THE ESSENTIAL IDEAS OF ELECTRODE KINETICS

Paul Delahay

Department of Chemistry, New York University, Washington Square
New York, New York 10003

The fundamental concepts in electrode kinetics are introduced. General references in English, or available in translation, include books (1-4), reviews-volumes (5-6) and reviews (7-8).

Historical (only key ideas)

1. The description of electrode kinetics in terms of current-potential (overvoltage) relationships is primarily based on:
   (a) the concept of exchange current (Butler, 1924)
   (b) the introduction of the transfer coeffecient (Erdey-Gruz and Volmer, 1930)
   (c) the correlation between electrode kinetics and double layer structure (Frumkin, 1933)
   (d) the correlation with adsorption at the electrode (Frumkin and Ershler, 1940; also Temkin)

2. Elucidation of reaction mechanisms involves:
   (a) the introduction of stoichiometric numbers in the analysis of current - potential relationships (Horiuti and Ikusima, 1939)
   (b) reaction orders studies (Vetter and Gerischer (1950); also Essin (1940)
   (c) the detection and, if possible, quantitative estimation of intermediates by various techniques
   (d) other approaches: double layer effects, detailed analysis of the effect of coupled chemical reactions, isotope effects, etc.

3. "Molecular" interpretation of electrode kinetics requires the development of theories of electron transfer (Marcus (1956)). These had as a precursor the introduction of potential-energy diagrams (Horiuti and Polanyi, 1935; Butler, 1936).

Descriptive Kinetics in Terms of Exchange Current and Transfer Coefficient

1. Introduction of the concept of exchange current by consideration of forward and backward reactions at equilibrium.
2. Discussion of transfer coefficient from potential-energy diagram.
3. Definition of overvoltage and discussion of current-overvoltage characteristics.

Correlation with Double Layer Structure

1. Correction for the concentrations of reactants (and products) in the plane of closest approach.
2. Correction for the drop of potential across the diffuse double layer.
3. Other effects: solvent structure, specific effects, etc.

The first two corrections can be made quite well, in the absence of specific adsorption, on the basis of the theory of the diffuse double layer. Specific adsorption poses problems. Solvent and specific effects do not lend themselves to quantitative analysis at this stage.

Correlation with Adsorption

The problem is to write current-overvoltage characteristics taking into account the coverage by reactants and/or products. Adsorption equilibrium follows some isotherm, e.g., the Langmuir or Temkin isotherms. The exchange current can then be correlated to the standard free energy of adsorption, and the effect of the nature of the electrode can be investigated. Formulation can be developed for parallel or consecutive reactions.

The effect of potential on adsorption, e.g., organic reactant on mercury, can also be introduced in the current-potential characteristic.

Elucidation of Mechanisms

Analysis of current-overvoltage variations in terms of stoichiometric numbers, reaction orders, Tafel plots, etc., provides fundamental criteria for the elucidation of reaction mechanisms. These criteria may suffice for simple processes (e.g., overall reaction identical with rate determining step) but in general, they do not allow unambiguous assignment of mechanisms for more complex reactions. Other methods must then be applied (see Historical).

Mass Transfer

Complication by the finite rate of mass transfer of reactants and products can be avoided when the exchange current is sufficiently low (vigorous stirring, large excess of reactants and products). This complication cannot be avoided with high exchange currents. Diffusion in electrode processes was already understood in the early work of Sand and Cottrell (about 1900) and was extensively studied in polarography (Heyrovsky, 1922; Ilkovic 1934). Combination of kinetics and diffusion has been vigorously studied for the last 20 years (Brdicka and Koutecky, 1947). Hydrodynamic problems can also be attacked (rotating disk electrode, Levich 1942).

"Molecular" Electrode Kinetics

This is a difficult problem but at least a way to introduce modern chemical physics in electrochemistry (which is mostly prequantum in its present concepts and orientation). Satisfactory treatment has been developed only for processes that do not involve the breaking or making of a bond. Application of theory has been made mostly to homogeneous redox processes, but there are unexploited applications to electrode kinetics. No prediction is ventured about treatments involving a bond-breaking or bond-making process.

Topics not Treated

The double layer, anodic films, processes with mixed potential (corrosion), semiconductor electrodes, methodology and techniques, etc.

References

1. G. Kortüm, "Treatise on Electrochemistry", 2nd edition, Elsevier, Amsterdam, 1965.
2. K.J. Vetter, "Elektrochemische Kinetik", Springer, Berlin, 1961. English translation by S. Bruckenstein and B. Howard, Academic Press, New York, in press.
3. P. Delahay, "Double Layer and Electrode Kinetics", Interscience-Wiley, New York, 1965.
4. B.E. Conway, "Electrode Processes", Ronald Press, New York, 1965.

5. "Modern Aspects of Electrochemistry", J.O'M. Bockris editor, Butterworths, London, vol.1 (1954), vol.2 (1959), vol.3 (1964).

6. "Advances in Electrochemistry", P. Delahay and C.W. Tobias editors, Interscience-Wiley, New York, vol.1 (1961), vol.2 (1962), vol.3 (1963), vol.4 (1966), vol.5 and 6 in press.

7. Ann. Rev. Phys. Chem., 5, 477 (1954); 6, 337 (1955); 8, 229 (1957); 12, 227 (1961); 15, 155 (1964).

8. Ann. Reports Chem. Soc., 51, 103 (1954); 54, 17 (1957); 55, 67 (1958); 56, 32 (1959); 61, 80 (1964).