Heyrovský ‘s drops

Jaroslav Heyrovský (1890-1967)

I recently re-read a short story by the great Italian writer Dino Buzzatti. It is the story of a man who lies awake at night listening with dread to the sound of a drop of water – “tic tic” – as it hops *up* the stairs of his apartment block in the dead of night. It suddenly brought back a practical I did as an undergraduate. If today I have absolutely no recollection of what I actually measured, I have never forgotten the strangeness of the apparatus, which included a small burette filled with mercury, droplets of which fell through a solution at regular intervals. I’m sure I had no idea of the significance of the technique that had revolutionised electrochemistry: polarography.

Alongside the development of the atomic theory, the nineteenth century is also the time when electricity shifted from a being a strange mystery, to take over almost every aspect of the scientific laboratory. After Volta’s invention of his pile (CK46, June 2011) it was transformed by Humphry Davy and others into a tool to tear matter apart into its components. After Faraday linked electricity quantitatively with chemistry, the search turned to trying to understand how electrical currents could decompose solutions. Nernst and Helmholtz coined the term electrode potential and developed the link between concentration and the potential itself. Nernst expressed the hope that electrochemistry would one day become as simple and useful as spectroscopy. Chemists like Max Le Blanc (CK89, January 2015) to begin to plot “polarisation” curves to investigate the electrochemical processes – his invention of the hydrogen electrode would anchor all measurements to a common standard.

But measurements in solution remained difficult and dogged by problems of reproducibility. These issues would be swept away by a young Czech postgraduate student, Jaroslav Heyrovský. Hooked on science since childhood he started a degree at Prague’s Charles-Ferdinand University where his father was Rector. Heyrovský was soon so excited by the latest discoveries that he begged his father to study at University College, London, where William Ramsay had been discovering the noble gases. But Heyrovský’s dream of working with Ramsay crumbled; the year he graduated, 1913, Ramsay retired.

By now Heyrovský was a true Anglophile; he wrote his notebooks in English to the end of his life. Awarded a demonstratorship (a fixed term lectureship) at UCL, he made plans to adopt British nationality and began to work with a newly appointed Frederick Donnan, whose recent paper on membrane potentials had cemented his academic reputation.

Donnan suggested that Heyrovský determine the reduction potential of aluminium. The oxide layer on the surface meant that its position in the “electropositivity” series had been a matter of speculation and debate – some measurements placed it as high as zinc or magnesium, others suggested it was as low as iron or even lead. With the pure metal giving inconsistent results, In his earlier work Donnan had been using mercury capillary electrodes similar to those developed by Gabriel Lipmann (see CK97-August 2015). Donnan suggested that by using mercury amalgam, as Gilbert Lewis had done for the alkali metals, it would be possible to obtain a fresh surface, free of an oxide layer.

Heyrovský used a platinum/hydrogen reference electrode, using the stream of hydrogen bubbles not only to stir the solution but also to maintain an “inert” atmosphere around his amalgam electrode. He established not only the reduction potential of aluminium but also gained insights into the speciation of aluminium in water by making measurements across a wide pH range.

He was on holiday with his parents in Bohemia when war broke out in 1914 and he found himself stuck on the wrong side of the battle lines. For a few months he managed to work at the Chemical Institute in Prague, but was called up to serve in the Austro-Hungarian army. He was lucky to be appointed as pharmacist in a hospital, a job that left him time to write up his work.

When the Armistice was declared in 1918 he submitted a thesis to the University. One of his examiners, the physicist Bohumil Kučera was an expert in electrocapillarity and the examination turned into a deep discussion of the curious effects that Kučera had observed deviated from Lippmann’s earlier work. Impressed, Kučera invited Heyrovský to the lab to show him his set-up: a capillary electrode from which mercury was allowed to drip as the potential was changed – the weight of each drop was plotted against potential – Kučera was having trouble making sense of the curves. Heyrovský spent two years making these excruciatingly tedious measurements, and gradually concluded that Kučera was wrong – what he was seeing was an electrochemical effect associated with chemistry on the surface of the droplets.

In February 1922 Heyrovský got his hands on a very sensitive mirror galvanometer. He measured the current as a function of the potential applied to the drops immersed in a molar solution of sodium chloride. As the voltage reached –1.9 V Heyrovský saw a huge surge in the current. He knew immediately that he was onto something important. He called the S-shaped curves he plotted “waves”, whose potential indicated reduction and found that he could easily distinguish one ion from another. Over the next seven weeks he filled 200 pages with notes. The news started to attract students. When a young Japanese chemist Masuzo Shikata visited his lab in the autumn, they designed an automated instrument to speed up the experiment – polarography was born. Experiments could be done in minutes and scans could be read almost like spectra just as Nernst had hoped.

Polarography spread like wildfire, becoming the electrochemical technique for choice for all manner of electroanalysis and speciation studies until the 1970’s when it was gradually superseded by cyclic voltammetry. I’ve not seen a dropping mercury electrode in decades, but the memory of that polarography practical has never left me, along with its delicate tic tic tic sound – reassuring rather than unsettling.

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References

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