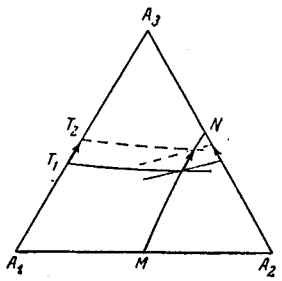
how the fold will move from its initial position with change in temperature. In most cases knowledge of data on the heats of evaporation of the pure components is in practice sufficient for this purpose.

Where a ternary azeotrope is present in a system, it belongs simultaneously to three equipartition curves. By determining the three regions of the composition triangle into which the three equipartition curves, the three folds, will be respectively displaced, we thereby determine that zone of the triangle (belonging to each of the regions) into which the composition of the ternary azeotrope will shift. Let us consider the simplest and clearest example, corresponding to the case in which the partial molar heats of evaporation of two components are equal. If the heats of vaporisation of the first and second components are similar, and this applies also to the heats of vaporisation of these components from ternary solutions whose compositions lie in the region of the fold, change in temperature will produce practically no change in the location of the given fold on the Gibbs triangle. This does not imply, of course, that a ternary azeotrope, if it exists, will not change its composition. It belongs also to two other folds, and with change in temperature will be displaced together with them. But, while changing its composition, it will not leave the first fold: it will move along the first fold, along the original position of the latter. This is illustrated by the accompanying diagram†. We have dealt with this case partly because quite different statements have appeared in the literature. Thus Świętosławski[6] concluded that in this case the concentration ratio of the first and second components in the ternary azeotrope $(x_1/x_2)_{az}$ would not vary with change in temperature: *i.e.* that the composition of the ternary azeotrope should then move along the secant towards or away from the corner representing the third component on the composition triangle. This contention, which at first sight seems very reasonable, is not correct. The ternary azeotrope would in this case move along the fold, roughly speaking, away from or towards the 1–2 binary azeotrope. The ratio $(x_1/x_2)_{az}$ will remain unchanged only in the limiting case examined earlier, when the direction of the fold coincides with that of the secant joining the composition of the 1–2 binary azeotrope with the corner representing the third component.



† In a system in which two components A_1 and A_2 have equal heats of vaporisation, the ternary azeotrope will be displaced, with change in temperature, along the fold starting at the A_1A_2 binary azeotrope: $L_3 > L_1 = L_2$.

The problems considered in the present communication are related thermodynamically to the problem of the change in composition of a binary azeotrope with variation in temperature. As can be readily sensed from the whole tenor of the paper, the question of the rules governing the location, on the concentration triangle, of projections of the fold in the pressure surface could be termed the problem of the change in composition of the binary solvent azeotrope produced by addition of the third component.

The writer expresses his gratitude to Professor A. V. Storonkin for the constant interest which he has shown in the work, which also owes much to the rigorous deduction of Vrevskii's laws due to Storonkin[7].

SUMMARY

1. The differential equations to the curve representing equal distributions of two components between coexisting phases in a solution–ideal vapour ternary system (the curve representing a constant relative fugacity of the two components of $\alpha_{ik} = 1$) have been used to examine the location of folds in the pressure surface on the composition diagram of the system and the displacement of these folds with change in temperature.
2. The laws governing the relative positions of ternary and binary azeotropes on the concentration triangle and the variation in composition of the ternary azeotrope with change in temperature have been elucidated on the same basis.

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THE PRESENT POSITION OF FUEL CELL DEVELOPMENT†

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Nowadays one of the more important problems of power engineering and transport is that of electrochemical combustion of fuel (the fuel cell problem). The efficiency of

† It is not an object of this paper to give a complete account of the work on fuel cells.

the steam and internal combustion engines can barely reach 40% and furthermore a considerable part of the energy is degraded to unusable dissipated energy. Thermodynamic calculations show that in the electrochemical combustion of fuel about 70 to 90% of the energy, depending on the type of fuel, may be converted into useful electrical energy.

The calculated values of the efficiencies and e.m.f.'s of fuel cells at various temperatures together with the current-generating reactions are given in the Table below.

The hydrogen–oxygen cell is of particular interest; in the temperature range 25°–227° its efficiency is ~ 83–90% and e.m.f. ~ 1.2–1.1 V, the optimum temperature being 200°–290°. It so happens that under these temperature conditions the electrochemical activities of the reacting gases (H_2 and O_2) may be greatly increased in the presence of some catalysts. The efficiency of the carbon monoxide–oxygen cell falls rapidly with rise in temperature, the most suitable conditions occurring in the range 25°–700° where the efficiency is 90–68%. The efficiency of the carbon–oxygen cell remains high (99.8–95%) at all the temperatures given in the Table.

It does not, of course, follow from the above that the best cell is the carbon–oxygen cell. The fact is that thermodynamic considerations do not decide whether it is possible to utilise these reactions in practice. The principal consideration is the reaction kinetics. At low temperatures the activity of carbon is low and therefore it cannot be used in electrochemical combustion. The basic difficulty in the development of fuel cells is that the usual fuels (solid, liquid, or gaseous) are electrochemically inactive or weakly active at low temperatures. At very high temperatures when the fuels become electrochemically active, the efficiencies of the fuel cells (with the exception of the carbon–oxygen cell) fall rapidly and the advantages of electrochemical combustion are lost. This explains why the efforts of investigators in many countries have been unsuccessful in this field up to the beginning of the Second World War. This gave rise to the view that the fuel cell problem cannot be solved in practice. However, the numerous unsuccessful experiments formed the basis of some new unexpected advances in the last decade. The new results are so encouraging that practical application of electrochemical power engineering is now seriously considered.

1. The author of this paper has worked on the electrochemical combustion of fuel since 1938. [1-5]

The early problems consisted of studies of the mechanism of current generation and development of a theoretical method for selection of the carrier-catalysts for processes at the negative and positive electrodes. Development work was devoted to the hydrogen–oxygen and carbon monoxide–oxygen cells.

As a result of theoretical and experimental work on the hydrogen–oxygen cell, a basis has been established for the theory of chemical polarisation of this cell (see Davtyan[1], pp. 38–82).

Using the theory of chemical polarisation, it has been shown that polarisation of hydrogen and oxygen on various catalysts is correlated with the hydrogen and oxygen overvoltage of these substances; the higher the overvoltage, the greater is the polarisation of the electrode and *vice versa*. This theoretical conclusion was fully confirmed in experimental studies of chemical polarisation on various carrier-catalysts for positive and negative electrodes. Thus a method has been found for selecting catalysts for the hydrogen and oxygen electrodes.

Further investigations showed that suitable catalysts for the hydrogen electrode are in principle all the hydrogenation catalysts (see Davtyan[1], p. 66). Attempts were made to employ the well-known foraminate hydrogenation catalysts (Raney nickel) with electrochemical activation. Unfortunately this work has not been completed. Later a study was made, under the supervision of the author, on the technology of preparation of diffusion electrodes with a foraminate catalyst[6].

Using the theoretical and experimental data a series of catalysts have been found which are now employed in hydrogen–oxygen cells. These include nickel, cobalt, silver, etc. for the hydrogen electrode and active carbon, nickel, silver, etc. for the oxygen electrode.

On the basis of experience with these catalysts a hydrogen–oxygen cell working at room temperature was developed. This cell operated at normal pressure of hydrogen and oxygen at a current density of 20–35 mA cm^{-2} and its efficiency was 60–70%.

It was found later (1944–1946) that by raising the temperature to 90° and static pressure to 2–3 kg cm^{-2} the electrical properties of the cell were very considerably improved; the current density at 0.7 V increased 4–5 times. Cells of this type, working at 2–3 atm and at 80°–90°, have been employed in studies of concentration of the heavy isotope of hydrogen. In the course of this work many improvements were made in the design of the cell and the electrodes.

In order to attain a definite pressure drop between the gases and the electrolyte, the surfaces of the electrodes on the side of the electrolyte were coated with a thin film of paraffin. This pressure difference prevented penetration of electrolyte into the large pores of the active layer of the electrodes and into the gas spaces. However, the protective paraffin film did not last long in an alkaline solution and was particularly unsuitable for cells heated to 80°–100°. For this reason, two types of cell were constructed: one with the single-layer paraffin film electrodes and another with electrodes having protective layers consisting of a copper or nickel coating deposited electrolytically.

Active three-phase contact may be achieved by rendering the system hydrophobic with a definite gradient of wetting by the electrolyte. In our investigations[1] paraffin and wax were employed as hydrophobic substances for the hydrogen and oxygen electrodes, but in this case the electrodes were impregnated with these substances from the

TABLE. Efficiencies and e.m.f.'s of some ideally working fuel cells, and some current-generating reactions.

Temp., °C	$2H_2+O_2\rightarrow 2H_2O$		$2CO+O_2\rightarrow 2CO_2$		$C+O_2=CO_2$		Temp., °C	$2H_2+O_2\rightarrow 2H_2O$		$2CO+O_2\rightarrow 2CO_2$		$C+O_2=CO_2$	
	eff., %	e.m.f., V	eff., %	e.m.f., V	eff., %	e.m.f., V		eff., %	e.m.f., V	eff., %	e.m.f., V	eff., %	e.m.f., V
25	82.8	1.227	90.5	1.336	99.8	1.02	1227	67.6	0.840	52.1	0.764	98.5	1.01
227	89.6	1.13	83.8	1.24	99.5	1.02	1727	52.8	0.656	36.9	0.533	97.8	1.00
727	77.2	0.991	67.7	0.999	99.0	1.01	2727	33.3	0.386	5.31	0.077	95.0	0.989

side of the gas. It has been found that paraffin and wax impaired the adsorption properties of the electrodes. Moreover, for the reasons given above, the working time of the electrodes was short.

Thus, apart from the catalytic activation of the current-generating processes, studies of the design principles of the cells are of considerable importance. In this respect the above method of achieving the contact of the gas with the catalyst and electrolyte is extremely important. The design of the cell proposed by the author forms in fact the basis for modern gas cells.

Very interesting results have been obtained in the course of development of the carbon monoxide–oxygen cell and the producer gas–oxygen cell. The latter is extremely attractive because it uses a common fuel.

This new approach is possible by application of a solid electrolyte. Numerous investigations have shown that sodium carbonate, either pure or especially with some admixtures, has a high ionic conductivity in the solid state at 500° and above. At 500°–700° it is no longer necessary to use any particularly active catalysts in the gas cells. The cell design is in fact very similar to that of the hydrogen–oxygen cell except that a solid electrolyte is used. A gas cell with a solid electrolyte constructed by the author had very good electrical characteristics. The cell was not subject to chemical polarisation. The drop of potential with an increase in load was due only to the internal resistance. The efficiency of the cell was ~60–70%.

The new trend in the utilisation of fuel cells was to study the possibility of application of the hydrogen–oxygen cell for production of heavy hydrogen with a low power consumption. It has been shown that this is possible because hydrogen isotopes separate during the working of the cell as in the electrolysis of water (this had been first shown by the author). Moreover, by operating the hydrogen–oxygen cells with the hydrogen evolved in the electrolytic heavy water production, a considerable proportion of the electrical energy expended may be regenerated. The hydrogen–oxygen cells of the types described above have been employed, operating at 80°–90° and 2–3 kg cm^{-2} pressure.

In the work mentioned above it was necessary to use a theory of the cascade separation of isotopes so that a high degree of enrichment with heavy hydrogen could be obtained. Such a theory applicable to any method of isotope separation has been developed by the author[7].

It has been shown theoretically and experimentally[8-11] that the potential of a gas electrode results in general not from all the chemisorbed gas but from the electrochemically active portion. It follows from this that the electrode (catalyst) surface is heterogeneous. There are some centres which adsorb gas molecules and make them electrochemically active whilst others make them chemically active[12,13]. An electrode immersed in an electrolyte can supply ions to the solution only from these active centres. Our experiments and calculations have shown that the active centres usually cover only a small part of the total surface[9,10]. It has also been shown that an exchange reaction takes place between the active and non-active molecules (*i.e.* between the molecules adsorbed on the active and non-active centres) and after some time a dynamic equilibrium is attained. This process is accomplished by migration in which a definite potential barrier has to be overcome.

The electrochemical potential of a gas electrode depends greatly on the nature of the carrier (catalyst). When the chemisorbed layers are immobile on the carrier surface and there is no contact with the gaseous phase, the potential will depend on the number of active centres and their mean energy level. But if these limitations do not apply, then, depending on the nature of the carrier, the potential is determined mainly by the free energy of chemisorption of the given gas. In general the number of active centres and their activity level (determined by the activation energy of chemisorption and desorption) determine the kinetics of the current-generating processes.

Some results have also been obtained relating to the theory of chemical polarisation of electrodes and the mechanism of the current-generating processes. It has been established that the rate of the current-generating processes in the hydrogen–oxygen cell is determined by the following factors: (1) the rate of chemisorption of hydrogen and oxygen on the electrode surfaces; (2) the rate of migration of chemisorbed species to the boundaries of the three phases (electrolyte–gas–catalyst); (3) the number of the electrochemically active centres per unit surface area of the catalyst; (4) the total lengths of the boundaries between the three phases per unit area of the apparent electrode surface; and (5) the rate of ionisation of hydrogen and oxygen (with simultaneous transfer of positive hydrogen ions and negative oxygen ions to the electrolyte; in the case of oxygen hydroxide ions form in the electrolyte).

Contact between the three phases may be achieved in two ways: by producing a wetting gradient in the electrode by a liquid electrolyte and by producing a pressure drop between the reacting gas and the electrolyte. In practice the wetting gradient may be produced artificially by introducing into the electrode some hydrophobic substance which does not have a detrimental effect on the extent and rate of chemisorption of the gas. The distribution of hydrophobic substance through the electrode should be such that its concentration is highest in the part of the electrode adjacent to the gas. Organosilicon polymers and other substances may be used as hydrophobic agents.

Transfer of the reacting gas to the active boundary of the three phases is accomplished chiefly by migration from the unoccupied parts of the active part of the electrode surface accessible to gas chemisorption. Ionisation of chemisorbed species proceeds in the boundary region between the three phases and gradually decreases on moving away from this region. Thus the active region consists of a band in the flooded portion of the active electrode surface. The author's investigations have shown that the distribution curve of the active surface plotted against the radii of capillaries passes through a maximum. It has been found that in all cases the optimum conditions for the electrode activity corresponded to the maximum of the distribution curve of the active surface.

An important step in the development of the hydrogen–oxygen cell is to obtain mechanically strong and at the same time active hydrogen and oxygen electrodes. A suitable catalyst for the oxygen electrode in an alkaline solution is nickel monoxide with a small quantity of lithium oxide (in the form of solid solution)[15,17].

The oxides NiO, CoO, CuO, and MnO are *p*-type semiconductors. Chemisorbed oxygen atoms remove electrons from bivalent ions (Ni^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}) as a result of which holes (Ni^{3+}, Co^{3+}, Cu^{3+}, Mn^{3+}) are formed. There is a definite relation between the activation energy for the

hole migration (electrical conductivity) and the activation energy for the hole formation (chemisorption of oxygen). The activation energies for electrical conductivity and oxygen chemisorption are of similar origin. In these processes energy is required to overcome elastic forces in the lattice in the migration of holes (electrical conductivity) and in charge exchange (chemisorption). Thus all the factors which cause a reduction of the elastic forces in the crystal lattices of the above oxides should also cause a reduction in the activation energies for electrical conductivity and chemisorption. One of these factors is the presence of lithium in the crystal lattice of these oxides. This may partly be attributed to the fact that lithium ions have a high compressibility and therefore weaken elastic forces in the lattice.

The author's investigations have shown that the rate of the current-generating process on the oxygen electrodes with NiO, CuO, and oxides of Cu–Ni alloys used as carriers increases considerably when small quantities of Li_2O are introduced into their crystal lattices. The increase in the electrical conductivity, rate of chemisorption, and electrochemical activity of these oxides on incorporation of small quantities of lithium may be explained by the fact that oxygen ions are considerably less strongly bonded with univalent lithium ions and tervalent ions of the main metal (*i.e.* with Ni^{3+} or Cu^{3+} formed on the introduction of lithium) than with the bivalent ions of these metals (Ni^{2+}, Cu^{2+}, etc.) comprising the principal lattice points. For this reason, the oxygen ions associated with Li^+ and the holes have a high mobility. They migrate freely, pass into the electrolyte, and possess a high oxidising power. These investigations show that it is possible to make oxygen electrodes with controlled electrochemical activities and also to predict which systems are suitable to use as carriers for the oxygen electrodes. It may also be concluded from the above considerations that incorporation of lithium into the crystal lattices of transition metals should increase their electrochemical activity when they are used as carriers of the hydrogen electrode.

2. In recent years numerous research establishments and private firms abroad have concentrated on two lines of investigation: development of oxygen–hydrogen cells and batteries working in the range from room temperature to 300° and development of fuel cells with gaseous or liquid fuels including carbon monoxide, methane, propane, etc., working at temperatures above 300°.

In the field of hydrogen–oxygen cells the work of Bacon and his collaborators[14,15,17] deserves particular attention. The Bacon cell is essentially similar to our hydrogen–oxygen cell with a nickel catalyst and an electrolyte consisting of potassium hydroxide solution. However Bacon introduced some very important improvements, mainly in the electrode design. The electrode frameworks (electrode carriers) in the Bacon cell are made of porous nickel. The electrodes consist of two layers, one of which has a finely porous structure and serves as a protective layer. The electrodes are prepared by sintering and are capable of working at temperatures up to 250°–300° and pressures of 30–50 kg cm^{-2}. Another important feature of the cell is the circulation of the electrolyte. The Bacon cell operating at 200° and a pressure of 42 kg cm^{-2} gives a potential of 0.776 V and a current density of ~300 mA cm^{-2}.

Application of an ion-exchange membrane as an electrolyte in hydrogen–oxygen cells has been recently reported[18]. These cells operate at normal temperature and pressure. Although the current densities in these cells are small (3–4 mA cm^{-2}), they are more compact than the cells with a liquid electrolyte.

The work of Justi and his collaborators[19,20] on the hydrogen–oxygen cell operating at low temperatures (below 100°) also deserves consideration. Details of their investigations, reported in several papers[19–22], are discussed below.

The main aspects of Justi's work[20] are: (a) development of the so-called "DSK electrode"; (b) suggestion of the "principle" of making electrode carriers with homogeneous pore structure and equilibrium capillary pressures; and (c) theoretical interpretation of the mechanism of the current-generating process and chemical polarisation of electrodes. These aspects are discussed below.

(a) The so-called "DSK electrode" (double-porosity foraminate catalytic electrode) consists of a porous nickel plate, the pores containing an active catalytic substance in the form of finely dispersed nickel. Thus the "DSK electrode" is an ordinary diffusion electrode with a nickel catalyst of the type similar to those developed by the author[1] and Bacon[14,15,17], prepared (like Bacon's electrode) by the sintering method. Thus Justi's work was concerned with various methods of preparation of the diffusion electrode and its activation and not with a development of new types of electrode. Justi employed the well-known foraminate hydrogenation catalyst — Raney nickel — as a catalyst of the hydrogen electrode. Justi's contribution consists of improvements in the technology of production of laboratory diffusion electrodes with foraminate catalysts and detailed studies of these electrodes.

(b) Justi and his collaborators postulated that one of the basic principles of development of diffusion electrodes is homogeneity in the porosity of the electrode (electrode with "equilibrium" pores). This means that the pore sizes should be as uniform as possible. Furthermore the pore radius should be such as to satisfy the condition of equilibrium of capillary pressure. It can be easily shown that Justi's "principle" is quite incorrect. In fact in an ideal case, when all the pores have the same radius, it is not possible in practice to obtain conditions under which some of the pores are filled with the electrolyte and some with the gas. An infinitesimal change in the equilibrium pressure leads either to filling of the pores with the electrolyte or to its complete removal. Clearly, under these circumstances there are no active boundaries between the three phases (electrolyte–catalyst–gas) required for development of a current-generating process and consequently such an electrode cannot work. This applies not only to the single-layer electrodes but also to the two-layer electrodes (electrodes with a non-active protective layer).

(c) A substantial part of the monograph by Justi *et al.*[20] is devoted to the mechanism of the current-generating processes and chemical polarisation of the electrodes. Their theoretical treatment will not be discussed in detail and only its principal features will be examined. They assume that the rate of the current-generating processes and consequently the current density provided by the cell is determined by the following factors: (1) adsorption of molecular hydrogen on the dry part of the electrode surface; (2) dissociation of hydrogen molecules ($H_2 \rightarrow 2H$) on catalytically active centres; (3) chemisorption of hydrogen with formation of an M–H compound; (4) diffusion of hydrogen atoms to the boundary of the three phases; (5) passage of ions through the Helmholtz double layer in the electrolyte with liberation of electrons on the metal. Similar

processes proceed also on the oxygen electrode, the only difference being that in this case hydrogen peroxide and hydroxide ions are formed (Justi *et al.* [20], p. 553). The above description of the current-generating processes is incorrect. Thus according to their theory after adsorption hydrogen molecules dissociate on the catalytically active centres and then (in the third stage) hydrogen is chemisorbed with the formation of an M–H compound. This representation is wrong from the point of view of the theory of chemisorption. The dissociation process cannot proceed independently of chemisorption. Furthermore according to this theory the fourth stage is the diffusion of H atoms (?!) to the boundary of the three phases. Regarding the "diffusion" of atoms on the surface, in the author's opinion this may be not diffusion but migration of atoms, which involves overcoming a definite potential barrier.

Regarding Justi's suggestion that the diffusion electrode may be applied to the hydrogenation of organic substances, it should be mentioned that this method was first developed and applied by the author before 1954. [23] Finally some historical aspects of Justi's monograph should be briefly considered. The authors have stated on p. 751 of their monograph [20]: "When they (*i.e.* the authors of the monograph) started their investigations in 1948 the best known H_2 electrode was the Schmidt electrode consisting of a platinised carbon tube with random distribution of pore sizes". This refers to the hydrogen electrode of the Schmidt hydrogen–chlorine cell. It should be pointed out that application of platinum as a catalyst for the hydrogen electrode in an acid solution was first suggested by Mond and Langer as early as 1886. Cells with a platinum catalyst and their disadvantages have been discussed in a monograph [1] by the present author. The lack of objectivity in Justi's monograph is quite apparent to anybody acquainted with fuel cells. One gets an impression that Justi *et al.* are completely unaware of the author's work published in 1946–1947 although they have quoted many references in which the author's work is rightly regarded as a basis of the subsequent fuel cell development.

As already mentioned the second important stage in the fuel cell progress was the development of cells with solid electrolytes, the principal component of which is sodium carbonate. Several organisations obtained promising results in this field. Many of the investigators abroad admit that their cells are essentially modifications of the author's producer gas–oxygen cell [1]. The cell developed at the Sondes Place Research Institute (England) is claimed to operate between 500° and 700°. In this cell the solid electrolyte consists of a mixture of sodium and lithium carbonates held in the pores of a thin membrane made of magnesium oxide, while the electrodes are prepared from a mixture of zinc oxide and metallic silver. Batteries of these cells work at atmospheric pressure using producer gas, water gas, propane, butane, or even petrol and kerosene, with air instead of oxygen. Their efficiency is 60–70% at a current density of ~ 80 mA cm^{-2}.

CONCLUSION

The principal advantage of electrochemical power generation over heat engine processes is the high efficiency of fuel cells. This not only follows from thermodynamic considerations but has also been established in practice with the existing equipment.

In practice fuel cells have also other advantages. Their construction is very simple, they have no moving parts, work without noise, and do not produce noxious effluent gases. Fuel cells are ideal for traction purposes, especially for automobiles, since, in addition to the advantages listed above, they are not damaged by short-circuiting which is very important from the point of view of starting conditions. Moreover, fuel batteries will not consume fuel during periodic stoppages, unlike heat engines, which continue burning fuel while working at a low number of revolutions. It is probable that fuel batteries will first be applied to road and rail transport. There are also good prospects of their application as power sources for tractors.

Fuel cells may eventually replace accumulators. They may be used in the electrochemical industry as direct current sources in galvanoplastics, refining of some metals, etc. Hydrogen–oxygen batteries may be used in the production of heavy hydrogen.

In the author's opinion cells with gaseous or liquid fuels have the best prospects. This is because coal is one of the most valuable raw materials for chemical industry. The author believes that it will not be long before direct utilisation of coal as a fuel is prohibited.

Gaseous fuels will in future be obtained as by-products of the coking-chemical and petrochemical industry and from natural gas. It is possible that hydrogen will be obtained in the decomposition of water by direct utilisation of solar energy (photolysis of water) or by other processes (photoelectric cells). Utilisation of solar energy for production of hydrogen as a possible method of storing solar energy would be very desirable. Hydrogen may also be obtained by electrolysis of water using cheap energy from hydroelectric and atomic power stations and also the energy of winds. Thus electrochemical energy may be regarded as a possible basis of future transport; eventually it may be expected to be associated with atomic power production and also with the solar and wind energy.

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TRANSITION OF THE BURNING OF EXPLOSIVES INTO AN EXPLOSION. II. STABILITY OF THE NORMAL BURNING OF POWDERED EXPLOSIVES

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The concept of burning in parallel layers, which for brevity we shall call normal burning, was introduced long ago. One of the principal differences between smokeless powder and ordinary gunpowder, which led to the replacement of the latter by the former, is the greater stability of the normal burning of smokeless powder. However, differences in this respect between various explosives are as a rule only quantitative. Not only ordinary gunpowder but even pyroxylin in its usual form is capable of normal burning under certain conditions, in particular pressure. The stability of the burning of various explosives can be characterised by the pressure above which normal burning breaks down.

Another factor is the permeability to gases of the powdered explosive, which is determined by the particle size of the powder and its relative density. The stability of normal burning can also be characterised by the density at which it breaks down, other conditions remaining the same. Experiments have shown that at a constant external pressure normal burning breaks down at a lower pressure with a charge of low density than with very compact powders.

Similar experiments can also be carried out at increasing pressure, which by facilitating the penetration of the gaseous products of burning into the bulk of the charge favours the breakdown of normal burning. An indication of the stability in this case too may be the relative density (in other words the resistance to the penetration of gases) below which normal burning breaks down. This method has been used here to study TNT, picric acid, Hexogen, pentaerythritol tetranitrate (PETN), and mercury fulminate.

EXPERIMENTAL

The burning of powdered explosives under increasing pressure was investigated in a manometric bomb (internal volume 50 cm^3), the change in pressure of the gases formed being recorded tensometrically. The design of the tensometric pressure transducer (with an intrinsic vibration frequency of 18–20 kc/s) was such that in combination with the tensometric receiver UTS-12k and a No. 1 oscillator of an MPO-2 oscilloscope it made it possible to record fairly accurately pressure changes with peaking time not less than 1 msec. The explosive charge was prepared as follows. The explosive weighed to within 0.01 g was placed in a transparent plastic beaker (diameter 10 mm, height 30 mm, thickness of walls and bottom 2 mm) and compressed to the required density by means of a hydraulic press. The powder was compressed in several portions, whose weight was chosen so that the thickness of the charge corresponding to each portion should not be greater than its diameter. The height and diameter of the charge were measured to within 0.1 mm and its density was calculated. In most experiments 1 or 2 g charges were used, which corresponded to densities of 0.02 and 0.04 g cm^{-3}. Specimens of definite particle size were obtained by screening. When the particle diameter was less than 50 μ, its mean value was calculated from the specific surface area of the particles determined on a PSKh-2 apparatus. DRP-3 black powder (0.5 or 1.0 g) ground in a mortar was used for ignition. A weighed amount of the black powder was placed in a cigarette paper bag through which a Constantan wire (diameter 0.15 mm, length 8–10 cm) was threaded, its ends being connected to the firing terminals of the manometric bomb.

After the rapid pressure rise due to the burning of the igniter, the $p-\tau$ curves (Figs. 1–7) usually show a section of slow increase in pressure† whose duration varies within wide limits depending on the density, particle size, and the size of the charge. When the burning began to accelerate, the rate of pressure rise increased sharply. The intensity of the acceleration of the burning up to detonation was also estimated from the nature of the fragmentation of the beaker containing the compressed charge. Above it was shown that the characteristic of the stability of the burning of an explosive, the relative density δ_{rel}, reflects

† In some cases after the igniter had finished burning, the pressure fell due to the cooling of the gases which was not compensated by gas evolution from the explosive.