



Excerpts from the Nobel Lecture of J Heyrovský

December 11, 1959

The Nobel talk by J Heyrovsky starts with a brisk style and straightaway discusses the advantages of the mercury electrode. The fact that the geometry of a mercury drop in the dropping mercury electrode lends itself to precise mathematical analysis is a major advantage which is seldom emphasised in text books.

“The reason why I keep some 38 years to the electrochemical researches with the dropping mercury electrode is its exquisite property as electrode material. Its physical conditions of dropping as well as the chemical changes during the passage of the electric current are well defined, and the phenomena displayed at the dropping mercury electrode proceed with strict reproducibility. Owing to the latter property the processes at the electrode can be exactly expressed mathematically.”

The technical difficulties faced by some outstanding experimental scientists of that period, which may appear to be a simple problem today, is evident by the following statement:

“Until the year 1924 the galvanometer deflexions were plotted by hand on the ordinate against the voltage applied by pushing the wheel of the Kohlrausch drum to different values. It took a couple of hours to obtain a full graph, point by point from 0 to 2 V. To accelerate the plotting of the curves we have constructed with Shikata in 1924 an automatic device, the “polarograph” by rotating the Kohlrausch drum mechanically, and synchronously moving also a photographic paper. This mechanism draws the current-voltage diagram (the “polarogram”) in less than 10 minutes with all the advantages of automatic recording. The galvanometer has to be



damped to register, instead of the instantaneous current, the mean current during each drop. It is not advisable to damp the motion of the galvanometer mirror so far that the oscillations disappear; the regularity of the oscillations is a good check of the right functioning of the apparatus”.

In polarography, the double layer charging current is always an essential component of the total measured current. The other major component of the total current is due to electrochemical reaction and is known as faradaic current. There is a need to separate out these two components in order to obtain information on the concentration of the species or the mechanism of electron transfer reaction. This aspect has been discussed in the following part of the talk:

“Next, the forms of the current-voltage curves were classified according to the various processes occurring at the dropping electrode. The most fundamental of these is the “charging current” which accompanies every drop-formation conveying to the drop the charge corresponding to the externally applied potential. As this charge depends on the capacity of the dropping electrode and does not involve any electrolytic changes, the current is also termed “capacity current” or “nonfaradaic current”. It is very small, of the order of 10^{-7} amp per volt and ordinarily is regarded as negligible. However, the charging current plays an important role in oscillographic polarography where it is considerably greater. At a certain potential an electrolytic process starts, reduction or oxidation, which is shown by the passage of the current due to electrolysis. In the simplest case molecules or ions of the reducible or oxidizable substances interchange electrons with the electrode and hereby are removed from the electrode surface. Then new molecules of the electroactive substance – the depolarizer – diffuse from the interior of the solution to the surface of the electrode. Ilkoviè has calculated the current governed by diffusion to the surface of the expanding drop, deducing (in 1933) the formula of the “diffusion current”:

$$i_d = 0.627 nF \cdot D^{1/2} m^{2/3} t^{1/6} C$$

where n is the number of electrons involved in the reaction, F the charge of



Faraday, D the diffusion constant, m the rate of flow of mercury through the capillary, t the drop-time, and C the concentration of the depolarizer.”

The polarographic kinetic current is an important parameter where the electroactive species is generated by a chemical reaction at the electrode surface. This is an essential information to separate it from purely diffusion limiting current, which appears in the Ilkovic equation.

“In 1943 Wiesner discovered another sort of currents controlled by the rate of the chemical reaction yielding the depolarizer at the electrode. For example, formaldehyde or glucose give at ordinary temperature much smaller waves than expected from the Ilkoviè formula. Evidently a slower process than diffusion furnishes the depolarizer. In the case of formaldehyde the molecules of methylene-glycol $\text{H}_2\text{C}(\text{OH})_2$ have to be dehydrated to form the actual depolarizer which is H_2CO . The current is given by the rate of the dehydration, which of course depends on pH. Such currents are termed “kinetic” and bring the possibility to measure the rates of fast chemical reactions. Wiesner *et al.* obtained from the currents due to glucose the kinetic constants of mutarotation and calculated the amount of the free aldehyde in 0.655 M glucose at 25°C as 0.0030%. From the ratios of the two waves which appear in the reduction of a reducible acid, we are able to calculate the very high rates of the recombination of the ions.”

The so-called polarographic maxima has always fascinated researchers working in polarography. This phenomenon has the origin in the electrocapillary effect and was studied in detail by the famous Russian School of Frumkin. Very much related to this phenomenon is the study of tensammetry by Breyer and co-workers.

“Breyer and his co-workers introduced in 1944 the “tensammetric” method which uses the dropping mercury arrangement by applying a slowly increasing voltage with superposed alternating voltage of some 10 to 30 mV and 50 Hz frequency. The alternating current which passes through the polarographic cell is measured, and the current-voltage curve recorded. The method resembles the derivative method inasmuch as it gives peaks at the half-wave potentials of reversible depolarizers, but is very sensitive to



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adsorbable substances which change the surface tension of mercury electrode. Hence the name “tensammetry”. The changes of the capacity due to adsorption produce on the current-voltage curves peaks often 100 times higher than is the normal height of the wave of the organic depolarizers. The chief advantage of Breyer’s tensammetric method is that it can determine with high sensitivity many organic substances which are polarographically inactive, provided they are surface active.”

Obviously Heyrovsky had to contend with the criticisms as to the scope and extent of fundamental insight provided by the technique. He disagreed with this view and predicted correctly the copious amount of work in polarography that was to follow later.

“We meet often with the opinion that polarography did not bring anything new into chemistry except an improvement of analytical methods. That is decidedly not so, since in the study of reductions or oxidations many otherwise inaccessible physicochemical constants are determinable. Polarography helps the investigation of chemical structure of organic and lately even inorganic compounds.”

“Although the analytical application of polarography is highly advanced at present, the field of its utilization in basic chemical problems begins to open.”



Swedish king
Gustav Adolf VI
hands over the Nobel
Prize to Heyrovský in
Stockholm on
10.12.1959.

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