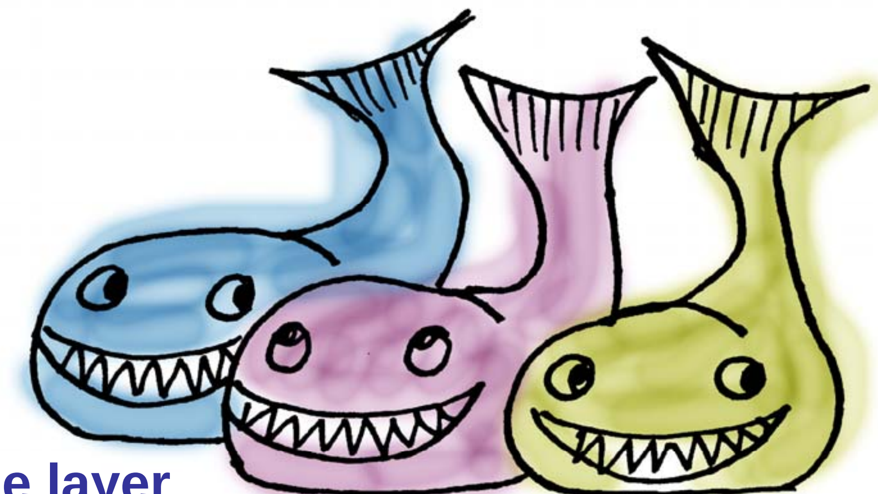
Department of

Electrochemistry
Moscow University

Diversity of electrochemistry: the specific problems of molecular models and their experimental verification

Galina A Tsirlina

Diversity, 50 years ago:



Double layer

Diffusion

Electrode kinetics

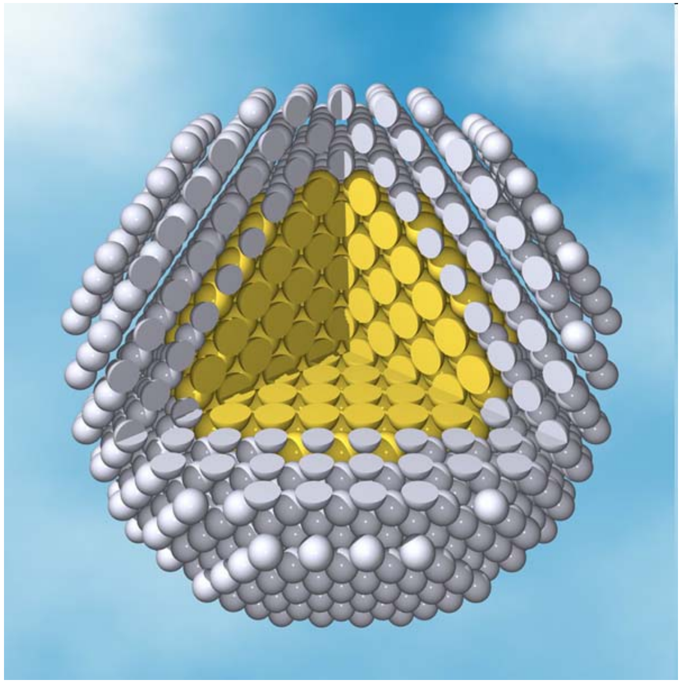
Where we are nowadays?

MolE, Aug 30, 2012

Physical chemistry is the particular case of electrochemistry for uncharged systems.

Prof. E.P.Ageev, MSU

- **Electrochemistry is a typical ‘core-shell’ science**
- **Shell: applications**
- **Shell: relative phenomena**
- **The former core: ionics**
- **Physics or chemistry?**
- **Core: electrified interface**
- **Core: electron transfer**



Shell: applications (where is high tech?)

Energy conversion (starting from Volta)
- primary batteries
- secondary batteries
- fuel cells

Electrolysis (starting from Davy and Faraday)
- industrial processes
- (organic) electrosynthesis
- crystal growth

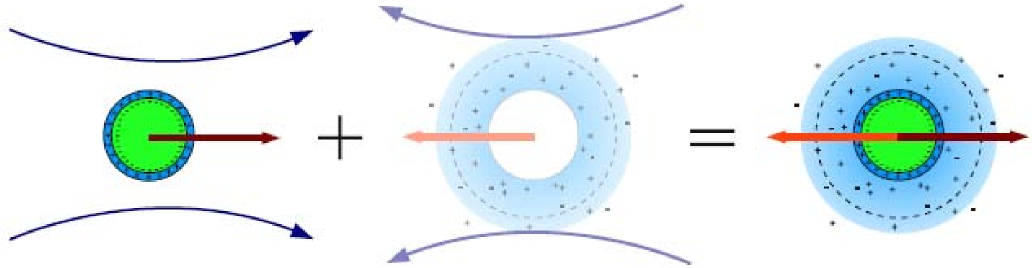
Surface finishing (starting from Jacoby)
- galvanics + "nanogalvanics"
- electropolishing, etching
- anodization, metal protection

Electroanalysis

Molecular electronics

Shell(s): relative areas

Electrokinetic phenomena

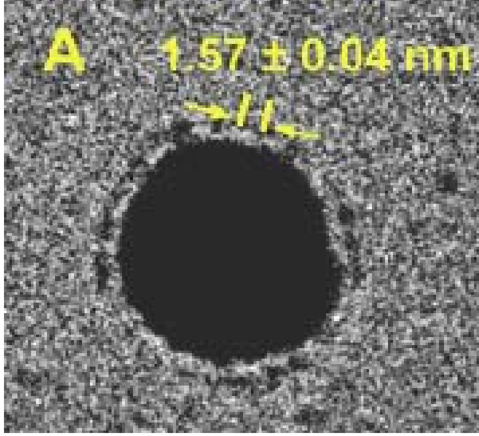


Solution redox chemistry

Liquid phase heterogeneous catalysis

etc

The former core: electrolyte solutions and molecular liquids ("ionics")

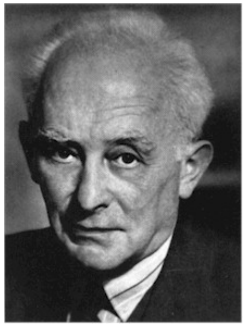


Basic concepts:

- Ionic atmosphere
- Solvation
- Dielectric relaxation

← Thermodynamics
+ other macroscopic observations

Peter Joseph William Debye



Max Born

Johannes Nicolaus Brønsted

Friedrich Wilhelm Ostwald

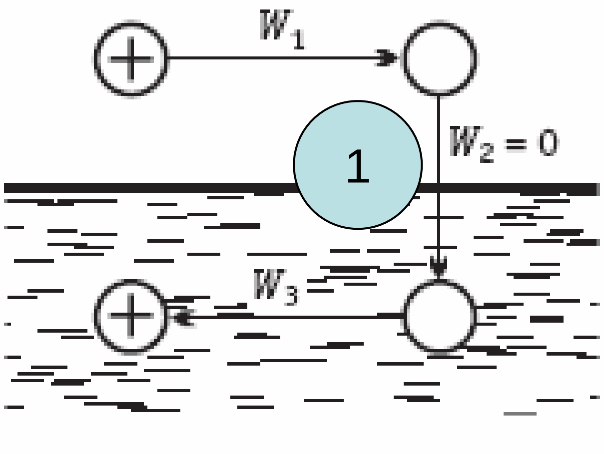
Svante August Arrhenius

Physical theory

Empty space for future

Correlations and empiric relationships

To explain what is ‘the model’



M.Born, *Z. Phys*. 1(1920)45

Solvation energy

$$\varphi = \frac{z_i e_0}{4\pi \varepsilon \varepsilon_0 r_i}$$

$$W = \int_0^{z_i e_0} \varphi \, dq = \frac{(z_i e_0)^2}{8\pi \varepsilon \varepsilon_0 r_i}$$

3

$$-\Delta G_s = N_A \frac{(z_i e_0)^2}{8\pi \varepsilon_0 r_i}\left(1 - \frac{1}{\varepsilon}\right)$$

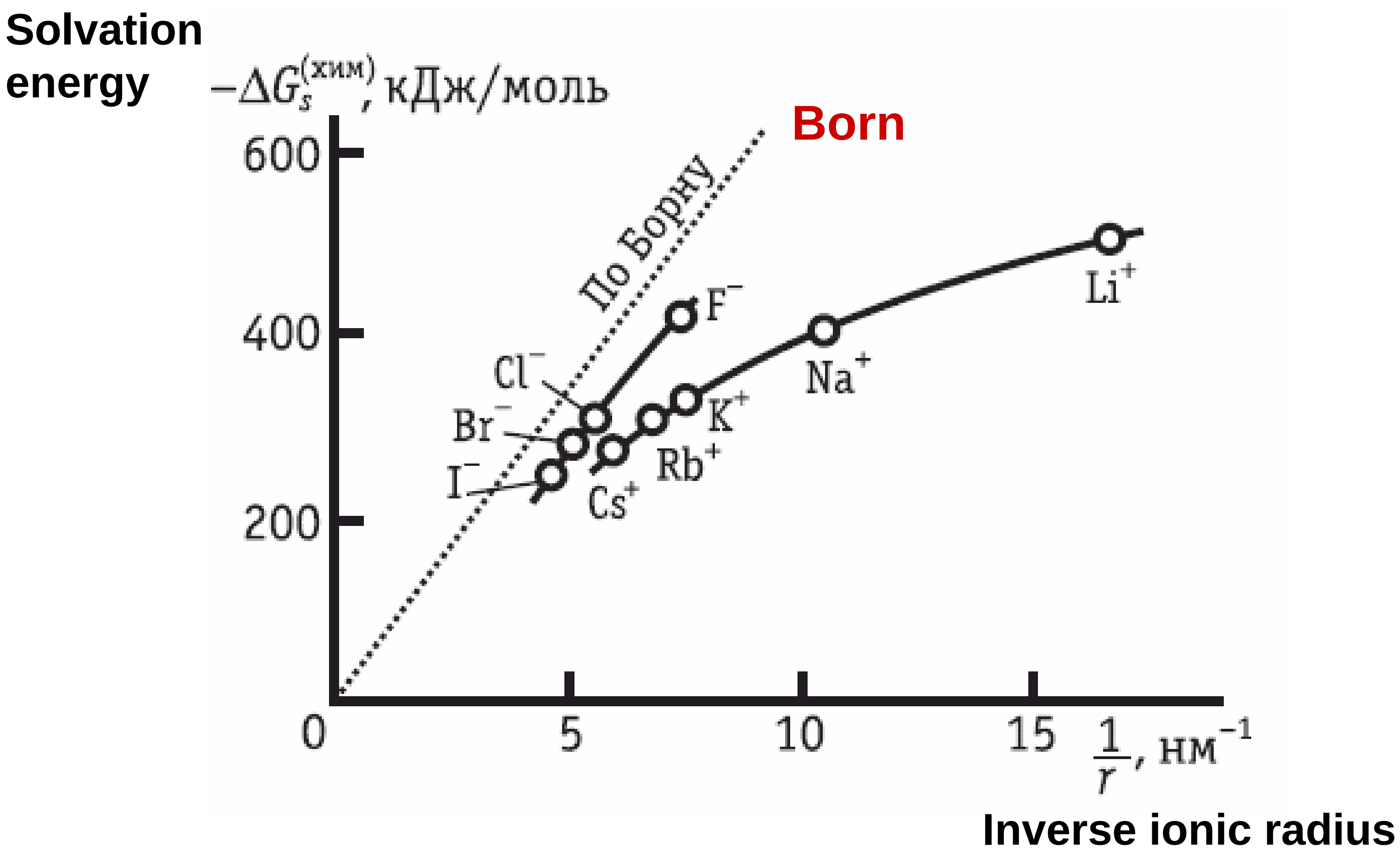
4

continuum

2

Differs from measurable value

Comparison with experiment: disagreement is more important than agreement



http://publish.aps.org/PACS/

Physics and Astronomy Classification Scheme® (PACS)

00 - General
10—The Physics of Elementary Particles and Fields
20—Nuclear Physics
30—Atomic and **Molecular** Physics
40—Electromagnetism, Optics, Acoustics, Heat Transfer, Classical Mechanics, and **Fluid Dynamics**
50—Physics of Gases, Plasmas, and **Electric Discharges**
60—Condensed Matter: **Structural**, Mechanical and Thermal Properties
70—Condensed Matter: **Electronic Structure, Electrical**, Magnetic, and Optical Properties
80—Interdisciplinary Physics and Related Areas of Science and Technology
90—Geophysics, Astronomy, and Astrophysics

81. Materials science
82. Physical chemistry and chemical physics
83. Rheology
84. Electronics; radiowave and microwave technology; direct energy conversion and storage
85. Electronic and magnetic devices; microelectronics
87. Biological and medical physics
88. Renewable energy resources and applications
89. Other areas of applied and interdisciplinary physics

81. Materials science

81.15.Pq Electrodeposition, electroplating
81.65.Kn Corrosion protection
(see also 82.45.Bb Corrosion and passivation in electrochemistry)
81.65.Ps Polishing, grinding, **surface finishing**
81.65.Rv Passivation ((see also 82.45.Bb)

82. Physical chemistry and chemical physics

82.45.-h **Electrochemistry and electrophoresis**

82.47.-a **Applied electrochemistry** (see also 88.30.G- Fuel cell systems, and 88.30.P- Types of fuel cells in renewable energy resources and applications)

88. Renewable energy resources and applications

88.30.-k Hydrogen **and fuel cell** technology (for hydrogen as a renewable alternative fuel, see 88.20.fn; for hydrogen as an alternative fuel in advanced vehicles, see 88.85.mh)

88.80.-q Energy delivery and storage

88.80.ff **Batteries** (for lithium-ion batteries, see 82.47.Aa; for lead-acid, nickel-metal hydride batteries, see 82.47.Cb; see also 88.85.jk, and 88.85.jm in advanced vehicles)

88.80.fh **Supercapacitors** (see also 82.47.Uv Electrochemical capacitors; supercapacitors)

Core: electrified interface

$$q = -F\sum_i (z_i \Gamma_i)$$

free charge

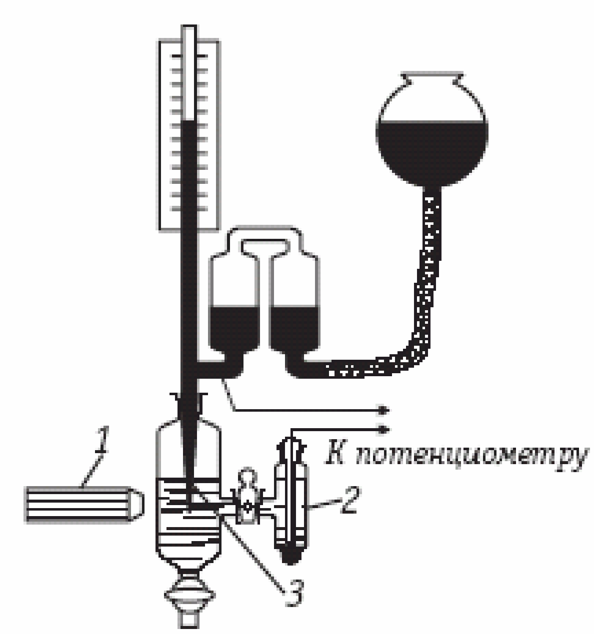
$$d\sigma = -\sum_i (\Gamma_i d\mu_i)$$

surface tension

Gibbs adsorption ('surface excess')

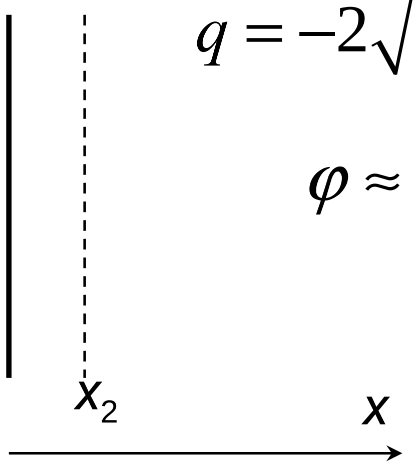
capacity $$C = \frac{dq}{dE}$$

Several measurable quantities (thermodynamic level)



$$q = -2\sqrt{2RT\varepsilon_0\varepsilon}\sqrt{c}\ \mathrm{sh}\left(\frac{F\varphi_2}{2RT}\right)$$

$$\varphi \approx \varphi_2 \exp(-\kappa x)$$



$$\sqrt{\frac{e_0^2}{\varepsilon\varepsilon_0 kT}\sum(n_{i0}z_i^2)}$$

Inverse radius of ionic atmosphere

Core: interfacial electron transfer

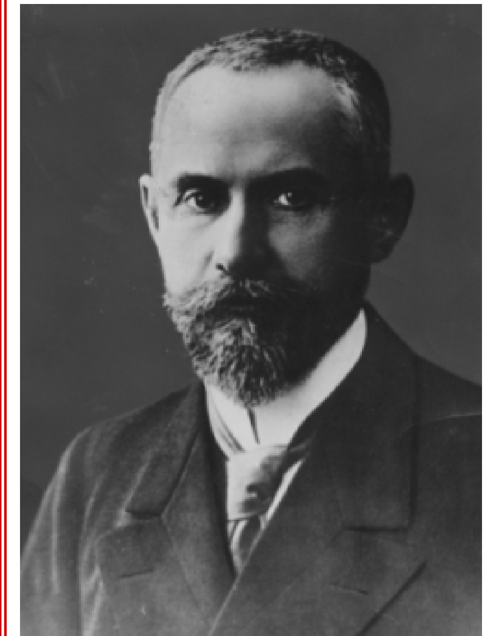
Über die Polarisation bei kathodischer Wasserstoffentwicklung.

Von

Julius Tafel.

(Mit 15 Figuren im Text.)

Z. Phys. Chem. 1905, Bd.50, S.641-712



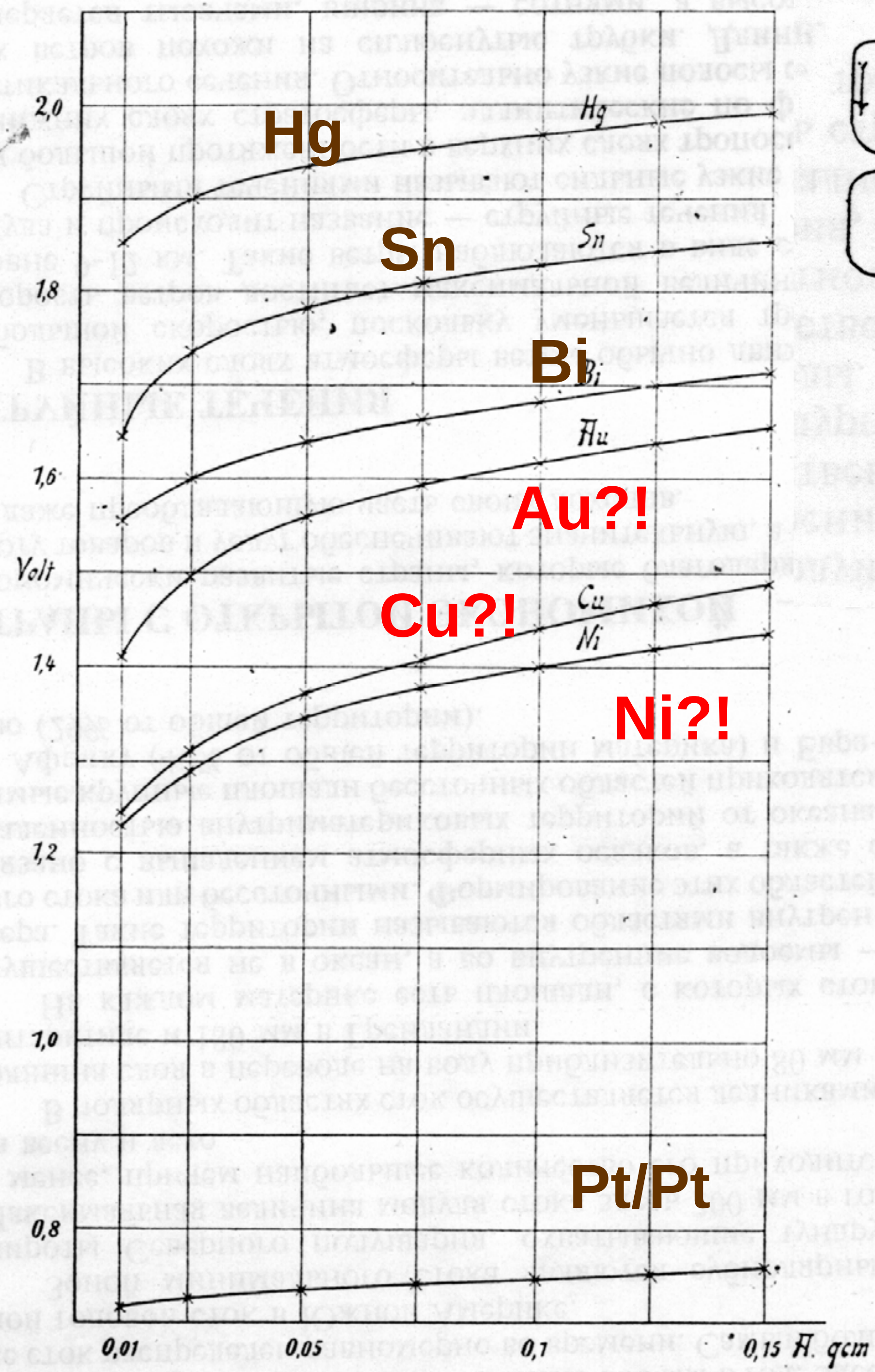
1862-1918

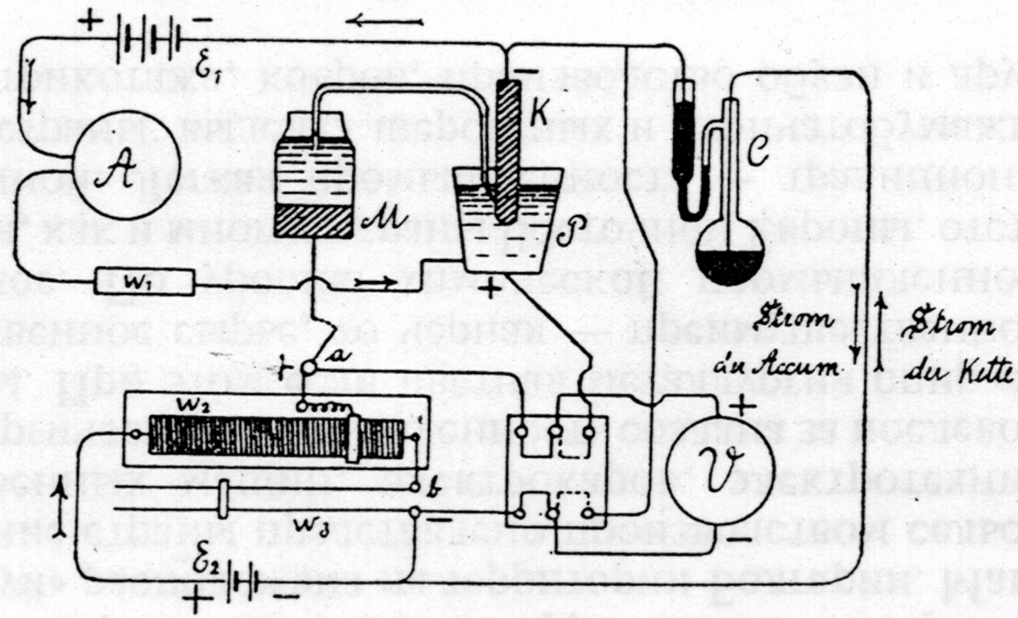
11. An Quecksilber (und annähernd auch an Blei und Kadmium) wurde für die Abhängigkeit des Kathodenpotentials ε von der Stromdichte J die Gleichung:

$$\varepsilon = a + b \log J$$

bestätigt gefunden, worin a und b Konstante sind. Der Wert für b fand sich bei 12° zu 0·107.

Empiric!





Interpretation was incorrect,

the data were approximate,

but Tafel equation is still widely used

because it is simple!

see K.Muller "Who was Tafel?" (J.Res. Inst. Catal., Hokkaido Univ., 17 (1969) 54

Can electron transfer be a limiting step?

R. Audubert, J. chim. phys., 21 (1924) 351

J.A.V. Butler, Trans. Faraday Soc., 19 (1924) 729, 734

T. Erdey-Gruz, M.Volmer, Z. phys. Chem. A, 150 (1930) 203

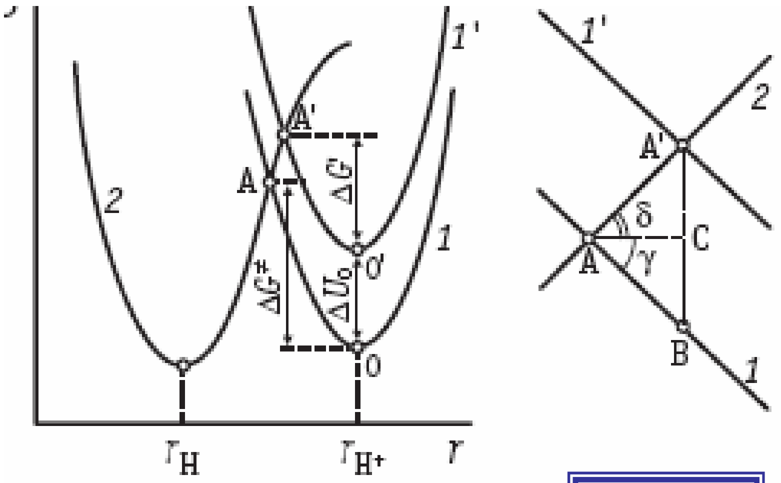
$$\eta = \mathrm{const} - \frac{RT}{\alpha F} \ln J$$

<u>**Overvoltage**</u> **(deviation from equilibrium potential)** → η

Current or current density → J

Phenomenological parameter (transfer coefficient) → α

Further consideration of the Tafel empiric constants



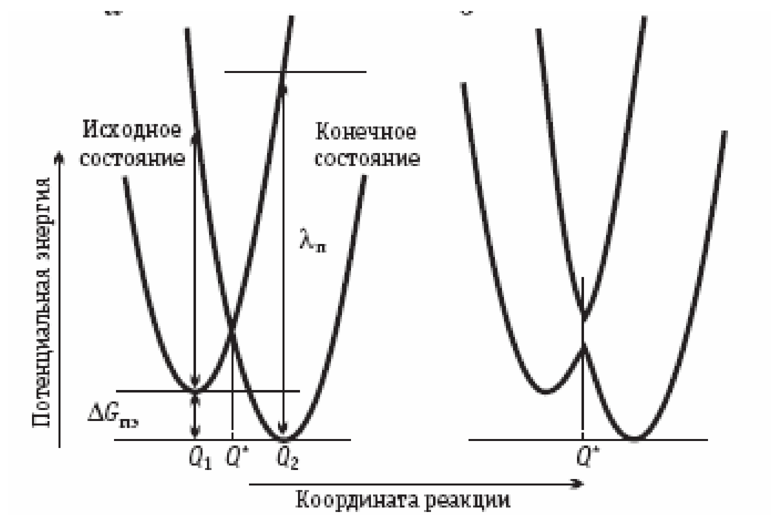
b

J. Horiuti, M. Polanyi,
Acta physicochim. URSS, 2 (1935) 505

a

J.A.V. Butler,
Proc. Royal Soc. 157A (1936) 423

P.I.Dolin, B.E.Ershler, A.N.Frumkin,
Acta physicochim. URSS, 13 (1940) 779



↓

The notion 'exchange current density'

Butler-Volmer and Tafel equations

$$i = i_0 \left\{ \exp\left[\frac{\alpha n F \eta}{RT}\right] - \exp\left[-\frac{(1-\alpha) n F \eta}{RT}\right] \right\}$$

$$\eta \gg RT/nF \quad \Longrightarrow \quad \eta \approx -\frac{RT}{\alpha n F}\ln i_0 + \frac{RT}{\alpha n F}\ln i$$

$$a = -\frac{RT}{\alpha n F}\ln i_0 \qquad b = \frac{2{,}3RT}{\alpha n F}$$

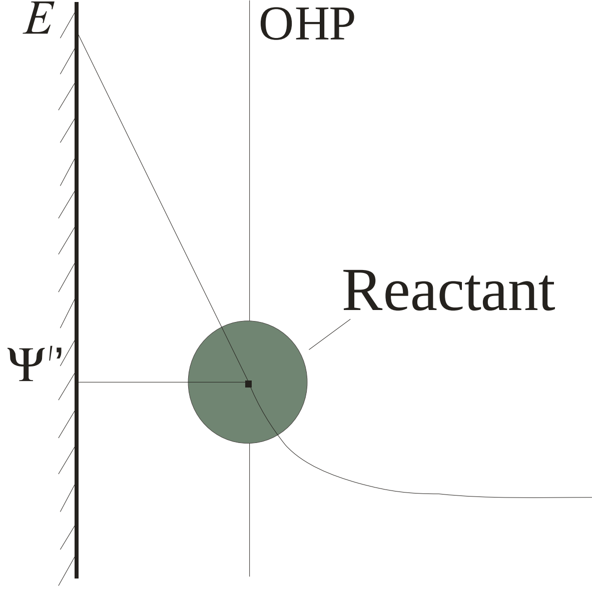
$$\eta = a + b \lg i$$

*** Explains temperature dependence of Tafel parameters**

Frumkin and Bakh, 1934
In Karpov Inst

A.N.Frumkin:

Z. phys. Chem. A 160 (1932) 116; 164 (1933) 121



$$\varphi + \varsigma = \frac{2RT}{F} \ln \left[H^+ \right]_s - \frac{2RT}{F} \ln i + const$$

Electrostatic electrode-reactant interaction

*** Explains non-linear and <u>non-monotonous(!)</u> Tafel plots**

*** Explains the dependence on supporting electrolyte concentration**

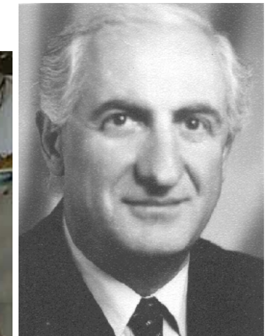
Theory: α(η)

R.Gurney,Proc. Royal Soc. A, 134 (1931)137

Rudolf Marcus

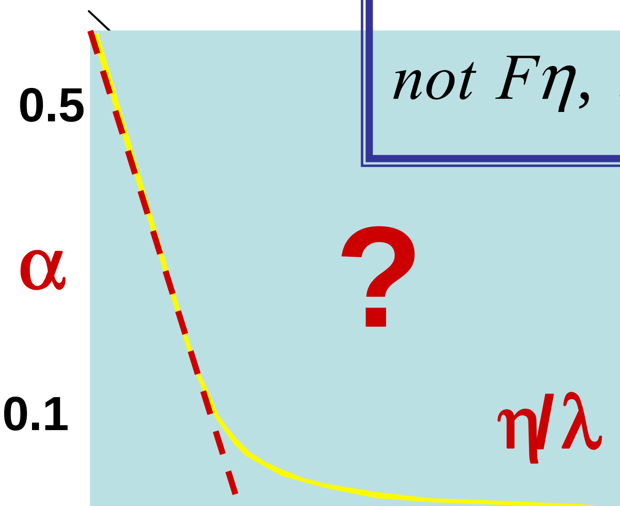
Chizmadzhev

Kuznetsov



Dogonadze

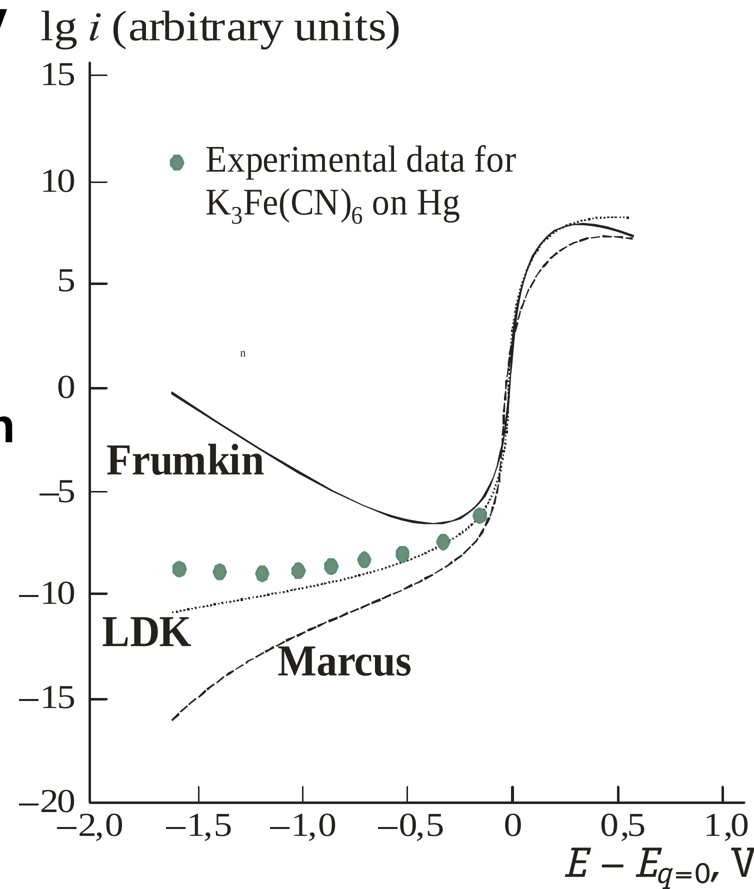
Levich

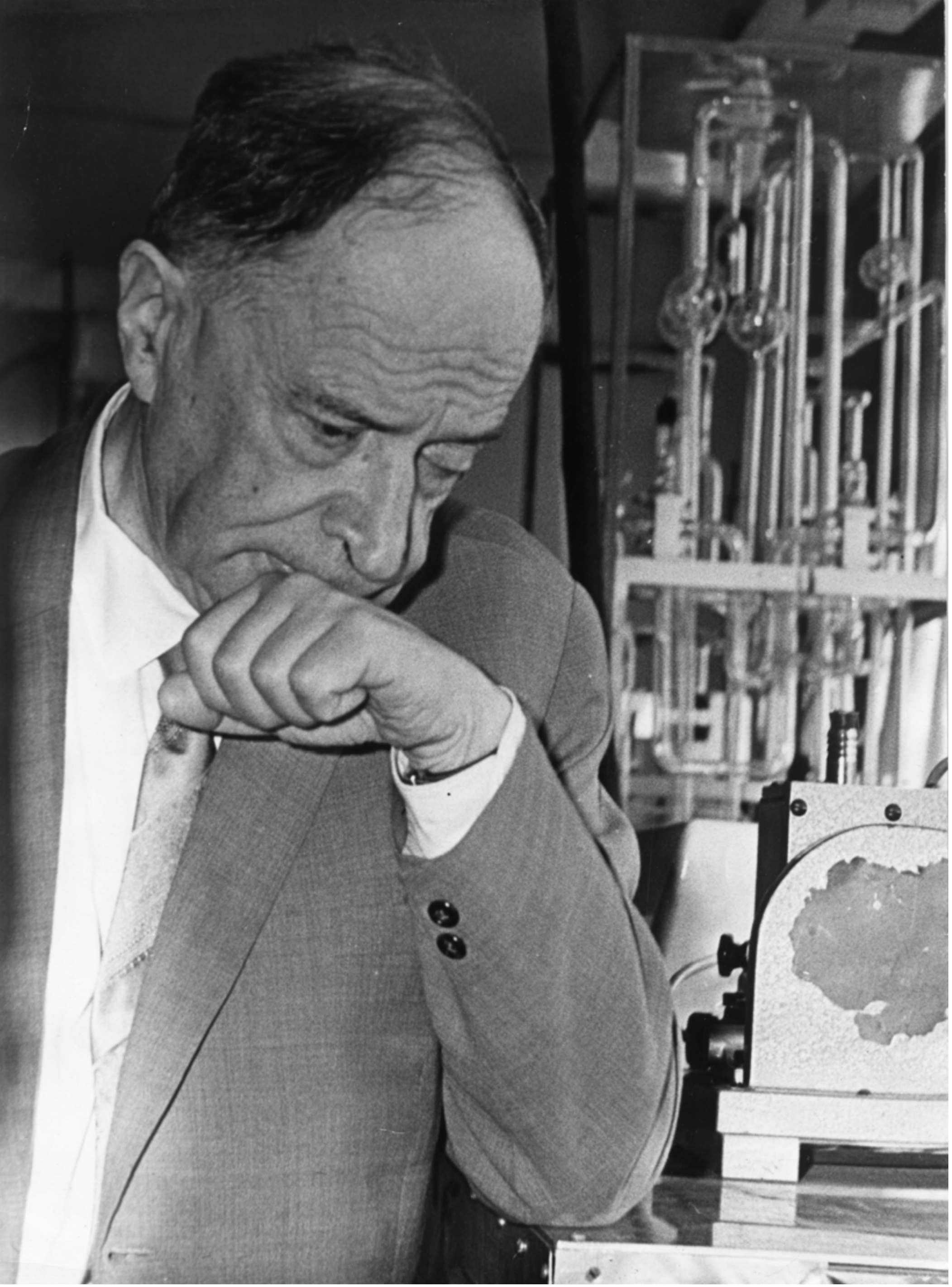


$$not\ F\eta,\ but\ \frac{(-F\eta+\lambda)^2}{4\lambda}$$

Reorganization energy

$$\lambda_p = N_A \frac{(e_0)^2}{8\pi\varepsilon_0}\left(\frac{1}{\varepsilon_{on}}-\frac{1}{\varepsilon}\right)\left(\frac{1}{a}-\frac{1}{2R}\right)$$





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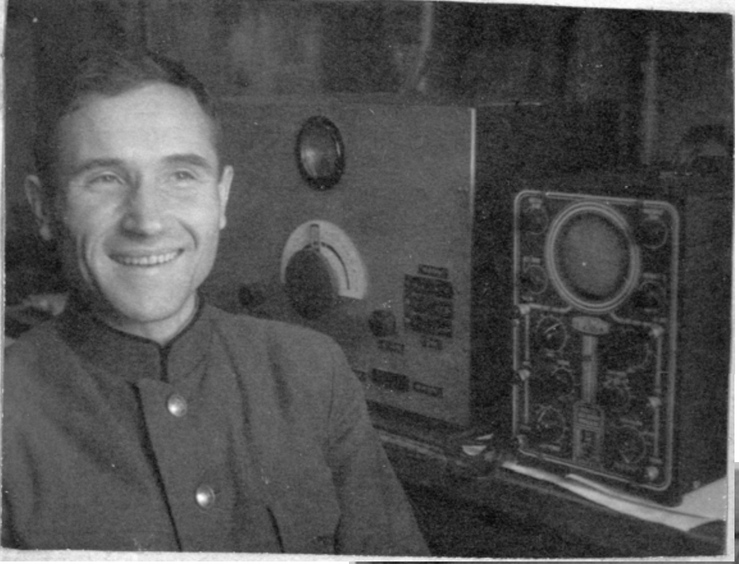
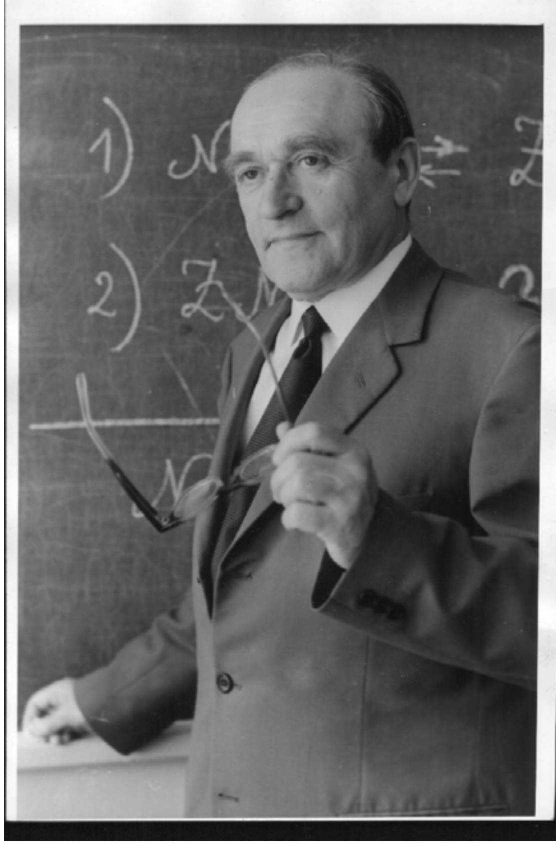


Petr Dolin

Boris Ershler



Mikhail Temkin

‘Electrochemical names’, still widely known

It is rather important to find new head for an old hat, so

You are kindly invited to visit www.elch.chem.msu.ru to get

- **some original Frumkin's and Levich's papers;**
- **current papers from our Dept,**

and also to ask any questions related to electrochemical aspects of your research.

Rare classical books in electrochemistry are available at the Dept, as well as some modern textbooks.

tsir@elch.chem.msu.ru