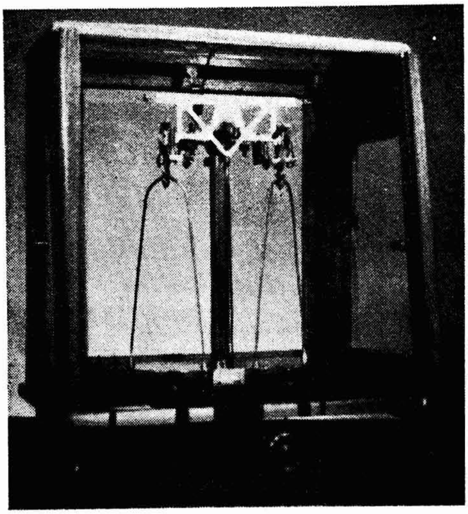

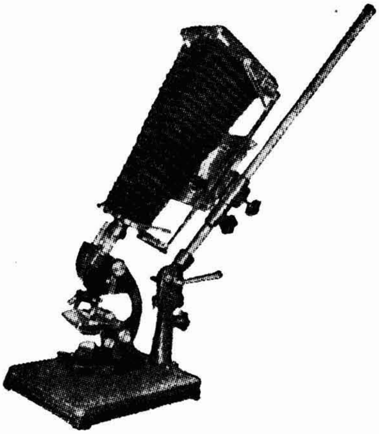

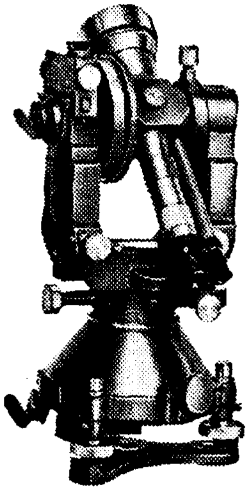

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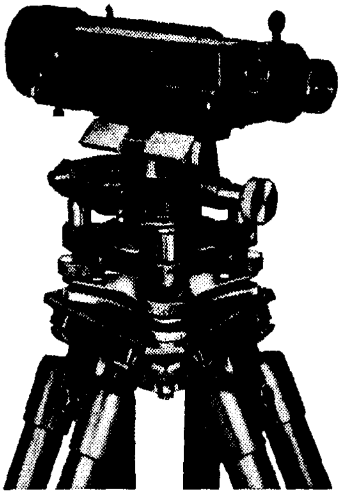

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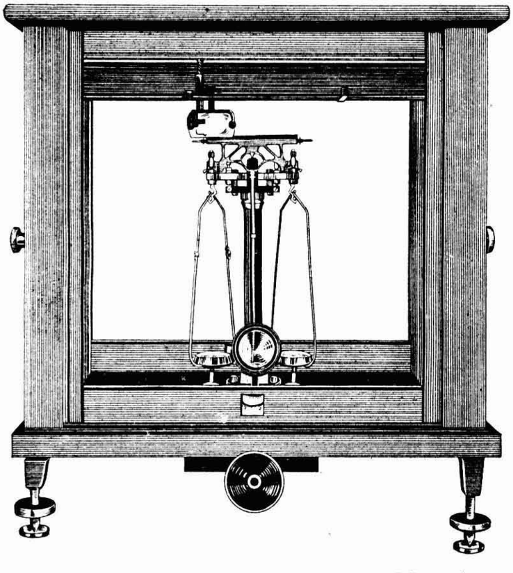

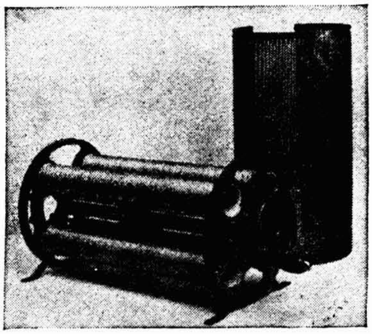

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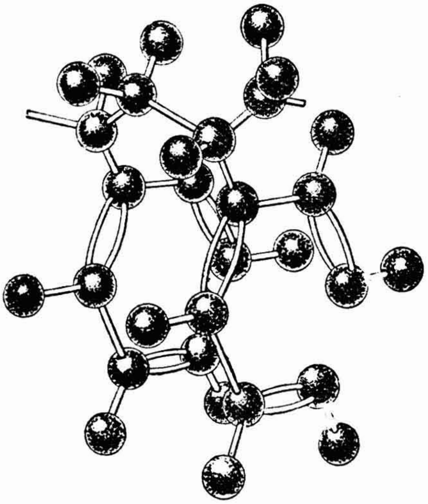

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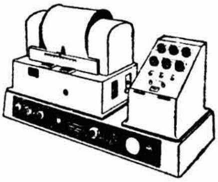

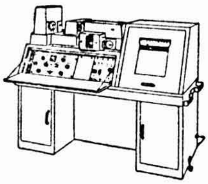

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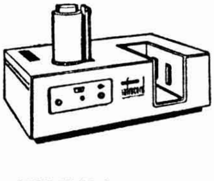

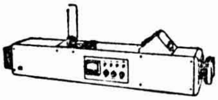

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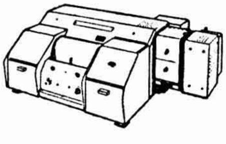

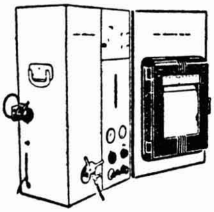

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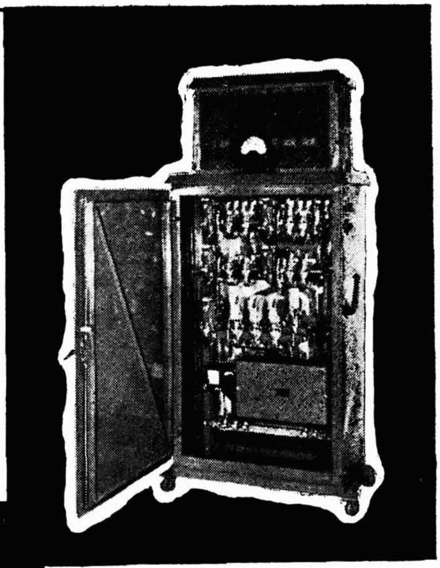

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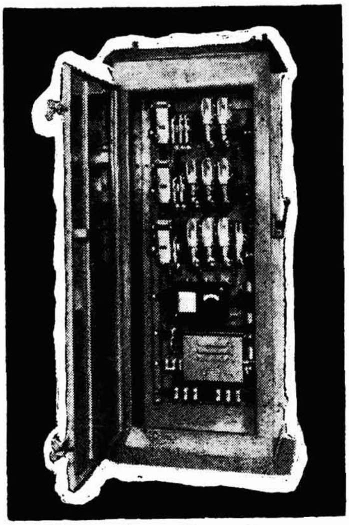

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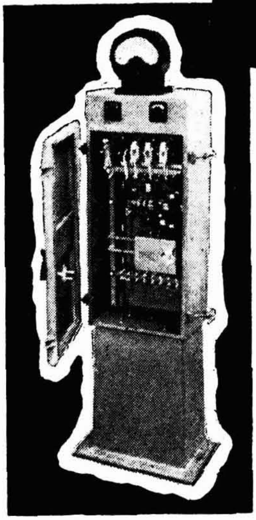

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The Rare Earths in Industry

K. VLASOV & B. KOGAN
U.S.S.R. Academy of Sciences, Moscow

AMONG the rare elements there is a group of 15 chemically kindred ones called the rare earth metals. They are: lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium. Two other elements — scandium and yttrium — possessing similar properties are also linked with this group.

For several decades the rare earths found comparatively small application, but within the last 5-6 years radical changes have taken place in their utilization.

An outstanding achievement was the introduction of rare earth metals into ferrous metallurgy. A small addition of these elements improves the plasticity, structure, impact ductility and other properties of steel, enhances the heat resistance of nichrome (an alloy consisting of 80 per cent nickel and 20 per cent chromium) and greatly lengthens its term of service under high temperatures; it improves the hot working of chrome-nickel stainless steels and eliminates the hot brittleness of the more complex alloy steels. Chrome-nickel-molybdenum steel, which as a rule can be used only for castings, becomes quite malleable when rare earth metals are added to it, so that sheets, bars, pipes and wires can be made out of it.

Rare earth metals improve the properties of light metals, such as aluminium and magnesium, and their alloys. Magnesium alloys with additions of zirconium and rare earth metals are very durable and creep-resistant under high temperatures. The most promising are the heat-resistant magnesium alloys containing neodymium.

Glass containing cerium possesses unparalleled properties; it remains transparent under the action of the strongest radioactive radiation. Cerium glass in nuclear reactors effectively protects personnel against the harmful effects of radiation and at the same time makes it possible to follow the process. This glass can also be used in the production of instruments for research work with radioactive materials.

Out of the six elements that most actively absorb heat neutrons five are rare earth metals, namely gadolinium, samarium, promethium, europium and dysprosium. A great future is predicted for gadolinium, especially in nuclear reactors for aeroplanes where it is important to decrease dimensions and weight. Metalloceramic material containing europium is successfully used for making rods for regulating nuclear processes.

By irradiating natural thulium-169 in a nuclear reactor a radioactive isotope thulium-170 is produced which possesses the remarkable property of emitting soft-radiation similar to X-rays. This has made it possible to create portable X-ray apparatuses which are extremely convenient for medical purposes. They are simple in working, do not require a source of electricity and can be used under all conditions. Thulium apparatuses are invaluable for field surgery, for use during geological or geographical expeditions and in alpine districts or remote villages where there is no electricity. With the help of thulium-170 it is possible to X-ray and make roentgenograms of such parts of the human body which are inaccessible to ordinary roentgen apparatuses. The gamma-radiation of thulium-170 is gaining practical importance in industrial defectoscopy of light metals and extremely fine articles made of heavy metals.

Another rare earth isotope — promethium-147 — in conjunction with a phosphorescent composition and minute photoelectric cells, has been used for the manufacture of atomic batteries of the size of a pill in which radioactive radiation is transformed into electricity. They can ensure the uninterrupted and exact working of a clock for about five years without winding.

By including fluorides of rare earth elements into the composition of searchlight candle coals an exceptionally bright light is produced approximating to the brightness of sunlight. Electrodes with rare earths have become indispensable for taking and projecting motion pictures.

The use of rare earth powders for polishing various kinds of optic glasses has received general recognition in the world glass industry. They surpass all other abrasive materials for this particular purpose; they accelerate by 50-100 per cent the polishing process and produce a polished surface of high quality.

The Soviet rare earth polishing preparation ' polirit ' has been tested not only in research laboratories but also under factory conditions. Its wide introduction into industry is saving millions of roubles by making it necessary to build polishing conveyer shops in the glassworks and by reducing working costs.

Cerium, lanthanum, neodymium and praseodymium compounds are used for the production of special coloured technical and remarkably beautiful decorative glass and also for decolourizing glass to increase its transparency. They are employed in the production of various types of glass which permit infrared rays to pass through but absorb ultraviolet rays, and are resistant to roentgen rays, and for the production of a number of special kinds of optic glasses, including photo lenses, periscopes and other instruments. It is planned to use them for the production of photo-sensitive glass which is of particular value for television cathode-ray tubes.

Rare earths are used as catalysts in organic and inorganic synthesis. In particular, much is expected of utilizing their catalytic properties in the process of cracking oil and in the production of artificial fibres and plastics.

Samarium, europium, terbium, praseodymium, erbium, thulium and gadolinium are activators of crystallophosphors — materials which can accumulate and preserve for a long time a large amount of luminous energy and then give it off. Yttrium, lanthanum and scandium serve as the basis for a number of industrial luminophors. Crystallophosphors combined with rare earths are employed for various purposes: in kinescopes of black-and-white and coloured television, in radar cathode-ray tubes, in high pressure mercury lamps, in luminescent daylight lamps, etc.

Very promising are rare earth compounds in the output of super-refractories and special heat-proof ceramics for nuclear reactors, and as dielectrics in radio engineering. Gadolinium is one of the few natural ferromagnetic metals, while yttrium, holmium, dysprosium, erbium and terbium are remarkably paramagnetic. That is why they are very promising in the creation of new materials with particularly high magnetic properties.

At present the industrial extraction of rare earths as separate metals is still very difficult, yet it has to be done. The technology of extracting yttrium and scandium has been mastered. Thus, 17 more elements, one-sixth of Mendelejeff's system, their isotopes and numerous compounds, are becoming available for scientific and practical purposes. This opens new possibilities for industry, the significance of which is as yet difficult to predict or appreciate.

Summaries of Addresses of Presidents of Sections, Forty-fifth Session, Indian Science Congress

MODERN ALGEBRA & THEORY OF ELEMENTARY PARTICLES

THE development of modern algebraic concepts such as matrices, differential operators, groups, integral operators, tensors, etc., and their increasing application in the solution of problems of theoretical physics formed the subject of the address delivered by Prof. B. S. Madhava Rao to the Section of Mathematics. The progress in theoretical physics as a result of these concepts, Prof. Rao said, has in turn led to the development of new algebraic concepts. The address reviews briefly the recent developments in modern algebra relating to invariance under charge conjugation, generalized gauge transformations, space and time inversions and conservation laws of isotopic spin and parity as applied to the ' strange ' particles. These developments are based essentially on the representations of the full Lorentz group and their topological significance. Prof. Rao has also referred to the mathematical implications of possible relativistic theories of discrete space-time and momentum-space of function spaces in quantum theory and of the logical foundations of causality.

The increasing use of abstract mathematics has been a striking feature of modern theoretical physics, specially in the field of the theory of elementary particles. This can be traced to a great extent to the change brought about by quantum mechanics in the meaning to be attached to a physical quantity, viz. as an operator yielding not one but a large set of numbers which can, however, be consistently used with the aid of a statistical theory. This widening of the concepts of theoretical physics has stimulated questions which have spurred on the progress of mathematics itself. A clear example of this is the development of the theory of abstract spaces and the knowledge that the analytical problems of quantum mechanics can be thought of in terms of linear transformations in an abstract Hilbert space.

The relationship between algebra and physics has been, until recently, rather a loose one. Although group theory has played a useful role in theoretical physics, it is perhaps true that progress in group theory and modern algebra has not always been chiefly motivated by physics. Researches on the theory of group representations, on abstract algebras and on continuous groups were carried on independently as a result of the fusion of several fundamental ideas in mathematics itself. But recent advances in theory of elementary particles have brought about an intimate connection between algebra and physics which is likely to help the growth of both the subjects.

In the early stages of the development of elementary particles when the Dirac theory of the electron, positron, proton and neutron, Pauli's neutrino and Yukawa's meson held the field, it was found possible to set up a general theory which could be used consistently so as to include the above-mentioned types of particles and their interactions. This theory consisted essentially of two stages, the c-number theory satisfying the postulates of special relativity, and the q-number theory making a transition from a one-particle to a many-particle picture on the basis of quantum mechanics. The former theory was based essentially on the setting up of a Lagrangian function L which is to be invariant under transformation of the proper Lorentz group, i.e. having the determinant $+1$, and not reversing the direction of time. The quantities transforming according to irreducible representations of the above group are the so-called spinors; of the three fundamental properties, the mass, charge and spin of elementary particles, the last which is perhaps not the simplest one from the experimental point of view, has come up, remarkably, as the first in the mathematical formalism. Spin could be easily defined in terms of spinors, and the c-number theory itself yielded some very general results, viz.

that for particles of half-integral spin, the total energy is not necessarily positive, and for particles of integral spin, the charge density is not necessarily positive. A deeper analysis showed that the uniqueness and definite positive character of charge and energy density is characteristic for the lower spins 0, $\frac{1}{2}$ and 1. Next, making the transition to the q-number theory, the essential step is the expression of the non-commutivity of the field quantities $\bar{U}(x)$ at different points of space-time x and x' in the form of the $\pm$ bracket expressions, the so-called commutation rules.

$$[\bar{U}(x), \bar{U}^*(x')]^{\pm} = D(x, x') \quad \ldots \; (1)$$

the $+$ or $-$ being taken according as the particles satisfy the Fermi and Bose statistics. The transformation properties of the $\bar{U}$'s under the proper Lorentz transformation require that the D's also should transform in a certain way. The requirements that D should be a function only of the invariant distance between x and x', and that $D = 0$ if each of x and x' lies outside the light cone of the other are stringent enough to determine the form of D uniquely. These considerations led to the well-known connection between spin and statistics, which is perhaps one of the most important applications of the theory of representations of the Lorentz group.

A further development was to put the wave equations of the particles in the Dirac form

$$\frac{\partial}{\partial x^K}\beta_K\Psi + \chi\Psi = 0 \quad \ldots\ldots\ldots \; (2)$$

representing particles of a single spin, and this form in which Dirac originally derived the wave equation of the electron and which was the basis of relativistic quantum mechanics, can be said to represent the particle aspect of the theory of elementary particles. The β_K's in equation (2) are matrices satisfying different types of commutation relations depending on the spin, and generate in virtue of these relations, a system of hypercomplex numbers. The theorems relating to representations of finite groups can be extended to group rings and hence also to hypercomplex numbers satisfying certain conditions. Thus an intimate connection could be set up between particles of specified spin and general types of algebras, e.g. the Dirac algebra, Meson algebra and so on. This also showed the possibility of several representations, with different orders, of the same algebra, being equivalent to different types of elementary particles having the same spin.

The limiting case of particles of rest mass zero could be brought into the general theory by the further requirement that the field quantities representing them be invariant under the gauge group. Similarly the other limiting case of particles of zero charge could also be treated satisfactorily by postulating invariance under transformations of charge conjugation or the so-called charge invariance.

Recent experimental work in high energy physics has resulted in the discovery of a large number of elementary particles, called the 'strange particles', like heavy mesons and hyperons of masses greater than that of the proton; the interactions between themselves, and between them and the known elementary particles, and also the decay of the strange particles are now of great interest. This has led to a re-examination of the questions of invariance under several types of Lorentz transformations like those confined to space-time displacements and rotations only, and those which are not. Questions relating to invariance under charge conjugation, generalized gauge transformations and space and time inversions, and conservation laws of isotopic spin and parity as applied to the strange particles have all raised problems of great algebraic significance. A new quantum number called the 'strangeness quantum number (S)' has been introduced to explain interactions among the new particles, and the relation between invariance of strangeness and invariance of parity (i.e. distinction between right and left) has been investigated. A particular problem of current interest is the question about the conservation laws in two types of interactions, viz. the strong ones including the electromagnetic interactions, and the weak ones like the decay interactions of mesons and hyperons and various Fermi interactions, specially the question of invariance of parity in these two types. Thus while parity is conserved in strong interactions, the same cannot be said of weak interactions, and the question of invariance of parity under these has recently been examined by Lee and Yang with reference to the heavy mesons θ^+ and τ^+ which have very close masses and they have come to the conclusion that they have the same spin but opposite parities, i.e. they are parity doublets. Thus one could speak of parity conjugation in relation to these two particles. It appears that we have here a new conservation law of physics, viz. that all particles of odd strangeness have parity doublets. Also, there does not exist at present experimental proof of the invariance of weak interactions under charge conjugation. A confirmation of the above conservation law is afforded by the hyperons, Λ and Σ, which have the same spin $\frac{1}{2}$ and the same parity, the value of S assigned being even.

RECENT DEVELOPMENTS IN EXPERIMENTAL DESIGN

IN his presidential address to the Statistics Section, Dr. K. Kishen has surveyed the important developments that have taken place in recent years in the theory of design of experiments as applied to biological, physical, chemical and industrial research. Dr. Kishen has, in this context, drawn the attention of statisticians to the necessity of familiarizing themselves with that branch of science in which research has been carried out and the problem is referred to him for solution. He is of the view that in research, the role of the statistician is that of a collaborator and not that of a leader, and that he should work in close collaboration with other research workers for achieving the best results.

Factorial designs — Considerable attention has been directed to the problem of constructing optimum confounded designs in the case of the general factorial experiment $s_1 \times s_2 \times \ldots \times s_m$, involving m factors $A_1, A_2, \ldots, A_m$, the i-th factor being at s_i $(i=1, 2, \ldots, m)$ levels. When $s_1 = s_2 = \ldots = s_m = s$, this leads to the general symmetrical factorial design. The problem of confounding in this case has been solved by Bose and Kishen when s is a prime positive integer or a power of a prime. When the s_i's $(i=1, 2, \ldots, m)$ are not all equal, asymmetrical factorial designs are obtained. Significant contributions to the theory of construction of these designs have been made by Yates, Li, and Nair and Rao. Dr. Kishen's work has provided two new general solutions, viz. (a) $q \times 2^2$ design in blocks of $q \times 2$ plots, and (b) $q \times p^2$ design in blocks of $q \times p$ plots, p being an odd prime or power thereof.

Subsequent to the work of Bose and Kishen, the theory of confounding in the general symmetrical factorial design was formulated by Fisher by the use of Abelian groups of order s^m and type (1, 1, ..., 1). However, as the elements of this Abelian group afford concrete representations of the Euclidean geometry EG (m, s), there exists a one-to-one correspondence between sub-groups of order s^k of the effect group and parallel pencils of s^k, $(m-k)$-flats $(k \leq m-1)$ in PG (m, s) representing $s^k - 1$ degrees of freedom belonging to main effects and/or interactions as defined by Bose and Kishen. This correspondence has been established by Kishen, who has shown that the two theories are exactly equivalent and interpretable in terms of each other.

Fractional and incomplete factorials — In problems of biological, physical, chemical and industrial research, in which a large number of factors have to be included at the exploratory stage of an investigation, the number of treatment combinations in the complete factorial scheme becomes unduly large, and adoption of even a single replication is beyond the resources of the experimenter. In such cases, it is imperative to resort to fractional replication in which only a fraction of the total number of treatment combinations required for a complete replication has to be tested. The device is of limited utility in that every measure of a treatment effect can be associated with two or more treatment contrasts, and careful planning is required so that this interconfusion in the effects does not vitiate the experimental results.

Fractionally replicated designs were originated by Finney and have been the subject of extensive research in recent years. Finney's theory was generalized by Kishen, who solved the problem of constructing fractional factorials in the case of the general symmetrical factorial design, that is an s^m design in $1/s^k$ replicate $(k \leq m-1)$. A significant recent advance, due to Plackett and Burman, Rao and Box and his co-workers, is the generalization of the concept of fractional factorials to incomplete factorials. The work of Box and his collaborators, particularly, broke new ground and is likely to be regarded in future as a landmark in the history of experimental design.

The concept of hypercubes and orthogonal arrays of strength 't' introduced by Rao is of fundamental importance in the construction of confounded factorial designs, fractional factorials and incomplete factorials. The method of analysis of an incomplete factorial design, which is an orthogonal array of strength $(t+k-1)$ represented by $(N, s^m, t+k-1, \lambda)$, has been given in the address.

Further work on orthogonal arrays has been done by Bush, and Bose and Bush, and the concept has been extended by Chakravarti to partially balanced arrays of strength 't'.

Incomplete block designs — Considerable progress has been made in recent years in the construction and analysis of incomplete block designs which were introduced by Yates to meet the needs of biologists confronted with the problem of testing a large number of varieties or treatments among which interactions do not exist or are of no particular interest. Special mention may be made of the extensive work on the classification and analysis of PBIB designs with two-associate classes done by Bose and his co-workers at North Carolina. Reference has also been made to simple, triple and near balance rectangular lattices developed by Harshbarger, the chain block design developed by Youden and Connor and the n-ary designs developed by Tocher.

Other recent developments — A significant trend in recent research in experimental designs is the evolution of special devices with a view to bringing about the maximum reduction in the amount of work required to be done in an experimental investigation. Besides fractional and incomplete factorials, another useful device for bringing about this reduction is sequential experimentation, developed as a consequence of the work on sequential analysis of Wald. The procedure has been found to be of particular utility in problems of medical research. Another useful device, based on the sequential procedure, is the ' up and down ' or staircase method developed by Dixon and Mood for the determination of the median lethal dose in biological assays.

Some important ideas regarding the optimum amount of experimentation required in developmental work have been introduced by Yates and further developed by Grundy, Healy and Rees. The results presented by these workers are likely to be of considerable practical value to the experimenter in deciding the optimum amount of experimentation under certain situations.

SOME GEOPHYSICAL PHENOMENA

SHRI S. L. Malurkar's presidential address to the Physics Section is devoted to a discussion of a number of geophysical phenomena which are related directly or indirectly to solar activity. The topical importance of this subject arises from the widespread interest shown in the current programme of the International Geophysical Year. Shri Malurkar has mainly dealt with phenomena accompanying solar flares, with particular reference to the flare on 23 February 1957, stability of top-heavy fluid layers in relation to the formation and characteristics of thunderstorms, and some aspects of tropical meteorology.

Solar flares, cosmic rays and geomagnetic storms — Solar flares may be accompanied by a radio fade-out or an ionospheric disturbance and a small crochet in the magnetic curves on the daylight side of the earth's hemisphere. Geomagnetic changes may occur a day after a geomagnetic storm or a disturbance in earth's magnetic field, which is sometimes accompanied closely by a change in cosmic ray intensity. Up to the year 1956, only four instances of large or sharp increases in cosmic ray ionization have been recorded at high geomagnetic latitudes. On 23 February 1956, the solar flare which occurred at 03.30 U.T. was accompanied by a cosmic ray burst which was recorded almost near the geomagnetic equator. This was the fifth instance. Two of these solar flares were followed by geomagnetic storms with simultaneous changes in cosmic ray intensities. In the three others, either there was no geomagnetic storm or they were followed much later by a slight change in cosmic ray intensity. Two intense geomagnetic storms have been recorded in the past 80 years at Alibag (Bombay) during which no cosmic ray changes have been observed. These were studied with respect to the evolution and the displacement from east to west (due to sun's rotation about its axis once in about 27 days) of the solar active regions and their flares along with the five instances of large solar flares.

When the corresponding solar active region had a long previous history of more than usual activity and when the flare was from near the central meridian or from near the western limb of the sun, sharp and sudden cosmic ray bursts occurred. In the former case a geomagnetic storm with corresponding cosmic ray changes followed. The flare at the western limb of the sun was not followed by a similar geomagnetic storm. The manifestation of asymmetry of cosmic ray bursts, when the flare was only near the western limb of the sun, shows that the particles have a definite type of charge. The need for the charged particles to be accelerated for many days in the active region and the rarity of such events indicate that the particles belong neither to the light nor to the heavy elements or even to one whose composition in the sun is relatively small.

Stability of fluid layers — Aichi, Rayleigh and Jeffreys have found that in a fluid layer, when the lower surface is heated, unstable conditions do not set in until the temperature of the bottom surface exceeds that of the top by a certain limit. By measuring temperatures and height above a hot road in the tropics whose form resembled a hyperbolic sine curve, it was found that the limit had been considerably exceeded. The form was arrived at by assuming eddy diffusivity and radiation from successive thin layers of the superincumbent air. By taking into account the actual distribution instead of a linear temperature-height distribution, it was found that larger temperature limits are maintainable before instability sets in. These ideas have been applied to the study of the formation of thunderstorms.

While dealing with the formation of thunderstorms, a consideration of the initial cause of convection, the conditions favouring maintenance of convection, once started, and the implications of dynamic instead of statical rising air masses is essential. The thunderstorms in the tropics are of the 'frontal' type (thunderstorm is accompanied by a fall in wet bulb temperature) and of the 'heat' type (no fall in wet bulb temperature). The frontal and heat thunderstorms occur on the northern (more poleward) and the southern (more equatorward) side respectively of the fluctuating upper air high pressure belt in sub-tropics of the northern hemisphere. The criteria would be valid everywhere in the northern tropics and sub-tropics. By interchanging south and north, they would become applicable in the corresponding regions of the southern hemisphere.

Tropical meteorology — Fresh air from south Indian Ocean crosses the equator as 'pulses' at intervals of a few days under specific determinable conditions to strengthen the south-west monsoon or to feed into a tropical cyclonic storm in the Indian Ocean area as a 'source' mass. The air stream from the same side of the equator as the depression or south-west monsoon has its ultimate source in the Far East — the northern Pacific high pressure area; its properties depend on season and locality. It exhibits great stability, though during the south-west monsoon it is hotter (pot-wet bulb is also hotter) than the fresh monsoon air. It delays the release of energy till vorticity is built up for a tropical depression. The stream of dry land air acts as a 'sink'. During the south-west monsoon if the 'pulses' do not cross the equator and move westwards, there is a break in the monsoon in India. When the Far Eastern air does not feed into the field, depressions are not formed and rainfall would be ill-distributed. When a monsoon 'pulse' empties into a depression, it has a westerly movement. The western or winter disturbances are split up into successive secondaries with independent evolutions and ENE paths for each. The Far Eastern air, which usually feeds into south Indian Ocean monsoon, feeds into a southern tropical storm and the winter disturbance over India, in the same longitudinal belt, produces less precipitation. If the same stream of air does not cross the equator but feeds into the western disturbance in North India, the precipitation would be more marked. Another important deduction is that two tropical depressions, one on either side of the equator and both moving westwards, could not for long coexist when the longitudinal separation is small (about 10°) and will result in one or both filling up or recurving. Thus, it can be concluded that when a cyclonic storm is moving westwards in the south Indian Ocean, a large part of India within a longitudinal sector of 15° to 20° experiences dry weather north of 10° to 12°N.

STABILITY OF LYOPHOBIC COLLOIDS

THE presidential address of Prof. S. Ghosh to the Section of Chemistry deals with the subject of Stability of Lyophobic Colloids principally from the following angles: general characteristics of lyophobic colloids;

measurement of stability; effect of ageing and radiations; kinetics of the process of aggregation; and gelation.

Lyophilic sols are highly stable due to their intrafacial tension, which is very nearly equal to zero, and this leads to an instantaneous dispersion of the particles in the surrounding medium. Lyophobic sols are thermodynamically unstable and the particles possess an inherent tendency to grow, which is prevented by the electric charge carried by the particles. Solvation has been considered by some workers as an important factor in the stability of colloids, for the coalescence linking across the solvent layer attached to the colloidal particle is likely to be weak. A large number of sols are, however, known to be highly solvated as evident from their high viscosities. Ghosh and co-workers have ascribed the high viscosities of sols to the development of pseudoplastic properties. Sols of vanadium pentoxide and phosphates and arsenates of iron, aluminium, chromium, etc., yield gels and, at the same time, like lyophobic sols, are sensitive to the action of electrolytes. The colloid particles of such sols do not carry the solvent at some points on their surface, where the aggregation starts leading to a loose structure and the formation of a gel.

Ellis and Powis consider the existence of a critical zeta potential produced by the addition of an electrolyte as a necessary factor in the process of coagulation. This conclusion has little experimental support. In the process of aggregation, the actual electric charge on the colloid surface plays a more important role than the zeta potential.

The stability of a lyophobic sol is usually measured by its coagulation by an added electrolyte. In the charge neutralization of a colloid particle by an added electrolyte the valency of an oppositely charged ion is significant, but the effect of (i) specific adsorption of both similarly and oppositely charged ions and (ii) the chemical interaction of the stabilizing ions with the added electrolyte are important. Ghosh and co-workers have emphasized the importance of similarly charged ions on (1) the stability of a sol related to its concentration, (2) ionic antagonism and (3) acclimatization. The phenomena of ionic antagonism and acclimatization are of great biological significance. They have also shown that when the adsorption of oppositely charged ions is considerable, negative acclimatization is developed.

Ageing and various radiations such as X-rays, α- and β-rays, ultraviolet, sonic and ultrasonic rays considerably affect the stability of lyophobic sols. Generally, the sols become unstable towards an electrolyte on ageing because of an inherent tendency of the colloid particles to grow, and the adsorbed ions imparting the electric charge are given out. The radiations also usually make the sols unstable. Ultrasonic radiations have been found to cause the dispersion of various hydrous oxides, mercury, sulphur, etc., in water, but it has been noted by Ghosh and co-workers that a sol of ferric succinate, when exposed to ultrasonic radiation, rapidly ages. Detailed investigation of the effect of various radiations on the stability of sols is likely to throw considerable light on their effect on several biological processes.

Smoluchowski studied the aggregation of the discharged colloid particles and obtained the relation:

$$\Sigma n = \frac{n_0}{1 + 4\pi D R n_0 t_0}$$

where Σn particles remain in the system out of the total number of particles n_0 after time t; D, the diffusion coefficient; and R, effective radius of attraction.

This relation is found to be true in the region of rapid coagulation but fails in the case of slow coagulation the factor $4\pi DR$ is multiplied by ϵ, when $\epsilon < 1$.

According to Smoluchowski, in the region of slow coagulation, all collisions of the colloid particles do not lead to aggregation due to a residual charge. Other workers have, however, shown that for slow coagulation, the value of R goes on changing so that the values become very small for coarser particles. It is probable that the value of R considerably diminishes in a greater proportion so that the value of DR becomes small with increasing aggregation. Undoubtedly, the value of R depends not on the actual size of the colloidal particles, but on the area of the colloidal surface active in the process of aggregation.

Ghosh has shown that for a sol with lyophilic character, the process of aggregation effected by the addition of an electrolyte has an induction period. In slow coagulation, therefore, charge neutralization also proceeds with a measurable speed. The stability factor W of Verwey and Overbeek is similar to $1/\epsilon$ and its value decreases by the addition of an electrolyte. An empirical relation between the time of coagulation and the concentration of the coagulating ion has been suggested by Paine *et al.*

The effect of temperature on the stability of lyophobic sols has not been fully investigated. The heat of activation for the gelation process was calculated by Hurd in the case of silicic acid using the equation

$$-\log t = \log Z - \frac{E}{2{\cdot}303RT}$$

where t is time for setting of the gel and E, heat of activation for gelation. The value came out to be 20 k. cal./g. mole silica.

According to Ghosh and co-workers the gelation of some inorganic substances is similar to coagulation process. Bose, Mushran and Ghosh determined the heat of activation for the gelation of ferric succinate sols peptized by ferric chloride by the addition of electrolytes. When ferric chloride is in a large excess, the rate of gelation is slow but the value of heat of activation is small; the reverse is the case when ferric chloride is in a small excess. These authors conclude that in the presence of large excess of ferric chloride, colloidal units are highly charged, so that the fraction of collision leading to gelation is very small. But, the size of the colliding particles being small there is a greater tendency for aggregation on account of the large surface. Hence the rate of gelation or coagulation can be expressed as

$$\frac{dx}{dt} = pZe^{-E/RT}$$

where Z represents the number of collisions in unit time and p, the fraction of successful collisions. The value of p is small when the residual electric charge on the colloidal particle is small, and E is large for coarser particles. Thus, the smaller the value of p and larger the value of E, the more stable will be the sol.

The coagulation process is, thus, closely analogous to a chemical reaction. The value of R is, however, of great significance and depends on the specific property of the surface of the colloidal particles.

GEOLOGY OF BUNDELKHAND GRANITES & GNEISSES

IN his presidential address to the Section of Geology & Geography, Dr. A. G. Jhingran has dealt with the geology of the Bundelkhand area which has not so far been studied systematically. Dr. Jhingran and his colleagues have mapped an area of over 3000 sq. miles of the massif lying between the latitudes 24°30′ and 25°30′N. and the longitudes 78°15′ and 80°0′E. The megascopic and petrographic data of granites and gneisses, and details of inclusions, quartz reefs, basic dykes and tuffaceous serpentine-calcite rock have been presented and discussed in the address. Mineralization of the granites is dealt with, and the genesis, age and correlation of the granites have been considered in the light of the existing knowledge. Dr. Jhingran is of the opinion that the Bundelkhand granites are younger than the oldest Dharwars and can be correlated with Berach granite in Rajasthan. He considers the term Bundelkhand gneisses applied to the typical rocks in this area a misnomer and Bundelkhand granite and gneisses as more appropriate.

Among the granites in the area those with pink felspar form the dominant types, the grey variety being subordinate. The pink granite has two dominant types: (1) coarse-grained variety with ferric minerals and (2) medium-grained variety poor in ferric minerals. The ferromagnesian content of these granites varies considerably. With the development of the large-sized crystals of felspars as phenocrysts, the rock assumes a porphyritic texture. At several places the medium-grained granite, with the development and gradual increase in the number and size of the felspar phenocrysts, passes into the coarse-grained group. These felspars have often been noticed to include the ferromagnesian constituents. Occasionally a pegmatitic variety is also present in the area. The granites bear a large number of inclusions of various types of rocks which include hornblende and chlorite-schists, quartz-schists, felspathic-schists, granulite, quartzite, etc. The granites are considerably jointed, the degree of development and the nature of joints in different portions of a single outcrop varying considerably.

The distribution of gneisses in the area does not show any regularity or pattern. Their outcrops vary in dimensions from small patches less than a foot in length to larger masses forming hillocks. They are often found associated with coarse-grained pink granite. Generally they are medium- to coarse-grained with varying proportions of pink and grey felspars, and clots of ferromagnesian constituents showing parallel orientation with high dips. Occasionally, when the foliation becomes ill-defined, the rock passes into a granitoid gneiss and gneissose granite. Smaller lenticular inclusions of amphibole-rich rock are often met within the gneisses, their long axes being oriented along the direction of foliation of the latter.

The different varieties of the granites occur often intimately mixed with one another, though occasionally a fairly extensive outcrop of a single variety is met with. The transition between the varieties rich in ferromagnesian constituents and those that are poor in them is comparatively sharp. Sometimes the coarse variety is found overlapping the fine-grained variety. Another significant feature is the repeated alternation in a vertical section of fine- or medium-grained pink granites and the coarse-grained pink variety with a fair amount of femic minerals. Intermingling of granites and gneisses is also frequent in the area.

Petrographically, these granites are formed essentially of quartz, felspars, a few ferromagnesian minerals and some accessories. The felspars present include orthoclase, microcline, perthite and plagioclases. In the porphyritic varieties the phenocrysts are usually of microcline or perthite. Hornblende, biotite and chlorite are the most common ferromagnesian minerals, while the accessories include apatite, iron ores, sphene, epidote and zircon. All the constituent rocks in the massif have been found to exhibit cataclastic effects such as bending and breaking of the twin lamellae of the plagioclase felspars, bending of biotite flakes, crushing of the component minerals, strain shadows in quartz, etc. From modal analyses it is seen that the rocks of this massif range from granite to granodiorite in composition, the latter being predominant.

A feature of the Bundelkhand granitic terrain is the presence of a number of parallel quartz reefs which form prominent narrow ridges. These run discontinuously for long distances, sometimes up to 18 miles. The vast majority of the reefs pursue a more or less common direction. The reefs are highly jointed, with three sets of prominent joint planes discernible. Their rock is of a composite nature, the most abundant constituent being a fine-grained compact cherty material of pinkish to greenish grey colour. The cherty material is found to be made up of angular to subangular grains of quartz with small quantities of microcline, perthitic felspar and plagioclases. Some milky quartz is also associated with the rock. A number of basic (doleritic) dykes also intrude through the granite massif. From observations on their relative occurrence, it is inferred that the basic dykes are younger than the quartz reefs. A tuffaceous serpentine-calcite rock has also been found in the massif, which is undoubtedly an intrusion.

A special feature of the Bundelkhand granite massif is the absence of any large-scale mineralization which probably is the reason for its neglect by geologists. Traces of malachite, azurite, covellite, pyromorphite and small quantities of galena have been reported from some of the quartz reefs and small encrustations of molybdenite have been observed along fracture planes in some medium-grained pink granites. The only mineral which occurs in somewhat workable quantity and in sufficient purity is pyrophyllite. The mineral, due to its ready amenability to dressing, is being used in pottery. From a close examination of the pyrophyllite and the other minerals occurring in the quartz veins it is inferred that certain amount of mineralizing solutions came along weak zones in the granite provided by the quartz reefs and the metasomatic alteration caused by them led to pyrophyllite. However, this activity seems to be very little resulting in an overall paucity of mineralization.

The heterogeneity in texture and mineral composition of these granites, both on the surface and in depth, appears to indicate that all the varieties of granite met with in this area are not of one single generation. From the consideration that the older granite should bear a larger number of undigested relics of the roof-rock in the form of inclusions and also from the nature of joints and shearing effect shown by these granites, the coarse-grained pink granite may be treated as older than the medium-grained granite. From the magmatic origin of the entire massif it may be concluded that the two principal varieties of granites were intruded into the country rock one after the other. This would explain the textural features and mineral variations of the massif. But lack of mineralization and the near complete absence of late-magmatic activity in the form of pegmatites throw doubt on the batholithic origin of the granites.

The petrographic features of the massif are largely explained by the assumption that two intrusions of magmas, formed by anatexis and paligenesis followed by metasomatism, occurred. The anatexial magma intruded in two phases: one being granodionitic in composition and the other adamellitic. The former gave rise to varieties of granites bearing ferromagnesian minerals and the latter to varieties free of femic constituents. This was followed by hydrothermal activity which caused metasomatism. During this phase the plagioclases got clouded and were partly replaced by potassic felspars. The quartz reefs came as the closing phase of the igneous activity. The whole massif was then subjected to tectonic movements which sheared the reefs and the granite, and gave rise to the mylonitic schist bands within the coarse-grained pink granites. Probably some gneissosity was also impressed on the granites at this stage which was followed by the doleritic dykes.

MOULDS, METABOLITES & TISSUES

RECENT advances in experimental plant pathology, particularly those dealing with pathogenic fungi and their host plants, formed the subject of the presidential address of Prof. T. S. Sadasivan to the Section of Botany. The species of wilt pathogens belonging to the genus *Fusarium*, which are responsible for wilt disease in cotton plants in India, have been treated in detail with special reference to the toxins produced by them, their nutritional requirements and behaviour in the root region of the host, effect of soil conditions and host physiology on fungi, and finally the development of resistance to wilt in cotton plants.

An important wilt toxin known to affect cotton plants in India is fusaric acid, a pyridine-carboxylic acid. This acid as well as dehydrofusaric acid are known to occur inside plant tissues when they are invaded by several species of the common soil organisms of the genus *Fusarium*. It is, however, not known if these acids are produced independent of each other, although it has been noticed that the unsaturated dehydrofusaric acid is produced earlier than the saturated fusaric acid molecule. Fusaric acid is known to be produced notably by *Fusarium lycopersici* (the tomato wilt pathogen), *F. vasinfectum* (the cotton wilt pathogen) and the non-specific *F. heterosporum*; *F. orthoceras*, a weak parasite, has been recently reported to produce the acid in much higher quantities. Another genus, *Gibberella fujikuroi*, is also known to produce fusaric acid, dehydrofusaric acid and two substances of the gibberellin group which are known to be growth promoters. The *in vitro* carbon and nitrogen requirements of these fungi for optimum production of the toxin have been worked out. The form and sources of carbon and nitrogen and the *p*H of the substratum are the main factors affecting the production of the toxin.

Much is not known about pathogenic fungi and their behaviour in the region of the root (rhizosphere). For instance, the cotton wilt fungus, *F. vasinfectum*, which is a serious pest in many cotton-growing areas in India, has been established as a typical inhabitant of the soils in these areas; as many as 14 species of this genus are known to occur in such soils. They are the primary decomposers of cellulose in the soils. The occurrence in soils of two other species, *F. lateritium* and *F. scirpi*, known to produce wilt of tomato, has also been noticed. The typical organism causing tomato wilt in other parts of the world is *F. lycopersici*; one of the wilt toxins produced by it is fusaric acid. *F. lateritium* and *F. scirpi* recorded by Sadasivan and his co-workers as potential pathogens of the tomato are not known to produce this toxin. Recently, a weak parasite, *F. orthoceras*, has been shown by Sadasivan and his coworkers to produce considerable quantities of fusaric acid, far in excess of what the cotton wilt pathogen *F. vasinfectum* can produce.

Many organisms, pathogens and saprophytes have been noticed in the rhizosphere. These organisms obviously depend on the root exudates for their growth. The pathogenic forms of the soil have been shown by many workers to produce toxins *in situ* and these remain stable in many cases for considerable periods. In sterilized soils amended with stable organic matter like green leaf and oats, *F. vasinfectum* has been found to produce fusaric acid up to 2·9 and 7·9 μg./g. of soil respectively. This organism can also be induced to produce mutants under ultraviolet irradiation, some of which are capable of synthesizing greater quantities of fusaric acid *in vitro* than the parent culture.

One of the heavy metals required by *F. vasinfectum* for normal *in vitro* production of fusaric acid is zinc. Fusaric acid is not formed when the concentration of the metal is below 0·08 mg./litre, the optimum being 0·24 mg./litre; levels higher than 0·4 mg./litre inhibit the production of the toxin. This work has a direct bearing on the field problem of wilt. In soils where cotton wilt by *F. vasinfectum* occurs freely, the level of zinc present is lower than in those harbouring the pathogen and not showing typical wilt.

It is obvious that the wilt fungus requires, *in vivo*, metals, pectins and presumably a good source of nitrogen for its development of toxin. The protein and non-protein nitrogen contents of both resistant and susceptible varieties of cotton plants differ widely and the susceptible varieties make available large quantities of non-protein nitrogen *in vivo* upon which the development of fungus toxin largely depends. This has been confirmed by *in vitro* tests where the fungus has been shown to depend on non-protein nitrogen sources for the elaboration of the toxin. Similarly, the roots of the susceptible varieties produce more of pectin *in vivo* than the resistant varieties and possibly the roots are another *in vivo* energy source on which the pathogen depends for developing its twin enzyme systems, the pectin methyl esterase and the pectin galacturonase, without which the organism cannot synthesize the toxin.

One of the factors contributing to the resistance of cotton plants to wilt is the presence of cystine in the resistant plants. There are two ways of inducing susceptible plants to produce cystine and induce resistance to wilt: (1) amending soils with zinc prior to growing the plants and (2) growing susceptible cottons at 37·5°C. The possibility of fusaric acid molecule splitting at the high incubation temperature (37·5°C.) and its utilization in respiratory processes of the plant tissue suggests itself as an alternative explanation. It also indicates the possibility of *in vivo* chelation of heavy metals with cystine, thus withdrawing these metals which are vital for the potentiation of fusaric acid. One of the effects of zinc amendment is retardation of tissue respiration in susceptible cotton plants grown in zinc-amended infested soils and bringing it down to the level of normal healthy plants. Increased respiration of the tissues of cotton plants grown in infested soils seems to be the major change occurring with the onset of toxaemia in the plants and the role of zinc in nullifying this effect needs further study.

Investigations on the uptake of ions and their derangement in wilt-susceptible cotton plants have indicated that, apart from the loss of potassium and an increase in manganese *in vivo* there is strong evidence of the appearance of ionized calcium during pathogenesis. Although the resistant plant also shows ionized calcium lines nearly as strong as the susceptible plant under toxaemia, the healthy susceptible plant shows very weak ionized calcium lines. Therefore, calcium ionization is essentially ascribable to the possible dissociation of the fusaric acid molecule *in vivo* and the consequent changes it would bring about in respiration and in the ionization of the neutral ion — calcium.

SOME ASPECTS OF REPRODUCTION IN INDIAN FARM ANIMALS

AN understanding of the pattern of reproduction in farm animals, an important factor in livestock improvement, was stressed by Dr. P. Bhattacharya in his presidential address to the Section of Zoology & Entomology. Dr. Bhattacharya observed that in view of the newer knowledge gained, the old concept that pre-coital sex play, the act of coitus and the presence of seminal plasma are not essential for reproduction has to be somewhat modified. Pre-coital sex play affects the quality of semen in the male, and influences the mechanism of ovulation in the female. Seminal plasma appears to play a role in causing full development and maturity of uterus and genitals in the female. One of the important problems facing the livestock expert, he said, is to find ways and means of improving fertility of farm animals. Concluding, Dr. Bhattacharya pleaded for more intensive research in this field.

The researches on reproductive physiology of Indian farm animals have shown that the physical characteristics of semen of Indian animals do not markedly differ from those reported for European livestock. In the buffalo, the volume of ejaculate and ascorbic acid content have been found to be significantly lower than those in bulls. In Kumauni hill bulls, a significant correlation between seminal ascorbic acid and fructose content has been observed but this relationship is non-existent in buffalo semen. In buffaloes, rams and goats, a linear relationship has been found to exist between the volume of ejaculate and concentration of fructose; a similar relationship has also been observed between sperm concentration and fructolysis. The initial fructose content of semen and the rate of fructolysis have been found to be reliable indices for assessing the concentration of active spermatozoa in the ejaculate of the buffalo.

The life span of buffalo spermatozoa in the preserved sample has been considerably extended by using glucose-bicarbonate diluting agent containing egg yolk and sulphamezathine powder. Egg yolk-glycine as a diluent has been found to preserve buffalo and ram spermatozoa appreciably longer than egg yolk alone. Semen preserved at sub-zero temperatures has been found to be active and 3-year-old frozen semen has effectively impregnated cows and yielded healthy calves. Preservation of semen at room temperatures (20°C.) is an important development, particularly for countries like India, and more attention has to be paid to this aspect of the work.

The quality of semen of the farm animals has been found to vary considerably during different seasons of the year. There is deterioration of semen quality during autumn when the atmospheric temperature and relative humidity are both high. Seasonal effect on the different endocrine glands has also been observed, the activity of adrenals, thyroid and the testes decreasing during summer.

The reproductive phenomenon in female farm animals has engaged the attention of workers in India only recently. Such aspects as the age at puberty and at first calving, duration of oestrus, length of oestrus cycle, gestation period, sex ratio and incidence of twinning and multiple births in certain breeds of Indian cattle have been investigated. The age of puberty and first calving is higher in Indian cattle as compared to European breeds; the incidence of twinning is higher in European cattle. In other respects the European and Indian cattle resemble each other. The duration of oestrus and the gestation period in buffaloes have been observed to be longer than in cows.

The methods developed for inducing ovulation, super-ovulation by the use of gonadotrophins and ova transplantation have enormous potentialities in improving the animal wealth of our country.

VARIATION IN MAN

THE presidential address of Dr. G. M. Kurulkar to the Section of Anthropology & Archaeology, entitled 'Variation in Man', deals with the subject in three parts. In the first part, ancient Indian concepts on the variation in man have been discussed from the points of view of *Ayurveda*, *Kamasastra* and *Samudrika Sastra*. The second part is concerned with the part biological sciences, particularly genetics, are playing in modern anthropological investigations. The third part discusses the new concepts incorporated into the science of physical anthropology and how they could be used to effect improvements in the work of medical care and health organizations and also to gain a better understanding of the concept of disease. It is concluded that for a better understanding of the causes of disease, medical sciences have to take into consideration cultural anthropology, sociology and philosophy.

Anthropology, in the past, was directed to taking measurements of external form only. The new physical anthropology tries to understand primate evolution and variation in man with the help of genetics. Population genetics presents the anthropologist with a clearly formulated and experimentally verified conceptual scheme. An essential condition is that a gene must get a chance to be transmitted and to influence a population in generations, it must get successive similar chances, so that its frequency in a population would increase. Such chances would depend upon (1) tendencies of a population in selecting mates, (2) rate of fertility in an individual, (3) size of a population, (4) stable or migrating nature of a population, (5) facilities for mixing up of different populations, and (6) isolation of a population.

Of the various genetic traits in man, the different types of blood groups and the presence of haemoglobin are the universal ones. Other genetic traits are also recognized. Taste reactions, patterns of superficial veins, presence or absence of some muscles, colour blindness, papillae on the tongue, hair pattern, dermatoglyphics, finger and toe irregularities, deafness, visceral asymmetry are some of the important genetic traits being studied. Of all these, blood groups offer several advantages in genetic study, because they are inherited in a known way according to Mendelian principles, and they are not altered by differences in climate, food, illness or medical treatment. There is a considerable correlation between geography and the distribution of different blood groups with the relevant antigenic substances, and their frequency in the population is steady so far as the present observations go.

Population studies are closely associated with ecological studies. Effects of climate, nutrition, density of settlement and of natural resources on selection and adaptation of human organism are fertile fields for coordinated study. The influence of social organization on biological make-up of a population may be approached with an ecological slant. Ecological studies can also serve as a framework for the study of the relation between size and structure of a population on the one hand and biological change and the nature and relation of genetic and non-genetic factors in man's adaptation to his environment on the other. Thus, studies of physical anthropology rest on judicious physical measurements and observations and genetic study, integrated with population studies and human ecology.

In the field of medicine, anthropological knowledge would be useful in two directions: firstly towards the improvement of medical care and the work of health organizations, and secondly towards understanding the cause of disease. In order that health programmes or medical care work should be of utmost benefit to the society, it is necessary to investigate the social processes which would be influenced by these undertakings. As cultural changes occur with least conflict along lines of established community patterns, the need for conducting such programmes along these patterns becomes evident. When new health programmes are contemplated in India, this aspect should not be lost sight of.

In the understanding of disease, anthropology is assuming great importance. Recent advances in medicine have increased the life expectancy of man. But it looks as though this will result in mortality being replaced by morbidity. The chief causes for this are: (1) multiple stresses and strains to which a person is exposed under the present-day conditions, (2) a person is required to give up a part of his freedom of action in the social set-up, and (3) the strain to which a person is subject to by trying to adapt himself to the environment to which his physical and mental make-up may not be quite capable of adjusting itself.

Concepts of disease are changing. The earlier concept based on disturbance in the cell as a cause of disease is likely to be replaced by a new concept. Environment is constantly influencing the personality of an individual. If his response systems can cope with the demands of the environment then nothing may happen, otherwise there will be psychological disturbances followed by functional disturbances. Once the functional disturbances start, cellular damage will take place producing structural alteration.

SOME PROBLEMS OF HEART DISEASE IN INDIA

DR. A. K. Bose's address to the Section of Medical & Veterinary Sciences deals mainly with the three principal heart diseases, viz. coronary heart disease, hypertension and rheumatic heart disease, which have a high incidence and cause as high a mortality in India as in other countries. The present state of our knowledge regarding the epidemiology, etiology, clinical diagnosis, treatment and prevention of these diseases has been discussed with special reference to research carried out on these aspects. Another minor heart disease, the congenital heart disease, has been briefly dealt with. These diseases pose many problems to the medical men, and in the suggestions put forward to solve these problems and combat the diseases, Dr. Bose has emphasized the need for greater attention to research into the nature of these diseases.

Cholesterol and particularly β-lipoproteins in blood have been associated with atherosclerosis but it is not clear why the disease is confined to coronary or/and cerebral arteries. Though much work is being done on the biochemical factors in blood and their relation to atherosclerosis, no attempt has been made to study the influence of arterial metabolism and the physical configuration of arteries. These two aspects may throw light on the production of zonal atherosclerosis. The importance of dietary fat in atherosclerosis is recognized but has not been experimentally confirmed, since drastic reduction of fat in the diet does not prevent the progress of the disease. The people in different parts of India have definite but different dietary habits, and a rich field exists here for investigation into the relation between diet and incidence of atherosclerosis.

There appear to be no definite etiological factors associated with the occurrence of essential hypertension. For persistent hypertension, spasm of the arteries is a primary factor, but what conditions bring about the spasm are not known. Similarly, in hypertension caused by endocrine imbalance, carticohypothalamic imbalance, presence of renin or hypertension in blood, considerable scope exists for research, particularly on problems connected with the standardization of the several clinical types of hypertension for the development of definite therapeutic procedures.

Rheumatic heart disease is common in India and studies relating to the factors responsible for the rheumatic heart condition should receive greater attention. The mechanism of production of antihyaluronidase titre in rheumatic fever patients and hereditary aspects of rheumatic heart disease should be investigated. No specific laboratory diagnostic test for rheumatic fever, leading to heart infection, is available and the development of such a test would enable an early diagnosis which is essential for effective treatment. The public health aspect of rheumatic fever should not be ignored and its etiology and pathogenesis merit more intensive study. The disease should be made a reportable disease as in other advanced countries of the world and plans must be formulated for its control and treatment.

CYTOGENETICS & CROP IMPROVEMENT

THE presidential address of Prof. P. N. Bhaduri to the Section of Agricultural Sciences is of topical interest to India in the context of chronic food shortages in the country. Two factors associated with this shortage are matters of grave concern. They are: (1) the continuously increasing demand for foodgrains as a result of steadily growing population and (2) the average yields of our important crops are far below those achieved in other countries. That there are methods other than those traditionally employed for improving crop yields is not commonly realized. No doubt, better agricultural practices, use of improved and pedigree seeds and other aids play an important part, but one of the economical and effective methods of improving the quality and yields of crop plants is the breeding of superior varieties suited to specific ecological conditions. Thus, the importance of applying cytogenetical methods and techniques for breeding improved varieties of crop plants cannot be overestimated. Dr. Bhaduri considers that the introduction of such breeding practices can come about only by (1) encouraging research in genetics and cytology, (2) laying more emphasis on the teaching of modern genetics and experimental cytology, and (3) establishing zonal research centres for advanced training in modern methods of plant breeding.

The two principal methods which have been made available to plant breeders in recent years are mutation breeding and chromosome doubling (polyploidy breeding). Two other methods, which are offshoots of the polyploidy breeding method, are (1) genome substitution and genome alteration and (2) karyotype alteration.

One of the gaps in our knowledge of mutation breeding is that methods are still not available by which mutations of a desired kind may be induced with certainty in a particular crop. In spite of this, many improved strains of commercial crops have been developed. High yielding and leaf spot-resistant strains of peanuts, rust-resistant wheat and oat varieties, strains of white mustard and rape with higher oil content, etc., are examples of the success of the mutation breeding method. In India attempts have been made to artificially alter the germplasm of some economic plants for producing improved strains. Improved strains of wheat, high oil-yielding sesamum and tall jute mutants have been produced by X-ray irradiation. A mutant of dwarf habit paddy with large number of tillers has been developed; this variety has been found to be less susceptible to lodging and highly suitable for cultivation in rich soils.

The importance of polyploidy breeding becomes evident from the fact that most of our economic crop plants such as wheat, cotton, tobacco, sugarcane, potato, mustard, coffee, etc., are polyploids. One of the considerations in this type of breeding is that breeding programmes for self-fertilized and cross-fertilized plants should be chalked out differently. The problem of genotypical balance does not arise in the case of these plants; polyploidy breeding and selection of superior varieties of induced polyploid crops are very much favoured.

Adopting chromosome doubling technique, a triploid beet with 10-12 per cent higher sugar content than the normal beet has been developed. Similarly, a variety of hardy winter steel rye with superior baking qualities of flour and seed sprouting has been evolved. High yielding polyploid forage plants and superior tetraploid fruit trees have also been produced.

A recent finding that mutation can alter the reactions of plants to their normal environment and evolve new ecotypes has great scope for exploitation, as strains suitable for a particular climatic condition can thereby be produced.

Another recently developed method which holds great promise for adoption in India is the one based on genome substitution and genome alteration. This method can be employed only after a thorough analysis of the genomes of the particular crop in relation to its wild relatives has been made. Paddy being a secondarily balanced polyploid species as compared to allopolyploid crops like wheat, cotton and tobacco, methods applicable to these crops cannot be used straight away in the case of paddy. For this purpose, amphiploids involving different species of *Oryza* and related genera and different varieties of paddy including *indica-japonica* hybrid should be first produced. Study of genome substitution and analysis in these amphiploids is bound to provide valuable data leading to the evolution of new and improved varieties. From such studies a clearer understanding as to the origin of the cultivated *Oryza sativa* and its phylogenetic relationship to other related plants would also be gained.

RUMINANT METABOLISM

THE salient features of ruminant metabolism, particularly the role of microflora in helping the digestion of coarse feeds, were discussed by Dr. S. N. Ray in his presidential address to the Section of Physiology. While advocating the need for supplying balanced rations to cattle in India, Dr. Ray pointed out that the reason for lower nutritional value of milk in India, particularly the low level of vitamin A, is due to the shortage of green fodder during a major part of the year. It is, therefore, imperative to provide a year-round supply of green feed as such or in ensiled form.

The important feature of ruminant metabolism is the symbiosis between the host and the vast population of bacteria and protozoa which thrive in the rumen. The complex carbohydrate, cellulose, which is digested to a very slight extent by most of the single-stomached animals, is effectively broken down in the rumen into simple volatile acids like acetic, propionic, butyric and valeric which are absorbed into the system to supply energy. In order to carry out these fermentative processes, the rumen microflora require a source of nitrogen, which may be either complex proteins or simple nitrogenous substances like urea or ammonium salts. The latter compounds are useless in simple-stomached animals as sources of body or milk proteins, but certain bacteria and protozoa of the rumen can utilize them to synthesize body proteins provided sufficient starch is also present. These microbial proteins have been found to contain all the essential amino acids, and when digested later in the fourth stomach supply the host with all its requirements of high quality protein. Urea can provide all the protein required by a ruminant only in the presence of ample starch. However, as starch-containing feeds are rather costly and are in short supply in India and as cellulose-splitting organisms cannot thrive in the presence of urea alone, the proportion of urea should not exceed one-third of the nitrogen supply in the ruminant ration for efficient utilization of coarse feeds. Another useful function of the rumen microflora lies in the synthesis of B-vitamins, so that, unlike simple-stomached animals, the ruminants do not depend on a supply of preformed B-vitamins.

The conversion of roughage into useful products by the ruminants is not, however, a very efficient process from the thermodynamic point of view. Ruminants can utilize only 50-60 per cent of the gross energy present in straws and other roughage. This is due to the deposition of lignin in mature plants. Due to lignification of its tissues, cellulose and other components of the plant cells are not easily available to the rumen microflora. Treatment with dilute alkali is effective in increasing the digestibility of coarse fodders. In the utilization of digested nutrients also, the ruminants exhibit lower capacity. In single-stomached animals, about 15 per cent of the digested feed is utilized for heat generation and the rest for increasing the body weight or production of milk and work. In a ruminant, on the other hand, the heat losses amount to 30-50 per cent of utilized energy. All these factors emphasize the need for supplying a comparatively larger feed to ruminants. The total daily requirement of dry matter is 2 lb./100 lb. body weight. The energy requirement is 30 per cent more per unit body weight than in human beings. Due to greater loss of body nitrogen in the faeces, the requirement of proteins in ruminants is also much higher than in single-stomached animals of corresponding body weight. Indian breeds of cattle, however, require 25-30 per cent less energy and protein than the cattle in Western countries.

The requirement of minerals like calcium, phosphorus, iron, copper and cobalt is also higher in ruminants. Cobalt has a special place in ruminant physiology: only this class of animals has been found to require this mineral in the feed for the production of B-vitamins in general and of vitamin B_{12} in particular.

Of all the vitamins, vitamin A is the most important for ruminants. Herbivorous animals get it from the carotene present in young grasses. In India, green feeds are available only during the monsoon months. After the rainy season, the carotene content of grasses diminishes rapidly so that by the end of winter and during summer very little supply of this provitamin is available. The result is that vitamin A deficiency symptoms like night blindness and blindness of calves have been reported during these seasons from practically every State in India. Pneumonia and diarrhoea in young stock is also caused through secondary infections in animals deficient in vitamin A. The remedy lies in feeding berseem and lucerne in winter or ensiled green grasses in late winter and summer months. As vitamin A content of milk is dependent on the level of intake of carotene, a year-round supply of green feeds as such or in ensiled form is highly desirable.

One of the main causes for the poor quality of Indian cattle is the faulty feeding practices adopted in the country. Balanced rations will go a long way in improving the productive capacity of the cattle. In India the supply of energy and proteins from currently available sources of feeds falls short by 60 and 75 per cent respectively. This shortage can be met, without affecting human food supply, through a proper utilization of available land.

PSYCHOLOGICAL RESEARCH IN INDIA

DR. A. K. P. Sinha's presidential address to the Section of Psychology & Educational Sciences is largely a survey of the present status of psychological research in India and of the measures to be taken to improve it to meet the needs of a changing society. Dr. Sinha has stressed the need for a planned and co-ordinated research in psychology to solve the diverse social and economic problems arising as a result of technological development in the country.

A critical examination of research in psychology done so far in the country reveals many shortcomings. Adequate standardized tests on the basis of which human behaviour could be predicted and controlled, have not been developed and this is one of the important problems confronting the psychologist. Other problems which also demand urgent attention are those relating to mental health, social prejudices, national and international tensions. Research into these and many other problems is largely unco-ordinated and no planned research has been attempted. Group research on a countrywide basis has to be undertaken to achieve worthwhile results in these fields. There are other problems whose solution needs the co-operative effort of workers in such disciplines as psychology, sociology and anthropology. The problems arising in respect of tribal people and rehabilitation of refugees are examples which come under this category.

In order to stimulate planned and coordinated research in psychology in the country, the setting up of a Psychological Research Development Board is advocated. The main functions of such a body would be to plan research programmes and promote intra- and interdisciplinary co-ordination of research. The establishment of a National Institute of Psychology, under the auspices of the Central Government, has also been suggested. The Institute, in addition to conducting research into problems of national importance, will be charged with the task of training psychologists.

TRENDS IN ENGINEERING EDUCATION & RESEARCH

THE need for reorganizing engineering education and research in the country to meet the demand for engineering personnel required for the national developmental programmes forms the main thesis of Prof. C. S. Ghosh's address to the Section of Engineering. A portion of the address is devoted to computing machines and other aids in the solution of engineering problems, and to a detailed treatment of the principle of operation of the transformer analogue computer. The lines on which teaching and research in engineering should be reorganized and the role of industry in the training of engineers have also been discussed. Prof. Ghosh is of the view that the engineering curriculum in our universities should be suitably modified so that engineers with a sound knowledge of basic engineering sciences can be produced to fit into the pattern of industrial development in the country.

In the past, more importance was given in our engineering education to the training of 'practical' engineers than to imparting a fundamental knowledge of the basic engineering sciences. The technician or the 'practical' engineer is conservative and he does not readily take to the introduction of new materials and techniques. Modern engineering practice demands, on the part of the engineer, a sound knowledge of the sciences basic to engineering, and the use of mathematical tools. For example, electronics is playing an increasingly important role in electrical engineering, and a sound knowledge of electronics and electronic devices has become essential for an electrical engineer. In the field of mechanical engineering, the engineer is faced with problems of a fundamental character such as heat transfer, energy conversion and fluid mechanics. It is, therefore, necessary that in the education of the young engineer, the emphasis should not merely be on the 'how' but also on the 'why' of engineering. This is the job universities and technical institutions in the country should concern themselves with and the industry must concern itself with the task of training engineers in the 'how' of engineering.

Forty-fifth Indian Science Congress, Madras

THE Forty-fifth Session of the Indian Science Congress Association was held during 6-12 January 1958 at Madras and was attended by over 1800 delegates from India and abroad. Prof. M. S. Thacker, Director-General, Scientific & Industrial Research, presided over the session which was inaugurated by the Prime Minister. Sixty eminent scientists from Australia, Bulgaria, China, Czechoslovakia, France, German Democratic Republic, West Germany, Japan, Poland, Sweden, U.K., U.S.A., U.S.S.R. and Yugoslavia participated in the deliberations of the Congress. Specialized Agencies of the United Nations including FAO, Unesco and WHO, and learned societies such as the German Academy of Sciences, Polish Academy of Sciences and British Association for the Advancement of Science were also represented.

About 1500 technical papers were presented and discussed at the 13 Sections of the Congress as follows: Agricultural Sciences, 103; Anthropology & Archaeology, 30; Botany, 144; Chemistry, 460; Engineering & Metallurgy, 38; Geology & Geography, 127; Mathematics, 30; Medical & Veterinary Sciences, 68; Physics, 114; Physiology, 76; Psychology & Educational Sciences, 22; Statistics, 13; and Zoology & Entomology, 147.

A number of symposia and joint discussions were organized under various Sections. The subjects included: Impact of industrialization on society with particular reference to India; Biological assay; Energy metabolism; Isotope technique in physiology; Application of genetics in the breeding of economically important insects; Microchemistry; Recent advances in the chemistry of plant products; Radiation chemistry; Role of cytoplasmic constituents in cell metabolism; Fisheries and marine biology in India; Corrosion of metals; Design and manufacture of chemical plants and equipment; Design and manufacture of control and measuring instruments; Some problems of research in engineering and technology; Recent advances in statistical thermodynamics including reversible processes; and Magneto-hydrodynamics and its applications in astrophysics.

Fifteen special lectures and five popular lectures were delivered during the session by foreign scientists participating in the Congress. These included the following: *Oxygen in the manufacture of iron and steel* (Prof. I. P. Bardin, U.S.S.R.); *Some recent developments in industrial electronics* (Prof. P. H. Craig, U.S.A.); *Biological importance of nucleo-proteins* (Mme. Y. Khouvine, France); *Some aspects of the fluid state* (Prof. E. G. Richardson, U.K.); *History of the discovery of vitamins* (Dr. Leslie J. Harris, U.K.); *Syntheses of aminosugars* (Prof. Richard Kuhn, West Germany); and *The scientist in the modern world* (Prof. F. D. Rossini, U.S.A.).

At the Science Exhibition organized concurrently with the Congress Session and inaugurated by the Prime Minister on 6 January, a large variety of scientific instruments, apparatus and appliances, models, charts, and technical journals and other publications were displayed by 24 firms and organizations who participated in the exhibition.

The Executive Council of the Indian Science Congress Association decided to hold the Forty-sixth Session at Delhi during January 1959; Dr. A. Lakshmanaswami Mudaliar, Vice-Chancellor, Madras University, was elected General President of the Congress for 1958-59; Prof. P. Parija, Vice-Chancellor, Utkal University, was elected General President for 1959-60. The following sectional presidents were elected: *Mathematics* — Prof. M. Ray (Agra); *Statistics* — Dr. Anil Kumar Bhattacharya (Calcutta); *Physics* — Dr. A. K. Dutta (Cuttack); *Chemistry* — Dr. S. R. Palit (Calcutta); *Geology & Geography* — Dr. C. S. Chatterjee (Patna); *Botany* — Dr. R. Misra (Banaras); *Zoology & Entomology* — Dr. B. S. Bhimachar (Calcutta); *Anthropology & Archaeology* — Shri V. D. Krishnaswami (Aurangabad); *Medical & Veterinary Sciences* — Shri P. G. Pande (Lucknow); *Agricultural Sciences* — Dr. B. K. Kar (Barrackpore); *Physiology* — Dr. N. P. Benwari (Gwalior); *Psychology & Educational Sciences* — Prof. S. S. Jalota (Banaras); and *Engineering & Metallurgy* — Dr. M. Dutta (Calcutta).

Dr. A. K. Dey (Calcutta) and Dr. B. N. Prasad (Allahabad) were elected General Secretaries and Dr. B. C. Guha was elected Treasurer.

The Council decided to hold a symposium on Social Implications of Technological Advance in India during the 1959 Session of the Congress.

Studies in Coal Constitution

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DESPITE the view that "the constitution of coal is one of those puzzles that allow the seeker to discover a little here and there and lead him on like a will-o'-the wisp with just enough encouragement to keep him in the hunt", the subject of coal constitution has continued to engage the attention of scientists in many countries. Bone and his collaborators[1], by wet oxidation of coal and study of the resulting carboxylic acids, were able to postulate that coal contains basically aromatic structures. X-ray investigation by Mahadevan[2] and later by Riley[3] led to the concept of graphite-like crystallites in coal, graphite being the limiting aromatic structure produced by indefinite condensation of benzene rings. Later, Bangham and his collaborators[4] brought in the concept of colloid chemistry to bear on coal constitution problem. This led to the concept of micellar structure of coal and the so-called Bangham model of coal.

But despite considerable work on coal constitution which was carried out more or less on orthodox lines, the subject of coal constitution had remained till recently singularly intractable. During the past few years, however, a great impetus was given to the subject in countries like U.S.S.R., U.K., the Netherlands, Canada, Australia and India. It now appears that the basic structure in coal comprises of 3-5 fused benzene rings* connected with similar groups through peripheral groups which are maximum in the non-coking coals cross-linked in a manner which produces the typical toughness of coal. During coalification, the number of fused rings apparently remains more or less the same; the number of peripheral groups, however, decreases with metamorphism, particularly the reactive oxygenated groups like COOH, etc., and these become almost negligible in the coking coal region. In the anthracite region the number of these groups further decreases and the number of fused rings is believed to increase to 20 or more. Further, in the non-coking coals the nucleus and the peripheral groups are said to occur randomly, probably hydrogen bonded to each other through the reactive oxygen groups. In the coking coal region there is a tendency for the nucleus to occur in 2 or 3 layers assuming a 'liquid-like' structure, postulated by some X-ray workers.

Work carried out at the Central Fuel Research Institute, India, on coal constitution is reviewed in the present paper.

Reactive groups in coal

Studies carried out on the hydroxyl groups have shown[6,7] that oxygen as OH group is about 54 per cent of the total oxygen in vitrain of carbon content less than 85 per cent and in composite coals about 43 per cent. The ratio begins to decrease sharply at about 85 per cent carbon in vitrains and in composite coal, and becomes negligible at about 91 per cent carbon. Wyss[8], however,

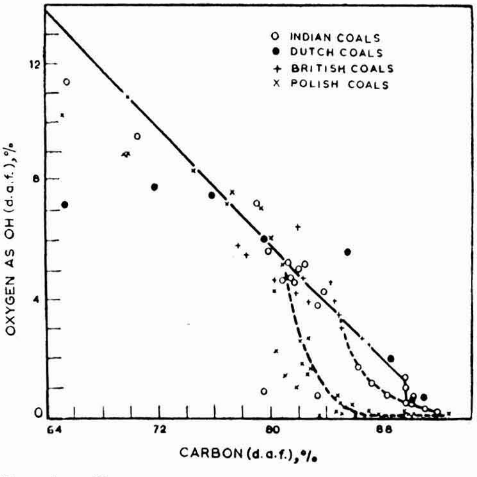

FIG. 1 — OXYGEN PRESENT AS HYDROXYL GROUPS IN DIFFERENT RANK COALS

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*Friedel[5] recently compared the extinction coefficient obtained in visible and ultraviolet range for poly-condensed compounds and coal samples and found that the latter had a very low coefficient. Based on this evidence, he has questioned the existence of fused benzene ring structures in coal.

finds that the discontinuity in the acetylable hydroxyl content occurs at about 90 per cent carbon for bright coals. According to him the readily acetylable hydroxyl is almost constant at 40 per cent of the total oxygen present, but at 90 per cent carbon, hydroxyl oxygen falls sharply to about a tenth of the total oxygen. Using ketene as acetylating agent, workers at Fuel Research Station, U.K.[9], found that 60 per cent of oxygen in coal is present as OH. Recently Van Krevelen[10] reported much lower values. The values obtained by different workers for OH group in different ranks of coal are presented in Fig. 1. The COOH groups, which are maximum in low rank coal, become negligible in coals with carbon content above 80-82 per cent. The values for COOH and CO are presented in Figs. 2 and 3 respectively. In Fig. 4, the total reactive group present in

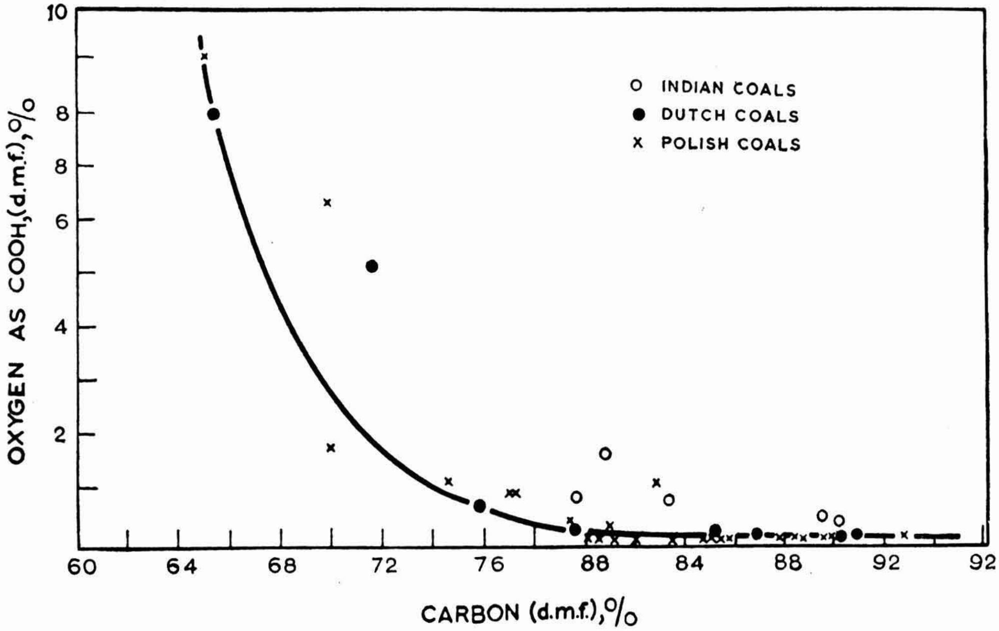

FIG. 2 — OXYGEN PRESENT AS CARBOXYL GROUPS IN DIFFERENT RANK COALS

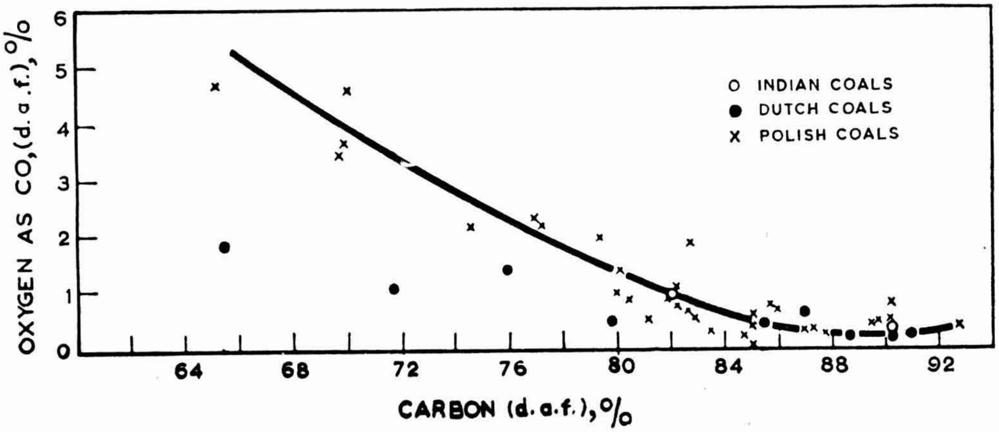

FIG. 3 — OXYGEN PRESENT AS CARBONYL GROUPS IN DIFFERENT RANK COALS

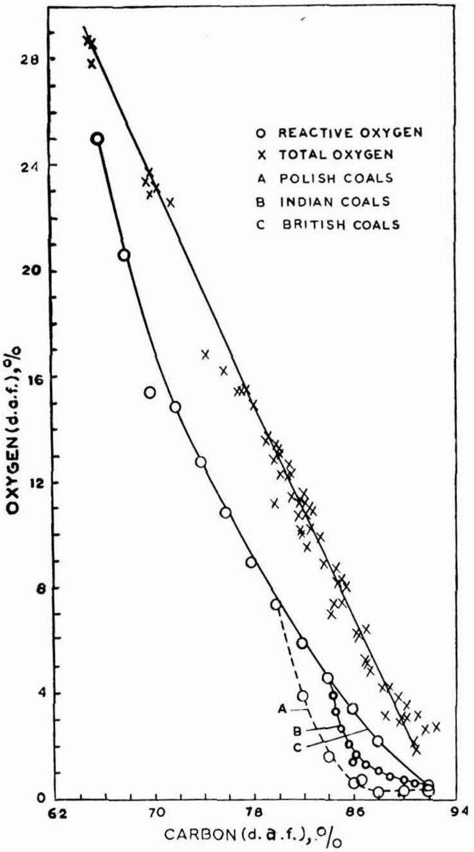

FIG. 4 — TOTAL REACTIVE OXYGEN IN DIFFERENT RANK COALS

different coals is given. It would appear that the development of coking properties in coals is closely connected with decrease in the total reactive groups.

When a comparison is made of the heat of wetting values in methanol, water and chlorobenzene of different rank coals and their corresponding hydrogen bonding energies calculated from their reactive oxygenated groups, it is found that only when it is assumed that the OH groups are chelated with their corresponding number of CO groups in coals containing up to 85 per cent carbon, that good correlation is obtained between the two values[11]. The sorption of water by different rank coals at different temperatures was also studied and it was found that the S_o in the BET equation represents the number of oxygenated reactive groups present in coal which are capable of hydrogen bonding rather than the so-called 'monolayer' (Fig. 5).

One way in which the CO. . .OH chelation can exist in coal is explained by the fact that coals contain quinone and hydroquinone structures and that these form quinhydrone structure[12]. Experiments carried out on the oxidation of coal (carbon content 80 per cent) at 70°C. for different periods indicate that whereas the total oxygen as OH and CO remains constant throughout the period of oxidation, oxygen as OH decreases with the progress of oxidation, and oxygen as CO increases[13] correspondingly. Further, when coal is hydrogenated at 375°C. at normal pressure as well as under pressure of 30 atm., it is found that the OH group increases from 2·4 to 4 per cent and the CO decreases from 1·1 per cent to almost zero[14]. This observation supports the concept of quinhydrone structure and it is also known that under certain conditions the quinone group is converted into semiquinone which has a lone electron and which behaves as a free radical. The presence of free radicals in coal has been postulated based on paramagnetic resonance[15] studies (Fig. 6). Assumption of 0·2 per cent oxygen as semiquinone gives $2 \cdot 5 \times 10^{19}$ radicals per gramme which is of the same order as that calculated from paramagnetic resonance measurements[15].

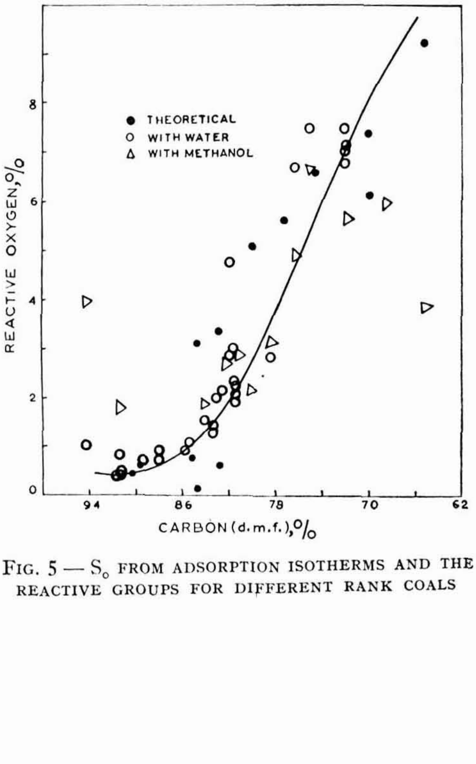

FIG. 5 — S_o FROM ADSORPTION ISOTHERMS AND THE REACTIVE GROUPS FOR DIFFERENT RANK COALS

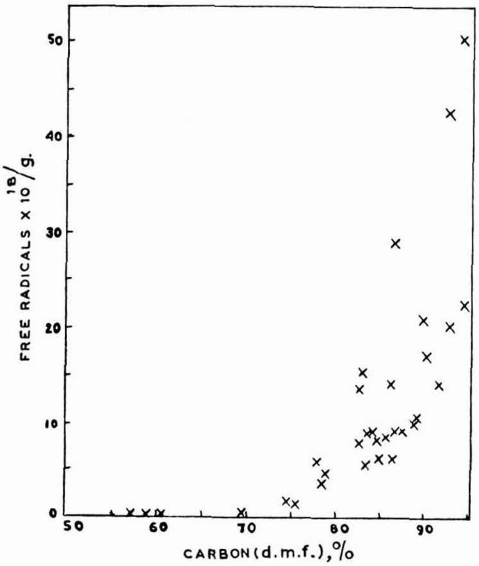

FIG. 6 — VARIATION OF FREE RADICAL CONTENT WITH CARBON CONTENT OF UNCARBONIZED COALS

When the reactive oxygenated groups are estimated by acetylation and their values compared with those obtained by Ubaldini's method for different rank coals, it is observed that excepting for lignite there is correlation between the two values for all ranks of coal[16]. The exception in lignite suggested the possibility of the OH groups existing partly in alcoholic and partly in phenolic form. When lignite is treated with alkali for about 20 min. and the ultimate analysis of the original lignite is compared with that of humic acid and of the residue, considerable difference is noticed in the carbon percentage which could only be attributed to hydrolytic fission occurring prior to the dissolution of humic acid in alkali[17] — the fission leading to an increase in the OH and COOH contents. These results have led to the concept of flavone and lactone structures in lignite.

Moisture in coal

Sorption-desorption studies on coal-water system at different temperatures have shown that while for low rank coals a rise in temperature decreases sorption (Fig. 7)[18], for coals of higher rank rise of temperature enhances sorption (Fig. 8). The rise in sorption with temperature indicates that water undergoes activated adsorption due to the presence of reactive groups. Although physical adsorption also takes place at the same temperature, activated adsorption can occur only in the presence of some activated groups or centres in the absorbent.

The sorption isotherms obtained for raw and degassed South Arcot lignite at 37·5° and 54·5°C. were subjected to thermodynamic analysis[19] (Fig. 9). These studies have indicated that the process is not a localized, non-interacting adsorption on a homogeneous surface but an interaction of adsorbate-adsorbent on a heterogeneous surface. The high heat of adsorption for low moisture sorption, the differential and free energy

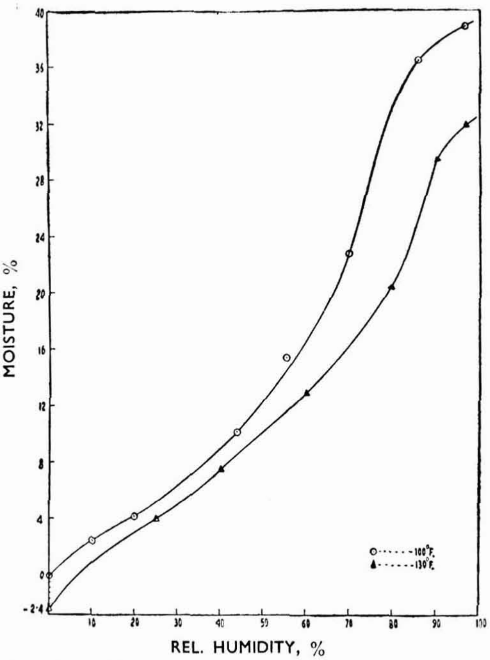

FIG. 7 — WATER SORPTION ISOTHERMS FOR SOUTH ARCOT LIGNITE

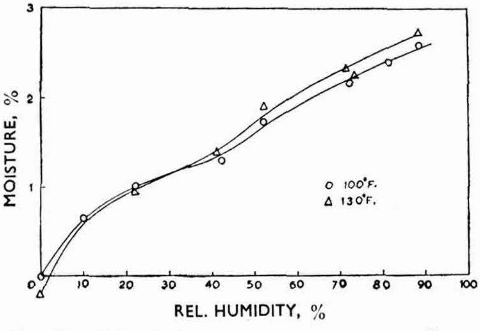

FIG. 8 — WATER SORPTION ISOTHERMS FOR JHARIA COAL

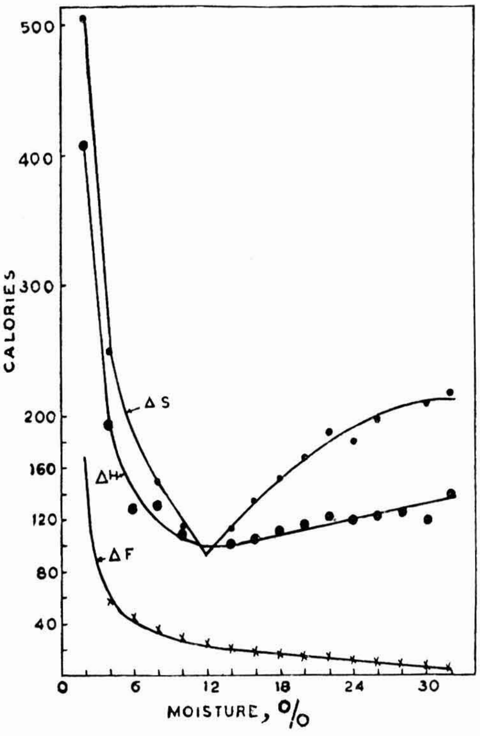

FIG. 9 — ΔH, ΔF AND ΔS FOR RAW LIGNITE

change, the general shape of the integral, free energy change and entropy curves indicate that forces other than physical adsorption are also involved.

Lignite contains carboxyl, carbonyl and hydroxyl groups. On the basis of the values of heat of adsorption at different moisture sorption levels it is assumed that the first 2 per cent of water sorbed forms hydrogen bonding with carboxyl groups and the next 6 per cent with effective hydroxyl groups. The values for oxygenated groups present in lignite calculated on this basis showed an excellent correlation with those determined by chemical methods.

The manner in which the rate and course of oxidation of coals are affected by the presence of moisture in the oxidizing stream of air has been investigated[20]. It has been possible to determine the rate of oxidation (as measured by the amount of oxygen used up in the process) by the rate of adsorption as well as reaction between coal and oxygen. For high rank coals the rate is found to be greater if the oxidation is carried out in a stream of humidified air. The reverse is true for coals of low rank. From a study of the variation in the CO_2/CO ratio in the exit gases, it is suggested that water participates in the reaction between coal and oxygen.

For coals of lower rank having a proportionately greater amount of active groups, the interaction with water results in partial blocking of the reactive sites with consequent decrease in the rate of oxidation. For coals of higher rank no such complication arises.

More direct evidence of the specific role of moisture has resulted from a study of the interaction between coal and water in sealed systems in the absence of oxygen at lower temperatures[21]. The reaction between coal and water under these conditions resulted in the evolution of gaseous products like CO_2, CO and H_2, hydrogen being the most significant entity indicating the reaction between water and coal. Thus, moisture which has been believed hitherto to be merely physically adsorbed, is actually chemically linked with the chemical constitution of coal and the rank, and therefore the properties of coal can be described by the single parameter of moisture alone.

Oxidation of coals

Determination of reactive groups in Jambad-Bowla and Jharia coals before and after subjecting them to aerial oxidation at 170°C. for different periods has shown that at any stage of oxidation, almost the whole of the incoming oxygen appears as reactive oxygen, the major part being in the form of carboxyl groups and the unaccounted oxygen which may be present as aromatic ether and/or heterocyclic oxygen remains unaffected throughout the course of oxidation[13]. Application of the ring indices method to the coals before and after oxidation indicates that the aromatic rings are not ruptured under the conditions of oxidation employed. Oxidation results primarily in the removal of the aliphatic and/or alicyclic carbon of the peripheral groups. The reaction may be different at higher temperatures. The suggested mechanism of oxidation has led to a method for the determination of ‘ cyclicity ’ of coals.

Different rank coals were oxidized under identical conditions in an air oven at 200°C. for 200 hr. and from the products of oxidation humic acids were isolated. It was observed that irrespective of the rank of coal the humic acids that result from oxidation are similar in character though not chemically identical[22]. The major active groups present in humic acid were COOH, phenolic OH and CO. The base-exchange capacity and equivalent weight, basicity, molecular weight, distribution of reactive groups were studied and it was found that the properties of the acids are related to the rank of the coal from which they are prepared.

The significant fact that emerges from these investigations is that high rank coals contain few functional groups like —OH, —COOH, whereas the acids obtained on oxidation contain a substantial amount of these groups. On the other hand, low rank coals which contain an appreciable percentage of oxygen as functional groups (especially —OH) yield humic acids which are more or less similar to those obtained from high rank coals. The major change that occurs during aerial oxidation is the formation of a preponderant amount of —COOH groups in coals, irrespective of rank. The other significant change that occurs during oxidation is reflected in the molecular weights of the humic acids isolated from coals oxidized to different extents (at 200°C.). The molecular weight of the acid declines slowly at a steady rate with progress in oxidation and after about 200 hr. of oxidation registers a sudden drop which may be ascribed to the breakdown of the ring structure of the parent material.

Viscosity of alkali salts of humic acids at different dilutions was also studied[23,24] and it was found that these acids behave as polyelectrolytes. The flow behaviour of humic acid can be explained in terms of association of the reactive groups through hydrogen bonding.

The study of reactive acidic groups in coal has also led to information on fixation of nitrogen in coal by reaction with ammonia resulting in the synthesis of a product which may find use as a fertilizer and soil conditioner.

Carbonization of coal

Active groups like OH, CO and COOH were determined in high and low rank coals, after subjecting them to different temperatures of carbonization under slight vacuum (Kini, K. A., unpublished data). The carboxyl groups disappear at about 400°C., but the percentage of hydroxyl group decreases and then again increases, showing a maximum between 400° and 600°C. This increase is relatively more in the case of high rank coals. The surface area by BET method using argon shows a maximum at higher temperatures, i.e. 600°-800°C.

It has been observed[12] that when non-coking coals are carbonized at 350°-420°C., there is a decrease in their reactive oxygen content and corresponding increase in the unreactive oxygen content. For example, in the case of 77·28 per cent carbon (d.m.f.) coal, the amounts of reactive and unreactive oxygen were 9·06 and 6·31 per cent respectively. On subjecting the coal to carbonization at 350°-420°C., the reactive oxygen decreases to 4·01 per cent and unreactive oxygen increases to 8·41 per cent. On the other hand, with coking coals there is not much significant change in the reactive and unreactive oxygen at these temperatures. The variation in the total reactive and unreactive groups with temperature of carbonization is shown for different rank coals in Table 1.

The above results enable a differentiation to be made between the behaviour of coking and non-coking coals on heating. In the coking coal, the units are loosely held through Van der Waal forces which are weakened on heating, and at a temperature between 350° and 450°C. the coal exhibits plastic flow. This is followed by a disproportionate reaction leading to the formation of compact condensed ring structures and formation of coke at higher temperatures.

On the other hand, the units in the non-coking coals are strongly held through hydrogen bonds at ordinary temperatures and when these are subjected to heat (350°-450°C.) the hydrogen bonds break and the functional groups which are already in juxtaposition undergo condensation reaction leading to the formation of chemical bonds which hinder plastic flow with the result that the coal is converted into semi-coke without undergoing plastic flow. It is interesting to note that up to the semi-coke stage the mechanical strength of the residue obtained from non-coking coals is higher than that corresponding to coking coals.

Free radicals are produced in coking and non-coking coals when they are subjected to a temperature below 600°C.[15], and they seem to influence the properties of the coke during the semi-coke formation stage. Their exact mechanism is, however, not properly understood. It has been suggested[25] that

TABLE 1 — REACTIVE AND UNREACTIVE OXYGEN IN COALS CARBONIZED AT DIFFERENT TEMPERATURES

C (d.m.f.) %	Room temp.		385°-420°C.				500°C.				600°C.				700°C.				900°C.			
	(O_{OH}+CO) %	O_{UR} %	O %	O_{OH} %	O_{CO} %	O_{UR} %	O %	O_{OH} %	O_{CO} %	O_{UR} %	O %	O_{OH} %	O_{CO} %	O_{UR} %	O %	O_{OH} %	O_{CO} %	O_{UR} %	O %	O_{OH} %	O_{CO} %	O_{UR} %
77·28	5·63	4·77	12·10	2·98	0·40	8·72	7·17	0·79	0·32	6·06	5·43	0·54	0·23	4·66	—	—	—	—	1·14	0·49	0·24	0·41
80·03	6·40	6·30	9·94	1·58	0·15	8·21	7·74	0·74	0·26	6·74	4·79	0·15	0·15	4·49	3·42	0·00	0·14	3·28	0·58	0·00	—	—
82·72	8·69	7·67	8·23	—	—	—	6·13	0·00	0·10	6·03	3·72	—	—	—	0·89	—	—	—	—	—	—	—
82·92	8·52	8·45	8·86	—	—	—	6·16	0·20	0·14	5·82	5·07	—	—	—	2·84	—	—	—	0·50	—	—	—
84·69	7·86	7·56	6·87	—	—	—	4·05	0·12	0·10	3·83	2·24	—	—	—	1·57	—	—	—	1·50	—	—	—
84·74	7·67	7·48	8·09	0·23	0·30	7·56	4·80	0·23	0·26	4·31	—	—	—	—	3·67	—	—	—	0·08	0·00	0·08	0·00
85·28	7·38	7·01	7·49	—	—	—	4·64	0·14	0·12	4·38	1·53	—	—	—	0·90	—	—	—	0·20	—	—	—
89·78	2·71	2·64	—	—	—	—	2·37	0·00	0·28	2·09	1·57	—	—	—	0·62	—	—	—	—	—	—	—
90·31	2·98	2·86	2·94 (450°C.)	—	—	—	2·21	0·00	0·19	2·02	2·17	—	—	—	1·60	—	—	—	1·00	—	—	—

the radicals produced in the coking coals are more stable than those produced in non-coking coals.

X-ray diffraction studies

A number of Indian vitrains of varying carbon content, and several fusains have been studied by the X-ray method, using a filtered X-ray beam and crystal reflected CuK radiation. The sharpening of the bands at 3·5 and 2·12A. with increase in rank of the vitrains has been confirmed (C content 76-91 per cent). The 20A. band has also been observed in photographs obtained with monochromatic radiation in vitrains with carbon content 88-91 per cent.

The fusains generally give a more diffuse pattern than the vitrains obtained from the same coal. The (002) band is not well marked on the low angle side and the scattering between this band and the direct beam is quite high. The band is also slightly shifted towards the low angle side. From general considerations, it appears that the broadening and the movement of the 002 band to slightly low angle region is due to increased distances between the condensed ring layers in a direction perpendicular to the layer plane, and the very appreciable amount of scattering between the 002 band and the direct beam is probably due to the large fraction of layers which occur singly. It has also been observed that the low angle scattering (up to about 25A.) is very diffuse, with no indication of a 20A. band, suggesting the variation in pore sizes in the fusains.

X-ray studies have been carried out on humic acids obtained from lignite and different rank coals (Ali, S. Z., unpublished data). The humic acid obtained from Palana lignite shows a very diffuse 002 bond (pattern obtained with monochromatic radiation) which appreciably sharpens up when small briquettes of the acid are subjected to a pressure of 50 tons/sq. in.

The humic acid obtained from vitrain of Jambad-Bowla coal (81·6 per cent C, d.m.f.) shows a pattern, the 002 bond of which bears a strong similarity not to the vitrain but to a vitrain of higher rank of about 89 per cent C. However, dialysis of this humic acid for about a week seems to reverse this trend towards a higher rank coal and in the case of a sodium salt of the undialysed humic acid, a highly diffuse pattern is obtained after long exposures of the order of 50 hr. (Ali, S. Z., unpublished data). A quantitative interpretation of this rather unexpected scattering pattern is being carried out.

Mechanism of briquetting of coals

Briquetting of lignite with polar and nonpolar liquids and with acetylated and barium acetate treated samples has shown that lignite briquettes are largely sustained by a hydrogen bonding mechanism involving the OH and COOH groups and the ' optimum moisture '[26]. This concept has been extended to other coals. It has also been found that all coals can be briquetted by the application of pressure only at an optimum moisture content corresponding to their air-dried moisture[27,28]. Further, the contribution of hydrogen bonds to the strength of the briquette depends upon the total reactive groups and the moisture present in the coals.

Heat of wetting of coals

Bond and Maggs[29] observed that for porous carbonaceous solids, the heat of wetting is essentially constant at 400 ergs/sq. cm. (or 1 cal./10 sq. m.). Based on this observation they evolved a method for determining the surface area of coals which varied from 20 to 200 sq. m./g. of coal depending on its rank. But in recent years several workers have questioned this technique and the results obtained therefrom[30-34]. Criticism was based not only on the consideration that 1 cal./10 sq. m. of internal surface is a rather doubtful value for the heat of wetting but especially on the fact that the application of the method of calculation of Brunauer *et al.*[35] to the measurement of absorption of nitrogen and argon at low temperatures (77°-90°K.) gave much lower values (0·1-10 sq. m./g.). In more recent publications[36-38], however, objections were raised against the BET method itself on the assumption that the values obtained from the adsorption experiments must necessarily be too low owing to the closing of the pores at the low measuring temperatures employed. Kini[39] has, however, shown that the effect of temperature, though significant, is not sufficient to explain the discrepancy between the values of surface area obtained by the BET method and the heat of wetting method. Recent work carried out at the Central Fuel Research Institute clearly establishes that the heat of wetting with methanol measures the heat liberated by the hydrogen bonding of the reactive oxygenated groups present in coal and the polar liquid, and is not a reliable method for measuring surface area. This method can, however, lead to important inferences regarding the structure and constitution of coal.

Heat of wetting of briquettes — The heats of wetting of different rank coals before and after briquetting were studied (Iyengar, M. S., unpublished data). The results obtained are presented in Table 2. From these results it is seen that the heat of wetting increases on briquetting and the extent of change brought about depends on the rank of the coal.

The values of BET surface area using argon at −183°C. and heat of wetting in methanol were obtained for a Raniganj coal before and after briquetting[34] (Table 3). These results show that while the BET surface area continuously decreases with increase in briquetting pressure, the heat of wetting remains constant or increases. The results obtained with the briquettes made at 35°, 80°, 100°, 150° and 200°C. were still more surprising. While the heat of wetting increases slightly with increase in briquetting temperature, the BET surface area exhibits a two-fold increase at 80°C. followed by a decrease at higher temperatures.

Heat of wetting of oxidized coals — The heats of wetting of different rank coals have been measured after subjecting them to aerial oxidation at 100°C., for different periods[40] (Fig. 10). The heats of wetting of medium

TABLE 2 — HEAT OF WETTING IN METHANOL OF BRIQUETTED COALS

(*Briquetting pressure,* 20 *tons/sq. in.*)

CARBON (d.m.f.) %	OXYGEN %	HEAT OF WETTING	
		Before briquetting *cal./g.*	After briquetting *cal./g.*
81·19	10·96	13·8	14·8
85·82	6·29	5·8	6·2
91·70	0·78	3·2	3·8

TABLE 3 — HEAT OF WETTING AND BET SURFACE AREA OF BRIQUETTED RANIGANJ COAL

BRIQUETTING PRESSURE *tons/sq. in.*	BET SURFACE AREA* *sq. m./g.*	HEAT OF WETTING* *cal./g.*
nil	51·2	20·5
35	17·4	20·5
50	13·4	22·6

*Expressed on d.a.f. basis.

rank coals have been found to increase with increase in the duration of oxidation. The heats of wetting of lower and higher rank coals have been found to exhibit an initial rise followed by a levelling off with increase in time. Excellent correlation exists between the change in the caking index and in the heat of wetting of these coals on oxidation (Fig. 11). These results showed that the greater the difference between initial and final heats of wetting of coals on oxidation, the greater was the difference in the initial and final caking index of coals.

Carbonization — The heats of wetting of Jharia coals (88 per cent C) and Raniganj coals (79 per cent C) before and after subjecting them to carbonization at different temperatures were examined and these values were compared with the corresponding values for surface areas measured by the BET method (Kini, K. A., unpublished data). These results show that in the case of medium rank Raniganj coals, the heat of wetting more or less continuously decreases with increase in temperature of carbonization but the BET surface area at first continuously decreases up to 400°C., then registers a small maximum at 600°C. only to increase sharply again at 800°C. and above. On the other hand, the h.o.w. and BET surface area of Jharia coals both decrease with increase in temperature of carbonization and then exhibit maxima at 600° and 800°C. respectively.

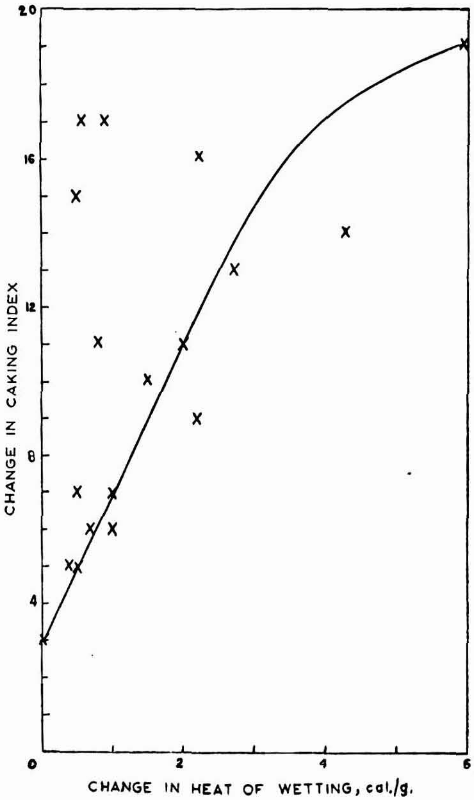

FIG. 11 — CHANGE IN CAKING INDEX WITH CHANGE IN HEAT OF WETTING

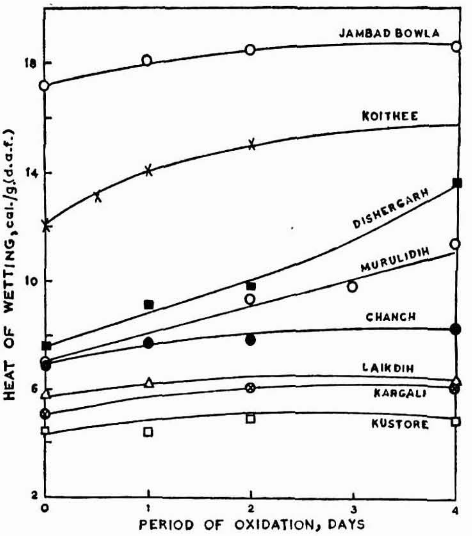

FIG. 10 — VARIATION OF HEAT OF WETTING WITH PERIOD OF OXIDATION

The heats of wetting of different rank coals were compared with the physical properties of their corresponding high temperature cokes[41,42] (Figs. 12-14). These results showed that with decrease in heat of wetting of parent coals, the Shatter index, Micum index and Haven index of their corresponding cokes continuously decrease. On this basis a classification of Indian coals has been evolved (Table 4) which enables the physical properties of the coke to be predicted with high accuracy from a knowledge of the heats of wetting of the coals.

There is an excellent correlation between the heat of wetting of coal and reactivity to CO_2 of the corresponding high temperature coke[43] (Fig. 15). In general, the reactivity of coke increases with increase in the heat of wetting of the coal.

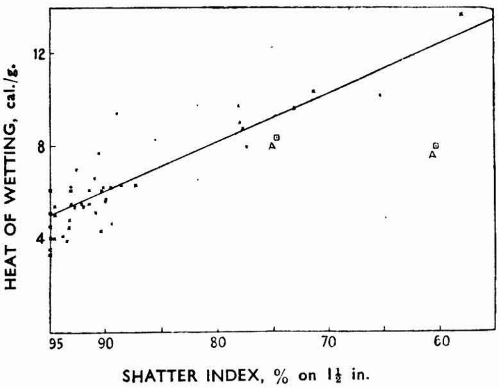

FIG. 12 — RELATION BETWEEN HEAT OF WETTING OF COALS AND SHATTER INDEX OF COKES

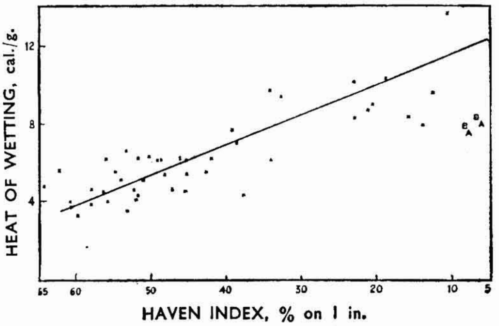

FIG. 14 — RELATION BETWEEN HEAT OF WETTING OF COALS AND HAVEN STABILITY FACTOR OF COKES

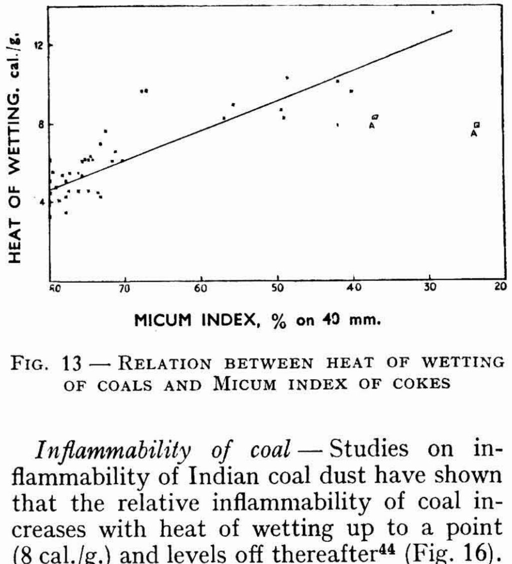

FIG. 13 — RELATION BETWEEN HEAT OF WETTING OF COALS AND MICUM INDEX OF COKES

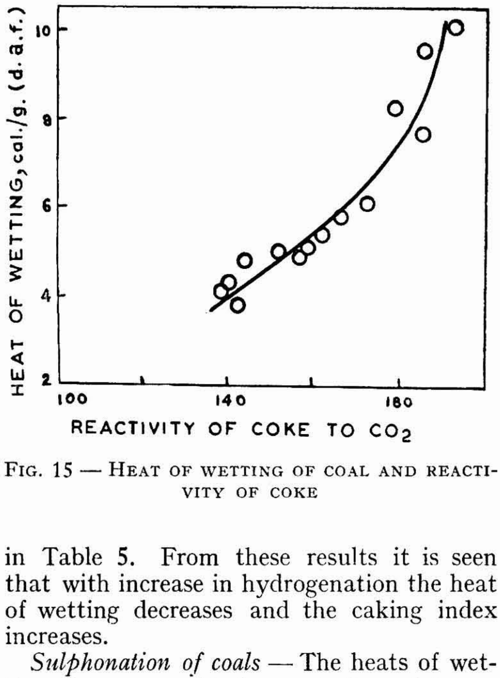

FIG. 15 — HEAT OF WETTING OF COAL AND REACTIVITY OF COKE

Inflammability of coal — Studies on inflammability of Indian coal dust have shown that the relative inflammability of coal increases with heat of wetting up to a point (8 cal./g.) and levels off thereafter[44] (Fig. 16). Inflammability is a rapid oxidation reaction and the kinetics of the reaction are governed by the surface reactivity of the material, the heat of wetting of coals giving a measure of this reactivity. Heat of wetting values of coals can, therefore, be utilized for predicting reactivity and, hence, inflammability and combustibility of coals.

Hydrogenation of coal — The heats of wetting of Jambad-Bowla coal (78·9 per cent C) after subjecting it to hydrogenation at 357°C. for 4 hr. with or without using different catalysts were studied and compared with the caking indices of the hydrogenation residues[14]. The results are presented in Table 5. From these results it is seen that with increase in hydrogenation the heat of wetting decreases and the caking index increases.

Sulphonation of coals — The heats of wetting of Assam coal before and after sulphonation and after subjecting the sulphonated product to hydrolysis using different concentrations of hydrochloric acid were studied (Iyengar, M. S., unpublished data) (Table 6). These results show that on sulphonation, the heat of wetting increases considerably but on hydrolysis it decreases progressively. In other words, the heat of wetting gives a measure of the formation and disappearance of sulphonic groups in coal.

Heat of wetting with polar and non-polar liquids — The heats of wetting of Madhya Pradesh coals (82·3 per cent C) in different polar and non-polar liquids were examined[34].

TABLE 4 — CLASSIFICATION OF INDIAN COALS ACCORDING TO THEIR HEATS OF WETTING AND PHYSICAL PROPERTIES OF COKES

Coals			Heat of wetting (d.a.f.) *cal./g.*	Physical properties of cokes					Quality as indicated by Micum test*
				Shatter index		Micum index		Haven test, stability factor, % on 1 in.	
Group	Type	Source		% on 1½ in.	% on ½ in.	% on 40 mm.	% through 10 mm.		
1(a)	Strongly coking	(i) Barakar measure, Jharia coalfields (ii) Lower Karharbaree seam, Giridih coalfields	3·5-6·0	92-95	97-98	77-82	8-12	50-60	Hard to very hard
1(b)	do	(i) Barakar measure, Jharia coalfields (the higher seams XVI to XVIII) (ii) Barakar measure, Laikdih seam, Raniganj coalfields (iii) West Bokaro X seam and Kargali seam, Bokaro coalfields (iv) Kanhan Valley, Rakhikole, M.P. coalfields	4·5-6·5	90-92	97-98	75-80	9-12	45-55	Hard
2	Medium	(i) Raniganj measure, Mohuda seam, Jharia coalfields (ii) Barakar measure, Ramnagar, Chanch and Begunia seams, Raniganj coalfields (iii) Kanhan Valley, Damua/Kalichhapar, M.P. coalfields	6-9	80-90	95-98	68-75	9-16	40-50	Soft to medium hard
	Weakly coking	Raniganj measure, Sanctoria and Dishergarh seams, Raniganj coalfields	8-10	70-80	94-96	40-60	10-15	10-25	Soft
4	Poorly coking	(i) Raniganj measure, Poniati seam, Raniganj coalfields (ii) Assam coking type	8-14	60-70	91-93	30-40	15-25	8-12	do
5	Non-coking	Coal from all coalfields	Over 14	(Yields pulverulent residue on carbonization)					

*Micum index on 40 mm. × 1·05 = Breslau index on 40 mm. (approx.)

Quality of coke	*Micum index on 40 mm.*
Very hard	82 and over
Hard	75 and over but <82
Medium hard	72 and over but <75
Soft	<72

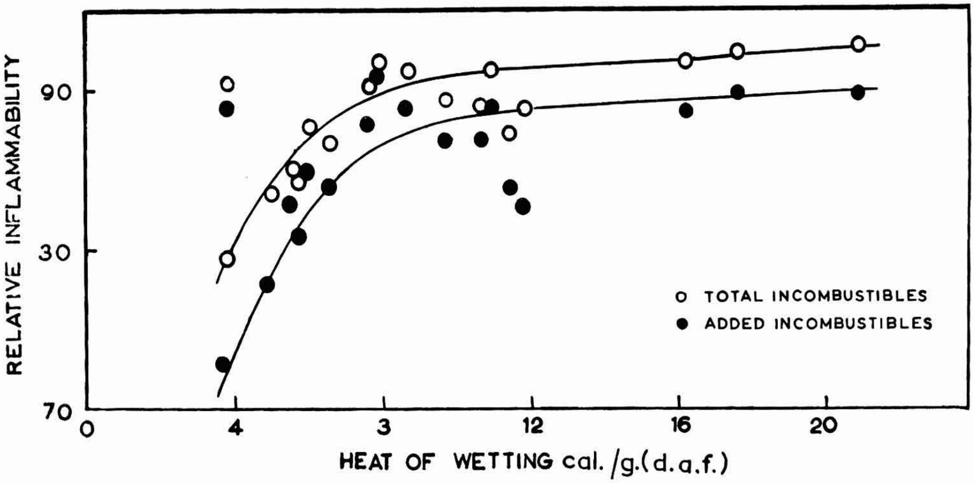

FIG. 16 — HEAT OF WETTING OF COAL AND RELATIVE INFLAMMABILITY

TABLE 5 — HEAT OF WETTING AND CAKING INDEX OF JAMBAD-BOWLA COAL AFTER HYDROGENATION

TREATMENT	CARBON (d.m.f.) %	OXYGEN (d.m.f.) %	CAKING INDEX	HEAT OF WETTING (d.a.f.) *cal./g.*
Original coal	78·93	13·60	2	17·5
Heated at 375°C. for 4 hr. in nitrogen	82·81	10·28	3	13·1
Heated at 375°C. for 4 hr. in hydrogen	88·33	5·37	3	11·7
Hydrogenated at 375°C. for 4 hr. at 30 atm. pressure	83·70	8·61	3	4·2
Hydrogenated at 375°C. for 4 hr. at 70 atm. pressure	83·64	8·35	3	4·1
Hydrogenated at 375°C. for 4 hr. at 200 atm. pressure	86·46	5·05	17	3·5
Impregnated with 2·5% Fe_2O_3, hydrogenated at 375°C. for 4 hr. at 30 atm. pressure	86·40	5·19	4	2·8
Impregnated with 2·5% Fe_2O_3, hydrogenated at 375°C. for 4 hr. at 30 atm. pressure	84·39	7·11	5	3·6
Impregnated with 2·5% Fe_2O_3 and 0·25% MO_3 and hydrogenated at 375°C. for 4 hr. at 30 atm. pressure	45·48	5·54	12	3·1

TABLE 6 — HEAT OF WETTING OF ASSAM COAL AFTER SULPHONATION AND HYDROLYSIS

SAMPLE	STRENGTH OF HCl %	HEAT OF WETTING *cal./g.*
Namdung coal	—	3·9
Sulphonated coal	—	34·0
Sulphonated coal (after hydrolysis for 16 hr.)	5	29·2
do	10	29·2
do	20	25·3
do	30	25·0

The heat of wetting showed a general increase with increase in dipole moment of the wetting liquid. But the relationship was not regular. On the other hand, when the heat of wetting is compared with the electronegativity of the wetting liquid there is excellent correlation.

The heats of wetting of different rank coals with chlorobenzene, benzene and methanol were also studied. These results showed that the difference between the heat of wetting values in chlorobenzene and benzene gives a measure of the OH groups and that between benzene and methanol gives a measure of both CO and OH groups present in coals. The value for reactive oxygen obtained in this manner is greater than that calculated from the amount of hydrochloric acid and methyl amine irreversibly sorbed by coals. This suggests that anthrone structures are present in coals.

TABLE 7 — HEAT OF WETTING AND MOISTURE CONTENT OF A VITRAIN AND ITS ACETYLATED PRODUCTS

	VITRAIN (O=13·5)	ACETYLATED (AT 100°C.) VITRAIN (44% O'BLOCKED)	ACETYLATED (AT 140°C.) VITRAIN (54% O'BLOCKED)
H.o.w. (in methanol), cal./g., of dry ash free material	23·1	13·8	11·8
Air-dried moisture, % (at 60% R.H.)	12·5	5·6	3·5

TABLE 8 — HEAT OF WETTING AND CAKING INDEX OF ABNORMAL COALS

COAL SAMPLE	CARBON %	OXYGEN %	SULPHUR %	B.S. SWELLING No.	HEAT OF WETTING *cal./g.*
Rasa, Istria, Croatia	75·4	6·6	10·90	9	3·2
Laitrengew, Assam, India	81·1	9·3	2·95	5	4·9
Lyngkyrdem, Assam, India	81·2	9·1	2·72	7½	3·9
Thanjinath, Assam, India	83·5	5·7	3·57	8	4·0
Cherrapunji, Assam, India	80·8	8·9	3·26	6	5·0
Cherrapunji, Assam, India	81·4	7·5	4·25	7½	5·3
Khost-Shrig, Pakistan	74·0	10·0	7·70	5½	5·0
Salt Range, Pakistan	74·6	13·6	5·50	—	19·8
Mach-Bolon, Pakistan	73·3	16·3	4·10	0	26·2

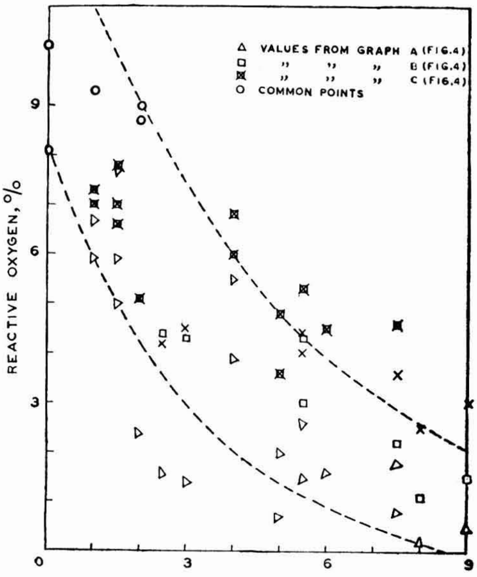

FIG. 17 — REACTIVE OXYGEN AND SWELLING NUMBER OF ABNORMAL COALS

That the heat of wetting gives a measure of the reactive groups in coal, can also be seen from the fact that on acetylation, the heat of wetting values decrease[45] (Table 7).

Heat of wetting of abnormal coals — A study of the heats of wetting of abnormal coals, i.e. high sulphur coals which exhibit the dual characteristics of both low as well as high rank coals, reveals interesting properties (Table 8). In general, coals which have developed coking properties have low heat of wetting. Further, in these coals there is a remarkable correlation between the caking index and total reactive groups — the lower the groups the higher is the caking index (Fig. 17).

Heat of wetting of normal coals — In the case of normal coals, the heat of wetting gives an excellent correlation with the other fundamental properties of coal like the calorific value of unit volatiles (Fig. 18), moisture content (Majumdar, B. K., unpublished data) (Fig. 19), volatile matter[46] (Fig. 20), oxygen and grindability[47,48] (Fig. 21), etc., and, therefore, measures a more fundamental property of coal than simply its surface area.

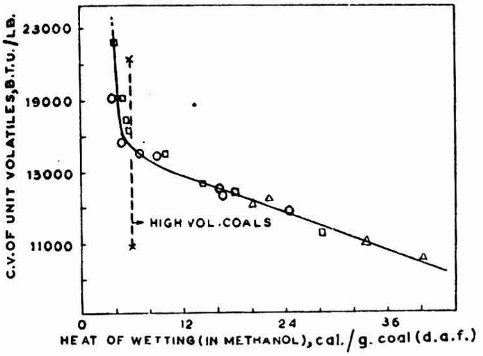

Fig. 18 — Heat of wetting (in methanol) vs. moisture content (at 25°C. and 90 per cent R.H.; expressed on ash-free coal) of different rank coals

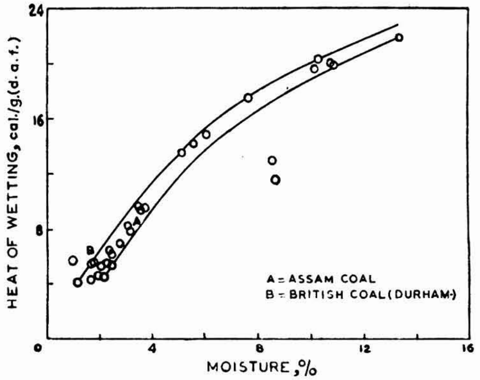

Fig. 19 — Heat of wetting vs. moisture content (at 25°C. and 90 per cent R.H.; expressed on ash-free coal) of different rank coals

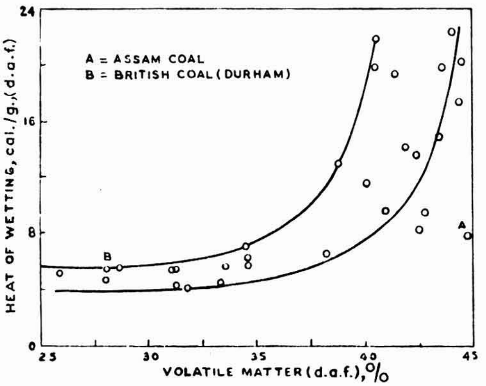

Fig. 20 — Heat of wetting vs. volatile matter for different rank coals

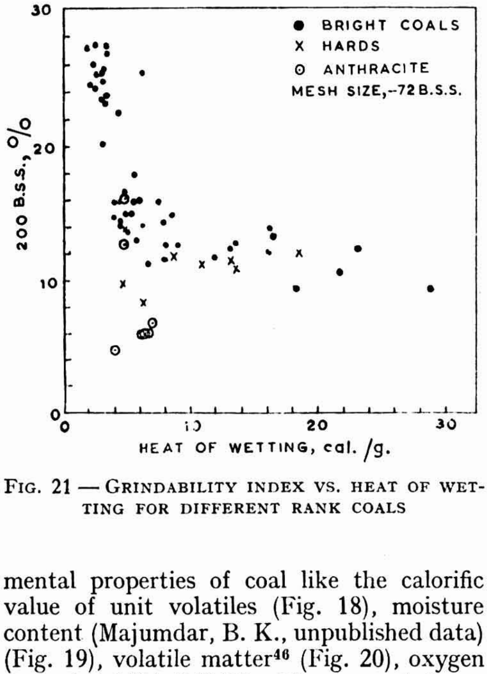

Fig. 21 — Grindability index vs. heat of wetting for different rank coals

Conclusion

The concept of reactive groups has been useful in explaining a number of properties of coal. For instance it has now become possible to explain the anomalies in the surface area measurements of coal in terms of the reactive groups. Measurements of surface area involving polar liquids or gases give large surface areas due to polar interaction. Similarly, it has been possible to explain why in binderless briquetting of coals maximum strength in the briquettes is obtained at an optimum moisture corresponding to the air-dried moisture content. It has also been possible to show that moisture (usually corresponding to air-dried moisture) exists in a hydrogen bonded form with the reactive groups present in coal.

It is likely that the key to the understanding of the mechanism of coke formation may also be in the reactive groups, particularly their behaviour during the pre-softening stage. Because of the presence of functional groups in the non-coking coals, it is probable that a condensation reaction takes place between 300° and 420°C. which by imparting a rigidity hinder plastic flow.

While much remains to be learnt about the constitution of coal, fundamental researches described above have led to the selection of a few parameters (e.g. heat of wetting or equilibrium moisture content) which not only help in differentiating coals according to their rank, but have also helped in the selection of coals suitable for industrial uses. They have also helped to assess the behaviour of different types of coals under different environmental conditions.

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REVIEWS

THE ENCYCLOPEDIA OF CHEMISTRY. Editor-in-Chief: George L. Clark; Managing Editor: Gessner G. Hawley (Reinhold Publishing Corpn., New York), 1957. Pp. xvi + 1037. Price $ 19.50

This is a valuable book of reference covering the entire field of pure and applied chemistry. The contributors are authorities on the subjects which they treat, and the names include Roger Adams, Jerome Alexander, R. C. Anderson, W. L. Badger, Lyman Craig, J. T. Edsall, C. A. Elvehjem, Henry Eyring, K. Fajans, Henry Gilman, David Green, E. A. Hauser, F. D. Rossini, R. N. Jones, V. I. Komarewsky, Herman Mark, C. P. Smyth, E. W. R. Steacie, S. A. Waksman and Roger Williams. The articles are clear and readable, and within the prescribed limitations of space they give a surprising amount of information; the editors' claim in the preface that they are 'near miracles of condensation' is largely justified. The articles on topics in applied chemistry and chemical engineering are particularly well written. To quote only one example, the brief one-page note on pilot plants gives a very clear account of their nature and purpose.

Occasionally the content of an article is not relevant to the title; for instance, the article on the Raman effect deals mostly with Raman and does not explain the Raman effect. For some mysterious reason it is stated under 'Quaternary ammonium compounds' 'see Chelation'; but the excellent article on Chelation naturally does not deal with quaternary ammonium compounds. Quantum theory is casually mentioned in the article on Periodic Law. There is an article on steric inhibition of resonance, but none on resonance. The space devoted to meteorology and other topics with no direct bearing on chemistry might have been used to better purpose. The 'biographies of outstanding figures in past chemical achievement' are interesting, but the choice of names has been somewhat carelessly made and a glaring omission is Emil Fischer. 'Past chemical achievement' is interpreted as excluding the achievement of chemists who are alive, and names such as those of Pauling, Robinson, Karrer and Woodward are, therefore, excluded. The numerous articles on societies and research institutions are restricted to the United States, although this is not stated in the preface, and they include several of little interest to readers outside the U.S.A.

The index is inadequate. Except in the article on chemical literature there are no references to books; a carefully chosen list of books, at least on the major topics, would have added to the usefulness of the encyclopedia.

K.V.

LABORATORY MANUAL OF ORGANIC CHEMISTRY by B. B. Dey, M. V. Sitaraman & T. R. Govindachari (S. Viswanathan, Central Art Press, Madras), Third Revised Edition, 1957. Pp. xiv + 457. Price Rs. 12.00

This is an extremely useful book for the teaching of organic chemistry in our universities. The earlier second edition has been out of print for a number of years and the present third edition has long been needed. Previous books on practical organic chemistry have usually belonged to two categories: (1) books dealing with organic preparations, (2) books dealing with qualitative and quantitative analysis. In the present volume these two aspects find a happy combination.

The book contains 13 chapters and starts with a brief introduction containing general directions and precautions to be observed in practical organic chemistry. The first two chapters deal with manipulations. The treatment is quite modern and contains semi-micro-methods which are more convenient to carry out than the older macro-methods. The next two chapters give the reactions of common organic compounds of various types and provide the necessary ground work for undertaking qualitative analysis which is the subject of the following two chapters. First, the systematic procedure is given for finding the group to which a given compound belongs and then the preparation of derivatives. Chapter seven gives a number of model analyses and it is followed by the treatment of the analysis of mixtures in chapter eight which also includes typical examples. Chapter nine is the biggest in the book, covering 130 pages. It deals with the preparation of organic compounds. One hundred and twenty-one compounds belonging to various types are dealt with. The selection has been made with a view to provide experience of various chemical reactions and groups of compounds. Chapters ten and eleven contain a treatment of quantitative organic analysis, first the estimation of groups and next the estimation of the elements. Semi-micro-methods of estimation are discussed. The last two chapters are also quite useful and deal with preparation of pure solvents and reagents and with certain general manipulations. The appendix which runs over 15 pages contains tables of derivatives of important compounds belonging to different groups. Though the scope of the list is limited, it will be enough for junior students. The senior students will have to refer to special books. The scope of the appendix could probably be increased in future editions. The index is also rather small and could be considerably increased in order to help ready reference. One example may be given — chromatography which is definitely dealt with in the book does not find a place in the index.

The book is a valuable one for the post-graduate students in chemistry. There are portions which are useful even for those who are doing research at the Ph.D. level. It is possible that it does not meet the full requirements of the senior students, but it does to a large extent and it may be hoped that it will receive the popularity it so fully deserves. Printing errors are few. For its value the price is quite low.

T. R. SESHADRI

QUANTITATIVE INORGANIC ANALYSIS by G. Charlot & Denise Bezier. Translated by R. C. Murray (Methuen & Co. Ltd., London), 1957. Pp. x + 691. Price 84*s*.

Advances in inorganic quantitative analysis have been so rapid and tremendous during the past few years that it is a tribute to the scholarship, ability, enthusiasm and energy of some of the leading workers in the field for successfully presenting the results achieved in a number of excellent treatises, text-books and compendiums covering different specialized branches of the vast subject. The book under review, whose title in French is *Methods modernes d' Analyse quantitative Minerale*, is a valuable addition to the field.

The book consists of two parts. The first part covers 319 pages and is divided into 32 chapters, and deals with all the well-established methods — chemical and physical — elucidating the general principles and logic of the methods. The electrochemical methods have received adequate attention. The theory of electrolysis, in the context of analytical work, is a well-condensed exposition of the subject in less than 20 pages. The sections on determinations in solvents other than pure water and separation by extraction are well presented and are especially valuable. The emphasis throughout this part of the book is on the theoretical and not on the descriptive side. Thus, the aid of other specialized treatises should have to be taken for detailed descriptions. Even so, the amount of information presented in the volume is great and this has been rendered possible by crispness of thought and expression. All that is non-essential is omitted. One sentence (page 16) is sufficient to illustrate the approach: " We shall not use the classical definition of acids and bases; Bronsteds definition is more general ".

The second part of the book is concerned with the determination of elements. The most up-to-date methods and reagents have been dealt with and essential details of ' know-how ' given. Reference to original sources are given then and there under particular methods, thus helping the reader. Judged by the standards of conventional text-books, this volume has dealt with 66 elements in the short space of about 318 pages, which is indeed creditable. This has been rendered possible by the method of treatment which is indicative rather than descriptive.

The book considered as a whole is a small-scale road map of a big continent. All important highroads, shortcuts and bypaths have been written on it. It is intended for the seasoned traveller, who knows his map and has learnt to walk, run and use all the quicker means of transport. There is definite need for a compendium like this on the shelf of every analyst. The format of the book is what should be expected of Methuens — excellent; but, what can we say of the price which is quite in keeping with the modern trends in book prices, 84 shillings for

650 pages? It is, from the viewpoint of the average analyst, to use a laboured word, unconscionable.

A. N. KAPPANNA

THE DESIGN & CONSTRUCTION OF ENGINEERING FOUNDATIONS by F. D. C. Henry (McGraw-Hill Book Co. Inc., New York), 1956. Pp. xviii + 547. Price $ 9.00

The author states in the preface, "The object of the book is to sow the seeds of ideas by linking the design of foundations to the methods of structural analysis and soil mechanics, by indicating how other engineers have constructed foundations, and by examining the whole subject in the light of relevant research". On going through the wealth of information contained in the book one can see that the author has very largely succeeded in his effort and the book is recommended as a very useful and comprehensive treatise on foundations for a student as also for a practising engineer.

The author has drawn liberally from recent research publications and codes of practices in U.K. and U.S.A. and for detailed study the reader has been referred to Appendix A which contains a comprehensive list of references. A notable chapter in the book is on Mining Subsidence and the measures adopted to guard against its damaging effects. This is usually lightly passed over in other engineering treatises. Appendix H, in the end, contains interesting and constructive design problems in foundation engineering.

The only criticism that may be made against the book is that not much use appears to have been made of the research publications by the contemporary European workers. For example, the Dutch deep sounding apparatus has only been lightly touched, while on the Continent, Belgian and Dutch engineers are using it extensively for design of pile foundations and for measuring settlements in deep layers of sandy soils.

DINESH MOHAN

SOLID STATE PHYSICS, Vol. 3. Edited by F. Seitz & D. Turnbull (Academic Press Inc., New York), 1956. Pp. xiv + 588

This is the third volume in a series intended to cover the wide field of solid state physics. Review articles from material often widely scattered by well-known specialists, are the most convenient media for research workers and others interested in the subject to keep pace with advancing scientific knowledge of the subject. In such a series, overlapping of topics cannot be possibly avoided (e.g. order-disorder phenomena and semiconductors in Vols. 1 and 3), but it need not disquieten the reader since the presentation is different in each case.

The present volume consists of six articles. The first article deals with the semiconducting properties of 'Group III-Group V compounds' by Welker and Weiss. After a general introduction of the subject, the preparation, binding properties, conductivity, Hall effect, resistivity, heat conductivity, infrared absorption surface-recombination, etc., of these compounds have been discussed and illustrated with many graphs. In the last section the binding energy of the compounds is considered from resonance and band structures. In 'The continuum theory of lattice defects' by Eshelby, the theory of elasticity is applied to lattice defects in crystals. The formal theory is discussed with respect to elasticity, internal stress, dislocations and interaction energies. Later, the point defects (i.e. distortion, solid solution, etc.), dislocations and surface and volume defects are considered.

The third article on 'Order-disorder phenomena in metals' by Guttman deals first with the structures of ordered alloys including short and long range order, pair density functions and their measurements and then the thermodynamics and kinetics of the order-disorder transition and also the further development of the Ising model. Various transition processes are discussed with illustrations.

The next article by Turnbull deals with the mechanism of 'Phase changes'. The thermodynamics and stability of phases have been treated, and the formal theory and the theories of nucleation and growth processes discussed. Phase transition in liquid/solid and solid/solid systems of constant composition are also dealt with.

In the fifth article on 'Relations between the concentrations of imperfections in crystalline solids' by Kröger and Vink, the defects have been treated on the basis of the law of mass action. After describing the various disorders in stoichiometric and non-stoichiometric compounds, the influence of foreign atoms on the energy level, ionic and electronic conductivity, and optical and magnetic properties of such compounds, and of their solubility in them have been discussed. The last article is on 'Ferromagnetic domain theory' by Kittel and Galt. After a brief survey of domain theory, the various domain energies (exchange, anisotropic, magnetostatic, magneto-elastic), and the thickness and energy of the Bloch wall have been considered. Experimental techniques for determining domain structures have been described and the coercive forces of small particles and bulk materials, and the motion of domain walls have been discussed.

The articles are all well written and are absorbing even to the uninitiated. This volume will, no doubt, be a valuable addition to the series, and will be of great help to the workers in the field of solid state physics. However, considering the cost of each volume, the series may not be within the reach of many individual workers for their personal library.

A.G.

SYSTEM ENGINEERING — AN INTRODUCTION TO THE DESIGN OF LARGE-SCALE SYSTEMS by Harry H. Goode & Robert E. Machol (McGraw-Hill Book Co. Inc., New York), 1957. Pp. 551. Price $ 10.00

In many branches of human activity one is inevitably led to the concept of a system-design team, a small group of engineers or scientists, to lead a large-scale project and organize the system effort. Such men have been variously called engineering scientists, system engineers, system analysts, or large-scale system designers. The technique has been named system approach, or the team development methods. The present book makes an attempt to instruct these classes of men, i.e. the generalists, by introducing to them the various techniques and problems of the specialists.

The book deals with both the aspects of system design: the *exterior system design* which concerns itself with the requirements on the system and its environment and the *interior system design* relating to design choices pertaining to equipment, procedures and people.

The first part has for its tools probability, mathematical statistics, design and analysis of experiments whilst the second part calls for such scientific disciplines as queing theory, information theory, servomechanism theory and human engineering.

The major portion of the book concerns itself with an exposition of the fundamental concepts and principles of the above subjects. The treatment is lucid and direct and is amply illustrated with examples: the example of exterior system design treated in Chapter 13 is particularly instructive. The concluding chapters on human engineering are interesting and instructive and are well worth the readers' close study.

Although the authors feel that virtually all the contents of the book can be comprehended with a knowledge of elementary calculus, one is inclined to the view that the reader should have a mathematical and technical discipline as a prerequisite if he were to profit more than a mere understanding of principles enunciated.

K. SUKUMARAN

INTRODUCTION TO BACTERIAL PHYSIOLOGY by C. E. Clifton (McGraw-Hill Book Co. Inc., New York, Toronto, London), 1957. Pp. xi + 414. Price $ 8.50

In this book, modestly entitled *Introduction to Bacterial Physiology* and aimed at analysing and summarizing the tremendous development that has occurred during the past fifteen years in the comparatively new field of bacterial physiology, the author has admirably achieved the objectives and has placed before the students in a clear and simple way the most complex problems associated with the numerous activities of bacteria. What is even more commendable is that the author has succeeded in a large measure in retaining throughout the text " an open-minded approach and a willingness to balance ideas against one another and in relation to the facts upon which they are based ", not to mention the successful efforts made to explain *what, how* and *why* of things connected with bacterial physiology.

After a short but crisp introduction in which are summarized the modes of evolution of morphological types of bacteria as proposed by Kluyver and van Niel, and Bisset, and the nutritional groupings as suggested by Knight, the first three chapters are devoted to physico-chemical and cytological aspects of the cell, a subject which has in recent years been in no small measure responsible for explaining the dynamic functions of the cellular components, cell metabolism and division. Herein one finds answers or interpretation to several problems in bacteriology. The succeeding chapter on enzymes is ably dealt with and even a beginner would easily get an insight into the most complicated mechanism of enzyme action on reading through the same. The references are almost up to date and the matter dealt with would also be found useful by an advanced worker in the field.

The next three chapters on Biological Oxidation, Alcoholic and Bacterial Fermentations, wherein the Wieland's and Warburg's concepts of hydrogen and oxygen activation respectively are discussed, are remarkable for their clarity of expression. The function of cytochrome in biological oxidation and the role of high energy phosphate bond in fermentation are detailed with precision. The selective capacity of a specific organism in the production of a particular alcohol and/or acid has been pointed out with ample evidence.

In Chapter 9 on ' The Metabolism of Nitrogenous Compounds ' the author seems to have taken for granted that the reader is quite familiar with nitrogen utilization by bacteria. However, aspects of nitrogen utilization are briefly discussed in Chapter 12. The topic of nucleic acids in Chapter 9 could have been elaborated into an independent chapter inasmuch as the metabolism of nucleic acids and their essential components are receiving considerable attention currently; perhaps it is too much to expect this in a book designed and designated as the present volume is. Chapter 10 would appear to be an extension of Chapter 6. Herein Professor Clifton has taken great pains to make the subject lively and interesting by discussing all possible pathways of aerobic respiration which by themselves are most intricate. Here again the importance of high energy phosphate bonds in biological oxidation is clearly brought out and the fate of glucose breakdown schematically represented with reference to Warburg-Dickens, Emden-Meyerhof and other pathways. In Chapter 11 are presented the interesting and intriguing problems pertaining to thermophily. Chapters 13 and 14 deal with growth and death of bacteria and the factors influencing vital aspects of life. In Chapter 15 are discussed the complicated themes of mutation, adaptation and biochemical genetics in a most fascinating way.

The last three chapters deal with aspects of infection, bacteriophagy and chemotherapeutic agents. A brief survey is made of toxin-producing bacteria, host-parasite relationship and of the quantitative and other aspects of phage-bacterium interaction. A summary of the known and more important sulpha drugs, antibiotics and metabolic antagonists is also given. While recognizing the value of inclusion of these antibiotics in such a comprehensive treatment of the vast subject under survey, one feels that a more detailed exposition of the mode of action of these agents and their chemistry is called for; this becomes all the more obvious when it is viewed in juxtaposition with other aspects of bacterial physiology which have received detailed treatment in the earlier chapters. All the same, considering the vastness of the subject, the book has been very well planned, its get-up is excellent and it would be a most welcome addition (and also as a companion volume to the earlier one — *Introduction to the Bacteria* — by the author) to the libraries of biochemists and bacteriologists alike. In short, this remarkable treatise is a fitting tribute to the memory of Dr. Marjorie Stephenson and Professor A. J. Kluyver whose pioneering efforts have contributed so much to our understanding of bacterial physiology.

J.V.B.

PUBLICATIONS RECEIVED

MAGNETISM (Indian Association for the Cultivation of Science, Jadavpur, Calcutta), 1957. Pp. vi+232. Price Rs. 7 net

FBI REGISTER OF BRITISH MANUFACTURERS — 1958. (Federation of British Industries, Westminster, London), Thirteenth Edition, 1957. Pp. 1137

SURVEY ADJUSTMENTS AND LEAST SQUARES by H. F. Rainsford (Constable & Co. Ltd., London), 1957. Pp. viii+326. Price 50*s*. net

CITADEL, MARKET & ALTAR — EMERGING SOCIETY by Spencer Heath (Science of Society Foundation Inc.), 1957. Pp. xxiv + 359. Price $ 6.00

CORROSION AND WEAR HANDBOOK FOR WATER-COOLED REACTORS by D. J. Depaul (McGraw-Hill Book Co. Inc., New York), 1957. Pp. ix + 293. Price $ 6.00

ELECTROSTATICS IN THE PETROLEUM INDUSTRY by A. Klinkenberg & J. L. Vanderminne (Elsevier Publishing Co., London; *Distributors*: Cleaver-Hume Press Ltd., London), 1958. Pp. 195. Price $ 7.00

REPORTS ON THE PROGRESS OF APPLIED CHEMISTRY — Volume 16: 1956. Edited by H. S. Rooke (Society of Chemical Industry, London), 1957. Pp. 795

EPOXY RESINS by Henry Lee & Kris Neville (McGraw-Hill Book Co. Inc., New York), 1957. Pp. 305. Price $ 8.00

NOTES & NEWS

A new magnetic memory concept

A NEW CONCEPT IN MEMORY devices has emerged from the research work conducted at the Bell Telephone Laboratories. This concept, which has been termed the 'twistor', is expected to lead to memory systems which are simpler to fabricate and more economical to manufacture than the existing matrix or ferrite systems. This development enables to do away with the plating and threading operations necessary in the case of matrices or ferrite plates being used now, without affecting the speed of operation or output of the ferrite memory devices. The 'twistor' concept opens the way for the construction of magnetic memory arrays by merely interweaving horizontal copper wires and vertical magnetic wires. Such a device would be similar in appearance to a ferrite core array, but without the cores, and would operate in much the same manner as a core array. This new concept gets its name 'twistor' from a characteristic of wire made of magnetic material. Torsion applied to such a wire shifts the preferred direction of magnetization from a longitudinal to a helical path. The coincidence of a circular and a longitudinal magnetic field can then be used to insert information into this wire in the form of a polarized helical magnetization, and the magnetic wire itself can be used as a sensor and as a means of reproducing the information. Application of torsion to the magnetic wire in a final device may be unnecessary, as the helical path for the preferred direction of magnetization can perhaps be 'frozen' into the wire during processing.

In practice, the circular magnetic field is provided by a current pulse through the magnetic wire, and the longitudinal field by a current pulse through the copper wire which is perpendicular to the magnetic wire. Thus, storing a bit requires two coincident current pulses. Read-out is accomplished by overdriving the longitudinal field in the reverse direction. The read-out signal is sensed across the magnetic wire. Because the lines of magnetic flux along the helical path wrap the magnetic conductor many times, a favourable increase in the output signal is obtained.

A conductor plated with magnetic material seems to have some advantages. Diameters as small as one-thousandth of an inch appear to be feasible. At least 10 bits/in. may be stored on such a wire without adverse interaction. The drive circuits for a 'twistor' array can be readily transistorized [*News from Bell Telephone Laboratories*].

Magnetic moment of the neutron

A MORE PRECISE DETERMINATION than what has been hitherto possible, of the magnetic moment of the neutron has been achieved by V. W. Cohen, N. R. Corngold and N. F. Ramsey. The new method gives a more accurate value than the one used by Bloch and co-workers, the precision of the latter being limited by the degree of polarization of the neutrons attainable by transmission through magnetized iron, the low neutron flux and the short path of the neutrons in the magnetic field. The method of Cohen and others combines the favourable features, viz. sharper resonance lines and a high percentage of polarization, attained in two separate experiments by Ramsey (the separated oscillatory field method) and Hughes and Burgy (reflection of neutrons from cobalt mirrors) respectively.

In this method, a beam of slow neutrons was polarized by reflection from a magnetized cobalt mirror and then reflected from a similar mirror used as an analyser. Between the two mirrors, the neutrons pass through a region of uniform magnetic field where they may be depolarized by a resonant radiofrequency magnetic field, thus resulting in a drop in intensity of the neutrons reflected from the second mirror. The resonant frequency for depolarization is compared with the proton moment resonant frequency in the same transition region. For high resolution of the neutron resonance, the path length of the neutrons in the uniform magnetic field was made 110 cm.

The value obtained for the magnetic moment of the neutron (μ_n) from this experiment is $\mu_n = -1{\cdot}913148 \pm 0{\cdot}000066$ nuclear magnetons. The neutron resonance measurement is more precise than that for proton. With further improvement an accuracy of one part in a million may be attained [*Nature, Lond.*, **179** (1957), 955].

A new light source

A NEW LIGHT SOURCE MAY COME into common use as a result of the work conducted at the Westinghouse Electric Corpn., Pittsburgh, Pa., U.S.A. The method is based on light emission by phosphor powders embedded in an insulator and subjected to the action of an a.c. electric field.

Sandwich-like glass panels, ⅛ in. thick and 1 ft. square, are coated with a transparent, electrically conducting film. Over this is spread a thin layer of polyvinyl chloride, in which is embedded a zinc sulphide type phosphor. On the top of the phosphor is an aluminium conducting coating. The panel thus resembles a capacitor with two conducting layers separated by a dielectric. When 350 V., 300 c/s. a.c. current is applied, the panels give a brightness of 100-foot lamberts at an efficiency of 3 lumens/W. Due to the existence of more than one emission band in some phosphors, the colour emitted is affected by the frequency. The phosphor is green when a power frequency below 1000 c/s. is employed. Above 5000 c/s. the light emitted is blue. In between this range various shades of blue-green are emitted. White light is obtained by mixing red, blue and green phosphors. The brightness is proportional to both the frequency and voltage applied; hence by raising either of them, the brightness can be increased. The voltage can be increased up to 600 V. beyond which dielectric breakdown occurs; a brightness of 2000-foot lamberts is obtained using a 600 V., 20,000 c/s. a.c. power source. Peak efficiency of 9 lumens/W. was achieved at a few hundred cycles and a few hundred volts. Applying higher or lower values only decreases the efficiency [*Discovery*, **18** (1957), 413].

New crystalline ice

TWO INDEPENDENT INVESTIGATIONS on the electron diffraction pattern of crystalline ice, one carried out in the Physics Department of the Imperial College, London, and the other in Japan, have shown the existence of a new cubic form of ice at low temperatures and low pressures. The cubic ice has been produced directly from water vapour by condensation on to a suitable surface in vacuum at a temperature which lies between −150° and −120°C.; above this temperature region the normal hexagonal form is found, and below it, the deposit gives a diffraction pattern consisting of a few diffused rings which might be expected from supercooled water. This deposit can also be converted into cubic form by heating to about −120°C., the change taking place in a temperature interval of a few degrees. The existence of cubic form has also beem demonstrated with heavy water. The formation of the deposit should be sufficiently slow because if the formation is too rapid, there will be rapid heat release with the result that the deposit will get heated to the temperature (−80°C.) at which the hexagonal ice is formed [*Discovery*, **18** (1957), 367].

Continuous baffle beta-ray spectrometer

A CONTINUOUS BAFFLE FOR A short lens beta-ray spectrometer capable of measuring electron energies up to 4 MeV. has been designed and installed at the Institute of Nuclear Physics, Calcutta. The new baffle system accomplishes a resolution of 1·47 per cent at a transmission of 0·56 per cent (available methods till now are capable of a resolution of only 2·2 per cent).

Improvements have been made on the short lens beta-ray spectrometer originally fabricated at the Institute in 1954 in which the beta particles are detected by means of a stilbene crystal and the initial line-shape corresponded to 12 per cent resolution. The improvements effected relate to the alignment of the axis of the photographic chamber with that of the lens and to the design of a compound baffle composed of ten outer stops of aluminium and a central stop. The data for determining the caustic envelope of the electron trajectories was obtained by a series of photographs taken at different positions along the chamber axis. This improved the resolution to 1·54 per cent. Next the continuous baffle is designed and improvements in mechanical devices by which the error in placing the baffle was reduced from 1 cm. to 2 mm. have been introduced.

The continuous baffle is a solid cone of aluminium which is divided into two parts, mounted on two brass cylinders. These cylinders can be moved along the chamber axis by rack and pinion arrangements, which can be operated from outside the chamber. By this arrangement the baffle can be easily and accurately made to follow the caustic envelope. The central stop is also movable and can be placed at any position on the axis in the neighbourhood of the focussed ring correct to 0·01 cm.

With this continuous baffle, a resolution of 1·47 per cent is obtained. Both the K and L conversion lines are resolved. The complete spectrum of Cs^{137} is obtained at a resolution of 2·2 per cent. The positions and intensity ratios of the conversion lines agree well with the standard values, ensuring the reliability of the spectrometer [*Indian J. Phys.*, **31** (1957), 531].

Square wave polarograph

DEVELOPMENTS IN POLAROGRAPHY in the past decade have been directed mainly towards the improvement of the sensitivity and the resolution of the technique. Among the modern polarographs like cathode-ray polarograph, alternating current polarograph, etc., the square wave polarograph is the most satisfactory as regards its operation, sensitivity and resolving power. It overcomes the limitation encountered in the conventional as well as the other recently improved polarographs mentioned above. In the conventional polarographs, the determination of concentrations smaller than about 10^{-5}M is not possible because of the interference from the condenser current; the resolution between two steps is not very satisfactory unless the half-wave potentials are separated approximately 200 mV. Serious interference can also result from the previous reduction of a major constituent of the sample. Square wave polarograph is superior to other palarographs in both resolution and reproducibility of the polarographic peaks and is applicable to the direct analysis of complex mixtures with far less interference from earlier reductions. The interfering capacity current, occurring in alternating current polarography, has been eliminated by a small alternating square wave voltage ($\leq$30 mV.) which is superposed on the normal slowly changing d.c. voltage, and the amplitude of the resulting a.c. component of the cell current is measured shortly before each change in the sign of the alternating voltage. In this way a perfect separation of the electrode reaction (diffusion) current and the capacity current is achieved. It has been observed that diffusion current never decays to zero in the interval between successive voltage changes, but in the same time interval the capacity current decays exponentially with time and decreases to a negligible value sometimes before the next change in applied voltage. The a.c. component of the cell current is recorded by the instrument at a time when the capacity current has decayed to zero and it is thereby governed by diffusion at the dropping mercury electrode. Consequently the diffusion current can be measured with certainty, and suitable amplification of the response gives the required sensitivity.

This technique has been applied to the rapid determination of small amounts — in the molar concentration ranging from 10^{-4} to 10^{-7} and less — of various constituents in diverse materials. In many cases direct procedures, simply involving the initial solution of the sample followed by the recording and evaluation of the peak for required metal ions, have been developed for the analysis of such material as metallurgical alloys, foodstuffs, fertilizers and minerals. For concentrations of approximately 2×10^{-6}M the determination can be accomplished with an accuracy of ±2 per cent. However, an improved accuracy of ±0·5 per cent can be obtained for concentrations greater than 2×10^{-5}M [*Industr. Chem. Mfr.*, **33** (1957), 494].

New research reactor

A NEW U.S. NUCLEAR REACTOR designed for research in chemistry, physics, metallurgy, biology and medicine as well as for the custom production of radio-isotopes (the first reactor in U.S.A. for this purpose) and for practical training of technicians will be built by the General Dynamics Corpn. The multipurpose unit, to be called TRIGA, is one of three reactor types being developed to utilize a new solid homogeneous reactor core incorporating inherent safety. The core fuel elements consist of a solid mixture of uranium of 20 per cent enrichment; zinc hydride is used as a moderator. If excess reactivity is introduced, the reactor will shut itself down due to physical phenomena occurring within the core producing a negative temperature coefficient of reaction [*Chem. Tr. J.*, **141** (1957), 987].

A new television camera tube

A NEW TYPE OF TELEVISION camera tube developed at the Research Laboratories of Westinghouse Electric Corpn. promises to lead to an exceptionally sensitive camera pick-up tube which can record every photoelectron leaving the photosensitive surface as a distinct flash. The tube is called EBICON, after the phenomenon basic to its operation, i.e. electron bombardment induced conductivity. The important feature of this device is an amplification of 100 or more in the scanning section which more than compensates the noise inherent in the subsequent vacuum tube amplifiers. The device consists of a layer of selenium which is a good insulator. A scanning beam of electrons from a gun in the rear of the tube charges the surface of the layer uniformly to a potential at which no further electrons from the beam can reach the layer of selenium. In this condition, no signal is received on the lead connected to the opposite side of the selenium layer. If an electron from the photosurface on which the light image is projected is accelerated and driven into the selenium with high energy, it can produce an avalanche of conducting electrons, which flow only momentarily and discharge the back surface of the selenium. When the scanning beam returns to this spot, it will recharge the selenium, and a current will flow in the signal lead. This current is amplified by ordinary vacuum tube amplifiers and used as a video signal for the transmission of television images [*Discovery*, **18** (1957), 413].

Brittleness in chromium

INVESTIGATIONS CARRIED OUT AT the Defence Standards Laboratories, Maribyrnong, W. 3, Victoria, Australia, have led to a new explanation for the cause of brittleness in ' pure ' chromium.

Current theories ascribe this phenomenon to Cottrell locking, invoking the Mott-Stroh theory of crack formation as the operative mechanism of brittle fracture, and nitrogen as the associated interstitial solute atom. However, this theory does not explain all the features of the tensile behaviour of annealed chromium, viz. (1) embrittlement at temperatures (*c.* 350°C.) higher than those for other body-centred cubic metals of similar structure; (2) abrupt ductile-brittle transition and (3) the occurrence of the embrittlement at the bottom of a trough in the maximum stress/temperature and yield stress/temperature curves just below 350°C. and not on that part of the curve ascribed directly to Cottrell locking.

The evidence obtained suggests that embrittlement may be caused primarily by the strain-induced precipitation from highly supersaturated solid solutions of chromium nitride and possibly also of chromium oxide. The process appears to be highly sensitive to applied plastic strains and, to some extent, resembles the strain-age hardening occurring in α-iron containing nitrogen.

Extrapolation of current data suggests a solid solubility of *c.* 10^{-5} per cent nitrogen in chromium at 400°C. falling to 10^{-10} per cent at 200°C. It is, therefore, to be expected that the whole of the nitrogen in chromium of the present purity would be available for precipitation between 400° and 200°C., which is the ductile-brittle transition in the material in the annealed condition.

The observed lowering of the transition temperature (by lowering the nitrogen content) may be ascribed to the reduction of the mass-embrittling effects of precipitation consequent on a lower order of solute content. Pre-straining accelerates precipitation of nitride and under appropriate conditions (e.g. at *c.* 3 per cent strain at 400°C.) over-ageing advances far enough to depress the ductile-brittle transition to below room temperature. The precipitated chromium nitrides would be stable due to the strong affinity of chromium for nitrogen and would be unaffected by the dissolving effect of adjacent unsaturated dislocations. Precipitation at an intermediate temperature (400°C.) would thus be expected to remove nitrogen permanently from the solution and reduce the residual nitrogen causing brittleness at lower temperatures [*Nature, Lond.*, **180** (1957), 806].

High-purity thorium

THE FIRST COMMERCIAL PRODUCTION of pure thorium has been started by Metal Hydrides, Beverley, Massachusetts, and is based on the thermal dissociation of thorium tetraiodide formed by reacting crude thorium with iodine vapour. The batch refining process starts with charging of crude thorium chips of nuclear reactor grade into the annular space between the outer shell (made of Hastealloy) of the reaction vessel and a concentrically disposed perforated retaining screen of molybdenum. After evacuation the vessel is heated to 450°-500°C.; at this temperature a measured amount of iodine vapour is introduced which diffuses into the chips forming gaseous thorium tetraiodide. One or more heated filaments of pure thorium, suspended along the centre of the cylindrical screen, cause the tetraiodide to dissociate, and crystals of pure metal deposit on the filaments, free iodine vapours diffusing back into the crude chips to repeat the cycle. In the final product the oxygen content is reduced from 1000-3000 to less than 50 p.p.m.; iron from 1000 to less than 30 p.p.m.; and other elements from 100 to less than 40 p.p.m. For the production of moderate amounts of the metal the production unit need not be much larger than a laboratory set-up [*Industr. Chem. Mfr.*, **33** (1957), 531].

Rare earth separation

A PROCESS FOR THE SEPARATION of rare earths, which combines the high capacity of solvent extraction with the high efficiency of ion-exchange separation, has been developed in the laboratory of Horizons Inc., Cleveland, and is in the production stage. It is essentially a liquid ion-exchange process using 2-diethylhexylphosphoric acid (DHPA) in a petroleum ether carrier. DHPA (0·1 mol) in petroleum ether is able to extract mixed rare earth chlorides in water solution quickly from which they are extracted with ammonium citrate. By regulating the *p*H of the extractant and its weight ratio to the petroleum ether, preferential extraction of the individual rare earths is achieved. In the laboratory the separations have averaged 97 per cent recovery (as oxides) of individual rare earths at 99·5 per cent purity. Chief advantages of this method are sharp separations and adaptability to continuous operation [*Chem. Engng News*, **35**(36) (1957), 80].

Gold plating by ionic displacement

A WATER-SOLUBLE GOLD/AMINO complex which reduces plating costs by 25 per cent through use of less gold than in electroplating has been developed by Baker & Co., Newark, N.J. Objects to be coated are immersed in a heated bath containing the complex. Gold displaces metal ions from the surface and is reduced to metal on the spot. Deposed ions are inactivated by chelation and removed into the body of the solution. When a 24 karat film has been deposited over the whole surface, the process stops itself. On most metals (iron, steels except stainless, die casting alloys, soft solder), an average of 1 mg. of gold/sq. in. deposits in a few minutes. The higher the temperature, the more rapid is the deposition. The process has the possibility of being used on an industrial scale in the gold plating of copper in electric and electronic applications, trophies, costume jewellery and metallized plastics [*Chem. Engng News*, **35**(36) (1957), 81].

Mercury determination by direct distillation

AN IMPROVED DIRECT DISTILLATION method for the determination of mercury has been developed. The method, with slight modifications, is applicable to a wide variety of mercury-containing materials like inorganic mercury salts, organic materials, seed dressings and pharmaceutical preparations. The determination is rapid and the apparatus employed is cheap and simple to use. The method employed is to distil the mercury-containing material in the presence of iron filings and to pass the vapour through a mixture of calcium oxide and iron filings. The mercury is trapped on zinc wool in the receiver, the amalgam being dissolved in nitric acid and titrated with N/10 ammonium thiocyanate in the usual way. The distillation unit is a vertical retort consisting of a fused silica flask fitted with a delivery tube and receiver in one piece, so that the whole would go into a beaker to dissolve out the mercury. It has been reported that when the amount of mercury taken is small, the losses are of the order of 0·2 mg. With large amounts of mercury the loss is equivalent to 0·1 mg. mercury. An accuracy of 99·6 per cent is claimed for the method [*Chem. Age*, **78** (1957), 595].

Chromatography of trace metals

FOR A RAPID ROUTINE EVALUATION of trace elements in crops, a simple chromatographic method has been developed. In this method the final assessment is made by visual matching against standards, which has been found satisfactory.

For the preparation of the sample extract, a known amount of finely ground sample (10 mg.) is ashed at 550°C. Silica is precipitated by repeated (twice) evaporation with hydrochloric acid and heating for 2 hr. The ash is then dissolved in 0·5 ml. of 50 per cent hydrochloric acid. For the chromatographic separations, Whatman No. 1, Pattern CRL, slotted paper is used, so that ten separate aliquots can be treated simultaneously.

Copper, cobalt and nickel are determined in 0·02 ml. portion of the sample by upward-flow chromatography with ethyl methyl ketone-hydrochloric acid-water in the ratio 15 : 3 : 2 as solvent, followed by development with rubeanic acid (0·1 per cent solution) when the coloured bands due to nickel (purple-blue at the bottom), cobalt (yellow in the middle) and copper (olive green at the top) will appear. The coloured bands are matched against standard papers, the convenient range being 0·2-2 μg. Molybdenum is similarly determined in 0·02 ml. portion, *n*-butyl alcohol saturated with 10 per cent hydrochloric acid being used as solvent and development with toluene-3 : 4-dithiol. An apple-green band develops about halfway up the strip which can be matched against standards in the range 0·2-2 μg. Excess of iron which interferes in the estimation of molybdenum is removed by adding potassium thiocyanate and stannous chloride (in concentrated HCl) to the original extract and then extracting the molybdenum complex with a measured amount of butyl acetate and transferring to a narrow tube of 2 mm. bore. The yellow colour of the molybdenum complex in butyl acetate can then be compared with a set of standards in similar tubes in the range 0·2-2 μg. For the estimation of zinc, 0·01 ml. of the extract solution is pipetted into a 10 ml. stoppered test tube containing 1 ml. of 1 per cent hydrochloric acid and 1·0 ml. of *p*H 5·0 buffer (equal volumes of 2N sodium acetate and 2N acetic acid), 1·0 ml. of 25 per cent sodium thiosulphate are added, followed by 1·0 ml. of 0·002 per cent dithiozone in carbon tetrachloride. After vigorous shaking for 1 min. the layers are allowed to separate, and the colour in the carbon tetrachloride layer is matched against standards in the range 0·2-4 μg. The band produced does not permit a quantitative evaluation. Boron is determined chromatographically using curcumin as a colour reagent. The complex thus formed after treatment with alkali gives a blue-green colour, not produced by iron, titanium, vanadium or molybdenum. The intensity of this band is then compared with that of standards simultaneously prepared in the range 0·2-2 μg. Matching should be carried out within 20-30 min.

Manganese is determined by periodate oxidation to permanganate. To 0·25 ml. of extract in a 6×1 in. test tube are added 0·4 ml. H_2SO_4, 0·5 ml. HNO_3 and 0·1 ml. phosphoric acid, together with a few drops of silver nitrate to catalyse the reaction. The tube is heated to fuming, cooled and again heated after addition of 1 ml. of water. Then 7 ml. of water and 0·1 g. of potassium periodate are added and the tube boiled for 5 min. and placed in a boiling water bath for 2 hr. The solution may be suitably diluted according to intensity of the permanganate colour before matching against standards.

An accuracy of ±5 per cent has been obtained with suitable aliquots [*Chem. Age*, **78** (1957), 596].

Chemistry of heredity

A NEW STUDY WHICH MAY SHED light on the chemistry of heredity has been carried out by the scientists at Columbia University and Brookhaven National Laboratory. Investigations on the nucleus of a single cell of an English bean plant have shown that cell heredity-carrying chromosomes are composed of two strands which separate when the chromosomes divide or duplicate themselves. Using radioactive labelled desoxypentose nucleic acid (DNA), a constituent of chromosomes which apparently transmits heredity characteristics from one generation to another, it has been possible to find that both 'daughter' chromosomes which result from division in the presence of radioactive tag appear equally and uniformly divided. In division without the tagged DNA, the label appeared in only one of the daughter chromosomes. These findings show that DNA is synthesized as a unit which extends throughout the length of the chromosomes. These experiments have been carried out with tritium labelled thymidine, a natural component of DNA [*Chem. Engng News*, **35**(34) (1957), 27].

Penicillin as a growth factor

THE INFLUENCE OF PENICILLIN ON biological processes requiring thiamine has been assessed by its ability to support the growth, in the absence of thiamine or its thiazole moiety, of the mould *Phycomyces blakesleeanus* and the weanling rat. Investigations show that penicillin is able to support the growth of the mould, during a 14-day period at 20°C., on an artificial medium containing the pyrimidine moiety of thiamine. Penicillin can, therefore, replace the thiazole moiety of thiamine as a growth factor and the concentrations of penicillin and the thiazole moiety of thiamine or thiamine required to give a comparable weight of mycelium are in the ratio of 100,000 : 1. In addition to this, penicillin has also supplemented a suboptimal concentration of thiazole moiety (4×10^{-9}M) to give an increased mycelial weight. Investigations on the effect of intraperitoneal administration of penicillin, either alone or with pyrimidine moiety of thiamine, on weanling rats fed on a thiamine-free diet show that it delays the onset of thiamine deficiency and reverses the symptoms of thiamine avitaminosis induced by withdrawal of treatment. Further administration of penicillin prevented premortal convulsions of severe thiamine deficiency and effected recovery in several such animals. The work on the nature of the growth-promoting effect of penicillin is under progress [*Nature, Lond.*, **180** (1957), 657].

Amphotericin, a new antibiotic

A NEW ANTIBIOTIC WHICH IS effective against fatal brain-killing fungus disease, cryptococcal meningitis, was reported by the public health scientists to the Fifth Annual Antibiotics Symposium held in Washington D.C. The antibiotic is obtained from a species of Streptomyces fungus which was found along the Orinoco river in Brazil. So far it has proved relatively non-toxic to humans, and is still under investigation and not yet available for general use. Intravenous injections of amphotericin B were given to six patients suffering from the disease caused by the fungus. Five are still alive after follow-up studies ranging from five to ten months. In three of them all the symptoms of the disease have disappeared and they have resumed normal activities. It has been tried against a number of other fungus diseases which failed to respond to other antibiotics and is reported to be the first antibiotic effective against histoplasmosis [*Sci. Newslett., Wash.*, **72** (1957), 232].

New synthesis of sulphanilamides

A NEW AND CHEAPER METHOD FOR the synthesis of sulphanilamide drugs based on ammonolysis in the presence of copper catalyst has been developed at the Ordshonikidze Institute for Chemical and Pharmaceutical Research, Moscow. The ammonolysis of the chlorine derivatives of sulphanil leads to a series of *n*-monosubstituted derivatives of sulphanilamides.

Sulgine, *p*-aminobenzene sulphonyl guanidine, has been synthesized by the ammonolysis of *p*-chlorobenzene sulphonyl guanidine in the presence of copper catalyst. The best yields are obtained when ammonolysis is carried out below 145°C. using less than 30 per cent ammonia and 0·5 mol of copper. In the above preparation it is advantageous first to prepare sulphanilamide and then to convert this by cross-amidation into sulgine. It is possible to obtain a yield of 70 per cent of the theoretical by melting sulphanilamide with guanidine carbonate [*Industr. Chem. Mfr.*, **33** (1957), 530].

Synthetic geraniol

GERANIOL AND A RANGE OF TERpene alcohols of great significance to perfumers have been produced for the first time on a commercial scale from turpentine at the Glidden's Research Laboratories. The synthetic geraniol is of high quality, having a minimum total alcohol content of 98 per cent. Detailed information concerning these products can be obtained from Glidden International, C.A., Southern Chemical Division, Rootes Building, Nassau, Bahamas, or from A. Boake, Roberts & Co. Ltd., Aromatics and Perfumery Division, Stratford, London, England.

New pharmaco-convulsive agent

HEXAFLUORODIETHYL ETHER IS proving a useful pharmaco-convulsive drug for shock therapy in mentally disturbed patients because of its harmless nature on repeated administration to animals, as shown by studies of blood chemistry and by histological examination of the lungs, brain, liver, kidneys and bone marrow of the animals. It causes rapid onset of clonic and tonic seizures in rats which stop quickly when the agent is removed from the inspired air. It produces cortical dysrhythmia in dogs and monkeys without involvement of the skeletal muscle similar to that caused by Metrazol. Four patients suffering with mental disturbances in which electro-shock therapy was indicated were subjected to inhalation of hexafluorodiethyl ether without anaesthetizing them. Within 1-3 min., the convulsive seizure ensued and continued from 2 to 4 min. until the inhaler was withdrawn. The seizure episode resembled that of electro-shock therapy. Unconsciousness supervened following the convulsion for from 5 to 17 min. in three patients. The first patient was allowed to inhale the compound only until a few myoclonic facial twitches occurred. The patients recovered uneventfully, and there appeared to be no clouding of memory. Two of the patients who were combative assumed a more co-operative attitude [*Science*, **126** (1957), 355].

Systemic insecticides

AT THE FOURTH INTERNATIONAL Crop Protection Congress, held recently in Hamburg, four new systemic insecticides were reported. Phosphamidon has a half-life of only two days in the plant. It kills leaf-sucking insects and many grules, larvae and caterpillars. It is non-volatile and safe to use. The second product, phosdrin, is a vinyl phosphate, very short lived in plants. It is effective in small quantities and 1-8 oz. are sufficient for an acre of land. Its breakdown to non-toxic products in plants is very rapid and the crops are safe to eat 24 hr. after treatment. It is capable of controlling economically 35 kinds of insects on 25 different crops. The third insecticide, thiodan, is a chlorinated organic sulphur compound and acts on the insects both as a stomach poison and as a contact poison. It is harmless to the plants. The compound's toxic effect on mammals and birds is relatively high if swallowed, but there is no cumulative action and no poisonous effect from absorption through the skin, or inhalation of the vapour. The fourth is a polychlorinated hydrocarbon of very low toxicity to warm-blooded creatures. It is particularly effective against beetles and various human and animal parasitic insects. It has a marked selective action against plant pests [*Chem. Tr. J.*, **141** (1957), 928].

New instruments and their applications

AS IN THE PREVIOUS YEARS, THE 'Instrument Issue' of *Science* [**126** (1957), 3278] reviews the recent developments in instrumentation in a number of branches of science. The eight articles included in this issue covering applications in physical, biological, medical and technological sciences have been written by experts in the respective fields and should prove useful for specialists as well as those engaged in research in border sciences. The articles deal in detail, either with the principles, design, operation and applications, current or prospective, of the measuring instruments with emphasis on the automation of its operation, or with new techniques for investigation in specific branches resulting from fundamental advances.

The first article presents the principles, design and applications of the recently developed ultraviolet colour-translating microscope which offers immense possibilities for new biological and medical investigations. The second article gives a detailed exposition of the theory behind the latest progress in microwave amplifiers using the MASER principle, and indicates its possibilities as well as limitations. The feasibility of instrumentation and the degree of success achieved in tackling the problem of information storage and retrieval by mechanical means, with particular reference to the chemical literature and the structural formulae, have been dealt with in another informative article.

In the domain of medical and biological sciences, the design and performance of an electronically controlled respirator, suitable to patients affected by muscular paralysis following poliomyelitis, are described. The instrument permits the neurological and biochemical mechanisms of the organism to automatically control its respiratory needs. The methods by which human control of general anaesthesia can be replaced by servo controls and the present applications and, in particular, in the pharmacological evaluation of drugs form the subject matter of another article. Another instrument of interest described is an automatic particle and bacterial colony counter which automatizes the routine work in many bacteriological laboratories; it can also find application in many industrial fields with slight modifications. The counter is essentially a flying-spot microscope with special information processing circuits attached.

Other articles deal with the sensitivity and composition control of a glass electrode for measuring the sodium ion activity in ionic mixtures and in biological fluids and with an integrating automatic recording potentiometer, useful in quantitative analysis in fields like chromatography and spectroscopy.

New fossils from Madhya Pradesh

THE FOLLOWING COMMUNICATION has been received from Shri B. S. Tiwari, Geology Department, Lucknow University. The marine Permo-Carboniferous rocks obtained from Mahendragarh (82°12′: 23°13′), Jhagrakhand, in Madhya Pradesh, have been studied. Apart from two marine fossiliferous localities so far reported from this area, two new spots along the right bank of the river Hasdo and situated upstream of the two known localities, have yielded marine assemblage. It has been observed that the conglomerate immediately overlying the Archaean gneiss, as also the successive beds which are needle shales and a band of sandstone, yield marine fossils and are in a conformable sequence and dip at an angle of 30° towards the south and 5° towards the west. Besides the fossils already reported from the conglomerates, others such as *Spirifer nitiensis*, *Protoretepora ampala*, *Lima*, *Pterinea*, a small species of *Pleurotomaria* and badly preserved arenaceous foraminifers have been found. The fauna resembles that of Lower Permian of Kashmir and the Salt Range. Besides the two new spots mentioned above, a new locality of Intertrappean fossils, the specimens of which were found in a hard siliceous rock, has been observed at the south-east end of Naurozabad railway platform.

Ayurvedic Pharmacopoeia

AN EIGHT-MEMBER COMMITTEE for preparing an Ayurvedic Pharmacopoeia has been set up by the Government of Bombay. The Committee consists of: Pandit Shiv Sharma (*Chairman*); Wamanrao Vaidya, G. M. Waidya, P. B. Dhamankar, K. G. Gune, K. C. Barot, the Drugs Controller, Bombay and the Director of Ayurveda, Bombay (*Members*).

At present, there is no standard Ayurvedic Pharmacopoeia serving as a basis for judging the various kinds of *Asavas*, *Arishtas* and other Ayurvedic drugs available in the market. The Committee will suggest steps to be taken to publish an Ayurvedic Pharmacopoeia which lists the Ayurvedic medicines and compounds and the methods of preparing them as well as the exact weights and measures to be used in their preparation and other related information which lead to their proper standardization. Priority will be given to the compilation of the section relating to *Asavas* and *Arishtas*, particularly those in common use [*Press Information Bureau*].

Symposium on Meteorology and High-level Aviation

A SYMPOSIUM ON 'METEOROLOGY and High-level Aviation' (over India and surrounding areas) was held at New Delhi on 8 December 1957. Shri S. Basu, Director-General of Observatories, presided. Representatives of the Civil Aviation Department, the Air Headquarters, the International Civil Aviation Organization, the International Airlines, All India Radio and the India Meteorological Department participated in the symposium. Sixteen papers covering a wide range of subjects of vital interest for jet aircraft operations were submitted and discussed at the symposium. The discussions covered such subjects as air temperature, density and other factors and their significance for jet aircraft operations; clear air turbulence; radar study of thunderstorms; jet streams and other phenomena in the upper air.

The Consultative Conference on 'Meteorological Requirements of Jet Flights', which met the previous day (7 December 1957), considered, among others, pre-flight and in-flight meteorological requirements, and supply of temperature and surface wind data for take-off and landing operations. A number of broad conclusions have been drawn which are of practical utility in planning ahead meteorological services to meet the requirements of jet airline service [*Press Information Bureau*].

Announcements

- *CERN Synchrocyclotron Starts Operation* — The 600 MeV. synchrocyclotron, the third biggest of its kind in the world, built by the European Organization for Nuclear Research (CERN) in Geneva for the use of European scientists in high energy nuclear research, has been recently completed and put into operation at its full energy. The successful commencement of working of this machine was the result of two years' intense effort in research, design, fabrication and construction undertaken by the synchrocyclotron division of the CERN laboratory centre. Successful test runs have been carried out on the machine at the peak output of 600 MeV. The internal current during the first run was *c.* 0·1 μa. The intensity of the particle beam is expected to be increased later.

- *The Seventh International Mechanical Engineering Congress* will be held during 2-7 June 1958 at Scheveningen, Netherlands. Full particulars can be obtained from International Mechanical Engineering Congress, 10 Avenue Hoche, Paris 8e, France.

- *An International Conference on Solid State Physics in Electronics and Telecommunications*, sponsored by the Postal and Telecommunications Group of the Brussels Universal and International Exhibition, will be held during 2-7 June 1958 at Brussels, Belgium. Further information can be obtained from the Honorable General Secretary, Societe Belge de Physique, 18r. de Phillipeville, Loverval, Belgium.

- *The Seventeenth Session of the International Conference on Large Electric Systems* will be held during 4-14 June 1958 at Paris. Queries in this connection may be addressed to 112 Boulevard Haussmann, Paris.

- *International High-polymer Conference* — An international conference on high-polymers will be held at Nottingham from 21-24 July 1958 under the auspices of the Macromolecular Commission of the International Union of Pure and Applied Chemistry. The conference has been divided into two sections. Section A will discuss reaction mechanism and kinetics of polymerization (heterogeneous polymerization, trapped or inactive radicals, graft and block copolymers). Section B will discuss physical, thermodynamic and mechanical properties of high polymers.

- *The Association des Ingenieurs Electriciens Sortis de l'Institut Electrotechnique Montefiore (A.I.M.)* will organize a series of International Study Days on 'Modern Thermal and Hydraulic Power Stations' during 27-31 May 1958. The venue of the study days will be the Palais des Congres, Liege, Belgium. These days will be devoted to the discussion of technical papers and reports submitted by specialist scientists from America, Britain, France, Germany, Switzerland, etc., and Belgium. Papers, in any one of the three languages — English, German and French, are invited for discussion which should deal with any of the following subjects: boilers, hydraulic turbines, steam turbines and alternators. Further particulars in this connection can be obtained from A.I.M. Secretariat, 31 rue Saint-Gilles, Liège, Belgium.

- *Indian Botanical Society* — The following have been elected office-bearers of the Society for the year 1958: Dr. R. Misra (*President*); Dr. S. K. Pande and Dr. P. Maheshwari (*Vice-Presidents*); Dr. J. Venkateswarlu (*Hon. Secretary*); Dr. R. Misra (*Hon. Librarian*); Dr. T. S. Sadasivan (*Hon. Treasurer*); Rev. Fr. H. Santapau, Drs. A. C. Joshi, P. Parija, T. S. Mahabale, S. Ranjan, A. Abraham, B. Samantarai, J. C. Sen Gupta, R. P. Roy, V. Puri (*Councillors*); Drs. P. Maheshwari, B. P. Pal, A. C. Joshi, Rev. Fr. H. Santapau (*Members of the Editorial Board*); and Dr. T. S. Sadasivan (*Business Manager*).

- *Soviet Government Scholarships* — The following candidates have been awarded Soviet Government post-graduate study / research scholarships in U.S.S.R. for 1957-58: Beni Madhava Shukla and Amar Nath: Chemistry; Pandurang Narhar Joshi: Biochemistry; Satya Pal Talwar: Astrophysics; Pratap Singh: Botany; Moreshwar Shankar Huzurbazar and Tyakal Subbiah Bhanu Murthy: Mathematics; Arvind Bhalchandra Buche: Statistics; Velagapoodi Chandrasekharan: Metallurgy; Aditya Prasad Sinha: Chemical Engineering; and Kanak Chandra Mahanta: Dairying.

- *Award of Doctorate Degrees* — The following have been recently awarded the Ph.D. degree of the Poona University for the theses noted in brackets against their names: Shri Nilkanth Balkrishna Kulkarni (*Studies in the genus Piricularia*); Shri Prabhakar Shripad Borkar (*Studies on amino acid acylases of fungi*).

INSTRUMENTS AND APPLIANCES

MASS SPECTROMETER

Two special types of mass spectrometers, MS5 and MS7, have been designed by Metropolitan-Vickers Electrical Co. Ltd. for analysis of inorganic solids. The MS5 is a 12-in. radius, 90°-sector, single-focussing mass spectrometer for use with either the single or triple filament surface ionization technique. A sliding-bar vacuum lock system enables the sample to be introduced into the instrument in less than a minute and an ion collector system provides the simultaneous availability of a normal collector (noise level approximately 3 by 10^{-15}A.) and an electron multiplier (equivalent noise level less than 10^{-18}A.). A resolving power of 300 can be obtained. A few micrograms, and in some cases 10^{-11} g., of the samples enable approximate determinations of isotope ratio. Nearly 75 per cent of all the elements including most metallic elements respond to the surface ionization technique and the time required for an analysis varies from 10 min. to an hour depending on the element and the sample size available.

MS7 is designed for general analysis of solids by the spark ionization technique. It is a double focussing instrument producing positive ions of the sample composition when a high voltage spark occurs between two electrodes made of the sample material and placed close together in vacuum. The ions produced first pass through an electrostatic analyser and then through a magnetic analyser the ions come to focus according to their mass as a series of lines on a photographic plate. The instrument has been used in the analysis of impurities in solids. A concentration of the impurity up to 0·1 p.p.m. has been estimated from the intensity of the lines on the longer exposures. The whole mass number ranges from 7 to 240, covering all elements, and can be recorded in a single exposure of the photographic plate. Compared with emission spectroscopy, the spectra are simpler and the elements easier to identify [*Chem. Age*, **78** (1957), 145].

INDUSTRIAL X-RAY EQUIPMENT

The Newton Victor Raymax 150 has been designed to meet the demand for a light-weight radiograph equipment with enough ruggedness to make it suitable for use in the factory or in the open on erection sites. These advantages result from the use of non-toxic inert gas, sulphur hexafluoride, as the insulating medium, together with the absence of voltage cables, rectifier valves and the associated filament transformer. The equipment consists of a tubehead, gantry stand which provides a versatile support for the tubehead, a control unit and water cooler. Earthing the target of the X-ray tube obviates one of the complications of oil cooling. The equipment is cooled either from the mains supply or from a water/air heat exchanger. Pivots on the long and short axes of the tubehead permit the beam to be angled in all directions. For special work the tubehead and cradle can be easily removed from the stand.

Two tubes are available for use with the equipment, one for the general radiography of welded joints, light alloy castings and miscellaneous objects and the other, for the examination of circumferential welds, hollow castings and small specimens arranged in a circle. Tube voltage is continuously adjustable from 50 to 150 kV. and is sufficient for testing all light alloy castings, plastic mouldings or assemblies and welded steel plates up to 1½ in. thick. The portable control unit contains a synchronous motor exposure timer with a range of 1 sec. to 55 min. in steps of 1 sec. [*Beama J.*, **64** (1957), 130].

LABORATORY AND MEDICAL FILTERS

Messrs British Berkefeld Filters Ltd., London, have recently developed a self-sterilizing candle, the 'Sterasyl', which overcomes drawbacks of the former kieselguhr types. For instance, frequent boiling necessary to keep the germicidal properties of the former filter is not needed with the new type.

The new candle not only acts as an efficient filter but sterilizes as it filters. Germs are trapped and destroyed on the exterior surface of the candle. The filtered water can be stored and remains pure for long periods. The candles last long without renewal; they are cleaned by washing them occasionally with a soft brush in clean water; no soap or detergent should be used. For laboratory and medical purposes, filters are available for sterilizing all liquids and for filtering beef tea, infusions and other liquids containing bacteria. From fresh milk a perfectly clean colourless fat-free milk serum can be obtained. These filters are available in 4 sizes, with capacities of 100, 200, 250 and 750 ml. Large supply pressure filters suitable for all purposes where a constant supply of pure water is required are also available.

MICROFLAME DETECTOR FOR GAS CHROMATOGRAPHY

The Scott microflame detector is now available commercially for use in vapour-phase gas chromatography. The detector depends on the use of a carrier gas containing a considerable proportion of hydrogen, which is burnt in a small flame near the column exit. The presence of an organic vapour in the gas increases the length of the flame, and this results in a comparatively large response from a thermocouple situated just above the normal flame. The advantages of this detector are that it has an extremely small effective volume, resulting in a rapid response. The response is directly proportional to the calorific value of the vapour; this means that in the analysis of hydrocarbons, calibration of the detector for individual compounds is necessary [*Nature, Lond.*, **180** (1957), 530].

Progress Reports

INDIAN INSTITUTE OF SCIENCE, BANGALORE: ANNUAL REPORT, 1955-56

During the period under review twenty schemes sponsored by Government departments, research organizations and other scientific bodies were under investigation. One hundred and seventy-seven papers were published during the year. The following is a brief account of the research work carried out in the different departments of the Institute.

General Chemistry — The substitution of the pyrophosphate bath in place of the conventional cyanide bath has yielded fruitful results in the electrodeposition of brass, nickel tungsten alloy and tin alloys. The deposition potentials of tin and nickel in tin-nickel alloys and of tin and lead in tin-lead alloys are close to each other in pyrophosphate solutions and this facilitates the co-deposition of these metals from the pyrophosphate solutions. Studies on selective flotation of sulphides and oxide minerals employing caproic acid as collector and different *p*H values indicate that the theory of Schulman *et al.* is not universally applicable and that the selective flotation is dependent on the chemical nature of the mineral surfaces. Phosphate reagents prepared from diethyl and dimethyl substituted quaternary ammonium compounds in the *p*H range 9·0-9·5 have been found to give the best results for quantitative precipitation of lithium as phosphate. Studies on cobalt carbonate prepared under different experimental conditions and examined by different physico-chemical methods show that cobalt carbonate of identical chemical composition may be obtained by various methods, but their physical properties vary. It is inferred that the mode of preparation is an important factor in determining the nature of cobalt catalysts. Primary alcohols with a small percentage of water have been found to be most efficient eluting solvents for a clear chromatographic separation of the mixture of lithium, sodium and potassium salts.

Organic Chemistry — Experiments towards the synthesis of some of the important steroids, like testosterone, estrone and their analogues, have been conducted and a number of intermediates have been synthesized. In continuation of the work on the projected synthesis of Wieland's tricarboxylic acid, methyl-2-methyl-Δ^4-cyclopentene-1, 2, 3-tricarboxylate has been prepared from 2-methyl-2, 3-dicarbethoxycyclopentanone through cyanohydrin. In the field of synthetic and natural drugs, experiments are in progress towards the synthesis of reserpine and penicillin and intermediates have been prepared. In a series of experiments carried out with dipiperonoyl succinate and designed to synthesize sesamin, two products have been isolated which from their elemental analyses and ultraviolet absorption data appear to be two isomers of sesamin. In the field of terpenoids, the synthesis of carissone has been achieved starting from 2-carbethoxy-2-methyl-Δ^5-cyclohexenone. A new route to the synthesis of azulenes, involving the intramolecular acylation of a lactone to a cyclopentenone by polyphosphoric acid, has been developed.

Crude *neem* oil has been refined to a tasteless, odourless and practically colourless oil by adsorption chromatography over an alumina column.

Biochemistry — Evidence in support of the existence of Embden-Meyerhof glycolytic pathway in green gram has been put forward by the identification of all the enzymes taking part in glycolysis. A new antibiotic, guttiferin, has been isolated from the exudation of Mysore Gamboge tree. The antibiotic has no effect on blood pressure and respiration and is well tolerated through oral, subcutaneous and intravenous administration.

Studies on the influence of curds on the biosynthesis of B-complex vitamins indicate that the feeding of curd is beneficial to the rats inasmuch as the synthesis of thiamine, riboflavin in intestines and liver storage are significantly higher in the curd-fed group as compared with the control rats.

A simple technique of zone electrophoresis in agar gel has been developed for the study of proteins and polysaccharides. The serum protein patterns in various diseases have been studied by this technique.

A blood anti-coagulant factor has been isolated from the latex of *Carica papaya*. The anti-coagulant is active at a concentration of 1/5000 in human as well as dog's, cow's and sheep's blood and acts both as an anti-prothrombin and an anti-thrombin, the latter activity being more pronounced.

Physics — The second order Raman spectrum, using the resonance radiation of mercury λ2537, of a single crystal of caesium bromide has been recorded for the first time. The possible position of the double bonds in hydrocarbon cyperene II and its partially and completely hydrogenated products have been obtained from the Raman spectra of these compounds obtained with Hg λ4358 as the exciting radiation. These are in accord with the evidence derived from chemical methods. The thermal expansion of crystals of calcite and alkali halides have been studied. The expansion of calcite both parallel and perpendicular to the axis was studied up to 400°C. It was found that a_{11} showed a monotonous increase with temperature, a_T decreased in magnitude with the rise in temperature. Ultrasonic velocities and their variation up to 1 molar have been measured for solutions of strontium iodide, lead acetate, uranyl chloride, for the temperature range 25°-60°C. and the results have revealed some interesting features: (1) Contrary to the general case of electrolytes, the ultrasonic velocities decrease with concentration in these cases. The lowering of velocity is attributed to the presence of heavy ions; and (2) the slopes of the molar compressibility curves, for lead acetate and uranyl salts, are less than that predicted by the Debye-Huckel theory. This anomaly is due to the presence of intermediate complexes and undissociated ions which seems to be in accord with X-ray diffraction and conductance data.

Metallurgy — Zinc or boron, when present in very low concentrations in aluminium, increases the modulus of elasticity of aluminium significantly. This unexpected finding has been interpreted on the basis of the prevailing electron concentration. A machine has been constructed to fabricate ' flat grid ' electrical resistance gauges, which possess a great advantage over the helical type gauges on account of their smaller thickness. In the preparation of anhydrous aluminium chloride from bauxite, carbon has been found to be a cheaper reducing agent than sulphur. Direct smelting of zinc sulphide by manganese and ferromanganese to zinc metal, by-passing the intermediary roasting of the sulphide, has been studied in detail. Smelting is carried out in an electrically heated tube furnace and the zinc vapour formed is flushed out with argon and condensed. The studies on the effect of time of smelting, temperature employed, and the molar ratio of manganese to zinc sulphide employed in smelting show that increased temperatures within the range 1000°-1200°C. improve the yield. The yield at all temperatures and molar ratios increase with time until a maximum is attained. Yields below theoretical obtained even when the manganese is in excess of the stoichiometric requirement have been attributed to the solution of manganese sulphide in zinc sulphide thereby decreasing the activity of zinc sulphide, and to the possible formation of secondary manganese compounds which decrease the amount of free manganese available for reduction of zinc sulphide. The effect of cerium on the electrical and mechanical properties of aluminium has been studied. It has been shown that cerium, to the extent of about 0·25 per cent, exerts a moderately beneficial effect on the electrical conductivity, and this effect seems to be related to the formation of intermetallic compounds between cerium and the impurity elements.

Power Engineering — Investigations on the transient behaviour of d.c. shunt generators have shown that the transients caused by the rapid insertion of a resistance in the shunt field circuit will cause under certain conditions of circuit constants a reversal of the exciter polarity leading to the abnormal condition of operation of the system. A transient analyser is being built in the laboratory with a view to studying the transient phenomena of transmission lines.

The study of the effects of placing a battery of sluices through a dam on their discharge and pressures, made on an electrical analogy tray, Heleshaw apparatus and in hydraulic flumes, indicated that in a two-dimensional analysis of flow, the interference may result in the reduction of coefficient of discharge varying from 1 to 16 per cent depending on the number of sluices of the same size placed side by side and from 1 to 7 per cent in the case of a pair of sluices; the value depends on the centre to centre spacing and size of the sluices. The effect of admixture of two puzzolanic materials (*surkhi* and granite powders, passing through sieves No. 200 and 325 respectively) on the properties of cement mortars and concretes has been investigated. The lime reactivity test has shown that *surkhi* is a better puzzolan, but the alkali reduction test and the mortar bar test have shown that granite powder is more effective in counteracting the excessive expansion resulting from alkali aggregate reaction.

Electrical Communication Engineering — An automatic ionospheric recorder has been constructed. It consists of (1) a pulsed high power transmitter capable of transmitting the frequencies of 0·5-20 Mc/s.; (2) a receiver capable of receiving signal in this frequency range; (3) a pulse generator triggering the transmitter; (4) a height marker generator; (5) a frequency marker generator; and (6) a display tube with auxiliaries like frequency scan generator, height scan generator and gate wave form generators. An electronic differential analyser has been set up to solve linear differential equations of the second order with constant coefficients. To deal with non-linear relations arising from such factors as back-lash, hysteresis, saturation, etc., special circuits have been constructed and a few problems involving certain types of non-linearities have been solved.

Chemical Technology and Chemical Engineering — Results obtained on the application of fluidized solids technique to haematite-air system and fullers' earth-air system indicate the occurrence of both homogeneous and heterogeneous conditions of fluidization in solid-gas systems. The air velocity at which a fixed bed changes to fluidized condition is found to be independent of the initial bed height, but dependent upon the particle size and its related characteristics. The technique has also been applied for the gasification of charcoal by oxygen and steam. Several test runs, made under various conditions of temperature, particle size, etc., show that the continuous gasification depends mainly on the retention time of the particles in the reactor tube. An apparatus has been constructed for the analysis and enrichment of heavy water using the principle of vapour-phase chromatography and is now being tested for the various systems. Activated charcoal has been found to be a good absorbent for β-active isotopes of uranium and protactinium series existing in uranium nitrate and uranium acetate solutions.

Pharmacology and Fermentation — Studies on the effect of supplementation of some amino acids on the severity and the course of avian malaria (*P. gallinaceum*) have shown that glutamic acid, methionine, histidine and glycine in doses administered proved toxic to the host, causing the death of the animals, while threonine, phenylalanine, and DL-aspartic acid did not exhibit any suppressive action. Derivatives of isonicotinic acid with various amino acids have been investigated for *in vitro* anti-tubercular activity. Of these, compound 608 exhibited a fair degree of inhibitory action.

The biliary stimulant activity of the pigment curcumin, and the essential oil fractions of *Curcuma longa*, have been determined in dogs. The pigment has been found to possess an appreciable bile stimulant action and acts as choleretic and cholecystogouge and inhibits the growth of *Staph. aureus*. The essential oil of *Cyperus rotundus* has been shown to possess bacteriostatic action.

It has been demonstrated on a semi-industrial scale that supplementation of mulberry diet of the silk-worm (*Bombyx mori* L.) with small amounts of glycine and the antibiotic chloromycetin improved not only the health and development of the worms but also helped the silk-worms to synthesize greater amounts of silk.

A Process for the Preparation of *para*-Nitroacetophenone & Other Substituted Acetophenones*

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(*Manuscript received* 4 *October* 1957)

An improved method is described for the preparation of *p*-nitroacetophenone and other substituted acetophenones by the condensation of ethyl acetoacetate with the appropriate acid chloride in the presence of anhydrous sodium hydroxide or potassium hydroxide. The new method eliminates the hazards and the controlled conditions required in the handling of metallic sodium, potassium or magnesium which have hitherto been used in the preparation of substituted acetophenones. The yields obtained (72-75 per cent) compare favourably with those obtained by the conventional methods.

p-NITROACETOPHENONE has assumed considerable importance in recent years, particularly in view of its use as an intermediate in the manufacture of the synthetic antibiotic, chloramphenicol [D-(-)-*threo*-1-*p*-nitrophenyl-2-dichloroacetamido-1,3-propanediol].

A convenient method for the preparation of *p*-nitroacetophenone or other methyl ketones consists in the acylation of the sodium, potassium or magnesium-ethoxy derivative of a β-ketonic ester, e.g. diethyl malonate[1-4] or ethyl acetoacetate[5-10] with *p*-nitrobenzoyl chloride or any other appropriate acid chloride followed by hydrolysis and decarboxylation. Ethyl *p*-nitrobenzoyl acetate has also been prepared by the condensation of *p*-nitrobenzoyl chloride with ethyl acetoacetate in the presence of metallic sodium or magnesium alkoxide, followed by the cleavage of acetyl group by customary methods of hydrolysis[4,6]. Another recent method due to Forrest and his collaborators[11] for the preparation of *p*-nitroacetophenone involves the use of ethyl sodioethoxaloacetate instead of ethyl sodioacetoacetate or ethyl sodiomalonate for condensation with *p*-nitrobenzoyl chloride.

In the present investigation it was found that in the preparation of *p*-nitroacetophenone by the condensation of *p*-nitrobenzoyl chloride with ethyl acetoacetate, the use of sodium, potassium or magnesium alkoxide, hitherto employed, can be easily dispensed with and instead good yields can be obtained by the use of anhydrous sodium hydroxide or potassium hydroxide in the presence of non-polar solvent, e.g. benzene, toluene, chlorobenzene, etc. The advantages of this method are obvious. The use of sodium or potassium alkoxide involves the handling of metallic sodium or potassium and their interaction with alcohol requires considerable skill and special care in handling. Even with magnesium, though more convenient to handle, close control is necessary due to the highly exothermic nature of its reaction with alcohol. Its use involves an additional stage in the manufacture, i.e. breaking the magnesium complex of the condensation product with mineral acid and extracting the reaction product with an organic solvent. Disposal of the large quantity of hydrogen gas evolved during the reaction is another problem resulting from the use of magnesium.

In the new procedure described in this paper sodium or potassium hydroxide is added to a mixture of ethyl acetoacetate (II) and an anhydrous non-polar solvent, e.g. benzene, chlorobenzene, toluene, etc., and stirred at room temperature (25°-30°C.) for *c*. 16 hr. To this mixture is then slowly added, with continuous stirring, a solution of *p*-nitrobenzoyl chloride (I) in a non-polar solvent, preferably the same solvent as used with the ester. The reaction can be carried out at room or elevated temperature

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*Patent pending.

(40°-50°C.). The reaction mixture is then filtered to remove inorganic material and the filtrate distilled under reduced pressure to obtain the crude ethyl α-*p*-nitrobenzoylacetoacetate (III). It is not necessary to use the customary reagents like ammonia and ammonium chloride or ethanolic ammonia for the conversion of ethyl α-*p*-nitrobenzoyl acetoacetate (III) into ethyl *p*-nitrobenzoyl acetate (IV). Only stirring of compound (III) with dilute aqueous sodium hydroxide at room temperature is enough. Ethyl *p*-nitrobenzoyl acetate yields *p*-nitroacetophenone (V) on hydrolysis and decarboxylation by the usual methods. The crude *p*-nitroacetophenone is purified by stirring for 15-20 min. with a hot solution of sodium bicarbonate in water followed by filtration and washing with water. The filtrate on acidification with mineral acids gives *p*-nitrobenzoic acid, the starting material for the manufacture of *p*-nitrobenzoyl chloride, which can be reused.

The yield of *p*-nitroacetophenone by this process ranges from 72 to 75 per cent on the basis of *p*-nitrobenzoyl chloride, which compares favourably with the yields obtained by Long and Troutman[2] using magnesium alkoxide as the condensing agent. Whereas excellent yields of (V) are obtained using sodium hydroxide as the condensing agent in the reaction of ethyl acetoacetate with *p*-nitrobenzoyl chloride, no appreciable yields could be obtained by using diethylmalonate in place of ethyl acetoacetate under similar experimental conditions.

In addition to *p*-nitroacetophenone, acetophenone and substituted acetophenones like *o*-nitroacetophenone, *m*-nitroacetophenone and *p*-methoxyacetophenone have also been prepared by condensing ethyl acetoacetate with the appropriate benzoyl chloride in the presence of sodium hydroxide.

Experimental procedure

p-Nitroacetophenone — Sodium hydroxide flakes (5·6 g.) were added to a mixture of ethyl acetoacetate (27·3 g.) and benzene (250 ml.) and the mixture stirred at room temperature (28°-30°C.) for 16 hr. To this mixture was added, slowly under stirring, a solution of *p*-nitrobenzoyl chloride (26 g.) in benzene (50 ml.), the reaction temperature being maintained at 45°-50°. After the addition was complete, the entire mixture was stirred at 45°-50° for a further period of 4 hr. and allowed to stand for 16 hr. at room temperature. It was then filtered to separate the inorganic material. The filtrate was distilled under reduced pressure on the boiling water bath till no more of the distillate could be collected, when an oily residue was obtained. An aliquot of this residue was purified by crystallization from petroleum ether (b.p. 40°-50°), yielding yellowish needles of ethyl α-*p*-nitrobenzoyl acetoacetate; m.p. 54°-55°; mixed melting point with an authentic sample of ethyl α-*p*-nitrobenzoyl acetoacetate prepared by the method of Bulow and Hailer[5] showed no depression. (Found: C, 56·1; H, 4·5; N, 4·8. $C_{13}H_{13}O_6N$ requires C, 55·9; H, 4·7; N, 5·0 per cent.)

The crude ethyl α-*p*-nitrobenzoyl acetoacetate was suspended in 10 per cent aqueous sodium hydroxide solution (250 ml.) and stirred at room temperature for about half an hour till all the solid went into solution. The alkaline solution was filtered to remove the small amount of suspended solid and acidified with dilute sulphuric acid to obtain an oil which solidified on cooling. The filtration residue was suspended in hot water and treated with calcium carbonate under stirring till effervescence subsided. The entire mixture was then cooled and extracted with ether. The ether extract, after drying over anhydrous sodium sulphate, was freed from the solvent to give pure ethyl *p*-nitrobenzoyl acetate; yield 25 g. (75 per cent); m.p. 74°-75°C.; mixed melting point with an authentic sample prepared by the method of Bulow and Hailer[5] showed no depression. (Found: C, 56·0; H, 4·7; N, 5·5. $C_{11}H_{11}O_5N$ requires C, 55·7; H, 4·6; N, 5·9 per cent.)

Ethyl *p*-nitrobenzoyl acetate (25 g.) was suspended in a mixture of sulphuric acid (sp. gr. 1·8; 37 ml.) and water (185 ml.); the entire mixture was refluxed for 4 hr. till the effervescence had subsided. The reaction mixture was then cooled and diluted with ice water. The solid collected by filtration was stirred for 15 min. with a hot solution (80°-90°) of sodium bicarbonate (10 g.) in water (80 ml.). The mixture was then cooled and the separated *p*-nitroacetophenone filtered and washed; yield 16·75 g. (96·5 percent). Crystallization from aqueous ethanol gave long yellow needles of *p*-nitroacetophenone; m.p. 80°; mixed melting point with an authentic sample obtained by the method of Long and Troutman[2] showed no depression. (Found: C, 58·3; H, 4·4; N, 8·5.

$C_8H_7O_3N$ requires C, 58·2; H, 4·3; N, 8·5 per cent.)

Preparation of p-nitroacetophenone without isolating the intermediate compounds — Condensation between *p*-nitrobenzoyl chloride (52 g.) and ethyl acetoacetate (54·64 g.) was carried out as described above using sodium hydroxide (11·3 g.) and benzene (500 ml.) as solvent. After the reaction was complete the inorganic matter which had separated during the reaction was removed by filtration and the filtrate concentrated under reduced pressure. The residue after cooling was stirred with 10 per cent aqueous sodium hydroxide (450 ml.) for 1 hr. till most of it had dissolved. The clear alkaline solution obtained after filtration was carefully acidified with dilute sulphuric acid to obtain an oil which solidified on cooling. The solid collected by filtration was suspended in a mixture of concentrated sulphuric acid (75 ml.) and water (375 ml.) and the entire mixture refluxed for 4 hr. till the effervescence had subsided. The mixture was cooled and diluted with ice water. The solid that separated was filtered, washed and stirred with a hot solution of sodium bicarbonate (*c.* 18 g.) in water (200 ml.). The mixture was then cooled and the separated *p*-nitroacetophenone filtered and washed; yield 33·5 g. (72 per cent); m.p. 78-80°. After crystallization from aqueous ethanol, yellow needles with m.p. 80° were obtained. The alkaline filtrate obtained after filtration of *p*-nitroacetophenone on acidification afforded *p*-nitrobenzoid acid (11·9 g.).

o-Nitroacetophenone — *o*-Nitrobenzoyl chloride (6 g.) was condensed with ethyl acetoacetate (7 g.) using sodium hydroxide (1·3 g.) as described previously to give ethyl α-*o*-nitrobenzoyl acetoacetate (6·57 g.) which on treatment with dilute aqueous sodium hydroxide yielded the deacetylated product ethyl *o*-nitrobenzoyl acetate (4·8 g.) identified by conversion into *o*-nitrobenzoyl acetic acid[7] (m.p. 117°) by treatment with dilute sulphuric acid. Ethyl *o*-nitrobenzoyl acetate on hydrolysis and decarboxylation with dilute sulphuric acid afforded *o*-nitroacetophenone (3·1 g.). (Found: N, 8·2. $C_8H_7O_3N$ requires N, 8·5 per cent.)

m-Nitroacetophenone — Condensation of *m*-nitrobenzoyl chloride (7·8 g.) and ethyl acetoacetate (8 g.) was effected in the presence of anhydrous sodium hydroxide (1·7 g.) as described above to afford ethyl α-*m*-nitrobenzoyl acetoacetate (8·2 g.); m.p. 73°-74°[5]. (Found: N, 5·0. $C_{13}H_{13}O_6N$ requires N, 5·0 per cent.) It was deacetylated by treatment with alkali to obtain ethyl *m*-nitrobenzoyl acetate (5·9 g.); m.p. 78°[5]. Ethyl *m*-nitrobenzoyl acetate on hydrolysis and decarboxylation afforded *m*-nitroacetophenone[12] (3·5 g.); m.p. 80°-81°. (Found: N, 8·5. $C_8H_7O_3N$ requires N, 8·5 per cent.)

p-Methoxy acetophenone — *p*-Methoxybenzoyl chloride (12·75 g.) and ethyl acetoacetate (15 g.) were condensed using a suspension of sodium hydroxide (3 g.) in benzene to give ethyl α-*p*-methoxybenzoyl acetoacetate (16·5 g.). The latter was deacetylated with dilute sodium hydroxide to give ethyl *p*-methoxybenzoyl acetate[13] [b.p. 185°-90°/10 mm.; copper complex $Cu(C_{12}H_{13}O_4)_2$, m.p. 180°]. Ethyl *p*-methoxybenzoyl acetate (11·96 g.) was hydrolysed and decarboxylated to afford *p*-methoxy acetophenone[14] (6·9 g.) (b.p. 152°-54°/20 mm.; $C_9H_{10}O_2.H_3PO_4$, m.p. 85°-86°).

Acetophenone — Benzoyl chloride (35 g.), ethyl acetoacetate (35·7 g.) and sodium hydroxide (10 g.) were allowed to react as described above to yield ethyl α-benzoyl acetoacetate[15] (yield 43·8 g.; b.p. 136°-40°/2 mm.; copper complex, m.p. 224°). The method of simple treatment with aqueous sodium hydroxide having failed in this instance, it was deacetylated by the customary method using ammonia; yield of ethyl benzoyl acetate[16], 28·8 g. [b.p. 132°-37°/4 mm.; copper complex $Cu(C_{11}H_{11}O_3)_2$, m.p. 180°]. Ethyl benzoyl acetate was further hydrolysed and decarboxylated with dilute sulphuric acid to give acetophenone[17] (yield 15·9 g.; b.p. 93°-94°/20 mm.).

Acknowledgement

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Behaviour of Alkaline Accumulators in the Temperature Range 0°-50°C.

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The capacities and coulombic efficiencies of ordinary 'pocket' or 'tube' types of nickel-iron and nickel-cadmium alkaline accumulators have been found to decrease with rise in the working temperature in the range 0°-50°C. The loss cannot be fully made up by subsequent lowering of the working temperature, although partial recovery can be achieved by working the accumulators for a few weeks at 0°C. The capacities and efficiencies of the accumulators are slightly higher when they are worked in continuous cycle than in interrupted cycles with a time interval of about 15 hr. between charge and discharge cycle. Changing the charge-discharge interval from 6 to 12 hr. does not materially affect the capacity of the accumulators in the temperature range investigated.

THE data available in literature on the behaviour, particularly the variation in capacity and coulombic efficiency, of Ni-Fe and Ni-Cd alkaline accumulators at different temperatures are few. From crystallographic and electrochemical studies of single nickel-oxide electrodes[1-3] it appeared that due to the instability of nickel oxides exceeding NiO 1·5 in active oxygen content, the capacities of these electrodes are liable to decrease as temperature increases. The capacities of alkaline accumulators as a whole have, however, been reported generally to increase with rise in temperature in the range 0°-45°C.[4,6]. It was, therefore, considered worth while to examine some ordinary commercial 'pocket' or 'tube' type alkaline accumulators with regard to their working efficiencies at different temperatures.

Experimental procedure

Two types of accumulators were used: (i) Ni-Fe cells of low rated capacities (600 ma. hr.), and (ii) Ni-Cd cells of comparatively higher rated capacities (10 amp. hr.). Charge-discharge cycles of these cells were carried out at different temperatures between 0° and 50°C. and the capacities and coulombic efficiencies measured for different extents of charging.

Fresh cells were used in each experiment. Potassium hydroxide solution of sp. gr. 1·2 was used as the electrolyte. A manually operated apparatus was used for charging and discharging the cells.

Charge-discharge curves were obtained for different temperatures between 0° and 50°C. After earlier working at 50°C. some of the cells were subsequently operated at 0° and 10°C. using refrigerator-thermostats, and

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their capacities and efficiencies on cycling were measured during a period of several weeks to examine the rate of their recovery. The results were compared with those of other accumulators worked under identical conditions, but which had not been exposed to a temperature higher than 18·5°C.

Some Ni-Fe cells were also operated at different fixed, charge-discharge rates (roughly corresponding to 6, 8 and 12 hr. rates) under identical conditions to find the effect, if any, of current density on the capacity and efficiency at various temperatures.

Discharges were made both in continuous cycle and with an interval of about 15 hr. between charge and discharge, to study the effect of standing on open-circuit and full charge. The cells were discharged to a cut-off voltage of 1·0 V. at all temperatures.

The capacity as determined is the charge given out by the cell up to the point when its potential difference on load falls to 1·0 V. The cells were again charged at constant current rate and discharged to 1·0 V. so that

$$\text{Coulombic efficiency (\%)} = \frac{\text{Discharge obtained}}{\text{Charge given}} \times 100$$

For the sake of convenience, the extent of charging and the capacity derived are expressed as percentage of the rated capacity as given by the manufacturers.

Results and discussion

The data for capacities and efficiencies of cells at different temperatures, current rates and extents of charging are given in Table 1.

Ni-Fe cells — When the cells are suddenly changed from one temperature or discharge rate to another, their capacity and efficiency are higher for the first few cycles. So, the first two cycles in all the above measurements were neglected. Both capacity and efficiency of the cells fall progressively as the temperature is increased from 0° to 50°C. (Table 1). There is, however, a slight gain in capacity as the temperature is lowered from 18·5° to 0°C. On keeping at high temperature (50°C.) the cells gradually deteriorate with time and lose capacity. But on keeping at low temperature (0°C.) their performance improves. This effect is more marked in the case of cells which have just previously been worked at high temperatures. The period for which the cells are cycled also affects their performance.

The loss in capacity at higher temperature cannot be fully made up on subsequent lowering of the temperature and even working at 0°C., although partial recovery is gradually achieved by working for a few weeks at 0°C.

The recovery of cells worked at 45°C. seems to be greater than when they are worked at 50°C. (Table 1). This may be partly due to chemical action between the electrolyte and the active electrode material above 46·5°C. as suggested by some manufacturers.

The effect of changing charge-discharge current rate from 6 to 12 amp. hr. on capacity is not very discernible, except in cases where the cells are recovering at 0°C. after having been operated at 45°-50°C.

Usually the capacity and efficiency are higher when the accumulators are discharged immediately after charge than when discharged after an interval of 15-18 hr. This is probably due to self-discharge of electrodes on standing. The initial rapid fall in potential is probably due to the decomposition of higher nickel oxides also observed by Foerrester[7]. This difference between the

TABLE 1 — CAPACITIES OF CELLS CHARGED TO RATED VALUE AND DISCHARGED IN CONTINUOUS CYCLES AT DIFFERENT TEMPERATURES

CHARGE AND DISCHARGE RATE	CAPACITY (% OF RATED VALUE) AT						
ma.	0°C.	10°C.	18·5°C.	35°C.	45°C.	50°C.	0°C.*
			Ni-Fe cell				
50	81	75	75	60	40·0	—	64·5
80	80	79	75	61	40·0	29	43·0
100	—	68	75	—	43·5	—	55·0
			Ni-Cd cell				
0·0015	85	—	94	72	—	47	65(25)†

*For cells first worked at 50°C. and subsequently tested at 0°C.

†If the electrolyte is not changed after working at 50°C., the capacity subsequently obtained at 0° is very low.

continuous and interrupted cycles was more pronounced in the range 18·5°-35·0°C. than at higher or lower temperatures.

The relation between charge and discharge under different conditions is shown in a typical input-output graph (Fig. 1). In the beginning the output increases almost linearly with input, but at one stage the slope of the line quickly changes after which the output remains almost constant. This point of inflexion gives the optimum capacity and conditions of operation for the accumulator and after this most of the charge given is simply wasted in electrolysing the electrolyte. However, this optimum does not in any way represent the maximum efficiency which can often be increased to almost 100 per cent at the cost of capacity. Fig. 1 also brings out clearly the influence of temperature on the input-output curve.

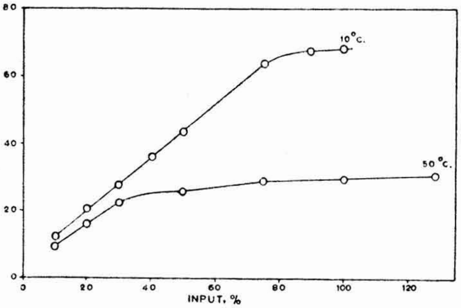

FIG. 1 — INPUT-OUTPUT CURVES FOR Ni-Fe CELLS AT DIFFERENT TEMPERATURES

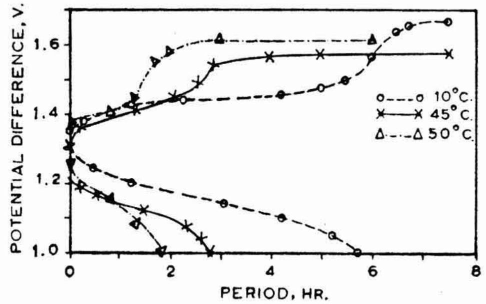

FIG. 2 — CHARGE-DISCHARGE CURVES FOR Ni-Fe CELLS WORKED AT DIFFERENT TEMPERATURES [Rated capacity, 0·6 amp. hr.; current strength, 80 ma.]

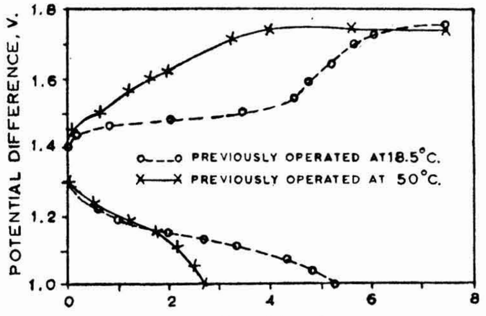

FIG. 3 — CHARGE-DISCHARGE CURVES FOR Ni-Fe CELLS WORKED AT 0°C.

Charge-discharge curves — The influence of temperature on the slope of time-potential charge-discharge curves is shown in Figs. 2-5. As the temperature is raised, the cell on charge usually starts gassing earlier and, therefore, the steep rise in the charge curve occurs at an early stage after which the

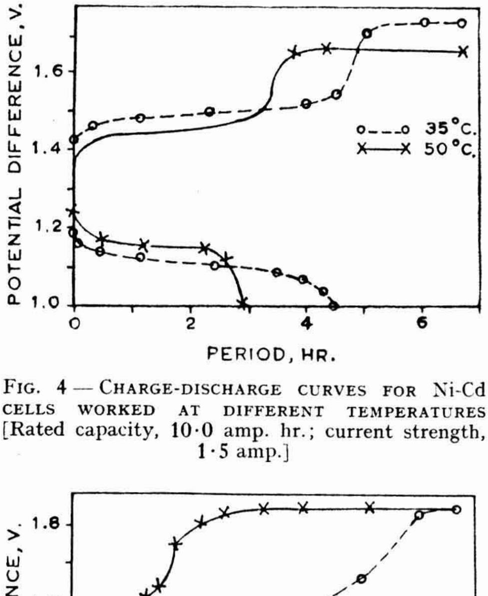

FIG. 4 — CHARGE-DISCHARGE CURVES FOR Ni-Cd CELLS WORKED AT DIFFERENT TEMPERATURES [Rated capacity, 10·0 amp. hr.; current strength, 1·5 amp.]

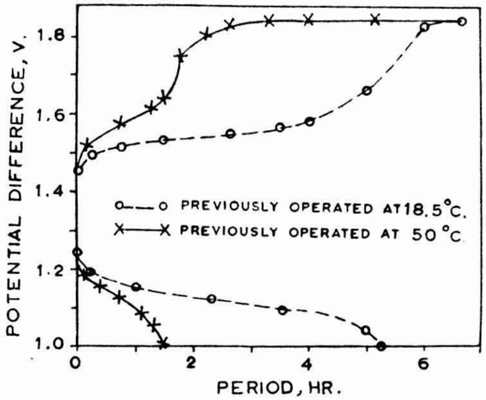

FIG. 5 — CHARGE-DISCHARGE CURVES FOR Ni-Cd CELLS WORKED AT 0°C.

voltage remains constant. After the start of rapid gassing little charge is utilized in charging the electrode and this partially explains the loss in capacity.

After earlier operation at high temperatures when the cells are again operated at 0°C., there is no steep rise in voltage. The potential continues to increase gradually for several hours before it becomes steady. In this sense the charging curves of ' recovering cells ' are distinctive.

Fresh cells start gassing at the later portion of their charge curve when they have a rise in potential.

As the operating temperature increases, the constant potential at which the charge curve becomes steady, decreases. This effect may partly be due to the fall in the over potential of oxygen evolution at the Ni electrodes with increasing temperature. It has already been observed that oxygen evolution starts earlier as the temperature is raised, i.e. at 50°C. within 30 min. and at 18·5°C. after about 3 hr. of the commencement of charge at 80 ma.

Ni-Cd cells — These cells also lose capacity and efficiency and gradually deteriorate when operated at 35° or 50°C. (Table 1).

There is a slight decrease in capacity and efficiency as the temperature falls from 18·5° to 0°C.

When the cells are operated at 0°C. after having been previously operated at 50°C. for about 8 weeks, at first further loss in capacity and efficiency occurs due to the presence of impurities and to the change in concentration and loss of electrolyte occurring while working at 50°C. On changing the electrolyte and allowing the cell to stand, it recovers as in the case of Ni-Fe cells.

As with Ni-Fe cells the average maximum steady potential attained in the charge curve decreases with increasing temperature, the potential at 0°, 35° and 50°C. being 1·84, 1·72 and 1·65 V. respectively.

The charge-discharge time-potential curves are similar to the corresponding curves of Ni-Fe cells (Figs. 4 and 5).

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Letters to the Editor

ELECTRO-DEPOSITION OF NICKEL ALLOYS FROM THE PYROPHOSPHATE BATH: NICKEL-ZINC & NICKEL-MOLYBDENUM ALLOYS

NICKEL-ZINC ALLOYS HAVE BEEN OBTAINED earlier from sulphate, chloride and sulphamate solutions[1]. The present note reports the results of studies on the electro-deposition of nickel-zinc and nickel-molybdenum alloys using pyrophosphate bath.

The solutions for nickel-zinc alloy deposition were prepared from nickel chloride, zinc pyrophosphate and potassium pyrophosphate. The concentrations and temperature were fixed on the basis of single metal deposition studies. Platinum electrodes were used in this study. The effects of varying current density and metal contents of the electrolyte on alloy deposit composition, cathode efficiency and cathode potential are shown in Table 1.

Adherent and dark to greyish white alloy deposits analysing 7-85 per cent nickel were obtained by varying the operating conditions. The nickel content in the deposit increased with increase in the nickel content of the

TABLE 1 — EFFECT OF CURRENT DENSITY AND COMPOSITION OF ELECTROLYTE ON Ni DEPOSITION

[*Temp.*, 60°*C.*; *bath voltage*, 2·0-4·6 *V.*; *p*H, 8·8-9·5; *ratio of pyrophosphate to metal* (*by wt.*), 7; *deposition was carried out with still electrodes*]

	CURRENT DENSITY (*amp./sq. dm.*)							
	0·25	0·50	1·00	2·00	4·00	6·00	10·00	15·00
Composition of plating bath: Ni, 0·05M; Zn, 0·5M								
Ni in deposit, %	76·00	10·00	9·00	8·00	7·00	7·00	—	—
Cathode efficiency, %	28·00	89·00	86·00	78·00	69·00	65·00	—	—
Cathode potential, −V.	0·79	1·13	1·20	1·24	1·32	1·38	—	—
Composition of plating bath: Ni, 0·2M; Zn, 0·5M								
Ni in deposit, %	83·00	75·00	51·00	16·00	16·00	15·00	16·00	—
Cathode efficiency, %	45·00	29·00	23·00	58·00	76·00	84·00	80·00	—
Cathode potential, −V.	0·75	0·83	0·94	1·21	1·28	1·37	1·44	—
Composition of plating bath: Ni, 0·3M; Zn, 0·5M								
Ni in deposit, %	85·00	78·00	73·00	21·00	18·00	18·00	—	—
Cathode efficiency, %	48·00	31·00	27·00	50·00	67·00	69·00	—	—
Cathode potential, −V.	0·74	0·80	0·83	1·21	1·28	1·35	—	—
Composition of plating bath: Ni, 0·3M; Zn, 0·3M								
Ni in deposit, %	84·00	—	74·00	52·00	42·00	21·00	21·00	21·00
Cathode efficiency, %	49·00	—	29·00	10·00	9·00	43·00	45·00	44·00
Cathode potential, −V.	0·74	—	0·84	0·90	1·04	1·33	1·35	1·54
Composition of plating bath: Ni, 0·3M; Zn, 0·2M								
Ni in deposit, %	85·00	—	75·00	53·00	44·00	40·00	25·00	24·00
Cathode efficiency, %	49·00	—	28·00	12·00	10·00	8·00	23·00	19·00
Cathode potential, −V.	0·74	—	0·84	0·92	0·99	1·07	1·43	1·42
Composition of plating bath: Ni, 0·3M; Zn, 0·1M								
Ni in deposit, %	85·00	—	79·00	69·00	51·00	44·00	30·00	—
Cathode efficiency, %	50·00	—	29·00	15·00	10·00	6·00	11·00	—
Cathode potential, −V.	0·74	—	0·85	0·94	1·03	1·09	1·31	—

TABLE 2 — CO-DEPOSITION OF NICKEL AND MOLYBDENUM

[*Electrolyte conc.*: *Ni*, 0·3*M* (*as chloride*); *Mo*, 0·1*M* (*as ammonium molybdate*); *pyrophosphate to nickel ratio*, 8; *p*H, 7·7; *bath voltage*, 3-5 *V.*; *other conditions same as in Table* 1]

	CURRENT DENSITY (*amp./sq. dm.*)							
	1	2	4	6	8	10	12	15
Ni in deposit, %	50·00	50·00	49·00	47·00	46·00	51·00	56·00	57·00
Cathode efficiency, %	2·00	2·00	7·00	11·00	13·00	18·00	22·00	19·00
Cathode potential, −V.	0·79	0·81	0·83	0·84	0·85	0·85	0·86	0·93

solution, temperature and agitation. Ammonium citrate (20 g./litre) considerably increased the nickel percentage, whereas gelatin (1 g./litre) decreased the same. The nickel content of the alloy decreased with increase in current density only up to a certain current density depending on the conditions; beyond this the composition remained practically constant. In the lower current density range there were sudden changes in plate composition and cathode potential, probably due to the deposition of alloys of different phases. The cathode efficiency was rather low.

The results of co-deposition of molybdenum with nickel from pyrophosphate solutions are shown in Table 2. The deposits were grey to dark grey in colour. Nickel was estimated using dimethylglyoxime and molybdenum by lead molybdate method.

Our thanks are due to Prof. K. R. Krishnaswami, Head of the Department, for his keen interest in the investigation.

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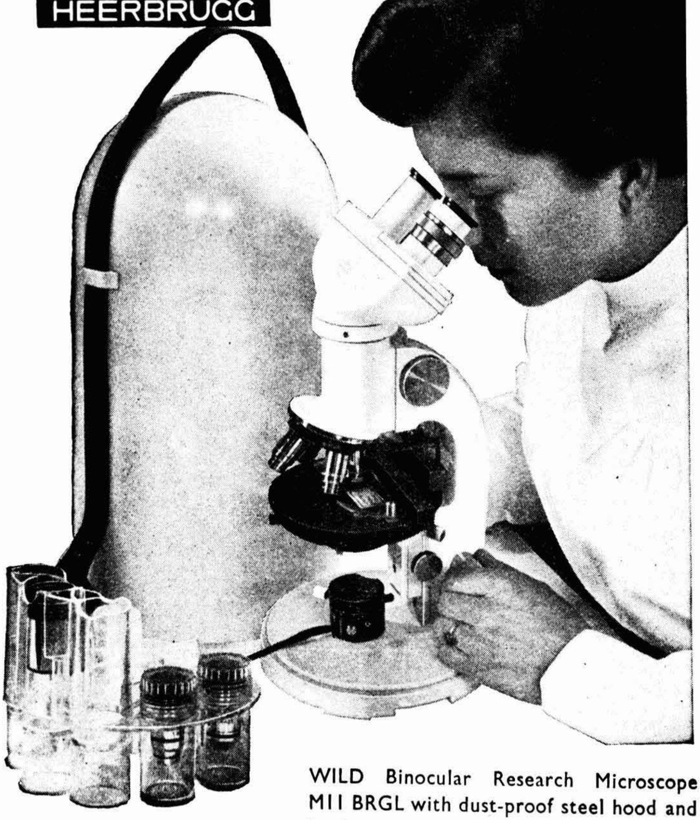
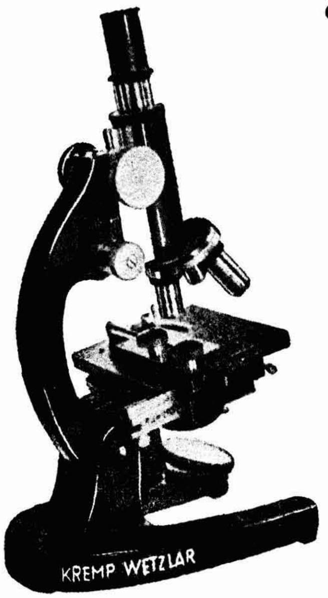


WILD Binocular Research Microscope M11 BRGL with dust-proof steel hood and leather carrying strap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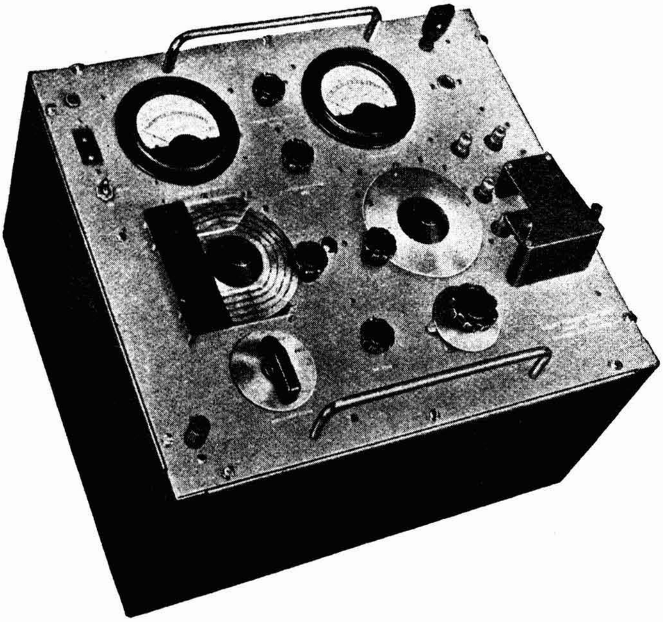

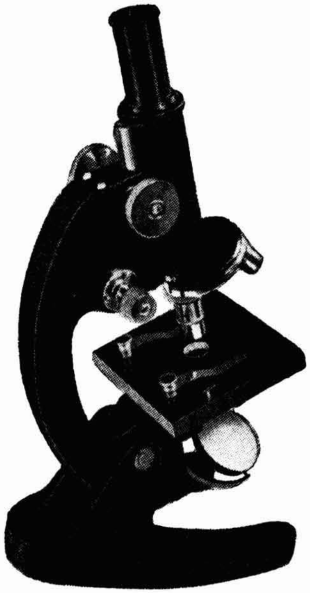

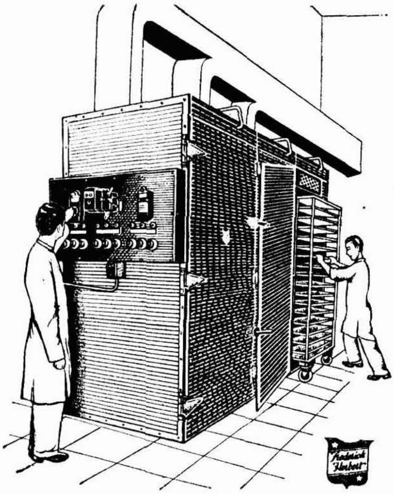
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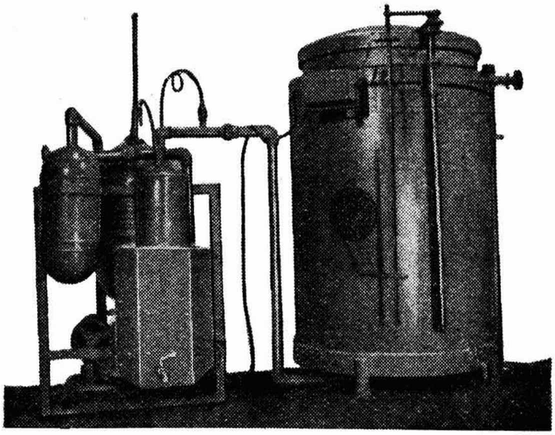

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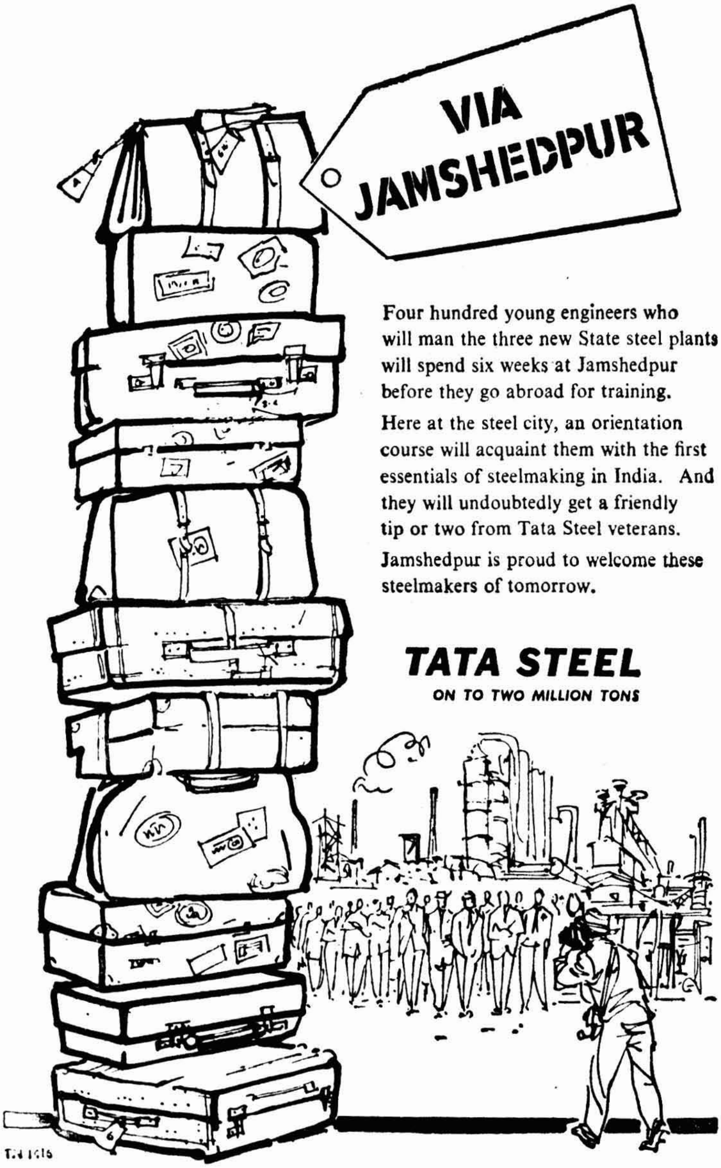
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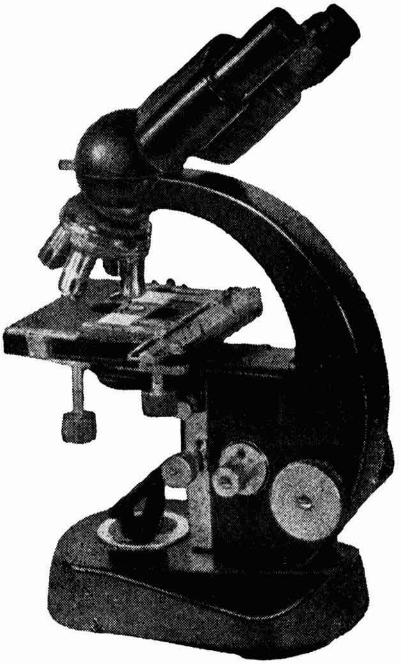

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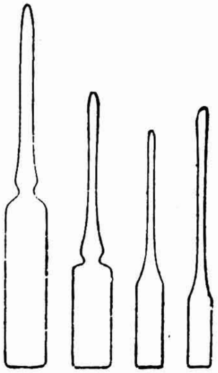

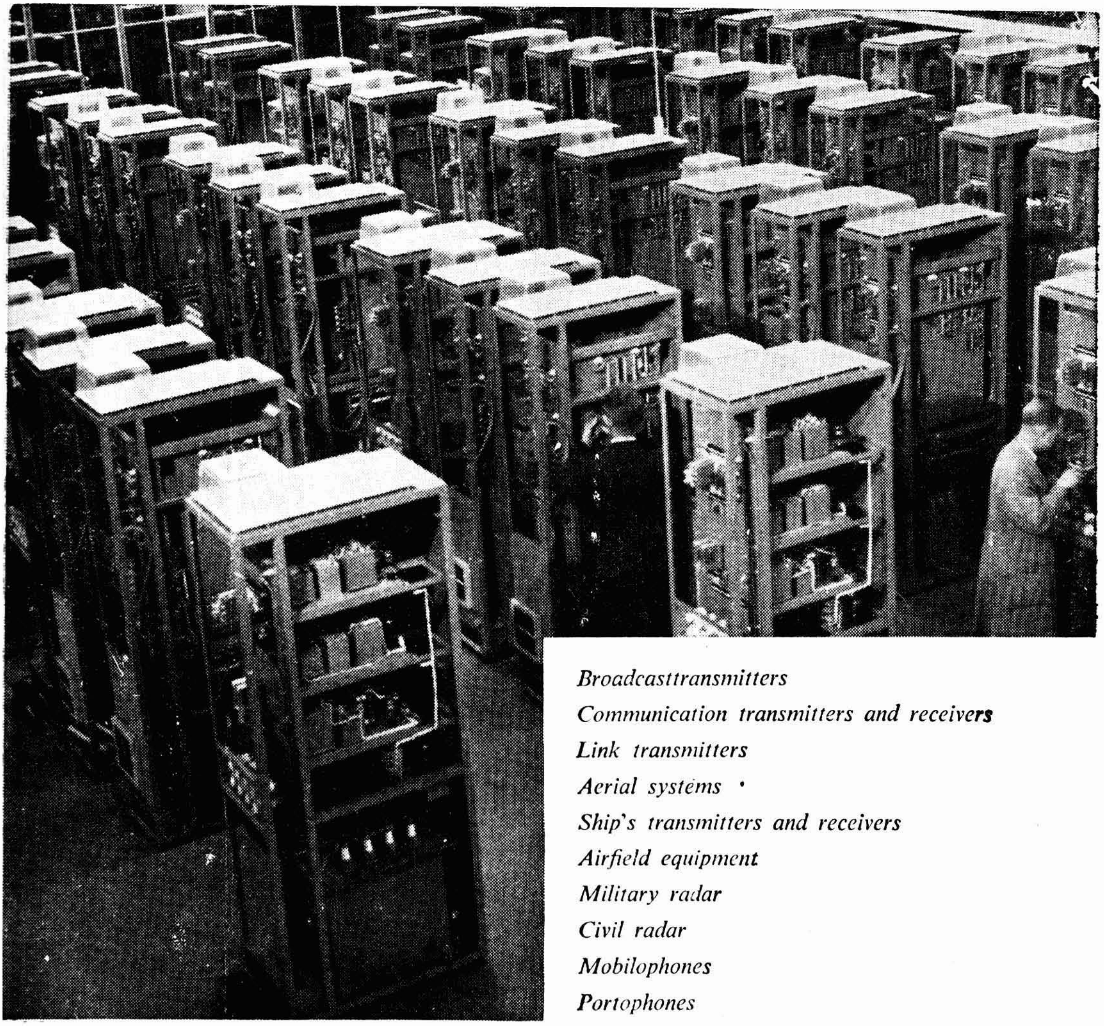

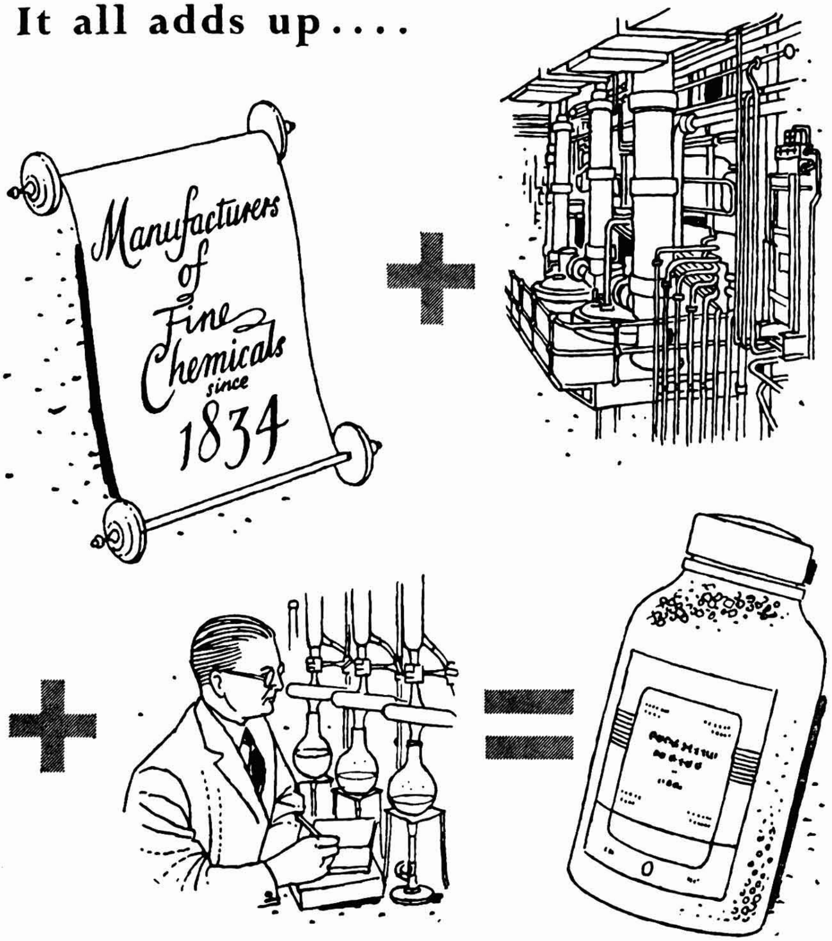

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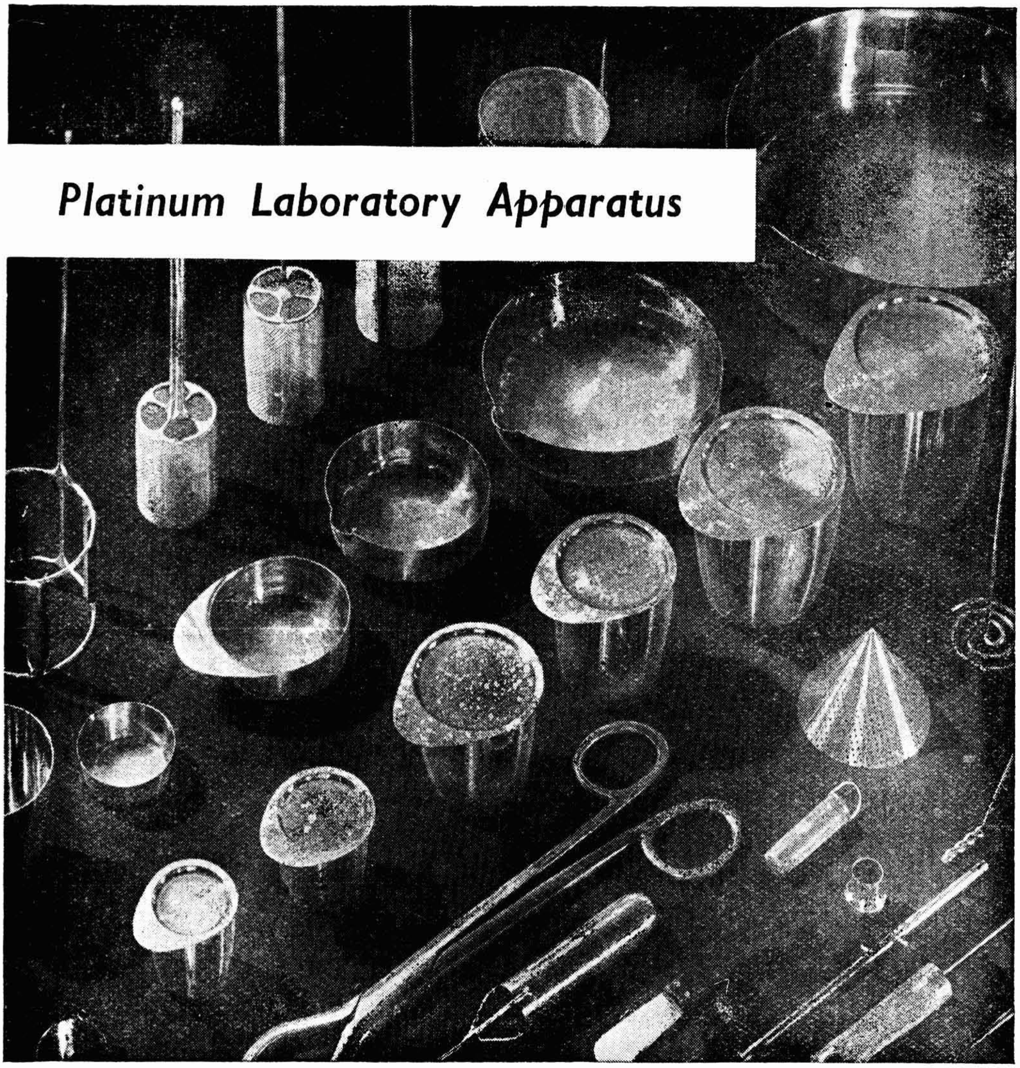

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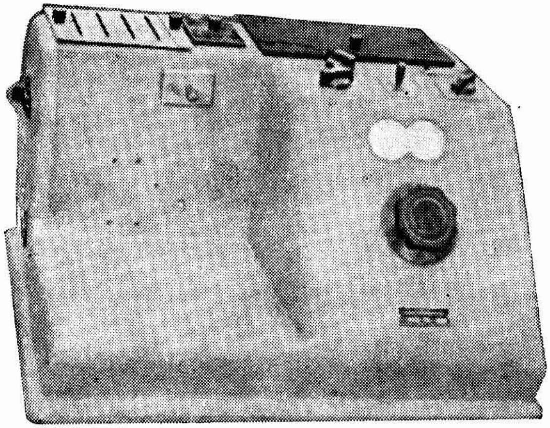

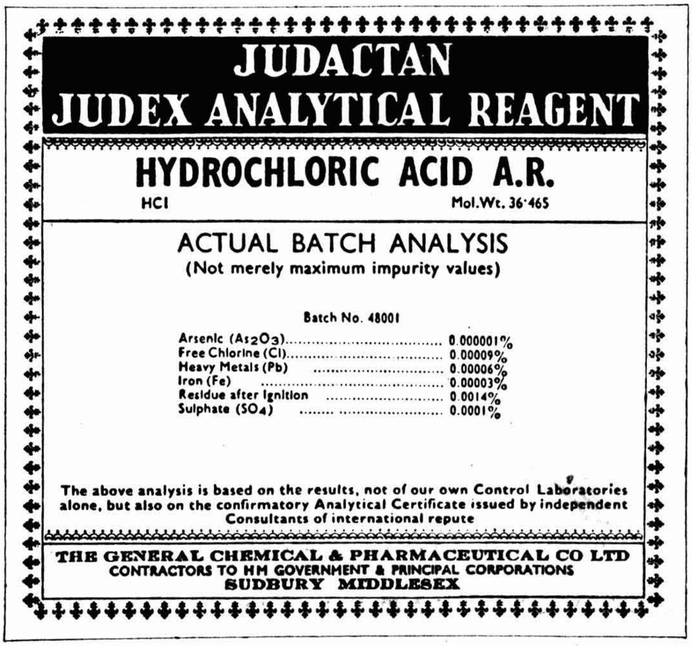

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