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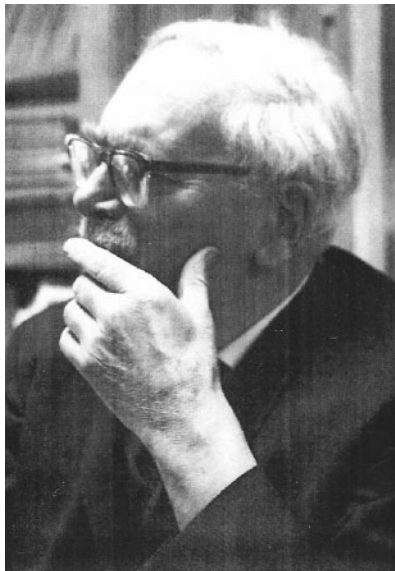
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# Butler and electrocrystallisation

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It is increasingly unusual for a scientist who is a specialist in a narrow field to make an outstanding contribution in another, albeit adjacent, field. John Alfred Valentine Butler was such a person – a chemist who made a profound contribution to electrode discharge reaction theory almost as an aside from his main work.

Born in Winchcombe, Gloucestershire, on 14 February 1899, he was educated at Cheltenham Grammar School and Birmingham University but, having to join the army in 1917, he was not free to continue his education until 1918, when he studied for his Inter BSc from the army, bought and read Bragg's new book on X-ray crystallography and joined the University in 1919 on an ex-army scholarship, taking a first in 1921. Being too young to receive the degree, he did a year's research with Dr S. R. Carter on 'A sulphur electrode' from which he later wrote his first paper and gained an MSc degree! He was then, successively, a lecturer in chemistry at Swansea (1922–1926), and Edinburgh (1926–1939) universities, teaching and researching in chemical thermodynamics.<sup>1</sup> This work provided the material for his second textbook which was widely used during the period from 1930 to 1970.<sup>2</sup> He took his DSc in 1927 and was Meldola Medallist of the Royal Institute of Chemistry in 1929. In 1939, he joined the Rockefeller Institute for medical research at Princeton University where his interests moved from the energetics of electrochemical reactions towards biological and medical aspects of chemistry. In 1941, he became an executive officer at the Commonwealth Scientific Office in Washington, returning to Edinburgh in 1944. In 1946, he moved to the Courtauld Institute for Biochemistry at Middlesex Hospital becoming, in 1952, Professor of Physical Chemistry in London University at the Institute of Cancer



Research. He retired in 1966. His biological interests are represented by other books.<sup>3–10</sup> (It has often been noted that all his books are characterised by great modesty, such that he does not always make reference to his own important research papers!)

Thus his remaining years were devoted to solution and electrochemical aspects of medical compounds notably DNA and the histones. In fact, from 1946 to 1968, he wrote 140 papers with an especial association with B. E. Conway until he left for Canada in the mid 1950s.

He was elected to the Royal Society in 1956 and died on 16 July 1977, having written over 200 papers and a series of books. He was married to Margaret Lois Hope, the botanist daughter of the Liberal MP for West Fife and had three children all of whom having good careers. His interests included painting (in the Cezanne/Van Gogh tradition), music especially Schubert and Mahler, and he was an active Anglican.

During the 1920s as a teacher of thermodynamics he was clearly fascinated by the implications of the Arrhenius equation and activation energies to characterise and describe reaction paths and rates. In particular,

he was concerned about the discharge of ions at cathode surfaces to become atoms in the surface metal lattice and the various energetic steps they passed through during the discharge process. Furthermore, he was driven by a need to justify Tafel's experimental equation of 1905,<sup>11</sup> and a desire to explain Nernstian potentials from a kinetic (current) point of view. This resulted in his proposal of an analysis leading to the Butler equation;<sup>12,13</sup> almost simultaneously Volmer in Germany published a similar analysis and the equation is now termed the Butler–Volmer equation. Other researchers later refined it, notably Erdey-Gruz,<sup>14</sup> while Butler himself moved on to other topics only returning to it, when invited to, for symposia presentations.<sup>15–17</sup>

Derivation of the equation can be found in all the major textbooks on electrochemistry but it incorporates a number of features of importance. The simple equation is the sum  $J$  of the forward and reverse reaction currents

$$J = J(-) + J(+) = J_0 \{ \exp[\beta n F \eta / RT] - \exp[-(1 - \beta) n F \eta / RT] \}$$

In this equation  $nF$  is the Faradaic equivalence,  $R$  the gas constant,  $T$  temperature, and  $\eta$  the overpotential. The important features are:

- (i) the concept of reversibility such that the deposition and dissolution reactions are noted. Clearly, at high currents, one dominates to the virtual exclusion of the other
- (ii) the concept of multiple activation energy stages in which solvation (or desolvation) is important as is the role of adsorption and adatom surface diffusion to least energy sites; the use of a symmetry factor  $\beta$  expresses the *skewness* of the activation energy–distance curves
- (iii) the definition of an exchange current density  $J_0$  at reversible potential

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- (iv) the means of measuring the exchange current density by extrapolation which could characterise the metal and its salt in solution
- (v) by making suitable approximations at various levels of overpotential, observed relationships between current and potential could be explained, notably the Tafel relationship of  $\eta = a \pm b \ln I$  which had hitherto been an experimental relationship only.<sup>11</sup> Using the Butler format, the Tafel equation now becomes:

$$\ln J = \ln J_0 + \{(1-\beta)nF/RT\}\eta$$

The theory of electrocrystallisation has since this time received huge attention and consequent publication listings. In particular, the role of hydrogen as opposed to metal discharge in cathodic electrodeposition processes, and the way in which ions become adatoms and then lattice atoms in the deposit growth process. The need to explain differences in grain size and even crystal structure at differing currents, the effects of surface-active additives,

the effects of differing solution anions, and the effect of pulsed current, etc. have all continued to provide a theoretical challenge to the original Butler–Volmer approach which remains the base point.

### Acknowledgement

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