



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



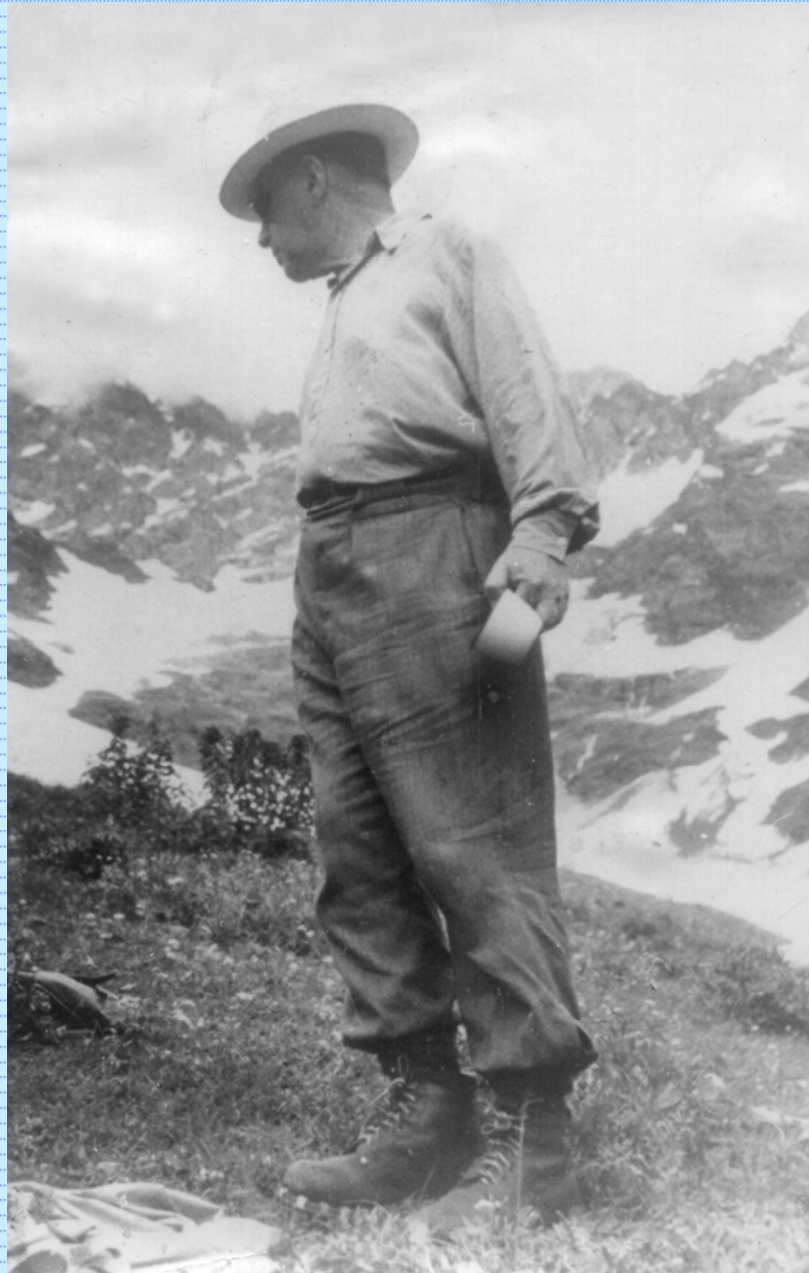
$\Delta t = 37$ years

My first meeting
with A.N.Frumkin

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

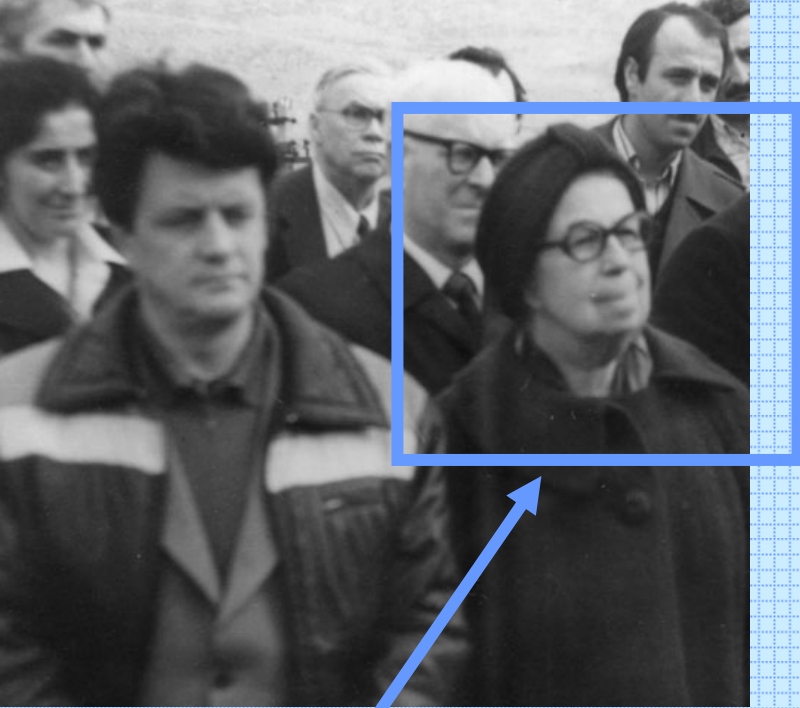


1951



**My first supervisor:
Prof. Nina V.Nikolaeva-Fedorovich**





Prof. Tatyana A. Kryukova



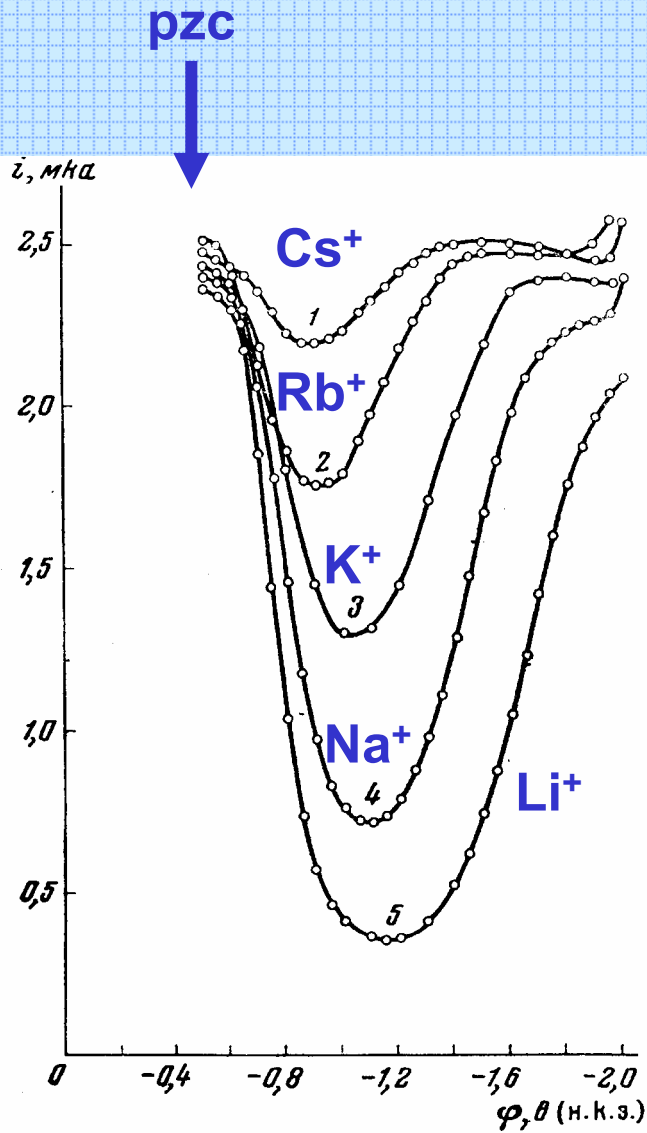
1953



"Белый корпус"



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



Adsorption of inorganic cations

Peculiarities of weak ionic adsorption

Unfortunately I had no Fr^+ ...

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!

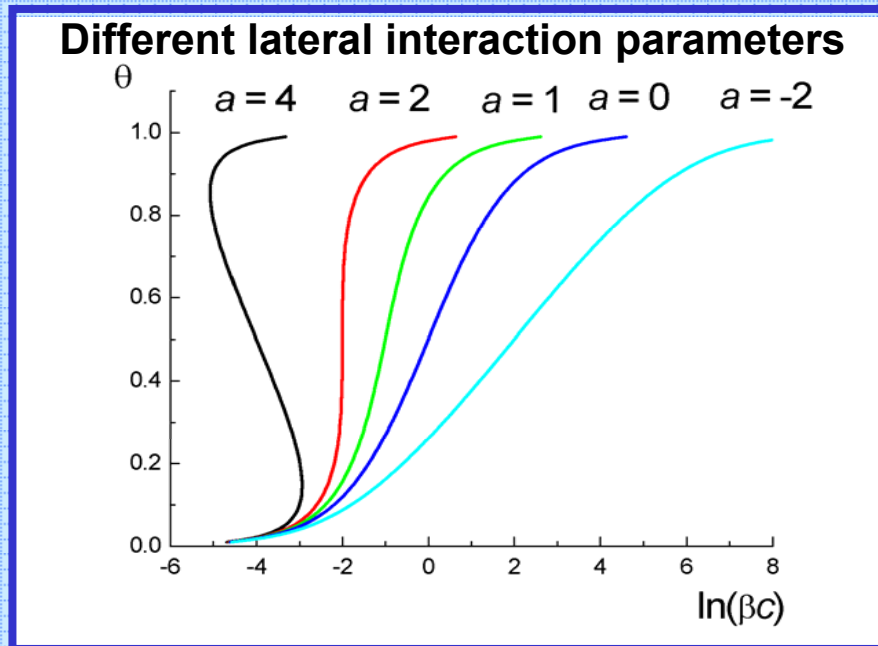




• Frumkin adsorption isotherm

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

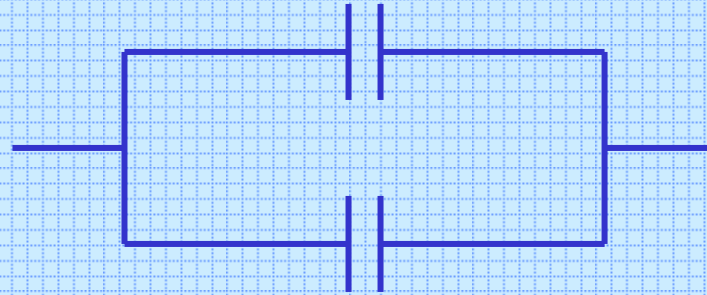
- c - bulk concentration of organic substance;
- θ - coverage of the electrode surface with organic substance;
- β - adsorption equilibrium constant
- a - parameter of lateral interaction





Model of two parallel capacitors

- Scheme



- Electrode charge density

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

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 $\theta = 1$;

$$\sigma_0 = \int_0^{E_0} C_0 dE$$



Model of two parallel capacitors

- Approximate Gibbs equation:

$$d\gamma = -\sigma dE - RT\Gamma d \ln c \quad (3)$$

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

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

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

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

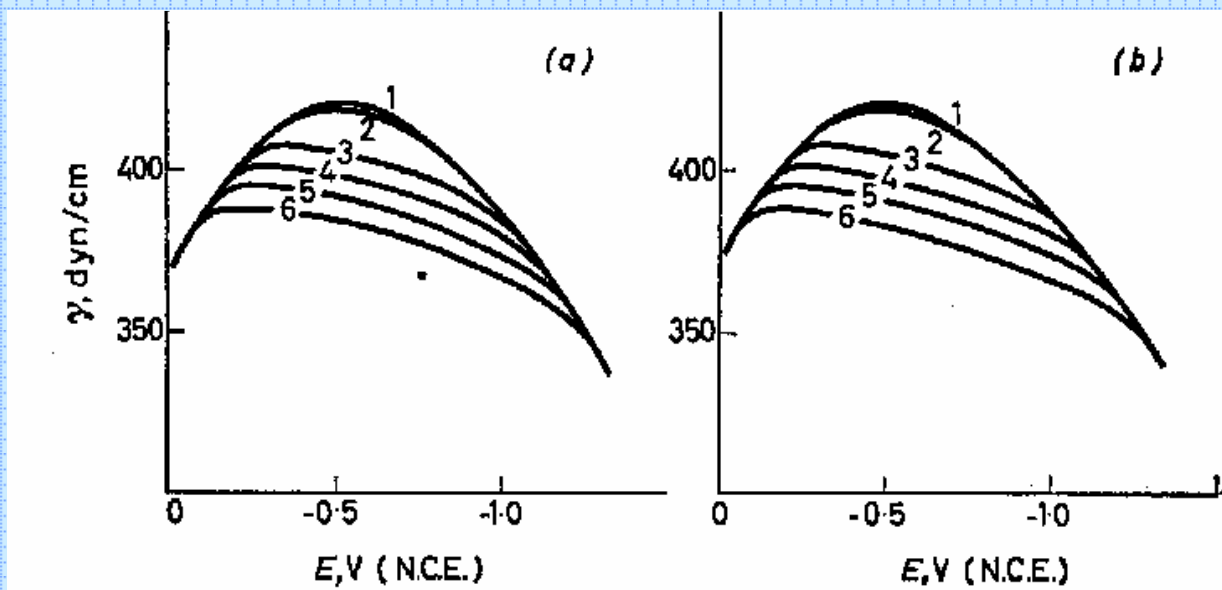
- Decrease of surface tension due to adsorption of organic molecules at $E_0 = \text{const}$:

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



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

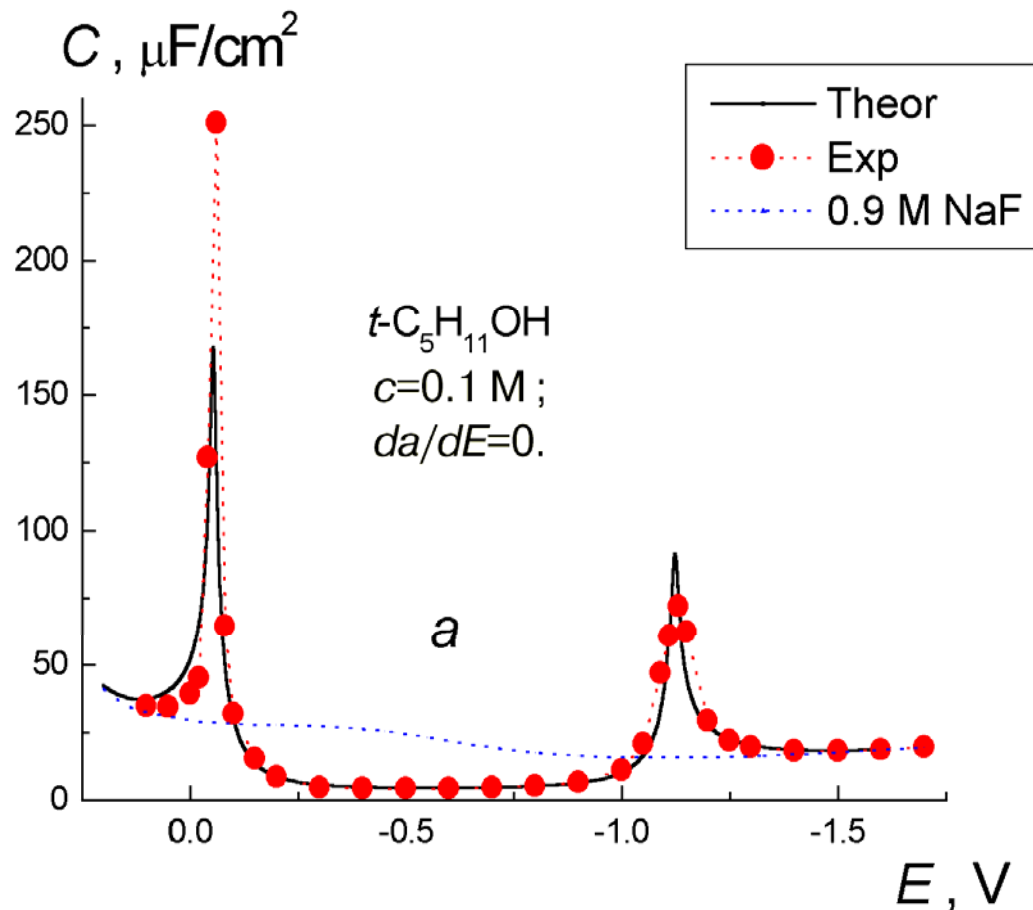


expression for equilibrium differential capacity can be derived:

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



Experimental and simulated differential capacity curves, $\alpha = \text{const}$





Lateral interaction parameter (“attraction coefficient”) vs. electrode potential

For an arbitrary dependence of a on E :

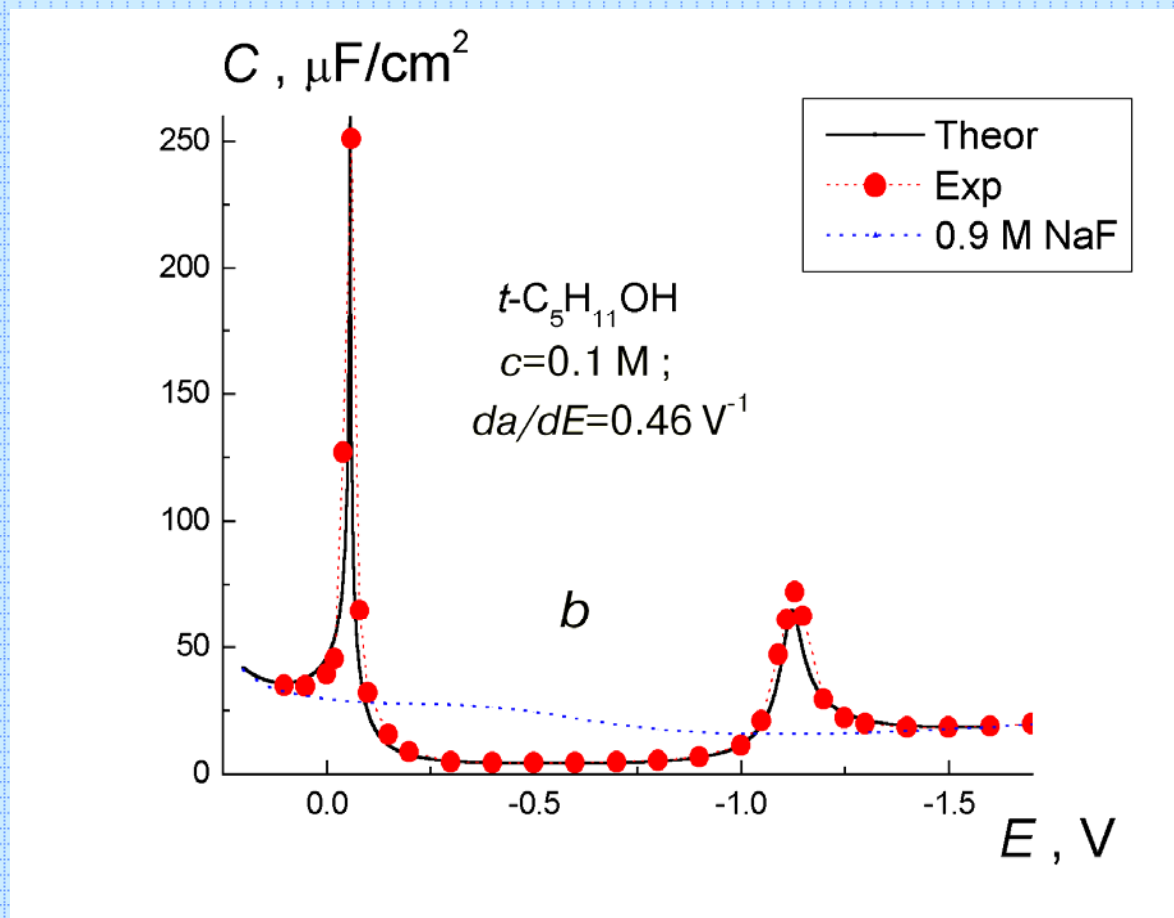
$$\ln \beta = \ln \beta_0 - \frac{\Delta\gamma_0 + C_1 E_0 (E_N - E_0 / 2)}{RT\Gamma_m} + (a_0 - a) \quad (7)$$

$$C = C_0(1 - \theta) + C_1\theta - RT\Gamma_m a' \theta(1 - \theta) + \frac{[\sigma_0 + C_1(E_N - E_0) + RT\Gamma_m a'(1 - 2\theta)]^2 \theta(1 - \theta)}{RT\Gamma_m [1 - 2a\theta(1 - \theta)]} \quad (8)$$

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

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

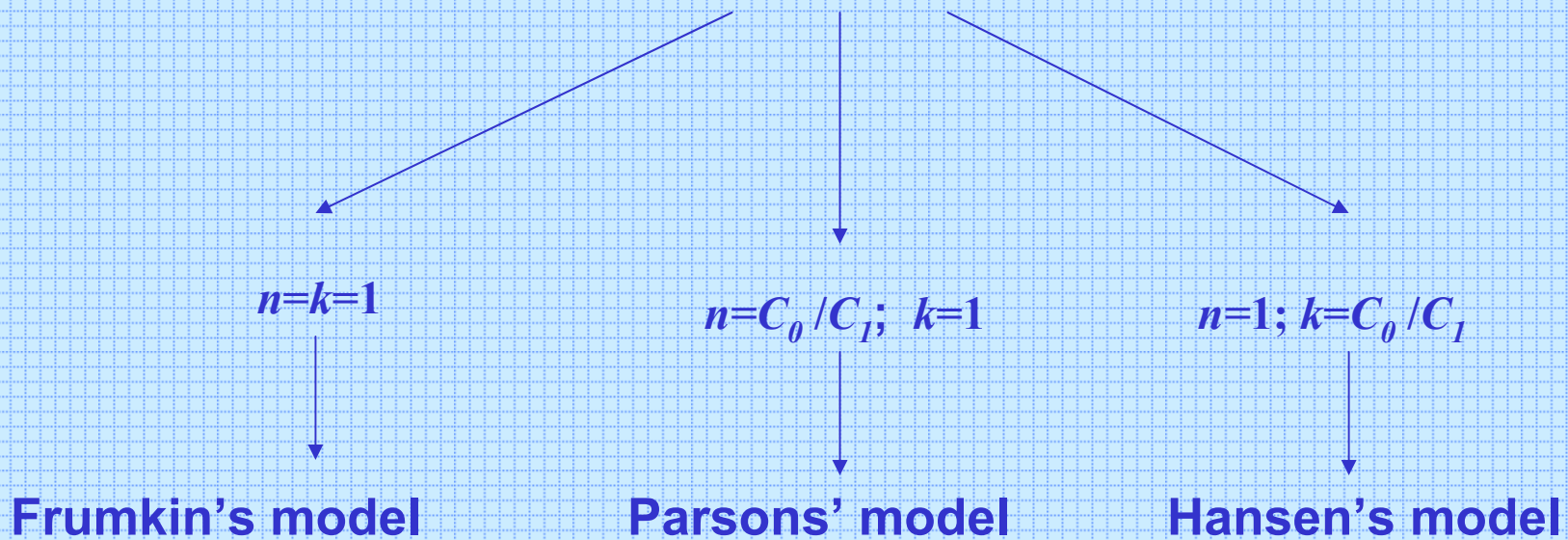
- Hansen's model

$$\sigma = (E_0 - E_N \theta) [C_0(1 - \theta) + C_1 \theta] \quad (10)$$



Generalization

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





Coadsorption of two solution components. Combination of two mixed Frumkin isotherms

$$\sigma = \sigma_0(1 - \theta_1 - \theta_2) + C_1\theta_1(E_0 - E_{N1}) + C_2\theta_2(E_0 - E_{N2}) \quad (12)$$

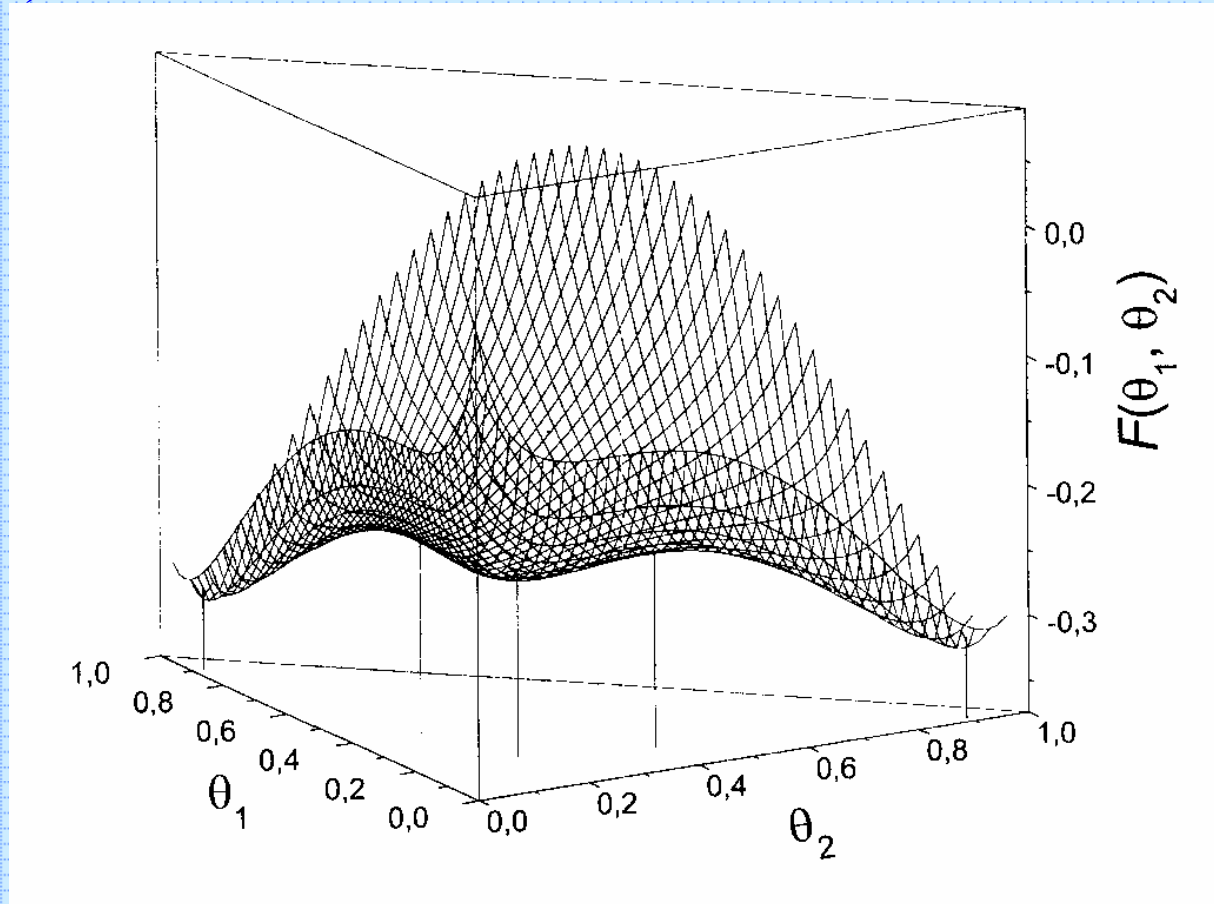
$$\beta_1 c_1 = \frac{\theta_1}{n_1 (1 - \theta_1 - \theta_2)^{n_1}} \exp(-2n_1 a_{11} \theta_1 - 2n_1 a_{12} \theta_2) \quad (13a)$$

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

One of the simplest equations in my life

$$F(\theta_1, \theta_2) = \frac{\Delta G}{RT\Gamma_m} = -a_{11}\theta_1^2 - a_{22}\theta_2^2 - 2a_{12}\theta_1\theta_2 + \frac{\theta_1}{n_1} \ln \left(\frac{\theta_1}{n_1\beta_1c_1} \right) + \quad (14)$$

$$\frac{\theta_2}{n_2} \ln \left(\frac{\theta_2}{n_2\beta_2c_2} \right) + (1 - \theta_1 - \theta_2) \ln(1 - \theta_1 - \theta_2) + \frac{\theta_1(n_1 - 1)}{n_1} + \frac{\theta_2(n_2 - 1)}{n_2}$$





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

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

Conditions of extremum:

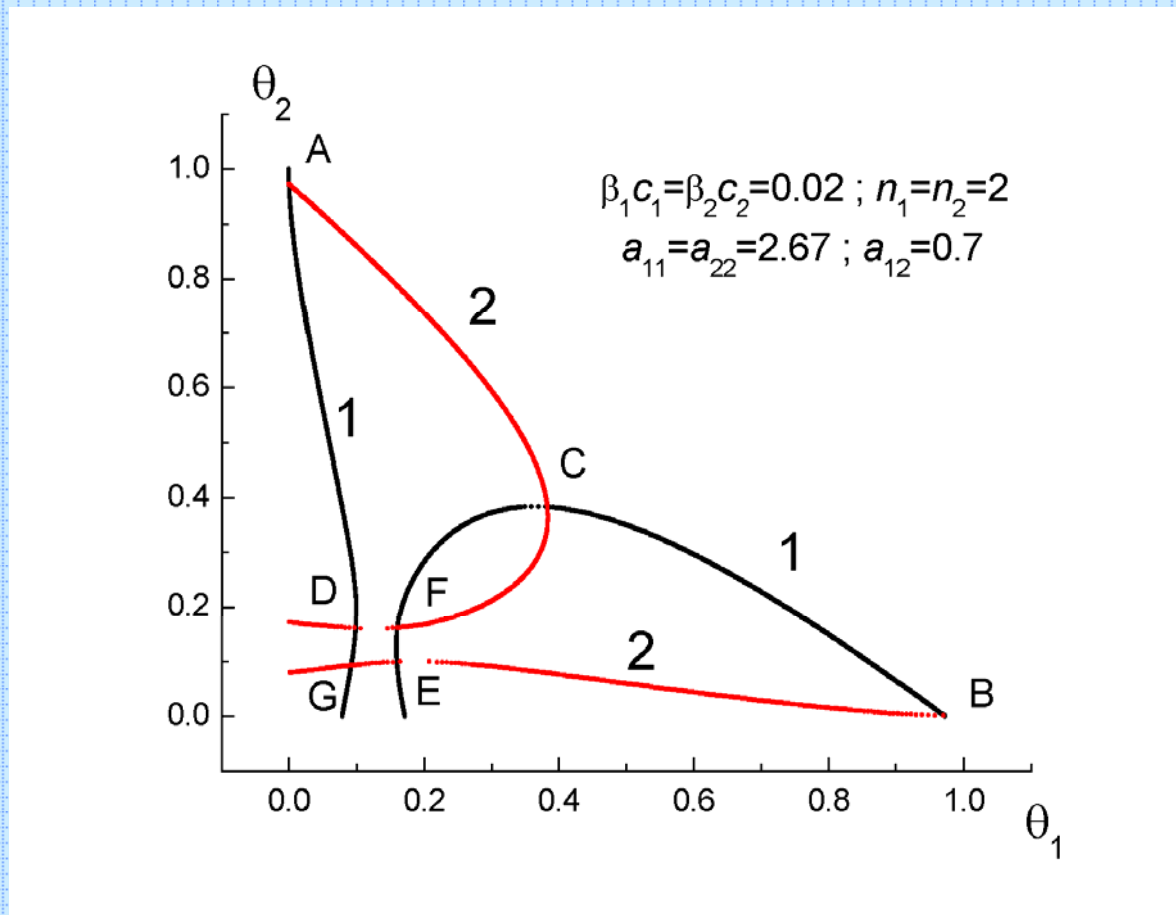
$p_1 > 0, p_2 > 0$ - minimum

$p_1 < 0, p_2 < 0$ - maximum

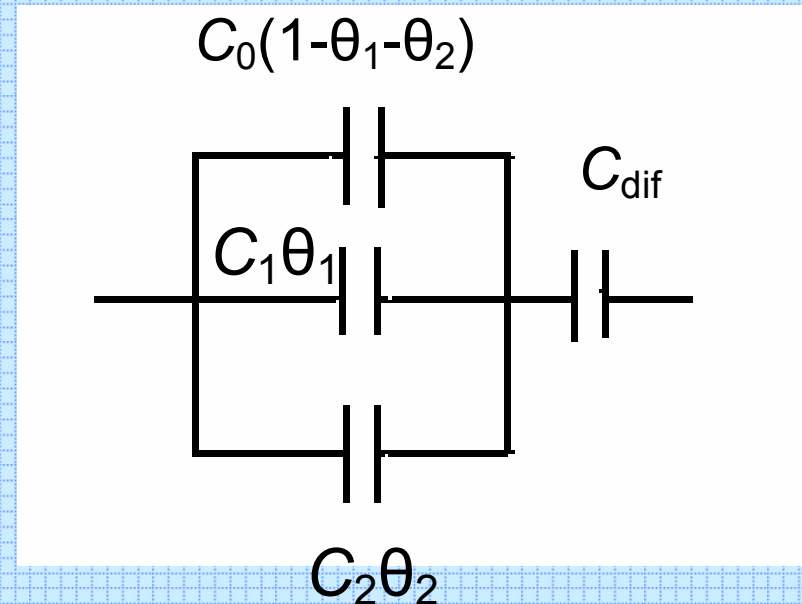
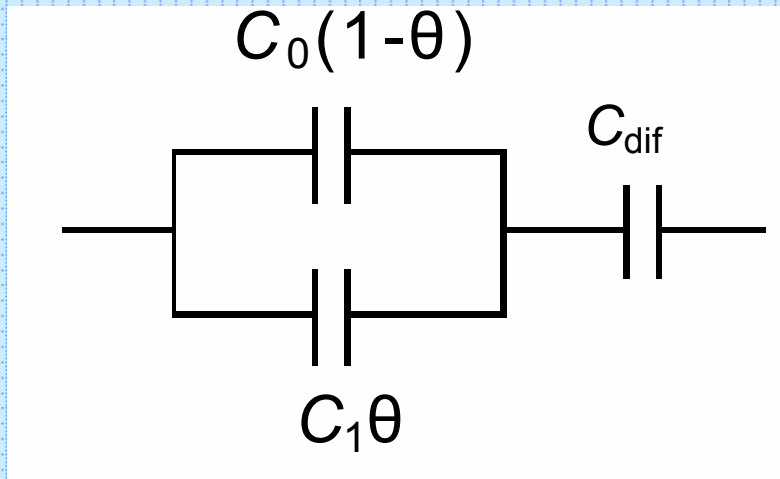
$p_1 > 0, p_2 < 0$ or $p_1 < 0, p_2 > 0$: saddle point



θ_2, θ_1 relationships 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



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