Jaroslav Heyrovský, the inventor of polarography

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Jaroslav Heyrovský (1890–1967) an eminent Czechoslovak scientist, was born in Prague on 20 December 1890. He invented polarography, an ingenious method of studying electrochemical phenomena using a polarizable electrode, and it fetched him the 1959 Nobel Prize for Chemistry.

Heyrovský used liquid mercury dropping regularly from a capillary orfice into the solution as an ideal polarizable electrode. By applying different voltages between the dropping mercury electrode (DME) and a suitable reference electrode (see Figure 1), he found that the changes in current in the circuit were characteristic of the depolarizer (oxidizable or reducible component) present in the solution. The change in current, caused by the oxidation or reduction process, when plotted as a function of the applied voltage, forms an S-shaped curve/wave (see Figure 2). The potential corresponding to the midpoint of the wave, called the half-wave potential, $E_{1/2}$, is characteristic of the redox couple, and the current corresponding to the height of the wave is proportional to the concentration of the depolarizer in the solution. Since the DME produces a constantly renewed fresh metallic surface, the current–voltage curves are perfectly reproducible. Thus the method tells us both about the kind and amount of the depolarizer present in the solution, even at very low concentrations.

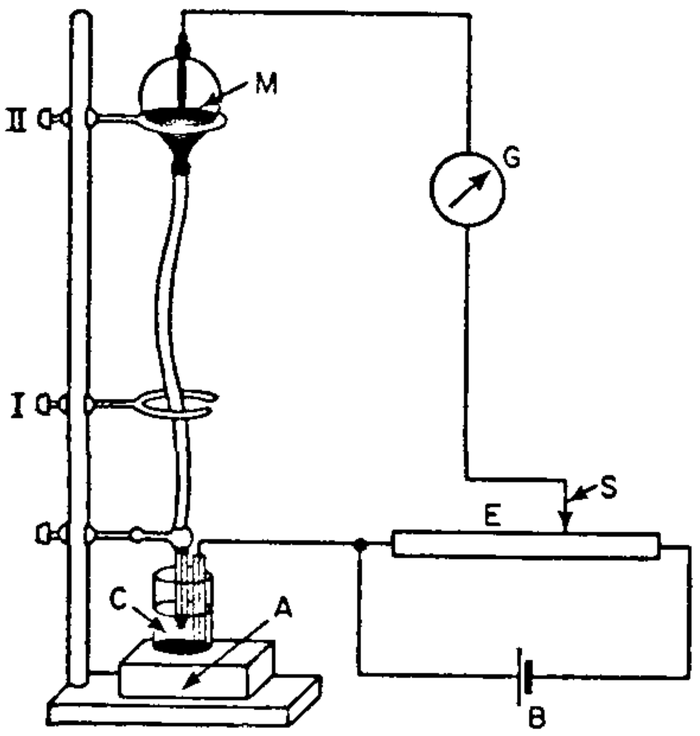

Figure 1. The polarographic circuit. Main parts: The electrolytic cell (C) with the tip of the capillary electrode dipping into the solution and a pool of mercury at the bottom as the reference electrode. Mercury from a reservoir (M) flows through the capillary. The e.m.f. from the battery (B) is applied to the cell through a potentiometer (E) and the current is measured by the galvanometer (G). (From *Practical Polarography*, by J. Heyrovský and P. Zuman, Academic Press, London and New York, 1968.)

This made polarography a very reliable and widespread analytical method. In addition, over the years, it has become an excellent method of studying various electrochemical and interfacial processes in inorganic, organic and biochemical contexts. Heyrovský's first polarograph (Figure 3) has been gradually improved into a versatile, portable and computerized version (Figure 4). Thus Heyrovský's wishful dreams have now become a reality.

Jaroslav Heyrovský's biography has been published on many occasions during his lifetime and after. Of these, the version published in the *Collection of Czechoslovak Chemical Communications* by his former pupil, R. Brdička in 1950 on the occasion of his sixtieth birthday, is considered as the most authentic account. He was born as the fifth child of Klára and Leopold Heyrovský, Professor of Roman Law at the then called Czech Charles-Ferdinand University. After completing the primary school in 1901, he studied in the Akademické Gymnasium and his favourite subjects were mathematics and physics. In 1909 he passed the maturity examination and joined the Philosophical Faculty of the Czech University in Prague and specialized in physics, chemistry and mathematics. He was most impressed by the lectures on inorganic chemistry by B. Brauner and on physics by F. Záviška and B. Kučera.

At this time, as he was very much taken by the achievements of Sir William Ramsay, he went over to London, matriculated in 1910 and started his studies in the University College. There he followed enthusiastically the lectures by W. Ramsay and W. C. Mc C. Lewis on general and physical chemistry, by F. T. Trouton and A. Porter on physics and by L. N. G. Filon on mathematics. His father financed his education. In 1913 he obtained the B Sc degree of the University of London. In that year Ramsay retired and was succeeded by the eminent physical chemist, F. G. Donnan. Through him Heyrovký turned to electrochemistry and soon became a demonstrator in the practical class of physical chemistry during 1913–1914. Heyrovký's experimental work was decisively influenced by the research topic for the D Sc thesis suggested by Donnan, viz. the determination of the electrode potential of aluminium. The passivity of this metal made it necessary to amalgamate its surface. However, the fluctuations of the electrode potential caused by the evolution of hydrogen led Donnan to advise Heyrovský to use a dilute aluminium amalgam dropping slowly out of a capillary, so that the electrode surface was constantly renewed. Donnan himself had used a dilute sodium amalgam dropping from a capillary for his study of membrane equilibria. The experience Heyrovský gained during these investigations laid the foundations for his future work; and his contacts with the eminent personalities left their imprints on him.

When Heyrovský returned home for the summer in 1914, his work at the University College got interrupted by the outbreak of World War I. He was then offered the facilities to continue his researches in the laboratory of J. S. Šterba–Böhm at the Chemical Institute of the University of Prague. In 1915 he was summoned for military service and due to his weak physical constitution, he was posted in a military hospital as a dispensing chemist and roentgenologist till the end of the war. This gave him enough time to complete his work and present his dissertation entitled 'The electro-affinity of aluminium' to the Philosophical Faculty of the Czech University in Prague. He thus obtained the degree of Philosophiae Doctor (PhDr) in 1918, after passing the final examinations. During the examination in physics, his teacher, Bohumil Kučera questioned him about the electrocapillarity of mercury. From the textbook on electrochemistry by F. Plzák and J. Baborovský, Heyrovský had prior

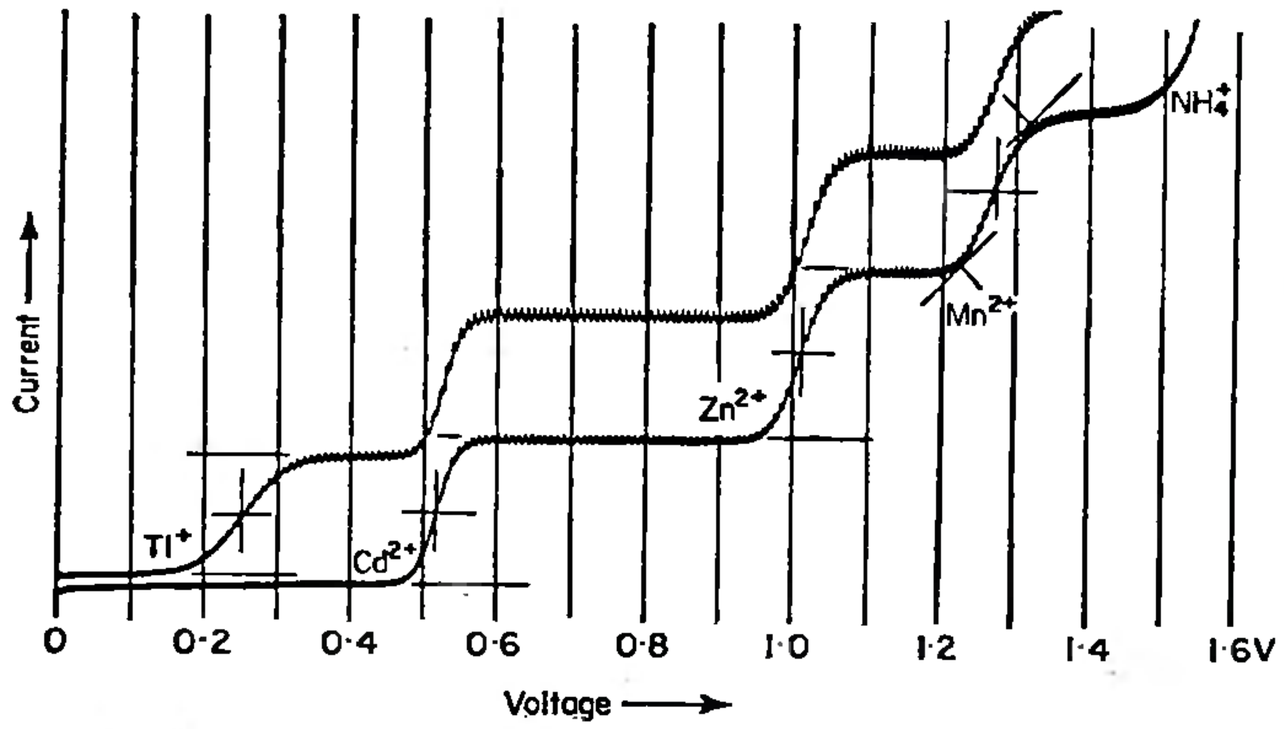

Figure 2. Polarographic waves. Right curve: A solution containing 0.0002 molar Cd^{++}, Zn^{++}, Mn^{++}. Left curve: The solution with the addition of 0.0004 molar Tl^{+}. Mercury pool is the reference electrode. Current is in the μA range. (From the same reference as Figure 1.)

Figure 4. The latest polarograh (From *Polaro Sensors*, Prague, 1994).

knowledge of Kučera's method of obtaining the 'electrocapillary parabola' by finding the weights of mercury drops at various applied potentials. So the examination in fact turned into a discussion and Kučera started describing some anomalous effects of distortion and secondary maxima on electrocapillary curves. He then said 'this mystery can be solved only by a physical chemist' and proposed to the surprised candidate researches on the surface tension of polarized mercury.

Soon Heyrovský found himself cooperating with R. Šimůnek, Assistant in Experimental Physics, in the tedious weighing of mercury drops at various potentials. In 1919 Heyrovský was nominated Assistant in the Department of Inorganic and Analytical Chemistry of the Czech University headed by Bohuslav Brauner. He was an intimate friend of D. I. Mendeleev and R. Abegg. He drew Heyrovský's attention to chemical affinity and valency and advised him to work on aluminic acid and the aluminates. Heyrovský submitted this as his habilitation work and was nominated Docent of Physical Chemistry in 1920 and as the first lecturer in this branch of science at the Czech University, renamed then as the Charles University. In 1919 Heyrovský gained the Fellowship of the Chemical Society, London, for which he had applied in 1914, at the outbreak of war. He also

Figure 3. The first polarograph (1924).

became a Member of the Faraday Society in 1919. He published his studies on aluminium as three papers in the *Transactions of the Chemical Society* in 1920 and submitted them as a thesis for the D Sc degree of the University of London, which he received in 1921.

From then on Heyrovský could devote himself more intensively to the Kučera's anomalies. A decisive step forward was made when Heyrovský determined, by the drop weight method, the decomposition voltages of some metallic ions, e.g., of Zn^{++}, Cd^{++}, Mn^{++} and Ba^{++}. He presented the results in a meeting of the Czech Mathematical and Physical Society in the presence of Kučera, shortly before the latter died in 1921. Subsequently, it occurred to Heyrovský to measure simultaneously the current that passed through the dropping electrode. For this he obtained a sensitive mirror galavanometer from his former teacher Záviška and set up his laboratory in the Chemical Institute. From the first current–voltage curves which he obtained, he immediately foresaw the potentialities of the method! He then put aside the problem of Kučera's anomalies and devoted himself to developing this new method. The first account of this innovation was published in the Czech Journal, *Chemické Listy* (1922, **16**, 256) and later more fully in the *Philosophical Magazine* (1923, **45**, 303). The first discussion abroad took place at the Meeting of the Faraday Society in November 1923, with two contributions to the General Discussion on Electrode Reactions and Equilibria. In the same meeting, a young Japanese co-worker of Heyrovský, M.

Figure 5. Jaroslav Heyrovský (taken in 1948).

Figure 6. Heyrovský with Raman in Prague, 1958.

Shikata presented a paper on the electroreduction of nitrobenzene at the dropping mercury cathode. The following year, Heyrovský and Shikata constructed an apparatus for automatically registering the current–voltage curves and called it the polarograph (see Figure 3). An account of this can be found in *Rec. Trav. chim. des Pays-Bas* (1925, 46, 496). With this device, polarographic researches began to speed up and Faraday's motto, 'Work–finish–publish' found its place on the walls of his laboratory. Thanks to Brauner's efforts, Heyrovský became an Assistant Professor in 1922 and Ordinarius Professor of Physical Chemistry in 1926. In 1922 he was appointed the Director of the newly established Department of Physical Chemistry of the Charles Univesity, at the extended premises of the Chemical Institute.

In 1925 Heyrovský went in pursuit of the element No. 75 using his new method to concentrate the nobler impurities in maganese salts. By X-ray analysis with the co-operation of V. Dolejšek (the discoverer of the N series of X-rays), Heyrovský and Dolejšek thought they discovered 'dvimanganese' (later called rhenium). However, this claim was withdrawn after more experiments. During this period in 1926 Heyrovský spent five months in G. Urbain's Laboratory in Paris as a Rockefeller Fellow. Since those years, Ramsay's remark 'Progress is made by trial and failure' also appeared on the walls of his laboratory.

In 1929, Heyrovský and Šimůnek found that the anomalous maximum observed on the electrocapillary curve by Kučera was associated with the reduction of air oxygen dissolved in the solution. The polarographic reduction of oxygen found extensive application in the determination of oxygen in biological contexts. By this time, Heyrovský's research group consisting of very able to enthusiastic scientists, was expanding rapidly and many aspects of experimental and theoretical polarography were gradually solved. A notable co-worker was D. Ilkovič who helped to quantitatively establish the equations for the current–voltage characteristics.

Around this period, in order to bring Czechoslovak science to the world platform, Heyrovský in collaboration with Emil Votoček, founded the Anglo-French Journal, *Collection of Czechoslovak Chemical Communications* and since 1929 practically all the polarographic papers were published in English in this journal. In 1933 Heyrovský was a Carnegie Visiting Professor and he lectured on polarography for six months in the Universities in Barkeley and Stanford and at Caltech and visited various Universities in the mid and eastern States. In 1932 as a result of the visit by the noted German analyst W. Böttger, Heyrovský wrote an account of his work in Volume II of *Physikalische Methoden der Analytischen Chemie*, which appeared in 1936. A Russian edition of Heyrovský's book on polarography (edited in Prague in 1933) appeared in 1937. Soon polarography spread to many corners of the world, both through his many pupils and by his visits abroad.

During World War II, polarography was found useful for quick metallurgical analyses. Thanks to the kindness of the anti-Nazi friend, Jan Böhm, Heyrovský could work in Böhm's laboratories. This enabled him to finish his large textbook, *Polarographie* in 1941 (Springer-Verlag, Vienna) and start oscillographic polarography using both the DME and the streaming mercury electrode. After the war, Heyrovský lectured in England in 1946 and for two months in 1947 in Sweden and Denmark. In 1950, the Czechoslovak Government enabled Heyrovský to establish the Central Polarographic Research Institute and he was nominated as its Director. As the research group was getting large, the Institure, belonging to the Czechoslovak Academy of Sciences since 1952, got gradually four or five buildings in different parts of Prague. From 1954, Heyrovský's office and some research laboratories were located in a building marked by three roses in Vlašská Street. Another motto on the walls of the Institute was that of Newton: 'A man must resolve either to produce nothing new or to become a slave to defend it.'

Heyrovský was very much attached to this Institute and remained an honorary Professor at the Faculty of Science of the Charles University, giving lectures and holding practical classes. He was fond of his students and research team, but was delicately firm as far as punctuality, non-smoking and devotion to research was concerned. He went around the laboratories daily and held regular seminars on Saturdays so that the whole group located in different buildings could gather for discussing the latest developments. The scope of polarography had now increased tremendously. His kind and magnetic personality gained for him research workers who respected and loved him and polarography and helped spread the method all over the world. Many scientists came from abroad to visit him and the Institute. Of these was also Sir C. V. Raman (see Figure 6) from Bangalore, in 1958. Those who stayed and worked with him went back with excitement and established active centers of polarographic research in their countries. To name a mere few, M. Shikata in Japan, W. Kemula in Poland, O. H. Müller in the USA, K. Wiesner in Canada, E.T. Verdier in France, G. Semerano in Italy, H. Berg in Germany and numerous others. Heyrovský's scientific merits were

recognized by many awards and his nomination to various distinguished scientific societies at home and abroad. The most prestigious award, the Nobel Prize, was awarded to him in 1959.

At the beginning of the sixties, since his health started declining, he retired from the post of the Director in 1963, but continued going to his Institute. However, his large circle of polarographers continued exploring various aspects of polarography both in his Institute and abroad. The highly successful and deeply respected Heyrovský breathed his last on 27 March 1967, leaving behind countless mourners which included his wife Marie, daugher Jitka and son Michael. A detailed biography of his life along with a complete list of his work was published in his honour in the same year in Volume 13 of the *Biographical Memoirs of Fellows of the Royal Society.*

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Rajalakshmi Heyrovská obtained her B Sc from the Maharani's College for Women, Bangalore and joined the Department of Inorganic and Physical Chemistry of the Indian Institute of Science in 1956 where she received her M Sc by research. Subsequently she was on the staff of the Department of IPC until 1964, when she left India and got her Ph D from the University of Cambridge, UK. Currently, she is working in the Academy of Sciences of the Czech Republic. She is the author of 'wet-and-measure' and 'current-spike' polarography, and has quantitatively interpreted (for the first time) the non-ideal properties of strong electrolytes in aqueous solutions in terms of partial dissociation and hydration 'from zero to saturation'.

She is married to Michael Heyrovský (son of J. Heyrovský), who is an active polarographer. They have a daughter, three sons and a little granddaughter.

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