

# SOME PROMINENT SCIENTIFIC ACHIEVEMENTS OF THE DEPARTMENTS OF THE FACULTY OF CHEMICAL ENGINEERING, POLYTECHNICAL UNIVERSITY, BUDAPEST\*

## Department of General Chemistry

In this Department, the number of reductometric determinations was augmented by ascorbinometry, a new volumetric method. The methods recently evolved in the Department, particularly the direct reductometric titration of metal ions, facilitate and accelerate, the performance of a number of tasks in industrial laboratories, such as determination of iron by ascorbinometry, determination of chlorate content in hypochlorite liquors and brines etc. The reaction taking place between hexacyanoferrate(III) and ascorbic acid can be utilized for the determination of various strong oxidizing agents.

In the course of investigations carried out in the field of volumetric analysis, the problem of a suitable redox-indication emerged. The application of reductometric methods and their widespread use in practice was greatly hindered just by the lack of an appropriate indicator. However, variamine-blue, the indicator recently introduced by the Department proved to be suitable not only for the indication of the end point in ascorbinometric titrations but also in iodometric, argentometric and chelatometric titrations, and even as colorimetric reagent. E.g. the argentometric determination of chloride content in waters can be carried out by end point indication with variamineblue in a markedly more accurate and more rapid way than with methods used earlier; while the argentometric determination of ammonia and nitrate through kalignost eliminates the distillation of ammonia, and thus appreciably shortens the time needed for analysis. The mechanism of oxidation of this indicator was studied in detail and elucidated in the Department. Further, the effect of substitution on redox potential and on the acidbase strength was examined. In this way, quite a series of variamineblue derivatives of various colour-change potentials were prepared which proved to be indicators suitable for using in various fields.

For the investigation on the behaviour of substances during heat-treatment, a combined new method of thermic analysis, *derivatography* was evolved. Namely, on the effect of heating, very different chemical and physical changes take place in the compounds, and these conversions are always connected with liberation or absorption of heat, and in certain cases also with changes in

\*A concise of the summary of the University's Year Book. (Edited by M. Polgár)

weight. The evolved apparatus, denoted as derivatograph operates in a completely automatic way, and simultaneously measures the temperature, the changes in temperature, the changes in weight and the rate of weight change of the sample, which is gradually heated to a higher temperature. The apparatus evolved in the Department, by the simultaneous measurement of the aforementioned four variables, further with an increased accuracy of the determination of changes in temperature and weight, makes the study of the chemical and physical alterations and conversions from quite new aspects possible, and thus, it must be considered as the introduction of a new method of investigation. The results of researches carried out so far proved that the recently evolved method successfully lends itself to the investigation of the qualitative and quantitative composition of raw materials of the ceramical and building industries, and, in general, of minerals and rocks as well. Besides, the method proved to be suitable for the precise determination of the mineral composition of bauxites, thus facilitating the evaluation of bauxite ores and the proper choice of the methods of processing. From the aspect of coking of coals, the experiences made during the investigation of the decomposition of coals on heat-treatment are of appreciable importance. Experimental evidences proved the suitability of derivatography for the control of the roasting process of ores, for the determination of water contents in drug preparations and foods, for the investigation of the mechanism of reactions of silicate chemistry and of other reactions taking place at high temperatures, for the investigation of heat resistance of catalysts and synthetic substances, for the study of crystal structure and composition of analytical precipitates, and for the analysis of ternary mixtures by distillation as well. The newest achievement in this field is the application of the method and of the balance, respectively, to investigations of sedimentation.

### Department of Food Chemistry

A simple, rapid and sensitive method was evolved for the detection of *sucrose* by Professor Dr. L. Telegdy Kováts Doctor of Chemical Sciences, assistant professor R. Kolta and associate professor Dr. D. Törley. On appropriately modifying the conditions of the Raybin reaction with diazo-uracyl, it is possible to reliably detect even 0.1% of *sucrose* in the presence of great quantities of glucose and fructose. This method is of great importance, in that eventual adulterations of must can be detected on the spot, on delivery of the shipment. Namely, sweetening by addition of sugar is often used by vine-growers when the weather is unfavourable. Owing to the rapid inversion of *sucrose*, the cumbersome laboratory methods known at present could not be used, and thus, it was difficult to choose the must samples on the spot for further investi-

gation. However, on using the method evolved by the Department, it became possible to instantaneously choose the must samples which were suspected of being adulterated with sucrose. This method has already been introduced by the Office for Wine Commerce of the Ministry of Food, as an obligatory test on the delivery of must batches, in order to protect the reputation of quality wines in the historical wine regions of the country. The scientists evolving the method twice received prizes for innovation.

Many fundamental studies were carried out in the field of investigation of up-to-date possibilities of food packaging, and of investigation of the interactions of foods and packaging materials. With the aid of a special instrument of high sensitivity, the theoretical and practical problems of the permeability of various synthetic foils to gases and vapours were subjected to a thorough study. On the basis of the obtained results, up-to-date methods of packaging were established for a number of foods, preserving their quality to an increased extent. The introduction of these methods was suggested to the industry and commerce. Of these suggestions which serve the interest of the people's economy as well as of the consumers; so far the new methods of packaging margarine and roasted coffee have been introduced. Remarkable results were obtained in the Department (associate professors R. Lásztity and Mrs. E. Szilasi) in solving the packaging problems of milk, table oil, raw meat and various products of the baking industry.

*The rheological investigation of foods* is already a conventional theme of the Department. Under the guidance of the Head of the Department, mainly associate professor R. Lásztity deals with these problems, and he attained significant results in various fields. On the basis of the penetrometer principle, a new instrument was evolved for the measurement of the elastic and plastic properties of the crumb of bakery products. Data were gathered in respect to the effect of various additives used in the baking industry, on the rheological properties of the crumb. On studying the curves obtained by plotting time against deformation, the plastic-elastic properties of the crumb were described by a new rheological model. With the aid of this model, on taking into account the curves time vs. deformation, the rheological constants of crumb could be calculated at a fair approximation. Of the known rheological instruments, the neo-laborograph was modified and was made suitable for the measurement of stress relaxation. Significant investigations were carried out in the Department in order to make possible the expression of the rheological properties of doughs in absolute physical units, instead of the empirical units applied so far. This fundamental research is of great importance in extending the instrumental methods of the food industry, and from the aspect of control and automation of the technological processes of food industry.

### Department of Physical Chemistry

A research team of the Department since a decade deals with studies on *physical adsorption*. Earlier investigations examined the analogy of physical adsorption and condensation. Then a new-type derivation of the Langmuir isotherm was published, where the presumption of localized adsorption sites is eliminated. Communications published since 1954 were devoted to a new method of measurement of adsorption. On utilizing the possibilities offered by frontal gas chromatography, it was possible to establish adsorption isotherms in a flowing system, and to extend this method to the measurement of mixed adsorption, absorption and mixed absorption as well. In the course of these investigations, the problem of the mechanism of wetting of the adsorbents and their carriers emerged. In connection with this researches into the mechanism of vapour adsorption were started, and they appear to elucidate a new mechanism in respect to adsorbents of large pores. The research workers of the Department succeeded in laying reliable foundations for the theory of gas chromatography by utilizing, for purposes of indication, the rate changes so far neglected in the theory of gas chromatography, further by the theoretical evaluation of this phenomenon.

In the field of the *growth of piezoelectric monocrystals* of substances other than quartz, as a substitute for quartz crystals, an organic substance, ethylenediamine tartrate was selected as a promising material. The methods for the preparation and appropriate purification of this compound were evolved by the research team of the Department. Then the experimental growth of monocrystals of given dimensions was started. The permissible rate of growth, together with the required stability of the parameters necessary for faultless growth (such as temperature, concentration, flow rate, stirring rate), and the period of growth (80 to 90 days) were established. The stability of these parameters could be maintained throughout the entire growth period, even in the case of failures of the current supply, by developing an appropriate automation.

### Department of Chemical Engineering

In the years 1947—1951, under the guidance of the Head of the Department, the late Professor Dr. J. VARGA, the aromatization of domestic motor gasoline distillates was studied. These investigations aimed at converting the gasoline distillates obtained in the course of distillation, into distillates of higher octane number, and thus, of greater value. Also *the thorough study of the catalysts of both dehydrogenation and hydrogenation* belonged to this range of themes. In this period, the reaction of methane and sulphur under high pressure, a process of great importance from the aspect of production of carbon disulphide

was studied by Professor Dr. J. VARGA and by associate professor Dr. P. BENEDEK, while associate professor Dr. K. POLINSZKY carried out experiments on the ahydration of Hungarian bauxites. These latter experiments aimed at raising the rationality of bauxite transport, and at utilizing the ahydrated bauxite for technical purposes. Besides these practical aims, also scientific results were attained by these investigations, in that the ahydration grades of Hungarian bauxite types were elucidated.

From 1952 to 1956, manifold experimental work was carried out in co-operation with the High Pressure Research Institute, with the participation of Professor Dr. J. VARGA, double Kossuth-prize winner, associate professor Dr. GY. RABÓ, Kossuth-prize winner, assistant professors E. HAIDEGGER and Dr. V. HESP, further with research engineers J. KÁROLYI, A. ZALAI, P. STEINGASZNER and A. SZÉKELY, aimed at the hydrogenating decomposition of mineral oils and distillation residues of petroleum, respectively. Widespread experiments were conducted with Nagylengyel crude petroleum and residues of atmospheric distillation, in the presence of oil mixed to the system. In these experiments, the effect of a wide range of reaction temperatures, hydrogen pressure, catalyst quality and concentration were studied. In the course of the extensive experiments conducted in connection with the development of the so-called Varga-process it was found that the effect of tetraline and other solvents which facilitate the decomposition of asphalt may be ascribed to the "loosening" of asphalt structure. Since then, the Varga-process has become known the world over, and its suitability was proved by a number of large-scale plant experiments. Just the existence of the Hungarian—German Varga Study Society founded recently, assures the use of this process in the near future at a large scale.

At the request of the Research Institute of Vegetable Oil and Household Chemical Industry, and of the Vegetable Oil and Soap Factory of Budapest, from May 1955, experiments on the hydrogenation of sunflower oil, on a batchwise operation, on applying a combined catalyst of copper, zinc, manganese oxide were carried out by the Department, in order to establish the optimum conditions of the production of fatty alcohols. On hydrogenating neutral sunflower oil triglycerides they succeeded, mainly with the co-operation of assistant professor E. HAIDEGGER and aspirant L. ÁDÁM, in establishing optimum conditions of reaction leading to 80% conversion rates of fatty alcohol.

The use of dinitrogen oxide as an anesthetic is becoming evermore widespread throughout the world. In this country, some difficulties arose, and the major part of the gas required for narcosis was only obtainable by foreign import. Therefore, in the early months of 1957, experiments were started in order to clear up the conditions for the preparation of dinitrogen oxide. Besides the literature researches, it is the merit mainly of assistant professor E. HAIDEGGER

and associate professor Z. ADONYI that some experiments to decompose ammonium nitrate were also conducted. The results of these experimental researches of fundamental importance, and the pilot plant erected on the basis of the results, facilitated the development of the technology for the production of dinitrogen oxide in Hungary.

In the researches carried out in the Department, also the investigation of the structure of ceramic dielectrics and semiconductors plays a significant role. These researches aim at elucidating the correlations existing between the structure and electrical properties of condenser substances of high dielectric constant, dielectric amplifiers and ceramic semiconductors used in telecommunication technique. On the basis of the results obtained, it was possible to start the industrial production of the condenser substance "Terradim".

The researches conducted by the group of electrochemistry resulted in also evolving the technology of zinc-silver accumulators, which is a merit of associate professor E. ZÖLD and assistant professor L. KISS. For this method, an official patent was granted to the Technical University of Budapest.

Professor M. KORACH, the present Head of the Department, in continuation of his researches carried out in the past, developed his *theory of tunnel furnaces*, and evolved a procedure for the treatment of the parameters of the tunnel furnace with the aid of analytical and analogous derivations, for the case of temperatures of batches of a quadratic cross section and of linearly increasing gas and batch temperatures. Under the guidance of Professor KORACH, research workers GY. SASVÁRI and K. SEITZ established the methods of calculation of the heating of the tunnel furnace, and, in general, of the direct-current and countercurrent heating, based on theories of analytical and analogous considerations, respectively, without any prescriptions for the shape of the heat curve, only on the basis of one single extreme value of temperature of the media delivering and accepting heat, respectively. Besides, the method of calculation of the mean temperature of bodies of any given shape was evolved for rapid heating.

The developed methods make possible the dimensioning of countercurrent heat-treating equipments, mainly of tunnel furnaces on a physically correct basis, and the calculation of plant parameters as well.

### Department of Mathematics, Nr. III

In this Department, prominent results were attained in mathematical sciences by Professor GY. ALEXITS and his earlier aspirant, K. TANDORI, Doctor of mathematical sciences. Both of them were particularly active in the field of the *theory of orthogonal expansions in series*, furthermore for the theory of Fourier series. One of the prominent achievements of Professor ALE-

ALEXITS refers to the characterization of the so-called Lipschitz classes of functions, while a number of detailed problems in respect to the characterization of the Lipschitz classes of functions by approximation theoretical way were elucidated by the Soviet scientist BERNSTEJN and the Belgian scientist DE LA VELLÉE POUSSIN. This problem was solved by Professor ALEXITS in 1941 for the Lipschitz function classes  $l$ , while in 1952 also for the more general function classes  $Lip(l, p)$ . These results are often quoted by foreign authors, such as e.g. the great two-volume monograph "Trigonometric Series" by the Polish mathematician ZYGMUND known throughout the world (published 1959 in Oxford). The scientific investigations of Professor ALEXITS in respect to the general orthogonal expansions in series are of great importance. Several new criteria were established as regards the summation  $(C, l)$  of orthogonal series, and these criteria are considered as being equal in rank to the classical criteria of the Soviet mathematician MENYSOV. The results of Professor ALEXITS in respect to the multiplicative orthogonal function systems received an appreciable international reception. All these results, together with many other new achievements are contained in his book "Konvergenzprobleme der Orthogonalreihen" published by the Hungarian Academy of Sciences in 1960. The proof of the great success of this work is that its English version will shortly appear, published by a London firm, and that its Russian translation is also in progress in the Soviet Union. Professor ALEXITS received greetings from renowned Soviet mathematicians as MENYSOV, NINI BARI and ULYANOV on the occasion of the appearance of this book, and they asked for his consent in the preparation of a Russian edition.

The theory of orthogonal expansions in series finds a widespread application in mathematical physics. Namely, here it is usual to establish the general solution of certain differential equations with the aid of expanding in series according to the own functions of the differential equation. The own functions form, in turn, an orthogonal function system. Therefore, the approximation theorems referring to orthogonal function series make the estimation of the orders of magnitude of the expansions in series of mathematical physics possible, i.e. the statement, how many members of the orthogonal series of which the function in question consists can be approximately calculated with a satisfactory accuracy.

The dissertation for the title of candidate of sciences was prepared by K. TANDORI in 1953 at this Department. In this work, TANDORI extends the results of HARD and LITTLEWOOD in respect to the strong summation of Fourier series to orthogonal polynome series. Since then, K. TANDORI as associate professor of the Szeged University, attained prominent scientific achievements in the field of orthogonal series. These results almost finally terminate this theme of research, started earlier by RADEMACHER and the Soviet scientist MENYSOV, who attained remarkable results in this field. Since, however,

these achievements were already attained at the Szeged University, they cannot be dealt with here in detail. Still, they must be mentioned here as earlier K. TANDORI belonged to the staff of the Department as an aspirant of Professor ALEXITS.

### Department of Agricultural Chemical Technology

The Department deals with researches on the chemistry of starch in the framework of its main research profile: researches into polysaccharides. This field was extensively studied by the Department.

Up to the present, more than 50 communications were published in this field. Above theoretical considerations, the Department many times gave advice to various industrial plants using starch, from pharmaceutical to textile factories, as regards the solution of their concrete plant problems.

The sub-themes of the greatest importance: the *kinetics of acid hydrolysis* and *experiments in connection with the synthesis of radioactive starch* which already extend beyond the boundaries of the starch research proper. Namely, the investigations in the former field aim at elucidating the general regularities of the hydrolysis of glycosidic bonds, while those in the latter field attempt at finding raw materials for the preparation of radioactive sugars.

In connection with the theme: *industrial microbiology and enzymology*, further the technology of vitamin B<sub>2</sub>, the Department dealt with the fermentative production of riboflavine. The aim of these experiments was in preparing a riboflavine concentrate from domestic raw materials, which is suitable for use as fodder. As a result, in a shaken culture, a concentrate containing 800 to 1000  $\gamma$ /ml. of vitamin B<sub>2</sub> could be prepared. In an aerated frame-culture, this yield could be raised by about 50%. Owing to the unfavourable economic conditions in 1955, the experimental results could not be realized on an industrial scale, though the animal experiments appeared to be promising. In Czechoslovakia, riboflavine is produced on an industrial scale, with the aid of an *E. ashybii* strain of identical activity.

Sorbose which serves as the raw material for the production of vitamin C can be very economically prepared by microbiological oxidation of sorbitol, using for this purpose the microorganism *Acetobacter suboxydans*. After an appropriate selection of strains, and on establishing the optimum parameters of oxidation, the method was developed by the Department to a process of semi-plant scale.

The *processing of flax and hemp* can be greatly hastened by an aerobic decomposition of pectin. The most important requirement of a method to be introduced into industry, is its economy. Therefore, a method of aeration was evolved by the Department, which maintains aerobic conditions by the use



of a quantity of energy much below that required by processes applied in foreign countries. In this method, in addition to establishing the degree of aeration, also the way of perforation of the tube system, and the practical location of the plant stems to be processed are taken into account. Using the suggested method, 30 to 50% of the time required for rotting can be saved.

During investigations of *pectin-decomposing enzymes* it was found that in the hydrolysis of pectin, instead of the —SH group, rather the —NH<sub>2</sub> group is essential. The enzyme preparation (*Botrytis cinerea* 5) produced in the Department was applied with success on processing grapes (in the case of direct-producing American varieties a juice surplus of 10—14%, while in the case of European varieties rich in juice surplus of 1.5 to 3% was attained). In the case of Tokay wines, the use of the enzyme preparation raised not only the extract contents but very favourably affected also the quantity and quality of the aroma and flavour substances of the wines. Thus, the wines processed in this way were richer in bouquet, had a better taste and showed a stronger raisin-wine character. The presence of *Botrytis cinerea* remarkably hastened the development of new wines, and reduced the period of ripening to about half the normal. This is of great economical significance.

The laboratory investigation of the *problems of drying, storage and conditioning* requires the adjustment of air to any desired content of relative moisture and temperature. The conventional statistical method (adjusting the desired vapour tension with the aid of saturated salt solutions, sulphuric acid, glycerol, etc.) is unfavourable, due to its time-consuming nature. In order to carry out measurements according to the dynamic principle, a simple laboratory conditioning equipment was designed with the aid of which measurements otherwise requiring 2—3 weeks could be conducted in a few hours. In essence, the apparatus operates as follows. Air supplied by a compressor is cooled below its dew point. Now this air saturated with moisture at low temperature is led over a water surface of accurately controllable temperature, where the air may take up more or less water vapour, depending on the temperature of the water. Air adjusted to the desired water contents now passes a heating system where its temperature is also adjusted to an accuracy of  $\pm 0.05$  C°. When the measurement of the equilibrium moisture contents or of the relative tension, or the plotting of drying isotherms etc. is necessary, then the air is introduced into the appropriate part of a modified analytical balance where air is contacted with the sample to be investigated. In this way, also the study of the kinetics of drying becomes possible. By this method, the relative moisture contents of air can be controlled within a deviation of  $\pm 1\%$ .

## Department of Plastic and Rubber Industries

The factors affecting the properties of reinforced plastics are manifold. Therefore, these substances of heterogeneous material structure were, in the Department, classified according to their relative dimensions. Possibly such heterogeneous material systems were investigated which enable the variation of a single factor, and the evaluation of its effect on the properties.

*In the course of the investigations carried out with various threads and thread bundles*, valuable data were established in respect to the correlation of optimum condensation time and temperature of thermosetting plastics. The phenomena occurring on subjecting the system resin-carrier-resin to tensile stress were studied by microscopic methods.

For the evaluation of stress and strain tests the observations of the changes in microstructure are indispensable. For this purpose, the methods applied on the microscopic investigations of heterogeneous plastics are utilized and developed further. In realizing these aims, a special method of polishing was evolved.

The investigations based on the phenomena of orientation and stress birefringence offered an indispensable aid in the development of the technique of processing thermoplastic plastics. Investigations in this field are in progress since 1959, on using up-to-date adequate instruments.

The application of plastics linings for frame pedestals and adjusting jibs was suggested in steam locomotives.

The linings of adjusting jibs and frame pedestals of steam locomotives usually made from a brass alloy were first substituted by bronze, then by gray cast iron. This made an annual saving of about 10 metric tons of bronze alloy possible. However, the cast iron linings caused severe breakdowns, due to galling which took already place in a very short time. Moreover, also a non-exchangeable part of the locomotive, the surface-hardened pedestal case suffered galling. The problem was solved by the application of plastics lining.

The specimens from reinforced plastics are anisotropic from the aspect of stress. Therefore, the required strength was attained in the preferred directions by an appropriate technique of processing. In these experiments, plastics of cresol-resol type reinforced by a textile-fabric skeleton were applied. For the manufacture of these materials, a new technology was evolved.

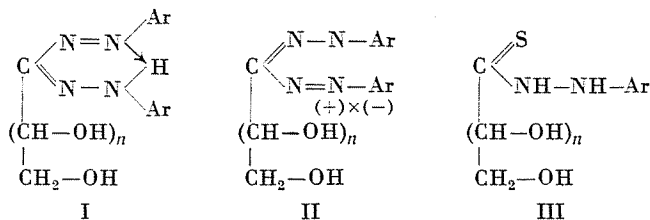
On the basis of the experiments it was proved that plastics linings from a practical aspect readily lend themselves to this purpose. According to experiences, the properties of plastics in this respect exceed those of the metals so far used to a great extent for this purpose.

Railway sleepers are a scarce article even in countries rich in wood as the industrial use of wood in other fields appears to be more important than the production of sleepers. It is attempted to eliminate this scarcity by the

use of pre-stressed reinforced concrete sleepers. The manufacture of such sleepers in Hungary attained a level which is high even at an international estimation. Plants of this type are being exported to several foreign countries. However, reinforced concrete sleepers cannot still be used on main lines, due to difficulties in fixing the rails to the sleepers. The requirements of a satisfactory solution of these problems are: certain degree of resistance to mechanical and electrical stresses, and to climatic and chemical effects. In the Department, experiments are in progress, aimed at solving the problem with the use of screw-setting fillings and plate retainers made of appropriate plastics.

### Department of Organic Chemistry

G. ZEMPLÉN, Academician, Kossuth-prize winner, the first Professor of the Department, and his co-workers (L. MESTER, A. MESSMER, E. ECKHART, E. MÓCZÁR and Á. MAJOR) succeeded in preparing sugar derivatives of a new type: sugar formazans (I), and from these, on oxidation with lead tetraacetate and N-bromo-succinimide, sugar-tetrazolium compounds (II), and, by reduction with hydrogen sulphide, thioaldonic phenylhydrazides (III)

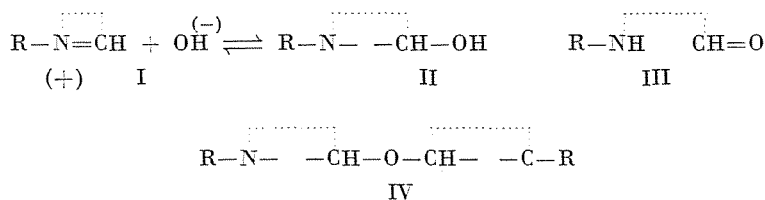


The reaction of formazan formation was utilized for the identification of aldoses, further for establishing the structure of various sugar derivatives, di- and polysaccharides. The cyclic and aliphatic nature of aldose-phenylhydrazones, the causes of the mutarotation of osazones were proved, and the structure of some sugar derivatives and disaccharides oxidized with periodate, together with the structure of some polysaccharides oxidized with periodate, nitrogen dioxide and ozone, respectively, and that of the anthrax-polysaccharide was elucidated.

The late D. BEKE, Kossuth-prize winner, the late Head of the Department, and his co-workers (Mrs. M. BEKE—BÁRCZAI, E. ECKHART, K. HARSÁNYI, D. KORBONITS, P. KOLONITS, Mrs. E. MARKOVITS, Cs. SZÁNTAY and L. TÓKE) solved a very old and much discussed problem of theoretical organic chemistry in an entirely new way by establishing the structure of the bases which can be liberated from heterocyclic quaternary ammonium salts. By this,

the proper theoretical interpretation of the chemical behaviour of this group of compounds disclosing manifold reactivity was made possible.

On the basis of their investigations carried out with a great number of natural and synthetic model compounds (mainly those with an isoquinoline skeleton), it was found that the real existence of the "triple tautomerism" postulated by Gadamer (1905) and since then generally accepted, namely the existence of the quaternary ammonium hydroxide (I), the pseudobasic aminocarbonol (II) and the aliphatic amino-aldehyde form (III) had never actually been proved. The above-mentioned "triple tautomerism" might mean the simultaneous existence of two basic types of tautomerism: of cationotropy and anionotropy. These are, however, processes opposite to each other. The more polar is the C—OH bond of the aminocarbonol, and, respectively, the stronger the equilibrium  $\text{II} \rightleftharpoons \text{I}$  shifts to the side of ions, the smaller the probability of the actual occurrence of the prototrop rearrangements II and III. Only in one single case, namely in the case of the bases liberated from 2-(2',4'-dinitrophenyl)-isoquinolinium chloride, it was possible to prove the existence of both members of the ring-chain prototrop system, and to verify the real tautomerism between them. However, the quaternary ammonium hydroxide form is absent here. Thus, the simultaneous existence of all three forms can only be expected with the basic aminocarbonols. In this case, however, the experimental conditions permit, in principle, the splitting of the ring, thus, instead of the aminoaldehyde, the "dimolecular" ether (IV) was always obtained. The formation



of the "dimolecular" ether (reaction of  $\text{S}_{\text{E}1}$  or  $\text{S}_{\text{E}2}$  type) and the formation of the aminoaldehyde (reaction of  $\text{B}-\text{S}_{\text{E}1'}$  or  $\text{B}-\text{S}_{\text{E}2'}$  type) are presumably competitive reactions. It is very probable that when the former reaction can take place, then the latter one is completely suppressed. — It was proved that the attack of nucleophilic reagents takes place on the hydroxylbearing carbon atom of the aminocarbonol, during formation of cyclic derivatives. The attack of electrophilic acylation and alkylation reagents, in turn, on the nitrogen atom of the aminocarbonol leads, by necessity, to an aliphatic reaction product. Thus, in order to explain the formation of these latter, one must not presume the existence of the ring-chain tautomerism.

## Department of Organic Chemical Technology

One of the principal fields of research of the Department, where a great number of communications were published and many lectures were delivered, is heterogeneous catalysis. For his work in this field, Professor Dr. Z. Csűrös, Head of the Department obtained a Kossuth-prize in 1953. The investigations referred to hydrogenations in liquid phase and to oxidation reactions. The role of the quantity of catalysts, further the kinetics and mechanism of the reaction were studied. In the course of researches carried out in the field of the theme: catalytic hydrogenations, in the last years, mainly Raney-nickel catalysts were investigated. It was found that the activity of catalysts is affected by their hydrogen contents. Depending on the conditions of preparation, it is possible to produce catalysts of various activity and various hydrogen contents.

During the hydrogenation reaction, the substrate, depending on its chemical nature and on the experimental conditions, is capable of reacting with various amounts of hydrogen adsorbed by the catalyst. This means, at the same time, that the activity of the catalyst changes. Substrates with a high affinity to the hydrogen adsorbed by the catalyst can react with this hydrogen more rapidly than the rate of hydrogen replacement from the gas area. Consequently, the hydrogen contents and with this latter also the activity of the catalyst decreases. This phenomenon may lead, in an extreme case, even to full inactivation. It was found that it is possible to reduce or to completely eliminate this detrimental process by an appropriate modification of the composition of catalyst or by complementing the ready-made catalyst with certain additives. The obtained results are also of great practical interest, due to the widespread use of Raney-nickel and to its relative expensiveness. On the basis of the aforementioned experimental data, a method was evolved for the *regeneration of Raney-nickel and palladium catalysts* as well.

A particular case of homogeneous catalytic reactions is that, where Lewis-acids capable of complex formation serve as catalysts. Since these catalysts are often used in industrial processes, such as the Friedel-Crafts reactions, the investigation of the mechanism of the catalytic action is, in addition to its theoretical interest, also of practical significance. In recent years, in the experiments conducted in the Department, the non-ionizing boron trifluoride and the ionizing titanium tetrachloride were applied, as characteristic representatives of both main types of Lewis-acids. In the course of these investigations, as the intention was to carry out kinetical measurements as well, mainly such an appropriate solvent was searched for, which makes the conducting of the reactions in homogeneous phase possible. On applying boron trifluoride complexes, the choice of the solvents depends on the nature of the complex in question. When acetic acid complexes were applied, glacial acetic

acid served as solvent, while on using an ethereal complex, also apolar solvents (such as chloroform) were applicable.

On using titanium tetrachloride as catalyst, some difficulties were met with, in that in an apolar solvent the reaction took place in a heterogeneous phase. On the basis of theoretical considerations and experimental evidences it was established that the titanium tetrachloride complexes are soluble in nitromethane, the reaction occurs in homogeneous phase, and the reaction kinetical measurements could be carried out.

Another important research trend of the Department refers to the chemistry of plastics and to rheology.

In this connection, researches are conducted in two directions:

a) preparation of *plastics by polymerization*,

b) rheological investigation of the prepared consistent products.

ad a) The study of polymerization and catalytic hydrogenation as competitive reactions was of importance from a theoretical aspect. In the case of polymerization activated with catalytic hydrogen, both mentioned reactions may take place at the same time, or the process may shift to the one or the other directions, depending on the concentration of hydrogen adsorbed by the surface of catalyst and on experimental conditions. It was possible to elucidate the kinetics and mechanism of polymerization activated by catalytic hydrogen (so-called hydropolymerization) in the case of several monomers.

In recent years, the significance of methods for the polymerization and copolymerization, respectively, of allyl compounds increased to a great extent, because polymers from these compounds can not so readily be prepared as from vinyl compounds. The favourable properties of the obtained allyl copolymers can be utilized in the field of synthetic fibres.

ad b) The rheological investigations aimed at evolving a technology suitable for the large-scale production of plastics. In this field, mainly the behaviour of the systems polyvinyl chloride (PVC)-plasticizer was studied as a function of processing parameters. Of the parameters, chiefly temperature proved to be of a decisive effect, and this may also have a theoretical significance, in addition to the practical aspects. Besides the solvents and plasticizers of PVC also the effect of other liquids was studied, and on the basis of their interactions, the liquids in question were classified into groups I, II and III.

### Department of Inorganic Chemistry

In this Department, a *catalytic Grignard method without any solvent* was evolved for the preparation of silicones. In the course of these researches, a study of fundamental importance was published by Professor J. PROSZT, Head of the Department, research worker I. LIPOVETZ and associate professor

J. NAGY. So far, six patents were granted for this process. By their method, on preparing tetraethoxysilane, polysilester is the first product. Polysilesters are applied in a precision foundry. On processing tetraethoxysilane by the catalytic Grignard method, all types of intermediates can be prepared, such as methyl, ethyl, phenyl, i.e. any alkyl or aryl silanes. The method offers the advantage of the ready control of the distribution of active groups, and of excluding the formation of products without functions. The mechanism of the catalytic Grignard reaction without any solvents was elucidated, and also various phenoxymethyl-siliconorganic compounds were prepared, and their physical and chemical properties established.

According to the afore-mentioned method, silicon intermediates could be prepared under atmospheric pressure, at a temperature of 100—150° C in a simple apparatus. In contrast to the synthesis of haloid silanes, the apparatus is not exposed to corrosion. On the further processing of alkoxysilanes, both substituted and condensed products could be obtained which can favourably be applied in the lacquer industry.

*Researches into polarography* was carried out in the Department since 1950, with the participation of J. PROSZT, K. GYÓRBIRÓ, T. DAMOKOS, J. KIS, E. MAJOR, J. PAULIK and L. POÓS. In the course of these investigations, methods were evolved for the polarographic determination of aluminium, ammonia, magnesium, beryllium and rhenium, for the measurement of the hardness of natural and industrial waters, and for the determination of contaminants in high-purity lead and zinc metals. The possibilities of polarographic separation of alkali metals and alkali earth metals were studied, and the complexes of these metals with various complexones were investigated by polarography. A new procedure was evolved for the derivation of polarograms, and a new-type polarographic cell with streaming mercury electrode was designed. Also the oscillopolarographic behaviour of alkali earth metals was investigated. The correlation between the polarographic behaviour and structure of cotarnine and relative alkaloids was studied. A method was evolved for the measurement of the alkaloid vincamine by polarography.

On designing an apparatus for the determination of liquid-vapour equilibria, which is also suitable for the investigation of heterogeneous systems, among other themes, the effect of electrolytes on azeotropic systems was studied. Examining the equilibrium curves, the significance of another preferred point, the so-called Raoult point was established, and the phenomenon of boiling point depression in certain liquid mixtures was interpreted. On dealing with the ebullioscopic behaviour of binary liquid mixtures, and introducing the term of the so-called mol-ratio ebullioscopic constant, it became possible to determine the Antoine constants independently of the tension curve, further to calculate the heat of evaporation and to establish the molecular state of the vapour phase.

In the field of investigations of *reversible and irreversible electrode processes*, researches were conducted in two main directions:

a) The so-called *thermogalvanic elements* consisting of two identical electrodes of different temperature were subjected to an experimental investigation. It was proved by associate professor N. LOHONYAI that the dependence of the electromotive force of thermogalvanic elements on the concentration of the solution can be interpreted with the aid of the irreversible thermodynamical laws.

b) The behaviour of the *aluminium anode* in aqueous solutions was studied by associate professor L. RÉDEY. These investigations are particularly important from the aspect of aluminium corrosion, respectively of the behaviour of the protecting surface layer of aluminium. Using the new-type equipment evolved for the investigation of polarization, it was possible to prove that the anodic polarization of aluminium in certain solutions deviates from the polarization phenomena known so far. On this basis, it was pointed out that the opinion of some authors, ascribing the strong aluminium corrosion observed in haloid solutions to the formation of "monovalent" aluminium ions, is erroneous.

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