Jaroslav Heyrovský and Polarography

The name of Jaroslav Heyrovský is unambiguously connected with polarography, the electrochemical method he introduced and to the development of which he dedicated his whole life. The Nobel Prize for chemistry in 1959 came as an apt appreciation of this single-minded devotion.

Jaroslav Heyrovský, called Jaro in the family, was born on 20th December 1890 in Prague which is now in the Czech Republic, then capital of Bohemia in the Austro-Hungarian Empire. He had three sisters and one brother and their father was a university professor of Roman Law. The two boys, from their childhood were keenly interested in nature. They collected interesting natural objects and kept a tame squirrel at home, which they had found injured in a forest. Leo, the younger brother, later became one of the leading Czech entomologists. Of the school subjects, Jaro preferred mathematics and physics (chemistry was not taught at that time in secondary schools in Prague) and read books on astronomy. He was strongly impressed by William Ramsay's discovery of the rare gas elements when this was internationally publicised in connection with Ramsay's Nobel Prize for Chemistry in 1904. This gave him the idea that physical chemistry was the subject that he would like to pursue. However, this subject was not yet established at the Prague Charles University, and so after the first year of study of chemistry in Prague, Jaro begged his father to allow him to continue his studies at the University College in London where William Ramsay was the head of the chemistry department.

Once the father's support had been granted, Jaro managed to learn English within six months to an extent that it enabled him to achieve admission to the London University College in 1910. During the first year, he could attend William Ramsay's course of lectures, the last one before the prominent chemist retired. The professor succeeding Ramsay at University College was the electrochemist F G Donnan who in the following years influenced decisively Jaroslav's orientation in physical chemistry. He appointed him as a demonstrator in the practical classes, and later he proposed the determination of electrochemical potential of aluminium as a topic for his PhD dissertation. From the pH value of aluminium in aqueous solution, it is known that it is either passivated by a layer of oxide or covered by bubbles of gaseous hydrogen. Therefore, Donnan suggested to his student to use dilute aluminium amalgam which would slowly flow out of a glass tube thereby constantly renewing its surface.

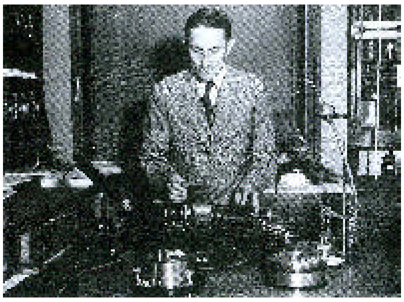
Heyrovský's experimental work was interrupted in 1914 when he visited his home for the summer holidays. At the end of July, World War I broke out and in 1915 he was called upon to join the Austrian army which was fighting, besides other states, also Britain, where he had his teachers and friends. Fortunately he was appointed to serve in military hospitals which allowed him occasional moments of peace that he utilised for continuing studies. This enabled him, in one of the last days of war in autumn 1918, to sit for the PhD examination at the Prague University. The examiner in physics was Professor Bohumil Kucera, author of the dropping mercury electrode method of measurement of surface tension of electrochemically polarized mercury. When asked about the method, Heyrovský knew the detailed answer, and a surprised Kucera invited the student to continue his research on certain anomalies noted with the dropping mercury electrode.

Shortly after the examination, Heyrovský, as assistant at the Department of Inorganic and Analytical Chemistry of Charles University, carried out experiments with mercury drops. He began to measure the exact weights of the collected amounts of 100 and later 80 drops of mercury falling into various solutions from the dropping mercury electrode. Using a potentiometer, different values of potential were applied to these drops with respect to the layer of mercury at the bottom of the measuring cell. The values of drop-weight, and later also of the drop-time, taken as the measure of surface tension, were plotted against the applied potential. The measurements were very tedious and the obtained curves did not provide satisfactory explanation for the anomalous maxima on the electrocapillary curves.

It was about 10 months after the untimely death of Professor Kucera, in February 1922, that Heyrovský carried out experiments in which he connected a sensitive galvanometer into the measuring circuit he had been using till then. He measured, besides the drop-time, the mean current that passed through the dropping electrode under different applied potentials. The current-potential curves thus obtained turned out to be perfectly reproducible and, moreover, provided information about the electrolysed solution. The potential at which an increase of current occurred was characteristic of the electroactive substance contained in the solution, and the extent of current increase was proportional to the concentration of that substance. Thus a new physico-chemical method for studying solutions was born. The main reason for this successful result was the constant and spontaneous renewal, every few seconds, of the metallic electrode surface which being a liquid, was completely homogeneous and isotropic. The results were therefore, not affected by any products of electrode reactions, and the values of current were exactly reproducible. With the minute size of the drops, the concentration changes in the bulk of electrolyte during measurement were completely negligible. Besides, the high overpotential for the hydrogen evolution on mercury allowed application of extended range of negative potentials when the drop was negatively polarised. During the first three years the method was called 'electrolysis with the dropping mercury cathode', as initially only cathodic processes known at that time were studied by it. Later, it was shown that anodic processes – limited by the potential of anodic dissolution of mercury – can be equally well studied by the dropping electrode.

The first Heyrovský's report about the new type of electrolysis was published in 1922 in Czech, followed by an English article in the *Philosophical Magazine* in 1923. That met with the interest of several specialists abroad. The first one who came to Prague to learn about the method on the spot was a young Japanese scientist, Masuzo Shikata from the University of Kyoto. Originally the polarization curves with the dropping mercury electrode were plotted manually, point-by-point, which could take as long as one hour. Shikata and Heyrovský in 1924 automated the measurements by constructing a motor-driven potentiometric drum combined with a cylindrical photographic cassette in which a photosensitive paper was revolving synchronously with the motion of the contact sliding along the potentiometric wire. The small mirror of the sensitive galvanometer was illuminated by a lamp and the reflected luminous spot was directed to the slit of the cassette. The current-potential curves were thus recorded photographically, which considerably accelerated receiving an objective result of the measurement. This new instrument for automatic recording of current-potential or polarization curves was called 'polarograph' and the method itself came to be known as 'polarography'.

The leading personality in electrochemistry towards the end of the 19th century, German Professor Walther Nernst of the Göttingen University, intended to introduce an electrochemical equivalent to spectroscopy. He expected that electrochemical current-potential curves would provide both qualitative and quantitative information about the substances contained in solution, similar to the spectroscopic methods. His students and co-workers tried various modifications of different metallic electrodes and also ways of recording curves. However, the poor reproducibility of the measurements did not satisfy Nernst, who finally in 1905 abandoned electrochemistry and left Göttingen for Berlin. There he devoted his interest to thermochemical and thermodynamic studies which brought him the Nobel Prize for Chemistry in 1920. Among Nernst's co-workers in Göttingen was also the Swedish scientist W Palmaer who studied electrochemical potential of dropping mercury electrode. However, neither he nor his professor ever thought of using this electrode for measuring current-potential curves.



The new method attracted students and co-workers, both Czech and foreign, to Heyrovský's laboratory. A special issue of the Dutch chemical journal '*Recueil*', published in 1925, contained as many as 11 papers dealing with polarography. In 1926 Heyrovský became the first professor of physical chemistry at Charles University. In his department, polarography became the primary object of research. From his studies in England he brought several quotes of British scientists which he considered important for scientific work and which he displayed in printed form on the walls of the department laboratories. They were:

"A man must either resolve to bring out nothing new or to become a slave to defend it." (Isaac Newton)

"Work, finish, publish !" (Michael Faraday)

"Progress is made by trial and failure." (William Ramsay)

"A problem solved is dead." (Frederick Soddy)

This was the beginning of the 'Prague polarographic school' from which the method was spreading to other countries. The first place to be introduced is Japan by M Shikata. This was followed in Poland by W Kemula, in Italy by G Semerano, and in the nineteen thirties it was well-known all over the world. The use of polarography in USA was spurred by Heyrovský's five months of lecture tour of American universities in 1933. By the end of 1932 the total number of polarographic publications was 139 and by 1940 it exceeded 900.

From the very beginning polarography found straightforward applications in quantitative chemical analysis. However, soon it was found that it could help to solve problems in other branches of chemistry as well, as in the study of coordination compounds or in questions concerning structure of inorganic as well as organic compounds. By then, its importance in electrode kinetics was quite well established. Polarographic method of determination of oxygen and of certain proteins found applications in biology and medicine and in determination of metals in metallurgy and mineralogy, etc. The development of exact quantitative theory of polarography was started in 1934 by Heyrovský's assistant Dionýz Ilkovic who derived the equation for the general case of polarographic current controlled by diffusion of the electroactive compound to the dropping mercury electrode. This was followed in 1935 by the *Heyrovský-Ilkovic equation* for the whole polarographic current-potential curve of a diffusion-controlled reversible electron transfer process. Another Heyrovský's pupil and co-worker, Rudolf Brdicka, initiated theoretical studies of polarographic currents which are controlled by adsorption of the electroactive substance at the electrode, and the current controlled by rates of chemical reactions. Later many scientists worked out further, in exact details, theoretical equations of polarographic currents for different specific kinetic cases, so that polarography became an experimental method with a highly developed theory. This aspect has contributed essentially to the image of polarography as a well-established physico-chemical method.

When electronic oscilloscopes (or cathode-ray tubes) became available for scientific research, Heyrovský in an effort to accelerate his method, introduced with his co-worker J Forejt a new modification of polarography. They polarized the dropping mercury electrode by alternating current and followed on the screen of the oscilloscope the corresponding changes of potential of the electrode as a function of time. They also recorded the derivative of potential with respect to time as a function of potential of the electrode. The resulting curves of specific shapes were again exactly reproducible. This revealed new aspects of the corresponding electrode reactions, and provided fast qualitative and quantitative information about the solution that can be applied for chemical analysis. Heyrovský's co-worker A Ševcík later used the oscilloscope to accelerate polarographic analysis by applying a single pulse of linearly changing potential to each drop of the dropping mercury electrode. In this way the whole polarographic curve was recorded on one single mercury drop. This new type of diffusion-controlled current/ potential curves contained peaks of current instead of the usual 'waves'. These curves could be readily explained by exact quantitative theory. The method, also called 'cathode ray polarography' is an important development in polargoraphy as it provided highly reproducible polarization curves at much higher rate than the original method. Later, the progress in electronic instrumentation brought along further modifications of polarography which were introduced in order to increase the sensitivity, specificity and rapidity of the method. There appeared ac polarography, square wave polarography, pulse polarography and a number of other derived methods.

During World War II polarography found applications in various branches of war industry, including in the development of atom bomb. In the 'Manhattan Project', several polarographs were used for determination of transuranium elements. After the war, during the second half of 1940s, polarography was among the five most frequently used methods of analysis. In 1951 the first International Congress on Polarography was held in Prague followed by international congresses on polarography in Cambridge (UK) in 1959, in Southampton in 1964, in 1966 again in Prague in July and in Kyoto in September. Besides, regular polarographic meetings were held in Italy, Japan, England, Germany, Poland, Soviet Union and other countries.

In 1950 the Polarographic Institute was founded in Prague under the directorship of Heyrovský. This was incorporated into the Czechoslovak Academy of Sciences after it was established in 1952. The aim of the Institute was to carry out and to propagate research of theoretical as well as practical applications of polarography in inorganic,

organic and physical chemistry, to follow the instrumental development of polarography and to supervise it in Czechoslovakia, and to collect polarographic data and literature. Bibliography of polarographic publications by Heyrovský and coworkers was appearing regularly from nineteen-thirties; in his last years it was mainly collected and prepared for print by Heyrovský's wife Marie, who worked as her husband's secretary. In the Polarography Institute, Heyrovský could devote himself completely to polarography; his teaching duties at the university were taken over by his successor, Rudolf Brdicka. Many scientists and students who visited the Institute, both from Czechoslovakia and from abroad, stayed on to learn the method or to carry out a specific research work. Among the visitors from India were the distinguished professors Satyendranath Bose and Chandrasekhar Venkata Raman.

In 1959, The Royal Swedish Academy of Sciences in Stockholm decided that the Nobel Prize for Chemistry for that year should be awarded to Jaroslav Heyrovsky "for his discovery and development of the polarographic methods of analysis". This came as a fitting recognition of the significance of polarography in science as well as Heyrovský's personal contribution to its discovery. Heyrovský felt highly honoured by this acknowledgement of his life´s work which was bestowed upon him at his advanced age; On the official formulation of the Swedish Academy, he would only comment that he considered polarography a physico-chemical method in which its analytical application is also a component .

Due to failing health Heyrovský resigned from the directorship of the Polarographic Institute in 1964 in favour of one of his post-war students, Antonín Vlcek. He continued to go with his wife to his office-cum-laboratory at the Institute as long as his health permitted. With his health going down and after several days of stay at a state hospital in Prague he passed away on 27th of March 1967. The Polarographic Institute, which he founded, was merged with the Institute of Physical Chemistry in 1970 after the untimely demise of Rudolf Brdicka who was heading the Institute. It is now known as Jaroslav Heyrovský Institute of Physical Chemistry belonging to the Academy of Sciences of the Czech Republic.

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