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PROF. DR W. KEMULA – A CATALYST OF ELECTROCHEMICAL RESEARCH AND A FRIEND

Professor Wiktor Kemula influenced profoundly the development of electroanalytical chemistry in the twentieth century. He was instrumental in initiating research in numerous areas of electrochemistry, which played an important role in the later development of electroanalytical techniques. An important moment in his scientific career was a visit he paid to the laboratory of Prof. Jaroslav Heyrovský in Prague in the late twenties. Here in the Department of Physical Chemistry of the Charles University research was in progress which laid scientific and rigorous foundations to the development of polarography, using electrolysis with the dropping mercury electrode.

After return to Poland, Professor Kemula, in continuation of his work in Prague, first observed and reported the dependence of limiting currents on the weight of mercury and its surface area[1, 2]. This observation was one of the experimental facts, which lead later D. Ilkovič to the derivation of an equation, describing the dependence of limiting currents on concentration of the electroactive species, its diffusion coefficient, on the number of transferred electrons, rate of formation of mercury drops and on the size of these drops[3].

Similarly, Professor Kemula was the first to indicate the possibility of following electrolysis products by following their formation, after alternatively applying a potential and measuring currents corresponding to electrolyses of products formed[4]. This principle has been later developed by M. Kalousek and

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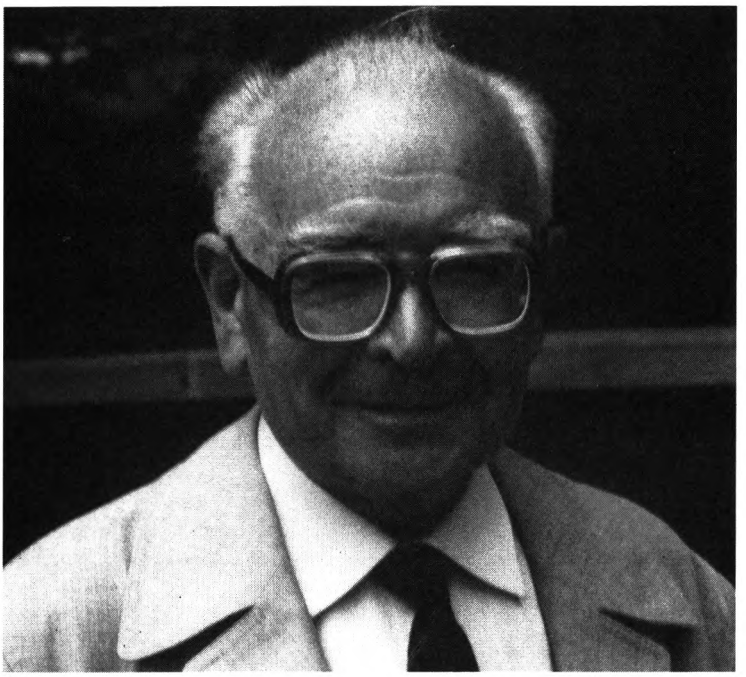


Fot. 26. Prof. Wiktor Kemula, 1983.

rectangular voltage polarization of the working electrode was used in his „commutator method"[5]. Basically the same principle was used by G. Barker in the pulse and square wave polarography[6, 7, 8], which, because of their high sensitivity, formed the basis of differential pulse polarography, and the variant of the square wave polarography introduced by J. Osteryoung[9]. These variants of polarography became the most widely used in practical analysis and their development saved the technique from obsolescence.

Another important contribution of Professor Kemula was the introduction of the hanging mercury drop electrode (HMDE) into electroanalysis in his work with Z. Kublik[10]. This type of electrode, that offers the clean surface of mercury and at the same time a constant electrode surface, is nowadays probably the most frequently used type of electrode for obtaining voltammetric current-voltage curves. The use of this electrode enables also accumulation of the analyte at the electrode surface. When such material is electrochemically stripped, the resulting current-voltage curves enable analyses of nanomolar, sometimes even picomolar solutions, which bring these electroanalytical methods to most sensitive existing ones. This electrode enables obtaining information bridging those, obtained with dropping mercury electrode (DME), mercury pool electrodes, and even solid electrodes. But whereas the potential of the DME remains during the life of each single drop practically constant, the potential of the stationary

Fot. 27. Na przyjęciu z okazji Konferencji Polarograficznej w Warszawie i przyznania prof. Heyrovskiemu doktoratu h.c. Uniw. Warszawskiego, 1956 r. Siedzą przy stole, od prawej: Michał Śmiałowski (Warszawa), Wiktor Kemula, przemawia Jaroslav Heyrovsk(, Maria Kemulowa, Alina Vincenz, Karol Butkiewicz, Stanisław Rubel.

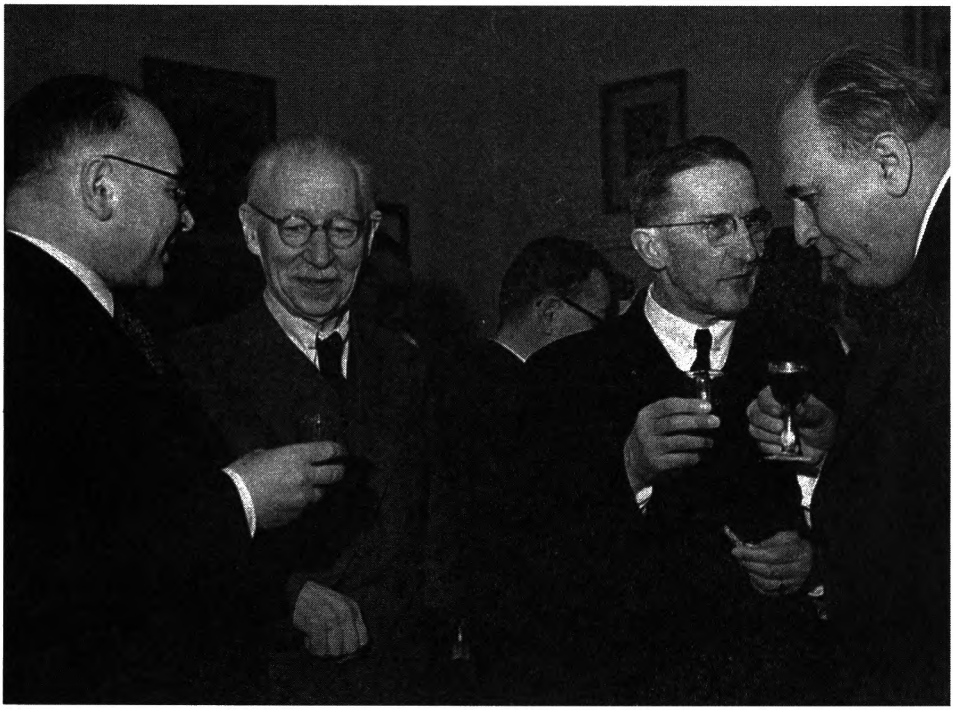
electrode is varied as a function of time during the recording of each current-voltage curve. This offers the possibility to use the scan rate as an additional parameter in investigation of electrode processes, but has the limitation that products generated at one potential may interact with species present or formed at a different potential.

When a triangular voltage sweep is used in cyclic voltammetry, HMDE proved to be very useful in investigation of reversibility of electrode processes and in the studies of chemical reactions of products or intermediates of electrode processes. Furthermore, HMDE is well suited for the use in controlled potential electrolyses (chronoamperometry), which also offers a further insight into mechanisms of electrode processes. It is to be regretted that in the view of its wide use, HMDE is not more frequently connected with names of its originators, Prof. W. Kemula and Z. Kublik.

The last area to be mentioned, in which Professor Kemula made a seminal contribution to the development of electroanalytical techniques, was the development of the first *hyphenated* method in analytical chemistry. By using a DME as a detector in column[11] and in paper[12] chromatography, by combining chromatography and polarography, a new method, „chromato-polarography" was born in the fifties, long time before other techniques were used in tandem with chromatography. Combination of various forms of separation techniques with electrochemical

detection is currently the most frequently used application of electrochemistry in analytical practice. Again, the importance and timeliness of Prof. Kemula's contribution to modern analytical chemistry is not as widely recognized, as would be deserved.

Yet in another aspect Professor Kemula made an important contribution to the development of contemporary electroanalytical chemistry. Professor Kemula had the ability to attract good, bright young collaborators. His enthusiasm and insight into electrochemical research rubbed off on his collaborators and resulted in a formation of a well renowned school. Some of his collaborators left the area of electroanalytical chemistry and became prominent in other areas of physical, analytical and inorganic chemistry, which reflects a healthy interbreeding of chemical disciplines. But considerable number of his collaborators remained true to their electrochemical credo and contributed to such growth of electroanalytical chemistry in Poland that this country became an exporter of electrochemical talent. Without doubt, Polish electrochemists currently represent the largest and strongest group of those, who have not been born West of the Atlantic, who achieved prominence in electrochemistry on the North American continent. Their contributions to the development and practical uses of electroanalytical techniques continue to have a large impact.



Fot. 28. Spotkanie naukowo-towarzyskie w mieszkaniu pp. Kemulów, 1956 r.. prof. Wiktor Kemula, prof. Wojciech Świętosławski, prof. Jaroslav Heyrovský, prof. Figurovskij (historyk chemii z Uniw. Moskiewskiego).

Professor W. Kemula understood well the importance of international cooperation in science. It was my pleasure to consider him an older friend, a relationship which was initiated during my first trip to abroad, when in 1953 I could spend 5 weeks in his laboratories. After that we met at meetings in some probable and even less probable corners of the world. We attended jointly the meetings of the Commission V-5 on Electroanalytical Chemistry of the International Union of Pure and Applied Chemistry, where he contributed considerably to international cooperation. His contribution was ackowleged as he became the President of the Analytical Division of IUPAC.

Last but not least, Professor Kemula was a man of culture. It was my pleasure at numerous dicussions we had at various localities to observe, how close were our opinions not only about science, but also about human relationships, history, politics and art. Professor Kemula was a real gentleman and it was of no surprise that he attracted friendship of colleagues from all over the world. His too early departure from this world was mourned by many friends in all parts of the globe.

References

[1] W. K e m u l a : *Les recherches sur les courants de saturation par diffusion des cations à l'aide d'une électrode à gouttes de mercure d'après Kučera-Heyrovský.* „Trabajos del IX Congresso Internacional de Quimica Pura y Applicada", Madrid 1934 Vol. **II** „Qimica-Fisica" s. 297–303.

[2] W. K e m u l a i B. W e n i g e r ó w n a : *Badania polarograficzne. Pomiary prądów granicznych w roztworach czystych soli za pomocą kroplowej elektrody rtęciowej Kučery-Heyrovský'ego.* „Roczniki Chemii" 1934 **14** 406–413.

[3] D. I l k o v i č : *Polarographical studies with the dropping mercury kathode.* Part XLIV. *The dependence of limiting currents on the diffusion constant, on the rate of dropping and on the size of drops.* „Collection of Czechoslovak Chemical Communications" 1934 **6** 498–513.

[4] W. K e m u l a : *Polarographic studies with the dropping mercury cathode.* Part XIV. *A study of the discontinuities on curves obtained in solutions of mercuric cyanide.* „Collection of Czechoslovak Chemical Communications" 1930 **2** 502–519.

[5] M. K a l o u s e k : *Processes at the dropping electrode with a discontinuously changing potential.* „Collection of Czechoslovak Chemical Communications" 1948 **13** 105–115.

[6] G.C. B a r k e r and I.L. J e n k i n s : *Square-Wave Polarography.* „Analyst" 1952 **77** 685–696.

[7] G.C. B a r k e r : *Square-Wave Polarography and Some Related Techniques.* „Analytica Chimica Acta" 1958 **18** 118–131.

[8] G.C. B a r k e r and A.W. G a r d n e r : *Pulse polarography.* „Zeitschrift für Analytische Chemie" 1960 **173** 79–83.

[9] J. O s t e r y o u n g and C. W e c h t e r : *Development of pulse polarography and voltammetry.* „Electrochemistry – Past and Present" (J.T. Stock and M.V. Oma, eds.) „ACS Symposium Series" 1989 **390** 380–395.

[10] W. K e m u l a i Z. K u b l i k : *Zastosowanie nieruchomej „wiszącej" elektrody rtęciowej do badań oscylopolarograficznych* . „Roczniki Chemii" 1956 **30** 1005–1008.

[11] W. K e m u l a : *Badania chromato-polarograficzne.* I. *Rozważania ogólne i opis aparatury.* „Roczniki Chemii" 1952 **26** 281–287.

[12] W. K e m u l a : *Chromato-polarograficzna analiza mieszanin jonów na bibule.* I. *Analiza mieszanin jonów o jednakowym potencjale pół-fali.* „Roczniki Chemii" 1952 **26** 694–696; II. *Analiza mieszanin jonów na bibule impregnowanej.* ibid. 696–697.