Александр Наумович
и
основные этапы развития теории адсорбции органических соединений

Б.Б.Дамаскин

INTERNATIONAL SOCIETY OF ELECTROCHEMISTRY

This is to certify that

Boris B. Damaskin

has been awarded the Frumkin Memorial Medal 2005
for his outstanding contributions to the quantitative
understanding of the electrical double layer at
electrode/electrolyte interfaces and the effects of
adsorption on its properties.

Juan M. Feliu
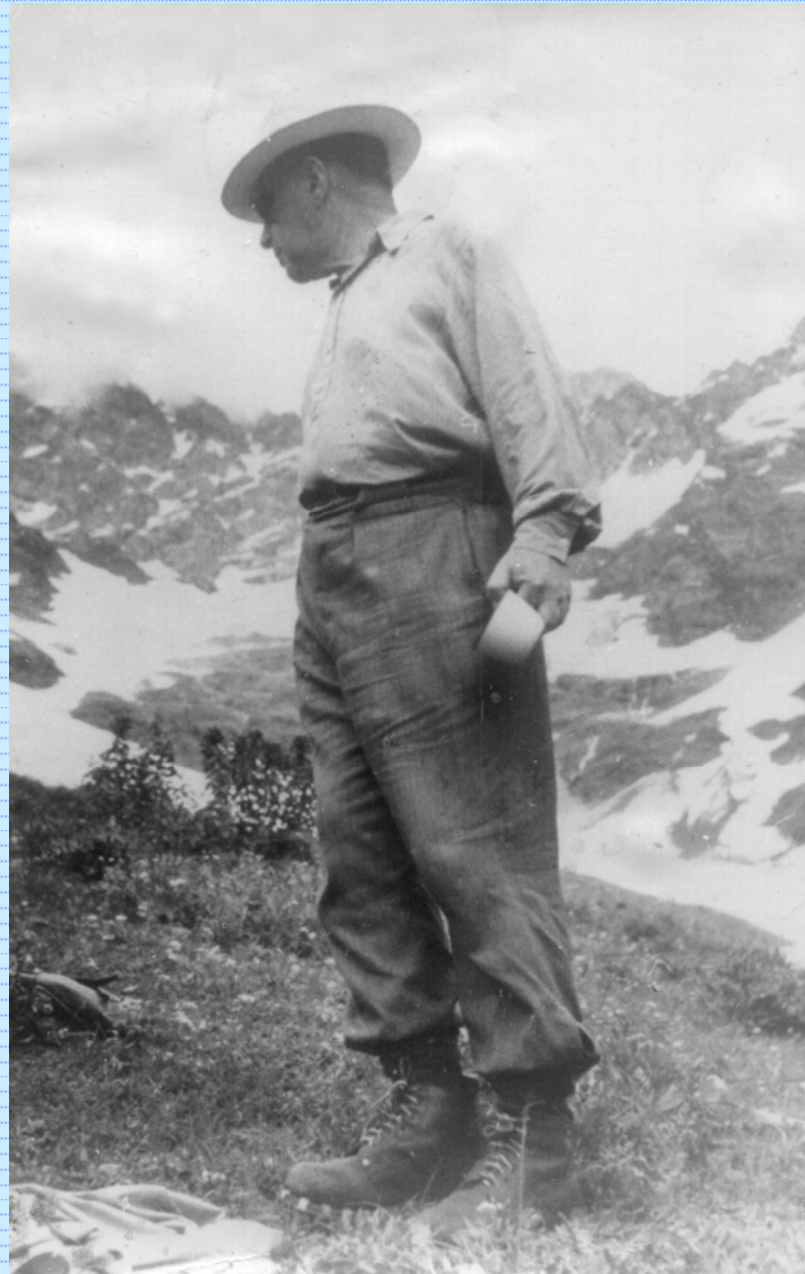President of ISE

1952

Δt = 37 years

**My first meeting
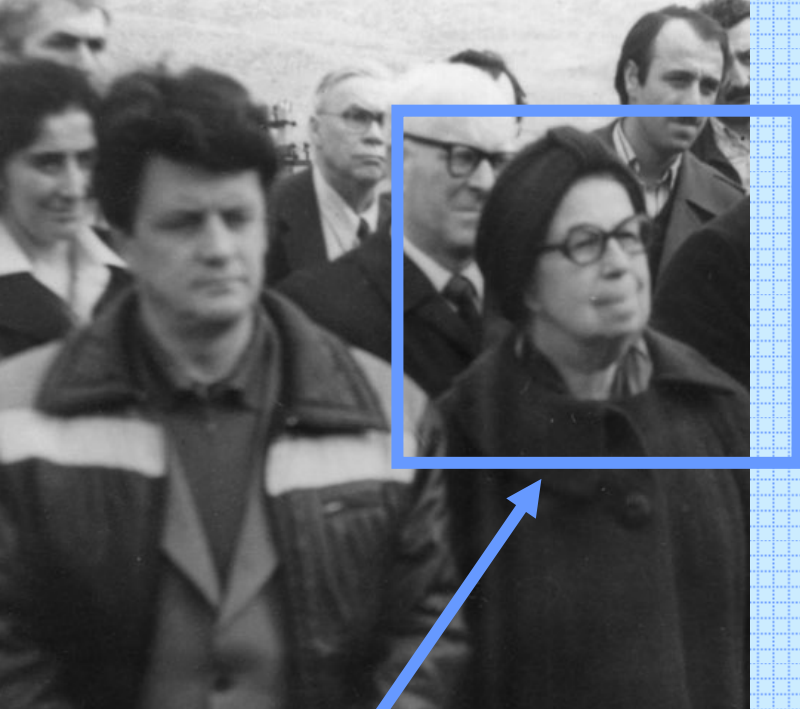with A.N.Frumkin**

My first teacher: Dr. Ol'ga I. Vorob'eva

1951

My first superviser:
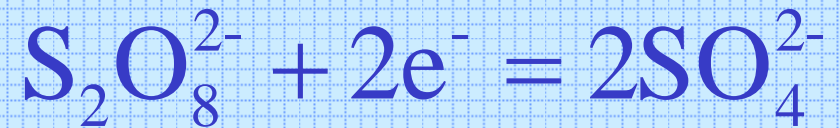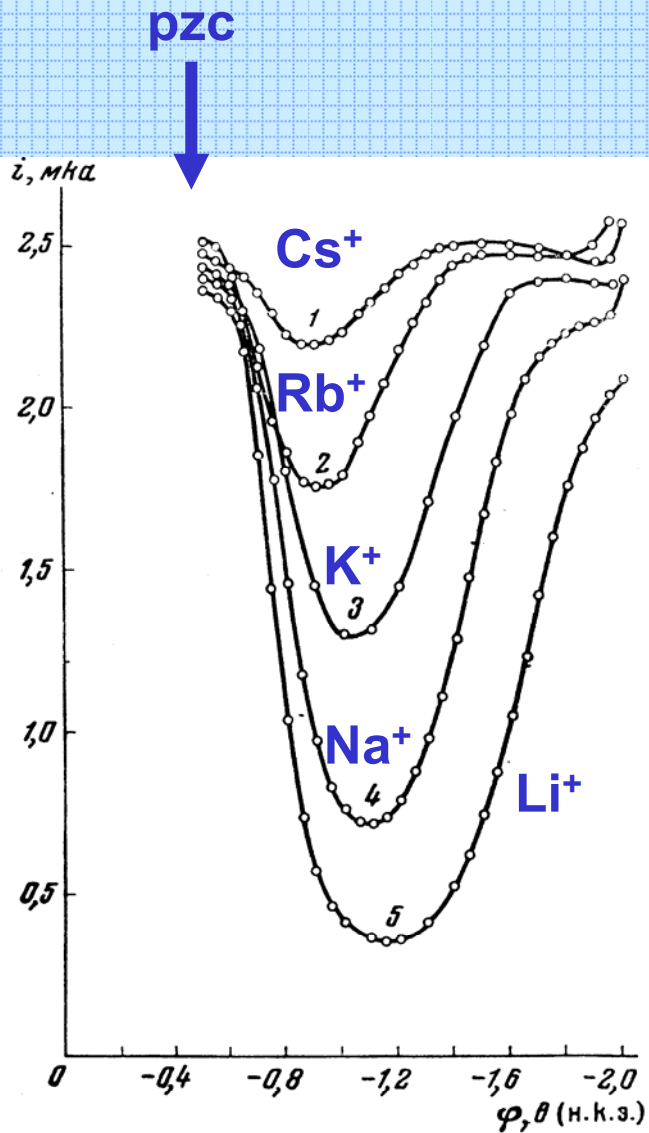## Prof. Nina V.Nikolaeva-Fedorovich

Prof. Tatyana A. Kryukova

1953

"Белый корпус"

pzc

Cs⁺
Rb⁺
K⁺
Na⁺
Li⁺

Unfortunately I had no Fr⁺…

My first topic, already in a new building of the Faculty of Chemistry :

$$S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$$

Adsorption of inorganic cations

**Peculiarities of
weak ionic adsorption**

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Three famous soviet scientists answer the student's question:

Mandel'shtam: Sorry, I gave you poor explanation, I shall propose something more simple and transparent;

Landau: If you are such a fool, I can repeat once again;

Frumkin: I do not understand how one can not understand it!
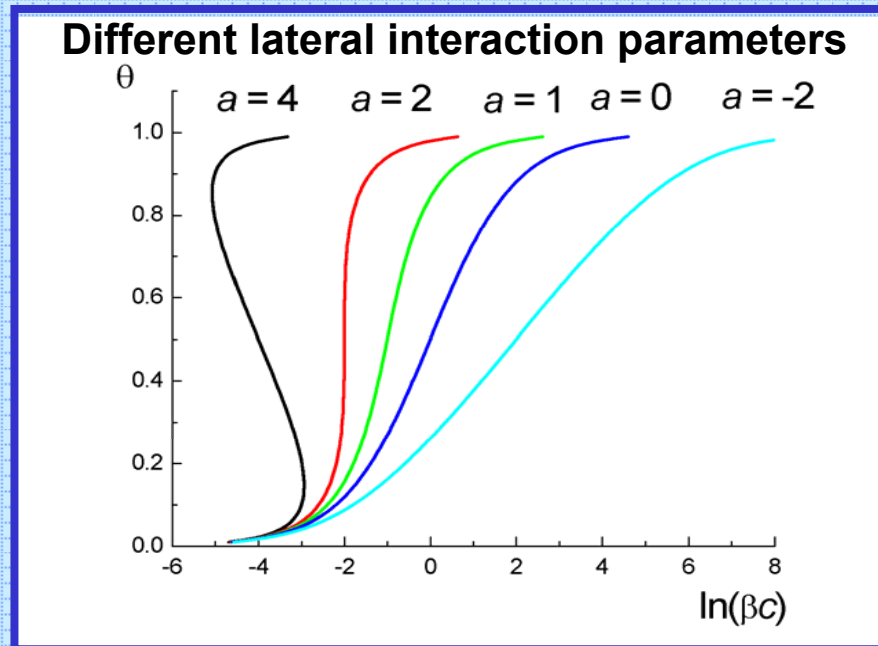
· Frumkin adsorption isotherm

$$\beta c = \frac{\theta}{1-\theta}\exp(-2a\theta) \qquad \textbf{(1)}$$

c - **bulk concentration of organic substance;**
θ- **coverage of the electrode surface with organic substance;**
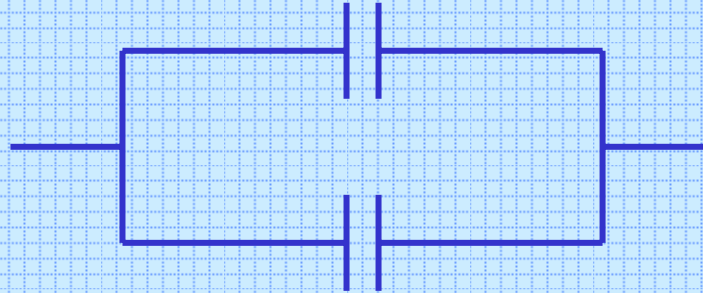β- **adsorption equilibrium constant**
a - **parameter of lateral interaction**

Different lateral interaction parameters

Model of two parallel capacitors

- **Scheme**

- **Electrode charge density**

$$\sigma = \sigma_0(1 - \theta) + C_1\theta(E_0 - E_N) \quad \textbf{(2)}$$

E_0 – electrode potential related to potential of zero charge (PZC) in the surface-inactive electrolyte;

E_N – shift of PZC when switching from $\theta = 0$ to $\theta = 1$;

$$\sigma_0 = \int\limits_0^{E_0} C_0 dE$$

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Model of two parallel capacitors

· **Approximate Gibbs equation:**

$$d\gamma = -\sigma dE - RT\Gamma d\ln c \qquad \textbf{(3)}$$

· **Expression for** $\ln\beta$ **as a function of** E_0 **:**

$$\ln\beta = \ln\beta_0 - \frac{\Delta\gamma_0 + C_1 E_0 (E_N - E_0/2)}{RT\Gamma_m} \qquad \textbf{(4)}$$

$$\Delta\gamma_0 = \int_0^{E_0} \sigma_0 dE$$

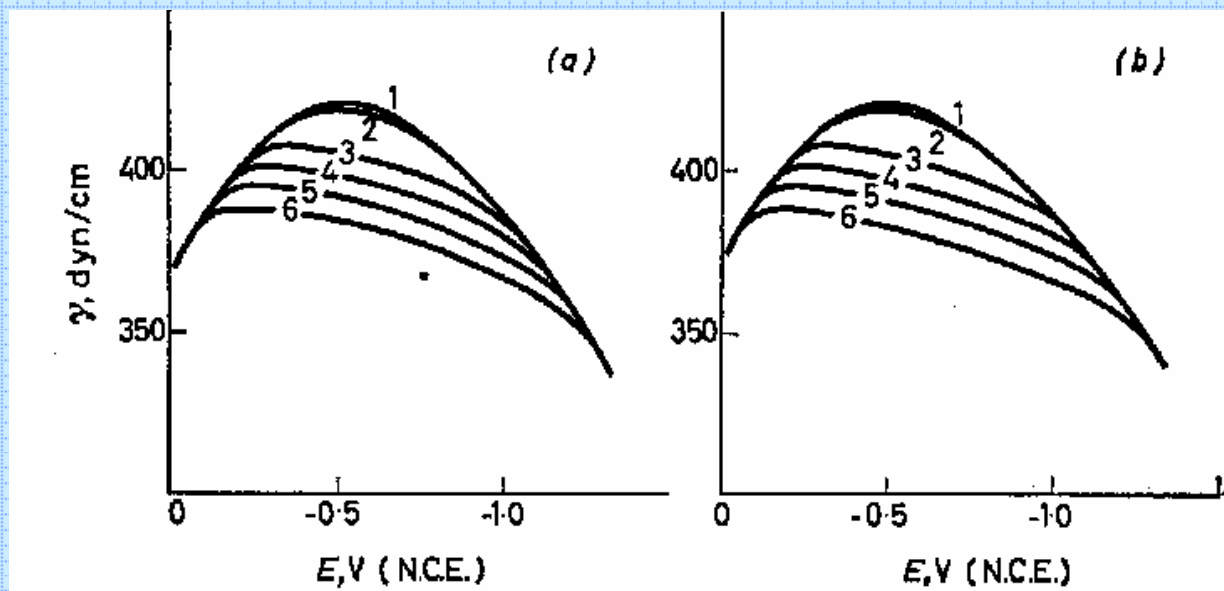*decrease of surface tension in supporting solution caused by deviation of potential from PZC*

• **Decrease of surface tension due to adsorption of organic molecules at** E_0 **= const:**

$$\Delta\gamma = -RT\Gamma_m[\ln(1-\theta) + a\theta^2] \qquad \textbf{(5)}$$

Electrocapillary curves of a mercury electrode in   1M NaCl solutions containing *tret-pentanol* additives:

1 - *0*; 2 - *0.01*; 3 -*0.05*; 4 - *0.1*; 5 - *0.2*; 6 - *0.4* M

Experimental data   Calculated

Starting from 1960

Frumkin's theory for interpreting differential capacity curves in solutions of aliphatic compounds

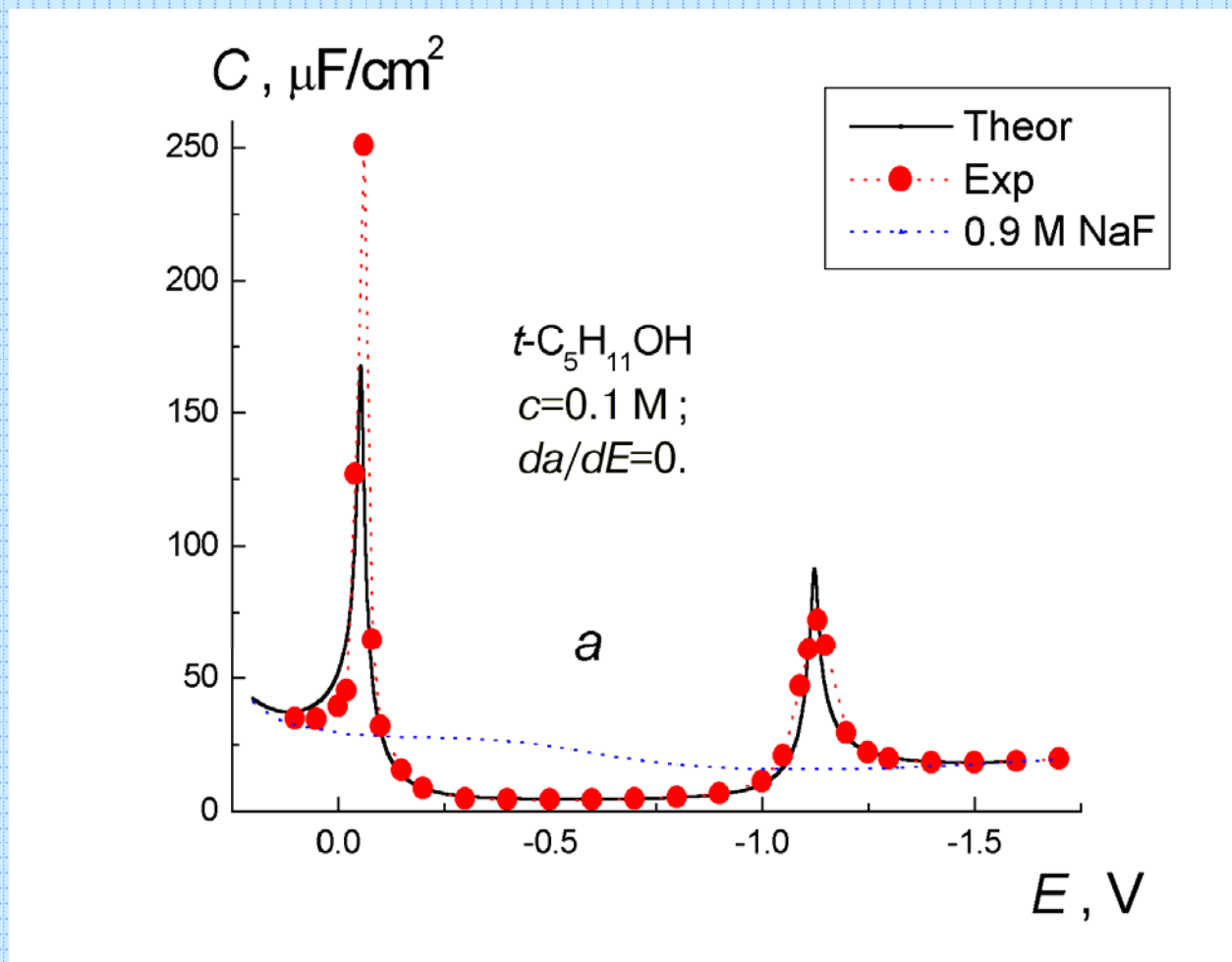**Five adsorption parameters (β_0, a , Γ_m , C_1 , E_N)**

- C_0,E_0**-curve in surface-inactive electrolyte solution**
- **Equations shown above**

expression for equilibrium differential capacity can be derived:

$$C = C_0(1-\theta) + C_1\theta + \frac{[\sigma_0 + C_1(E_N - E_0)]^2\,\theta(1-\theta)}{RT\Gamma_m[1-2a\theta(1-\theta)]} \quad \textbf{(6)}$$

Experimental and simulated differential capacity curves, *a*=const

Lateral interaction parameter ("attraction coefficient") vs. electrode potential
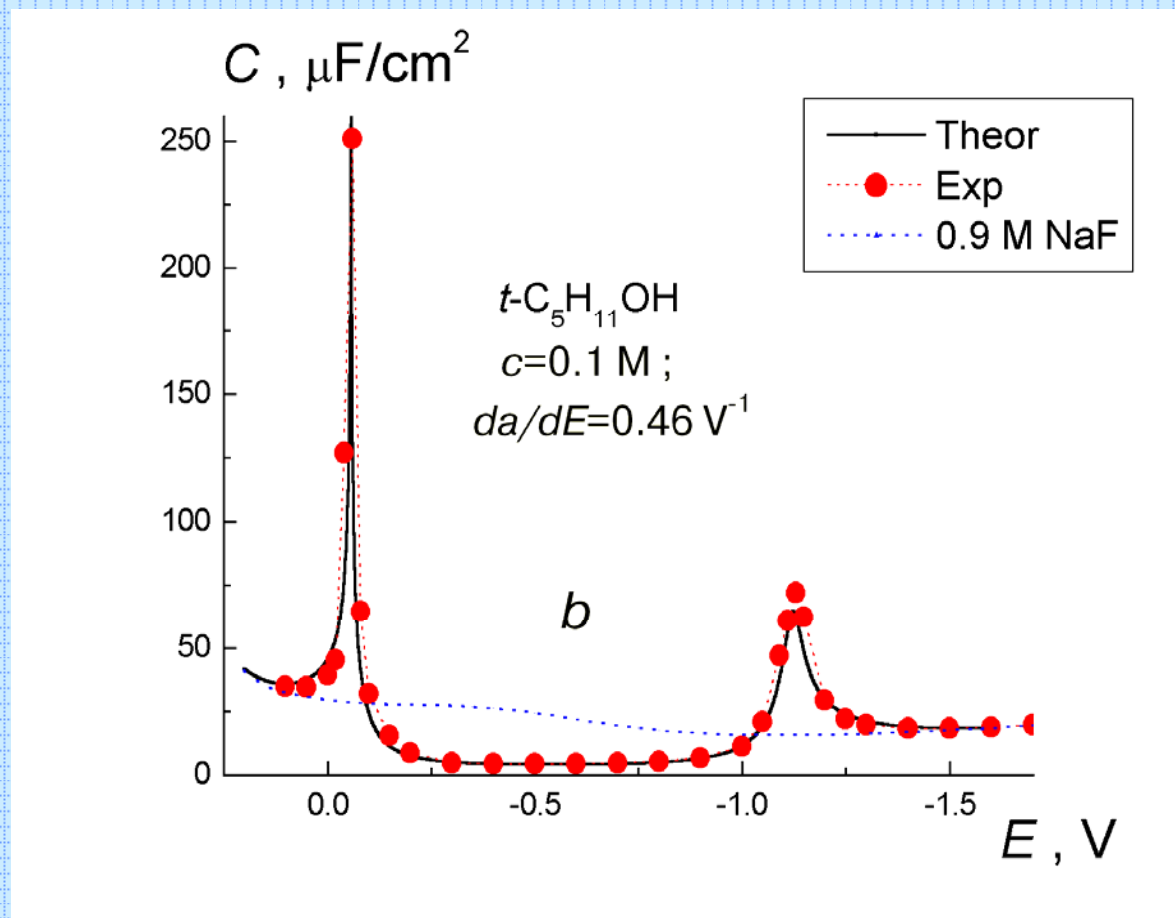
For an arbitrary dependence of a on E:

$$\ln \beta = \ln \beta_0 - \frac{\Delta\gamma_0 + C_1 E_0 (E_N - E_0/2)}{RT\Gamma_m} + (a_0 - a) \quad \textbf{(7)}$$

$$C = C_0(1-\theta) + C_1\theta - RT\Gamma_m a"\theta(1-\theta) + \frac{[\sigma_0 + C_1(E_N - E_0) + RT\Gamma_m a'(1-2\theta)]^2 \theta(1-\theta)}{RT\Gamma_m[1 - 2a\theta(1-\theta)]}$$

$$\textbf{(8)}$$

where $a_0 = a(E_0 = 0)$; $a' = da/dE$; $a'' = d^2a/dE^2$

Experimental and simulated differential capacity curves: linear a, E - dependence

Beyond the model of two parallel capacitors

- **Parsons' model**

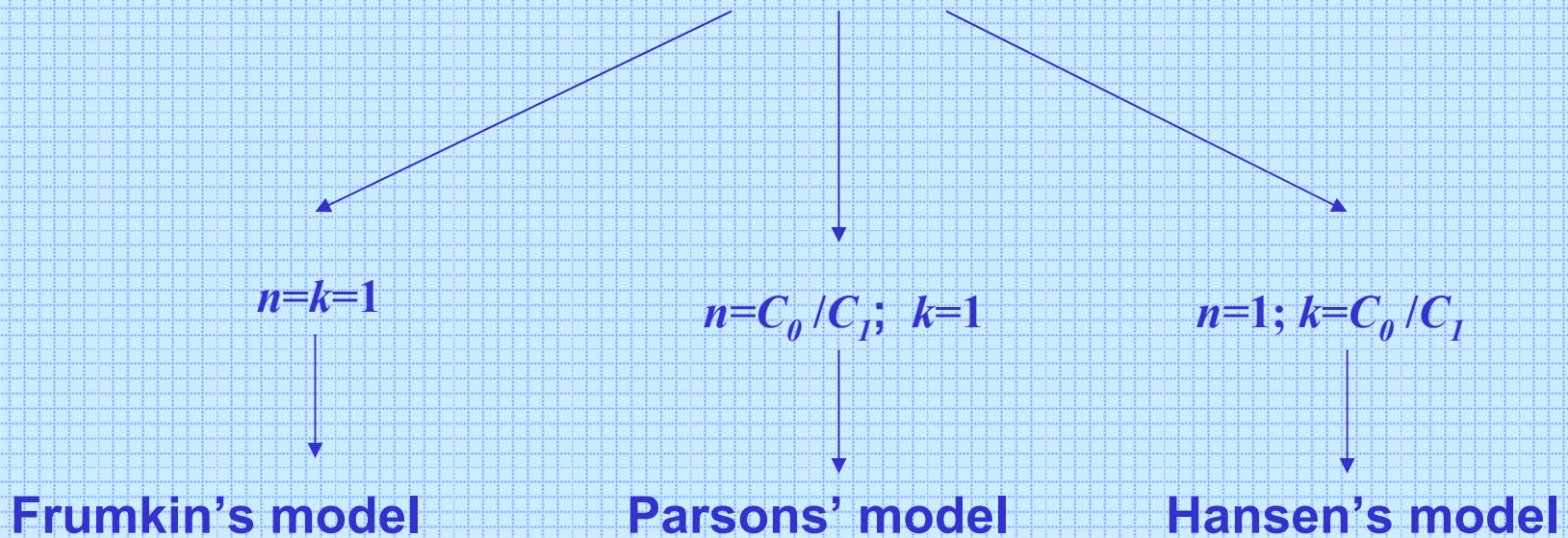$$E_0 = \frac{\sigma}{C_0}(1-\theta) + \left(E_N + \frac{\sigma}{C_1}\right)\theta \qquad \textbf{(9)}$$

- **Hansen's model**

$$\sigma = (E_0 - E_N\theta)[C_0(1-\theta) + C_1\theta] \qquad \textbf{(10)}$$

Generalization

$$\sigma = \frac{[C_0(1-\theta) + nC_1\theta]E_0 - nC_1E_N[k(1-\theta) + \theta]\theta}{1 + n\theta - \theta} \quad \textbf{(11)}$$

$n=k=1$

$n=C_0/C_1; \ k=1$

$n=1; \ k=C_0/C_1$

Frumkin's model

Parsons' model

Hansen's model

Coadsorption of two solution components. Combination of two mixed Frumkin isotherms
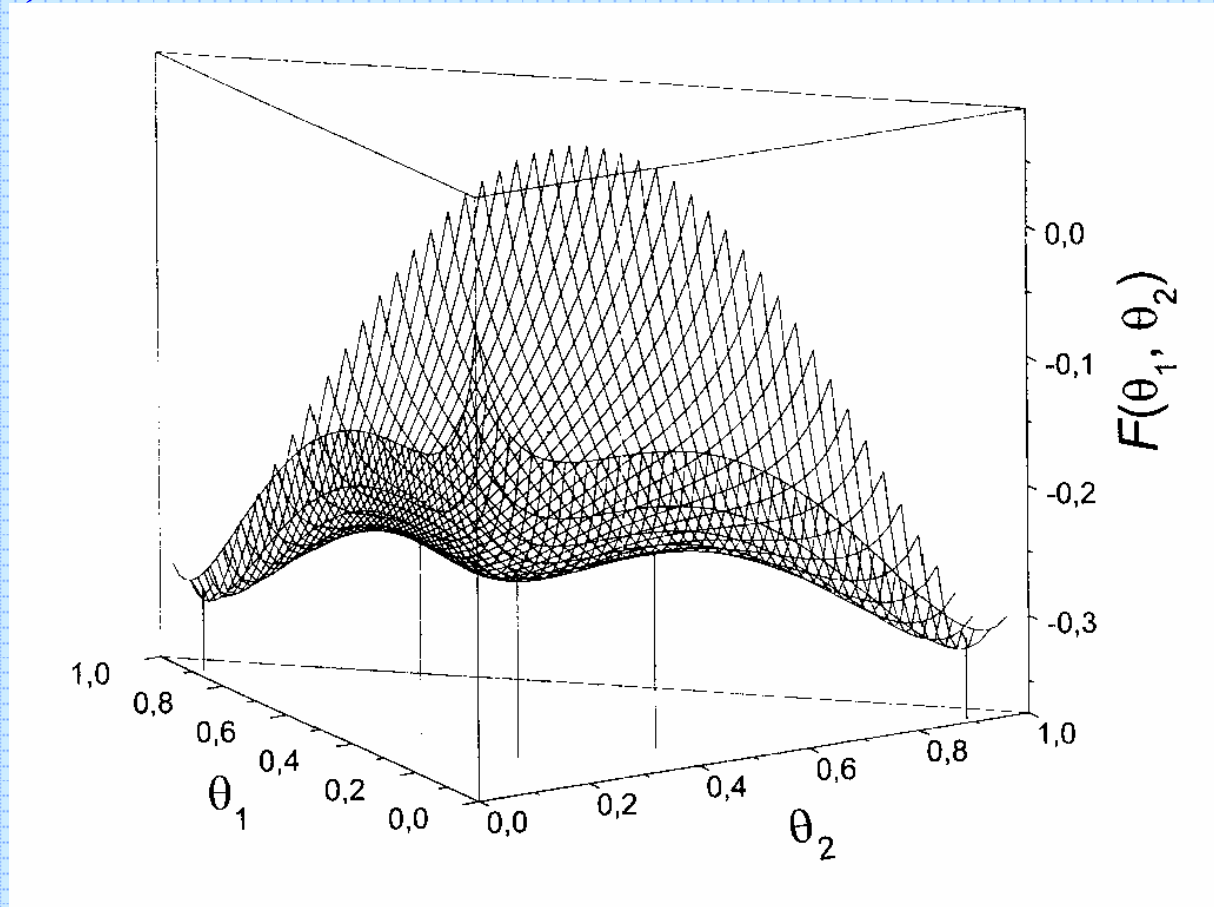
$$\sigma = \sigma_0(1 - \theta_1 - \theta_2) + C_1\theta_1(E_0 - E_{N1}) + C_2\theta_2(E_0 - E_{N2}) \qquad \textbf{(12)}$$

$$\beta_1 c_1 = \frac{\theta_1}{n_1(1 - \theta_1 - \theta_2)^{n_1}} \exp\left(-2n_1 a_{11}\theta_1 - 2n_1 a_{12}\theta_2\right) \qquad \textbf{(13a)}$$

$$\beta_2 c_2 = \frac{\theta_2}{n_2(1 - \theta_1 - \theta_2)^{n_2}} \exp\left(-2n_2 a_{22}\theta_2 - 2n_2 a_{12}\theta_1\right) \qquad \textbf{(13b)}$$

One of the simplest equations in my life

$$F(\theta_1,\theta_2) = \frac{\Delta G}{RT\Gamma_m} = -a_{11}\theta_1^2 - a_{22}\theta_2^2 - 2a_{12}\theta_1\theta_2 + \frac{\theta_1}{n_1}\ln\left(\frac{\theta_1}{n_1\beta_1 c_1}\right) + \quad \textbf{(14)}$$

$$\frac{\theta_2}{n_2}\ln\left(\frac{\theta_2}{n_2\beta_2 c_2}\right) + (1-\theta_1-\theta_2)\ln(1-\theta_1-\theta_2) + \frac{\theta_1(n_1-1)}{n_1} + \frac{\theta_2(n_2-1)}{n_2}$$

$$p_1 = \left(\frac{\partial^2 F}{\partial \theta_1^2} \right)_{\theta_2} = \frac{1}{n_1 \theta_1} + \frac{1}{1 - \theta_1 - \theta_2} - 2a_{11} \quad , \qquad \textbf{(15a)}$$

$$p_2 = \left(\frac{\partial^2 F}{\partial \theta_2^2} \right)_{\theta_1} = \frac{1}{n_2 \theta_2} + \frac{1}{1 - \theta_1 - \theta_2} - 2a_{22} \quad . \qquad \textbf{(15b)}$$
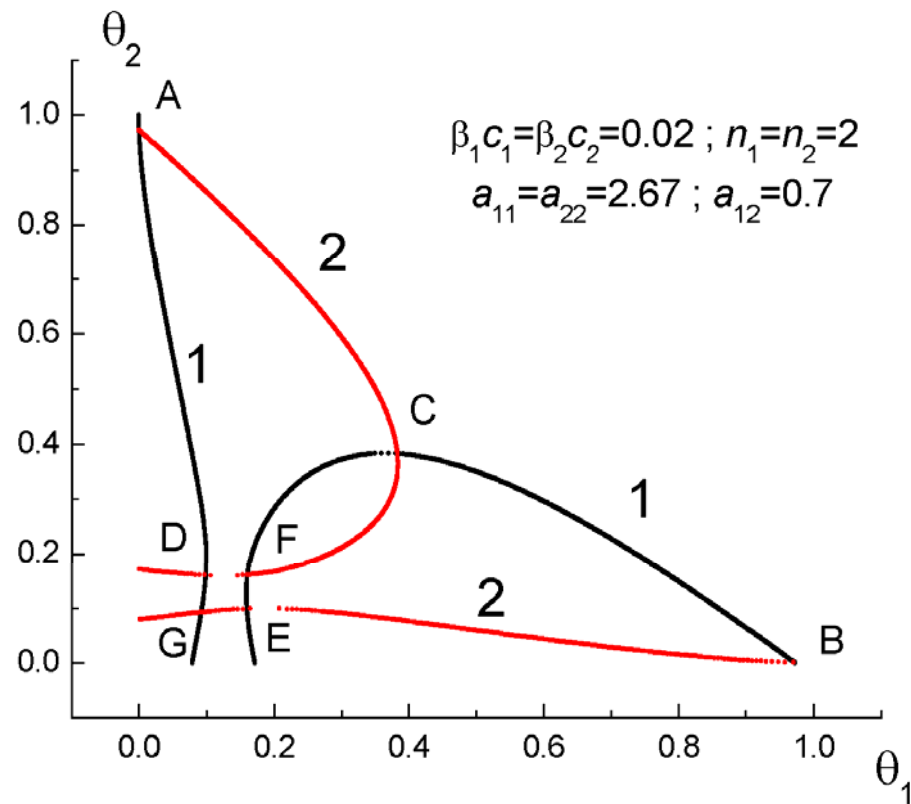
Conditions of extremum:

$$p_1 > 0, \, p_2 > 0 \quad - \quad \text{minimum}$$

$$p_1 < 0, \, p_2 < 0 \quad - \quad \text{maximum}$$

$$p_1 > 0, \, p_2 < 0 \quad \text{or} \quad p_1 < 0, \, p_2 > 0 : \text{saddle point}$$

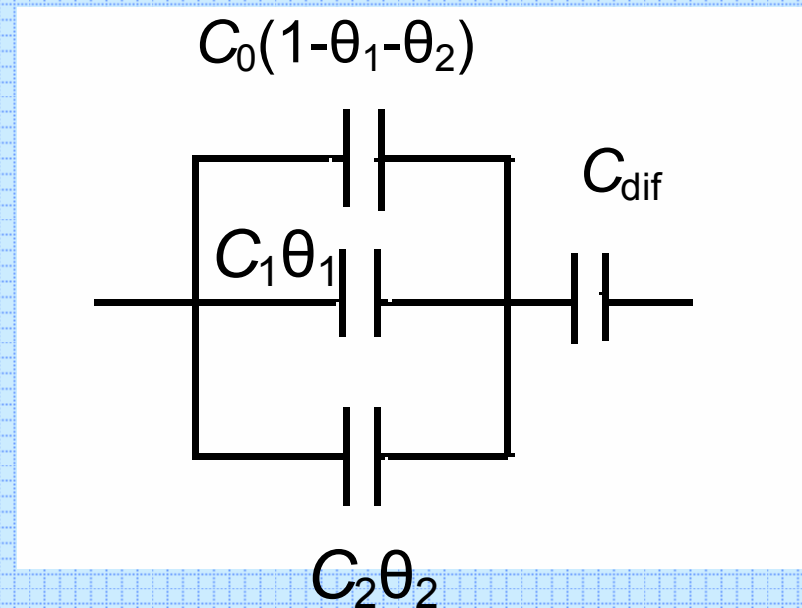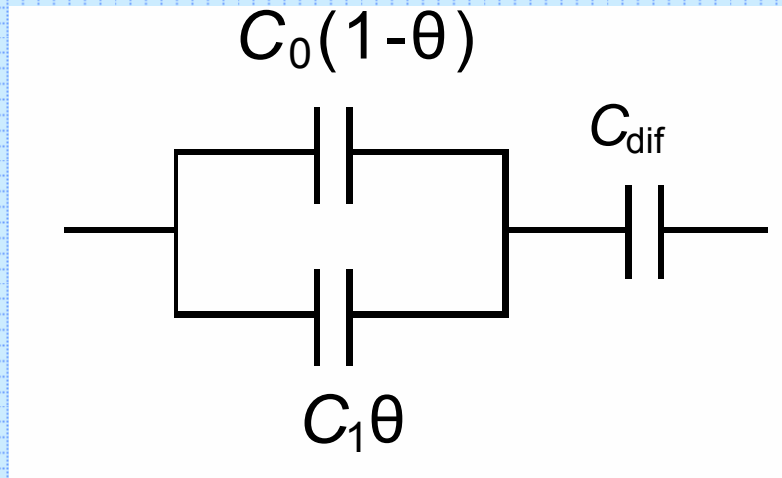# θ_2, θ_1 relartionships corresponding to two equations of mixed Frumkin isotherms

Models of two and three parallel capacitors taking into account diffuse part of the electrical double layer

$C_0(1-\theta)$

C_{dif}

$C_1\theta$

$C_0(1-\theta_1-\theta_2)$

C_{dif}

$C_1\theta_1$

$C_2\theta_2$

Further development of the theory of adsorption of ions and organic molecules on electrodes suggests transition to molecular models.
However, I would like to point out that conclusions of molecular models should not contradict phenomenological models I just talked about.

The longer I live the more I see that I am never wrong about anything, and that all the pains that I have so humbly taken to verify my notions have only wasted my time.

George Bernard Shaw