

ON THE 60th ANNIVERSARY OF PHYSICAL CHEMISTRY DEPARTMENT

A short historical survey or about the people who are responsible for this jubilee

The Physical Chemistry Department of the University of Chemical Technology and Metallurgy was created 60 years ago. At that time it was within the Industrial Chemistry Section of the State Polytechnics in Sofia. Professor Stefan Christov, an actual member of the Bulgarian Academy of Sciences was its founder



Stefan Christov
(1910-2002)

and with a Government's decree from July the 17, 1947 he was entrusted to head it. This brilliant and highly educated scientist and lecturer, who had left incredible impact on the development of physical chemistry, chemistry and physics in Bulgaria and worldwide, lead the department's development for 30 years. Within this period he was also elected and served as a Rector (1964-1968) of the recently structured Higher Institute of Chemical Technology (succeeded now by the University of Chemical Technology and Metallurgy).

Professor Dr. Svetla Raicheva (1977-1984), Professor DSc. Savin Ikonopisov (1984-1995), Professor DSc. Assen Girginov (1995-2000), Professor Dr. Stefka Veleva (2000-2004) and Associate Professor Dr. Mihai Christov (since 2004) were his successors.

The first Assistant Professors who joined the Department were Georgi Bliznakov (an actual member of the Bulgarian Academy of Sciences, Director of the Institute of Inorganic Chemistry of the Bulgarian Acad-

emy of Sciences, Vice-Chairman of the Bulgarian Academy of Sciences), Christo Noninski (Professor and Head of the Department of Electrochemistry and Electrochemistry Based Technologies of the former Higher Institute of Chemical Technology) and Dimitar Elenkov (Professor and Head of the Department of Chemical



Svetla Raicheva
(1929-2007)



Savin Ikonopisov
(1928-1996)

Engineering of the former Higher Institute of Chemical Technology, a corresponding member of the Bulgarian Academy of Sciences). Professor Tzvyatko Mutaftchiev was appointed as the second full-time professor at the Department. He was the first one to teach and develop studies in the field of Electrochemistry.

Svetla Raicheva (Professor, Head of the Department, Vice-Rector and Rector of the University of Chemical Technology and Metallurgy, Honorary Doctor of the Moscow Institute of Chemical Technology) was appointed as an Assistant Professor at the Department in 1952. The first post-graduate student at the De-



The staff in 1977



The staff in 2007

partment, Nikola Pangarov (Professor at the Institute of Physical Chemistry of Bulgarian Academy of Sciences), started his work in 1953. A new Assistant Professor, Dechko Pavlov (an actual member of the Bulgarian Academy of Sciences, Institute of Electrochemistry and Energy Systems) was appointed in 1954.

A new group of young people joined the Department in 1959. These were Savin Ikonopisov (Professor, Head of the Department, Dean of the Organic Technologies Faculty of the former Higher Institute of Chemical Technology), Eva Sokolova (Professor and Vice-Rector of the former Higher Institute of Chemical Technology), Ivan Nenov (Associate Professor and Head of the Department of Electrochemistry and Electrochemistry Based Technologies of the former Higher Institute of Chemical Technology) and Milko Azmanov (Senior Assistant Professor).

A photo-laboratory (Savin Ikonopisov and Milko Azmanov) and an X-ray analysis laboratory (Nikola Pangarov) were organized at the Department. Later they started serving the whole Institute.

In 1961 the Department was joined by Lyuba Andreeva (Associate Professor) and Zhivko Georgiev (Associate Professor at the Department of Electrochemistry and Electrochemistry Based Technologies). The following year the Department was joined by Raicho Raicheff (Professor, Head of the Department of Electrochemistry and Electrochemistry Based Technologies, Dean and Vice-Rector of the former Higher Institute of Chemical Technology), Tzanko Nikolov and Iliana Galabova (both Associate Professors at the Department).

In 1963 Eva Valcheva, Emilia Lazarova and Lyuben Avramov became members of the Department team. They all continued their work as Associate Professors. During the same period of time Stefka Veleva (Professor and Head of the Department, Vice-Dean and Dean of the Organic Technologies Faculty of the former Higher Institute of Chemical Technology) and Marin Parlapanski (Professor at Chemistry Department of the University of Mining and Geology) joined the staff.

Georgi Georgiev (Senior Assistant Professor) working at the Department of General and Inorganic Chemistry was reappointed in 1964 and became a member of the team of the Physical Chemistry Department.

In 1972 two new Assistant Professors were appointed – Alexandrina Zwetanova (Associate Professor) and Assen Girginov (Professor, Head of the Department, and Head of the Chemistry Sciences Department). Another two members joined the staff – Veneta Trifonova (Senior Assistant Professor) and Djina Zlateva.

In 1977 Dr. Sasha Kalcheva (Associate Professor) and Dr. Mihai Christov (Associate Professor, Head of the Department, and Director of the German Language Based Education Centre of the University) became members of the Department team.

Work on a number of research projects started at the Physical Chemistry Department. This required the appointment of the research fellows Maria Machkova and Eduard Klein (both now working as Associate Professors). Antonina Djambova (a chemist and a part-time Assistant Professor) also joined the team.

It was during this period of time when Professor Ikonopisov organized and managed the first at the Institute low-scale students' production where a number of electrochemical technologies were developed.

Nearly at that time Professor Raicheva started a new research laboratory solving different corrosion problems. It was joined by a large group of the Department staff. Investigations within several research projects and programmes connected with corrosion protection were carried there. Corrosion maps of problematic regions of the country were drawn up on the basis of prolonged corrosion studies. Four post-graduate students worked in the laboratory and defended their Ph. D. theses.

Ivan Kanazirski joined the team as a new post-graduate student in 1987. After he got his Ph.D. degree he continued his studies at the Department.

In 1998 Dr. Angelina Popova was appointed a Senior Assistant Professor after having working as a Ph. D. student and a chemist at the Department. Now she is working as a Senior Assistant Professor at Chemistry Department of the Technical University in Sofia.

The Research Fellow Dr. Tzveti Tzvetkov, working as a Head of the ElChemEngineering Laboratory for the University Research Centre was reappointed in 1997 as an Associate Professor at the Department. Since 2007 he is a Senior Research Fellow (DSc.) and a Head of the NATO Laboratory on Defence Technologies at the Department of Chemical Engineering.

Dr. Martin Bozhinov was appointed as an Associate Professor at the Department in 2005 in connection

with the further development of the Department's teaching activities in French.

Greta Radeva is the youngest Senior Assistant Professor at the Department. She was appointed after she obtained her Ph. D. degree.

During all those years the activities of the Department were facilitated by the laboratory assistants Katsarova, Atanasova, Stambolska, Christova, Todorova, Trifonova (Eng.), Kyateva (Eng.), Komitova (Eng.), Ivanova, Miyateva (Eng.), M. Mihajlova, M. Christova, T. Krusteva and the technicians Kurkelanov, Stoimenov, Krustev, Gerchev, Dinev (Eng.). At present N. Angelova and V. Dervenska (Eng.) assist the work at the Department.

During the jubilee 2007 the staff of the Department of Physical Chemistry enlists 2 Professors, 6 Associate Professors, 1 Senior Assistant Professor, 2 chemists and 2 laboratory assistants.

To our greatest regret Professor Christov, Professor Mutafov, Senior Assistant Professor Azmanov, Associate Professor Andreeva, Professor Ikonopisov and Professor Raicheva could not live out this jubilee but their numerous contributions will be always highly appreciated.

Teaching activities at the Department of Physical Chemistry

During all these 60 years the staff of the Department was actively involved in teaching Physical Chemistry. In fact all efforts were aimed at teaching the students how to think but not what to think. Thus this difficult discipline had never become a barrier in students' education.

The first lecture course in Physical Chemistry for full- and part-time students was read by Professor Stefan Christov. He had read lectures in Chemical Thermodynamics as well. When Professor Tzvyatko Mutafov joined the Department he started reading courses in Applied Electrochemistry and Corrosion of Metals. A course on X-Ray Analysis was read at the Department as well.

Numerous changes in curricula and study programmes have taken place within the period of time discussed. They were usually aimed at "increasing the fundamental competence of the students" but in fact resulted in a systematic shortening of Physical Chemistry curriculum. Without going into details, nowadays 6 lecture courses in Physical Chemistry are read at BSc.

Level, and 1 course in Colloid Chemistry at MSc. Level for students studying Biotechnology. Four elective courses at MSc. Level can be read. These are the courses on Chemical Kinetics and Catalysis, Dispersed Systems, Chemical Thermodynamics of Real Systems and Quantum Chemistry.

A course on Ph. D. Level on Contemporary Methods in Theoretical Chemistry has been read for several years.

The Department's staff has actively participated in organizing and carrying out the education at the University of Chemical Technology and Metallurgy in German, French and English. Courses in Equilibrium Thermodynamics and Physical Chemistry are read in German, Chemistry I, II and III, Theoretical Chemistry, Thermodynamics and Kinetics – in French, Physical Chemistry of Materials – in English.

The Department's staff was also very active in responding to the needs of the society. A few courses were read; a number of individual training programmes were organized and carried out. Systematic training in "Corrosion and corrosion protection of materials in chemical industry" was provided for groups of engineers coming from different works and industrial laboratories.

The laboratory exercises in Physical Chemistry experienced certain development. Initially they were carried out at Sofia University by E. Budevski, J. Malinovski (both Professors, active members of the Bulgarian Academy of Sciences, Directors of Research Institutes of the Bulgarian Academy of Sciences) and Kordova. Starting with only one laboratory, the Department has four thematically differentiated laboratories. Thermodynamics, phase equilibria, chemical equilibrium, chemical kinetics, electrochemistry, surface phenomena and colloid chemistry are the basic fields included.

Some 30 years ago members of the staff were among the beginners to assess students' knowledge and understanding using specifically designed teaching materials and machines. This was done with the participation of colleagues working at the Institute's Research Laboratory on Educational Problems.

During the same period of time joint laboratory exercises were carried out with the research fellows at the Central Research Laboratory.

Problem-solving workshops were introduced at the Department as their significance to the desired learning outcomes was taken into consideration.

All teaching activities at the Department of Physical Chemistry were provided with teaching materials. 25 textbooks and manuals for the students taught in Bulgarian and 4 other for those taught in German and French were published. The first textbook in Physical Chemistry, the first manual on problem solving in Physical Chemistry, the first book in Physical Chemistry with examples and problems were written by members of the Department's staff.

More than 40 Ph. D. theses were written at the Department. Professor Raicheva was the first lady at the Higher Institute of Chemical Technology and Metallurgy who had defended a Ph. D. thesis. Five members of the staff had got their DSc. degrees, three other had successfully gone through a habilitation procedure for full-time professorship. Many Ph. D. students were supervised by Raicheva, Ikonopisov, Sokolova, Girginov, Veleva, Valcheva, Lazarova, Tzvetkov. They all have found successful realization in the field of higher education and science.

A great number of diploma projects were carried out at the Department. Some of them resulted from the joint efforts of staff members as well as colleagues from other Departments or research groups.

Research activities at the Department of Physical Chemistry

On the work of Professor Christov

Professor Stefan Christov, an actual member of the Bulgarian Academy of Sciences, is one of the most eminent scientists in the world, known for new and important trends in theoretical and applied physical chemistry. His original scientific contributions can be summarized as follows:

- He developed a quantum-mechanical theory of charge transfer electrochemical processes. This theory refers to a great variety of homogeneous and heterogeneous reactions in acid-base catalysis, hydrogen evolution, electrodeposition and dissolution of metals, anodic oxidation of metals.
- He developed the theory of electron transfer through energetic barriers in solid systems. It refers to phenomena connected with emission of electrons from metals and semiconductors in vacuum, electron currents through thin layers of insulators and semiconductors between two metals or at metal-semiconductor interfaces.



Some pictures from the Scientific Conference dedicated to 60th Anniversary of Department of Physical Chemistry

- He offered a quantum-chemical theory of chemical reactions rates which is free from the limitations of the widely used active complex theory.

- He developed a general quantum-mechanical theory of the non-emission processes in crystals.

All these theories are universally acknowledged. They have found numerous experimental verifications by research groups in Bulgaria and abroad and are reviewed in hundreds of papers and monographic editions.

Of particular importance are the contributions of Professor Christov to the general quantum-chemical theory of the potential barriers – the tunnel effect theory. The equations he has derived find a wide application in chemistry and physics. It is especially important to note the tunnel-effect criterion known as “Characteristic temperature of Christov” used in the field of chemical kinetics, in solid state physics, in biophysics.

The scientific contributions of Professor Christov are mainly theoretical but they are of great importance for solving practical problems in the fields of chemical kinetics, kinetics of electrode processes, microelectronics. He had taken part in a number of experimental investigations, stimulated or supervised by him, which referred to metals corrosion, formation of oxides and their physicochemical properties.

Professor Christov is the author of several hundred scientific papers which have been cited more than 2000 times. The interest towards his work was the reason for him to take part in numerous international symposia, conferences, congresses and to read lectures in many universities on all five continents.

Professor Christov was an extraordinary university lecturer. He was greatly admired by colleagues and students.

The investigations carried out at the Department of Physical Chemistry are mainly in the field of elec-

trochemistry, chemical kinetics and surface phenomena.

The research interests in electrochemistry refer mainly to:

- Electrochemistry of anodic oxide films (Prof. DSc. S. Ikonopisov, Prof. DSc. S. Christov, Assoc. Prof. Dr. L. Andreeva, Assoc. Prof. Dr. I. Nenov, Prof. DSc. A. Girginov, Assoc. Prof. Dr. T. Nikolov, Assoc. Prof. Dr. E. Klein, Assoc. Prof. Dr. M. Machkova, Sen. Assist. Prof. Dr. V. Trifonova, Dr. I. Kanazirski)

The formation and the properties of the oxide films on metals and alloys in oxygen-containing media became a field of particular interest. The studies on the kinetics and the mechanism of formation and dissolution of these films are of importance in elucidating the character of the processes of passivity, transpassivity and corrosion stability of metals and alloys. These oxide films are extremely interesting from fundamental point of view. They provide to study the migration of electric charges through thin dielectric and semiconducting films in high electric fields. These are the only objects of investigation where one can get knowledge on ionic and electronic conductivity, on breakdown phenomena, galvanoluminescence in dielectrics contacting with electrolytes. These investigations are significant for the further development of the theory of metals corrosion and other electrochemical processes the kinetics of which are determined or are affected by the presence of phase oxide on the electrode surface. The anodic oxide films find a wide variety of practical applications as well.

The investigations carried out by Professor Ikonopisov and his group provided the development of: (i) an improved model of the ionic conductivity through anodic films. All further studies worldwide are based on this model; (ii) a theory of breakdown phenomena in anodization. It describes quantitatively the dependence of the breakdown voltage on the nature and the concentration of the contacting electrolyte; (iii) galvanoluminescence theory. It provides to generalize, systematize and interpret all experimental data reported in the field. It was used to predict a series of new characteristics of galvanoluminescence.

Nine Ph. D. and two D. Sc. theses were defended in the field discussed.

- Electrocatalytic oxidation processes (Prof. Dr. E. Sokolova, Prof. Dr. S. Raicheva, Assoc. Prof. Dr. S.

Kalcheva, Assoc. Prof. Dr. M. Christov, A. Djambova, Assoc. Prof. Dr. A. Zwetanova)

Thorough investigations on the kinetics and the mechanism of oxidation of oxygen-containing aliphatic and aromatic organic compounds, hydrogen and hydrazine at electrodes of Pt, Au, Pt/Au, Pt/Ru and WC were carried out. The effects of additional factors like the preliminary treatment and the modification of the electrode surface (bright and roughened electrodes, electrode surfaces modified by oxides or electroless deposition of metal clusters, membrane electrodes with nanodispersed electrocatalysts), the temperature, the nature of the supporting electrolyte (aqueous acid and alkaline solutions, PEM) were studied. Generalized mechanisms of chemisorption and sorption of the oxygen-containing organic compounds, kinetic models and mechanisms of their oxidative and electrooxidative transformations were offered.

The problems investigated are closely connected with the development of fuel cells and waste water treatment. Some of the studies were carried out with the active collaboration of Dr. P. Iotov (Associate Professor at the Department of Fundamentals of Chemical Technology of the University of Chemical Technology and Metallurgy), others were performed within joint research projects with groups from the Institute of Electrochemistry and Electrochemical Systems at the Bulgarian Academy of Sciences, from the Universities of Bonn and Poitiers, Max-Planck Institute in Magdeburg.

Three Ph. D. theses were defended in the field of electrocatalytic oxidation processes of organic compounds. The papers and presentations in this field have been cited more than 300 times.

- Corrosion of metals (Prof. Dr. S. Raicheva, Prof. Dr. E. Sokolova, Assoc. Prof. Dr. T. Nikolov, Assoc. Prof. Dr. M. Christov, Sen. Assist. Prof. Dr. A. Popova, Assoc. Prof. Dr. E. Lazarova Dr. D. Zlateva, Assoc. Prof. Dr. A. Zwetanova, Prof. Dr. S. Veleva, Assoc. Prof. Dr. M. Machkova, A. Djambova)

The investigations in this field were carried out in two aspects – atmospheric corrosion and metals protection from corrosion in aqueous media.

Corrosion maps of Sofia and the town of Stara Zagora were designed; specific corrosion problems of the chemical works in Stara Zagora were solved.

The interests in metals protection were aimed mainly at studies of the inhibitor behaviour of different

organic substances following the effect of their molecular nature and structure. Oxygen-, sulphur- and nitrogen-containing aliphatic and aromatic organic compounds, some of which synthesized just to serve the aim of the investigation, were extensively studied as inhibitors of copper, iron and steel in aqueous neutral and acid solutions. Various experimental conditions were intentionally varied in wide ranges and their effect was followed. The studies were carried out with the application of the gravimetric method, voltammetry and impedance spectroscopy. A new method for the determination of the potential of zero charge of solid metals was developed. It was also extensively used in the study of the various organic substances adsorption. All results obtained show that in general the protective efficiency of the compounds studied depends on the type of the heteroatom present, on the type of the functional group where it is found, on the chemical and the electronic structure of the compound. The prevailing effect of the area of the adsorbing molecule over its ionization potential was outlined. Different adsorption isotherms were applied. The values of the adsorption parameters obtained were discussed in connection with the inhibiting effect of the substances investigated.

A number of research projects were carried out. Six Ph. D. theses were defended in this field. Some of the investigations were carried out with the participation of Professor DSc. C. Noninski, Associate Professor Dr. L. Nikolova and Professor DSc. R. Raicheff from the former Department of Electrochemistry and Electrochemistry Based Technologies of the University. Joint studies with the Theoretical Chemistry research group at the Institute of Physical Chemistry of Bonn University were carried out as well.

Numerous papers and presentations were made. Some of these are among the most frequently cited corrosion papers in the world.

- Effect of the crystal modification and the phase state of metals on their electrochemical behaviour (Prof. DSc. S. Christov, Prof. Dr. S. Raicheva, Assoc. Prof. Dr. I. Nenov, Prof. DSc. R. Raicheff, Assoc. Prof. Dr. Z. Georgiev, Prof. DSc. M. Parlapaniski, Assoc. Prof. Dr. A. Zwetanova, Dr. D. Zlateva)

The effect of the phase state of gallium, of the crystallographic structure of chromium, of the surface treatment of various types of steel, of copper and nickel coverages in aqueous media, of silver and nickel in

molten salts was thoroughly investigated. Fundamental knowledge on the anodic and the cathodic behaviour of metals studied as well as on the mechanism of the processes of their dissolution and those connected with the expected corrosion stability was obtained.

Seven Ph. D. theses were defended in this field. There were many publications and presentations discussing the results obtained. The interest provoked was great.

- Passivity and trans-passivity of engineering metals and alloys (Assoc. Prof. DSc. M. Bozhinov, Sen. Res. Fellow DSc. T. Tzvetkov)

A generalized model of metals passive state (the mixed conductivity model) is developed. It considers the processes of the passive oxide film growth and the metal dissolution as a sequence of reactions of generation, transport and consumption of ionic point defects (interlattice cations, cation and anion vacancies). The model of mixed conductivity is specified for quantitative description of the passive state of Cr, Fe, Ni, iron and nickel alloys in sulphate and borate electrolyte media at ambient temperatures as well as in borate electrolytes at high temperatures. The model of mixed conductivity is extended to describe the passive state of iron and nickel alloys in electrolytes based on molten hydroxides and carbonates at temperatures below 470°C and in supercritical water at temperatures reaching 700°C.

Two Ph. D. and two DSc. theses were defended in this field. About a hundred papers were published. Numerous citations are found in the literature.

- New materials for the energetics and multifunctional coverages based on nanomaterials and nanotechnologies (Prof. Dr. S. Raicheva, Assoc. Prof. Dr. I. Nenov, Assoc. Prof. Dr. M. Machkova, Assoc. Prof. Dr. A. Zwetanova)

The investigations in this field have been carried out since 1993 within a joint research group headed by Professor DSc. V. Kozuharov from the Department of Silicates Technology of the University. This group takes part in research projects funded by the European Commission within the corresponding Third, Fifth and Sixth Thematic Networks. The results obtained refer to; (i) determination of the conditions which are required for the application of an electrophoretic method for layer formation in high temperature fuel cells based on yttrium stabilized zirconium ceramics; (ii) development of a procedure for the evaluation of the operational time

of stacks in hard-oxide fuel cells – it is based on thermodynamic and kinetic investigations of processes of degradation of their elements; (iii) modelling of the protective anti-corrosion properties of nanomaterials deposited on different supports.

The group has 10 papers and 9 presentations at international conferences and symposia.

The research interests in chemical kinetics refer mainly to:

- Kinetic and thermodynamic relations of chemisorption processes at inhomogeneous surfaces (Assoc. Prof. Dr. E. Valcheva, Prof. Dr. S. Veleva, Sen. Assist. Prof. Dr. G. Radeva)

The basic contributions of the numerous publications and presentations in this field refer mainly to the introduction of an entropy correction term to the models of uniformly and exponentially inhomogeneous surfaces. The relations derived were experimentally verified in studies of (i) the adsorption processes taking place in production, hydrolysis and whitening of pulp; (ii) kinetics of enzyme and topochemical processes; (iii) dyeing of different fibres. The kinetics of these processes as well as many others connected with dispersed dyes dissolution, of adsorption of water vapours, iron and copper ions, of steel corrosion was successfully described by an exponential function of the process rate on the system's kinetic variable. All results reported are of fundamental and practical importance.

The studies most generally described above were carried out with the active participation of Professor DSc. V. Valchev, Associate Professor Dr. I. Valchev, Professor DSc. S. Nenkova, Associate Professor Dr. S. Bencheva, and Professor DSc. R. Draganova, all from the Department of Cellulose, Paper and Polygraphy of the University. Professor DSc. R. Decheva, Professor DSc. E. Kunchev, Associate Professor Dr. V. Vassileva, Associate Professor E. Terlemezyan, Associate Professor Dr. D. Pishev, Senior Research Fellow A. Georgieva, all from the Department of Textile and Leather Technology of the University collaborated as well.

Four Ph. D. theses were defended at the Department; many other were based on the joint investi-

gations in the field. The professorship of Dr. S. Veleva was connected with the application of the exponential equation pointed above. It is important to note that the studies described had a definite impact on a number of stages in paper production and textile technologies.

- Topochemical kinetics of solid compounds thermal decomposition (Assoc. Prof. Dr. L. Avramov)

Investigations on the thermal decomposition of basic cobalt-containing compounds were carried out. Of great theoretical and practical significance was the behaviour of cobalt oxyhydroxide. Some of the results obtained were used by A. Ernberg in his theoretical derivations on the kinetics of thermal decomposition processes.

The research interests in surface phenomena refer mainly to:

- Synthesis, adsorption, ion-exchange and application of zeolites (Assoc. Prof. Dr. I. Galabova)

This is the field of research interests of Dr. I. Galabova who defended her Ph. D. thesis in 1970 at Imperial Collage of London University. The results obtained found theoretical and practical application. They were reported in numerous papers and at international conferences. Some of the studies were carried out in close collaboration with research groups from the Departments of Non-Ferrous Metals and Alloys Metallurgy and Inorganic Compounds Technology of the University.

- Dispersed systems (Sen. Assist. Prof. G. Georgiev)

The work was aimed at investigating the structure and the properties of dispersed systems. The focus was mainly on the determination of criteria providing to foresee the tyxotropic behaviour of the systems studied.

Summarizing all these 60 years of teaching and research activities at the Department of Physical Chemistry it is important to note that the people working and making the history shortly outlined here have always aimed at giving knowledge and understanding, interpersonal, intellectual and practical skills, ethical values. The future development of all students who have studied at the Department of Physical Chemistry reflects in fact the impact experienced.