

# История электрохимии. 4. Эволюция представлений о ионах в растворах

Работа Гротгуса (1805): будущее электрохимического материаловедения + важная гипотеза

Клаузиус, тепловое движение/спонтанная диссоциация

Обобщения Аррениуса и Оствальда (+ протесты Менделеева)

Активность как термодинамическая величина (Льюис)

Борн, первая физическая модель

**Дэви, Николсон  
Карлейль:**  
электролиз  
воды/растворов

**Фарадей:**  
законы  
электролиза

**ПРИКЛАДНАЯ ЭЛЕКТРОХИМИЯ**



**1800-1803**

**1833-1834**

**1805**

**1857**

**1874**

**1887**

**1907**

**1919**

**Гротгус:**  
механизм протекания  
тока через растворы

**Клаузиус:**  
ионы - не только  
под действием поля

**Концепция  
Аррениуса**

1853-59, Гитторф:  
числа переноса

1865, Фик:  
законы диффузии

**Льюис:  
активности**

**Борн: модели**

**Кольрауш: ионные  
электропроводности**

V

Not all dissolved metals are decomposed by galvanic electricity. From manganese nitrate I obtained gaseous bubbles at the negative pole<sup>2</sup> instead of a metallic deposit; and it seems that, when under the same circumstances the dissolved metal has a greater affinity for oxygen than that of hydrogen for the same principle, it is solely water which undergoes decomposition.

<sup>2</sup> I shall henceforth use the expression **positive pole** to refer to the tip of the wire **connected to the disc of zinc**, and the expression **negative pole** to denote the tip of the wire **in contact with the copper disc**.

**Работа Гротгуса существенно шире идеи переориентации диполей воды.**



*"Mémoire sur la Décomposition  
à l'Aide de l'Electricité Galvanique"  
Published in Rome, 1805  
Ann. Chim. (Paris) 58:54-74 (1806)  
Translation: Biochim Biophys Acta  
1757 (2006) 871–875*

Of all the metallic salts that I have subjected to the action of the electromotive apparatus, lead acetate and tin muriate<sup>3</sup> gave me most beautiful vegetations. That of lead takes the appearance of fern leaves; and on the ramifications of tin, I often observed, with a magnifying glass, octahedral crystals. It is remarkable that **arborisation** always grows from the negative pole to the positive one, regardless of their respective location, and that it is therefore always organised in the direction of the electric current. The vegetation of a metal obtained by means of electricity appears somehow to imitate that of natural plants, which constantly point towards the source of light, and release oxygen upon coming into contact with its rays.

<sup>3</sup> *I also obtained more or less similar results from nitromuriates of gold and platinum, from nitrates of zinc, copper, mercury, and cobalt, from sulfates of zinc and iron, from stannite of muriated potash, and from iron muriate.*

## XII

Following a prolonged application of galvanic electricity to a solution of **iron sulphate**, the latter became blurred, adopting a reddish hue in the region surrounding the positive pole. One then verifies that it contains a highly-oxidised oxygenated iron sulphate, by testing it with prussiate of potash, which instantly turns into a beautiful **Prussian blue** in that part of the liquid, whereas that surrounding the negative pole, in the presence of the same prussiate, merely turns into a greenish-white precipitate.

## XIII

Cold solutions of **molybdic acid** in concentrated sulphuric acid adopt a **beautiful blue colour** that disappears upon heating the solution.... at the positive pole, the liquor gradually becomes perfectly transparent, and molybdic acid partly precipitates as a white powder, whereas around the negative pole, it acquires a colour ever darker and dirtier. Switching the two poles around has the opposite effect: **the transparent part reverts to blue, and the blue part becomes transparent.**

### XIV

Upon prolonged application of galvanic current to an alkaline salt solution, the base of the latter gradually precipitates around the tip of the wire with the negative electricity. **These precipitates do not seem to me to be due to a decomposition**, judging by the infinitely small quantity of alkali generated at this location; but I presume that the acid of the salt is either destroyed or decomposed there, so that its alkaline base becomes free.

The glass tubes used to hold the solutions subjected to the experiments that I have just described often ended up **coated with a metallic layer** which seemed molten onto the glass inside the tube, and which came from the metal particles torn off from the conducting wires by the action of the apparatus: thus, when the tips were made of gold or of silver, the glass tubes became perfectly gilded with silver or gold.

## XVI

The voltaic column, which immortalises the genius of its inventor, is an electric magnet of which each and **every element** (i.e., each pair of discs) possesses **its own negative and positive poles**. Pondering this polarity suggested to me the idea that a **similar polarity might very well arise between the elementary molecules of water** solicited by the same electrical agent; and I must confess that this was for me an illumination.

## XXII

The theory of water decomposition that I have just presented leads to the following consequences. (a) The proportion of hydrogen cannot increase in water located in the vicinity of the **positive pole**, since the **oxygen of the whole liquid** traversed by galvanic **current tends towards that point, whereas hydrogen tries to move away from it**. (b) By the same token, oxygenation is impossible in the water surrounding the **negative pole**, since **hydrogen is constantly attracted to it, whereas oxygen is repelled by it**. (c) Even if the component principles of water could not be combined into any proportion other than that which constitutes water, the latter would still be decomposed as described; but neither oxygenation, hydrogenation, acidity, nor alkalinity would be observed in any of its parts.

**The polar arrangement**, such as is found in the elementary molecules of water traversed by galvanic current, **must also result in the elementary molecules of all other liquids**, provided that they are solicited by the same forces. In metallic solutions, electric polarity takes place among the elements of the oxide, whose oxygen is transferred to the positive pole, and whose metal is deposited at the negative pole. Acid reacts with these metallic particles which it holds in solution; but even though it has been decomposed either by this reaction or by the electric power, revival occurs nevertheless.



“Über die chemische Wirksamkeit des Lichtes und der Elektrizität”, *Jahres Verhandlungen der Kurländischen Gesellschaft für Literatur und Kunst*, **1819**, 1, 119-184

...in solution **even without electrical current** there is a **continuous exchange between molecules and their elementary parts**.



# *Ueber die Elektrizitätsleitung in Elektrolyten; von R. Clausius.*

Ann. Phys. 177 (1857) 338-360

$n$  positive Theilmolecüle in der positiven und  $n'$  negative Theilmolecüle in der negativen Richtung hindurchgehen, die Stromstärke mit  $C(n + n')$  bezeichnen.

Тепловое движение



СТОЛКНОВЕНИЯ



ДИССОЦИАЦИЯ



Rudolf Julius Emanuel  
**Clausius**  
(1822 – 1888)

(J.L. Gay-Lussac,  $\text{Na}_2\text{SO}_4 + \text{BaCl}_2$ )



S. Arrhenius, JACS 34 (1912) 353-364:

These ideas are, perhaps, a little abstract, but they are of the greatest interest, for they are more than eighty years old. They were expressed in 1839. And later on, in 1857, Williamson expressed absolutely similar ideas, and the same was the case with Clausius, the German mathematical physicist. Clausius came to this conclusion from quite different considerations. He did not care at all for chemical compounds

# Электролитическая диссоциация



**Сванте Август  
Аррениус**  
(1859 – 1927)



**Йоханнес  
Николаус  
Брønстед**  
(1879 - 1947)



**Якоб Хендрик  
Вант-Гофф**  
(1852 - 1911)



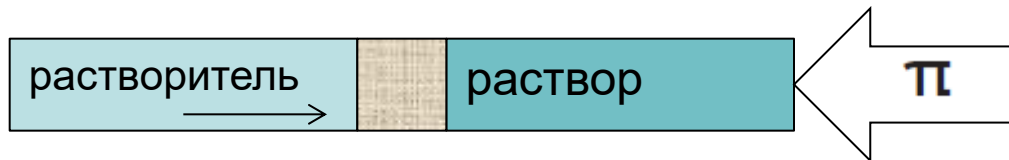
**Вильгельм Оствальд**  
(1853 - 1932)

# Осмотическое давление

$$\pi = cRT \quad \text{для не-электролитов}$$

$$\pi = icRT$$

для электролитов ( $i > 1$ )



## Давление насыщенного пара

$$\Delta p = \frac{p_0 M_0}{1000} c$$

$i$  для электролитов

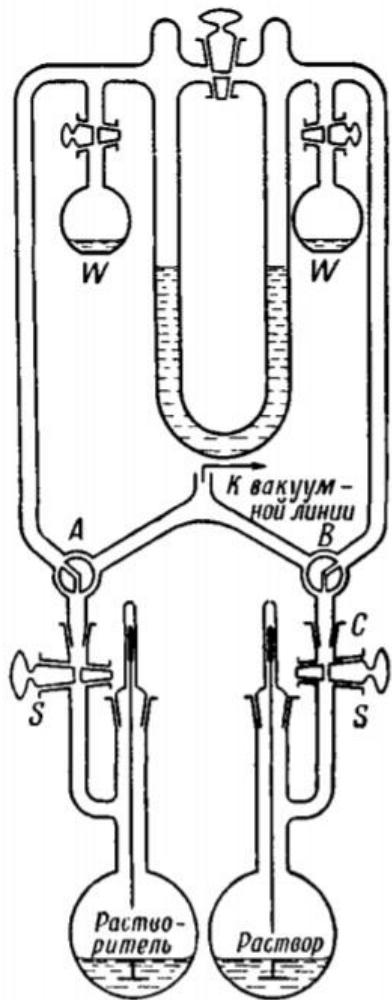
## Температуры плавления и замерзания

$$\Delta T_{\text{зам}} = \frac{RT_{\text{пл}}^2 M_0}{1000 \Delta H_{\text{пл}}} c$$

$$\Delta T_{\text{кип}} = \frac{RT_{\text{кип}}^2 M_0}{1000 \Delta H_{\text{пар}}} c$$

Величина  $i$  – фактор Вант-Гоффа (отношение величин, характеризующих одно и то же коллигативное свойство раствора электролита и раствора неэлектролита).

Подробнее см. в книге Р. Робинсона и Р. Стокса «Растворы электролитов»



HARPER'S SCIENTIFIC MEMOIRS

EDITED BY

J. S. AMES, Ph.D.

PROFESSOR OF PHYSICS IN JOHNS HOPKINS UNIVERSITY

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IV.

THE MODERN

THEORY OF SOLUTION

MEMOIRS BY PFEFFER, VAN'T HOFF

ARRHENIUS, AND RAOULT

NEW YORK AND LONDON

HARPER & BROTHERS PUBLISHERS

1899

Уже есть:

эксперимент по термодинамическим свойствам и электропроводности

Еще нет:

никакой модели ион-ионных взаимодействий

Еще долго не будет:

спектроскопических свидетельств и молекулярных расчетов

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## Arrhenius:

In a former communication "On the Electrical Conductivity of Electrolytes," I have designated those molecules whose ions are independent of one another in their movements, as active; the remaining molecules, whose ions are firmly combined with one another, as inactive. I have also maintained it as probable, that in extreme dilution all the inactive molecules of an electrolyte are transformed into active.† This assumption I will make the basis of the calculations now to be carried out. I have designated the relation between the number of active molecules and the sum of the active and inactive molecules, as the activity coefficient.‡ The activity coefficient of an

\* Clausius, *Pogg. Ann.*, **101**, 347 (1857); *Wied. Elektr.*, **2**, 941.

† *Bihang der Stockholmer Akademie*, **8**, Nr. 13 and 14, 2 Tl. pp. 5 and 13; 1 Tl., p. 61.

‡ *l. c.*, 2 Tl., p. 5.

electrolyte at infinite dilution is therefore taken as unity. For smaller dilution it is less than one, and from the principles

tive and active molecules. If, then,  $m$  represents the number of inactive, and  $n$  the number of active molecules, and  $k$  the number of ions into which every active molecule dissociates (e. g.,  $k=2$  for  $KCl$ , i. e.,  $K$  and  $Cl$ ;  $k=3$  for  $BaCl_2$  and  $K_2SO_4$ , i. e.,  $Ba$ ,  $Cl$ ,  $Cl$ , and  $K$ ,  $K$ ,  $SO_4$ ), then we have :

$$i = \frac{m + kn}{m + n} \quad a \leq 1 ??$$

SUBSTANCE.	FORMULA.	$a$	$i = \frac{t}{18.5}$	$i = 1 + (k-1)a$
Barium hydroxide.....	$Ba(OH)_2$	0.84	2.69	2.67
Strontium hydroxide...	$Sr(OH)_2$	0.86	2.61	2.72
Calcium hydroxide ....	$Ca(OH)_2$	0.80	2.59	2.59
Lithium hydroxide.....	$LiOH$	0.83	2.02	1.83
Sodium hydroxide.....	$NaOH$	0.88	1.96	1.88
Potassium hydroxide ..	$KOH$	0.93	1.91	1.93

smaller dilution it is less than *one*, and from the principles established in my work already cited, it can be regarded as equal to the ratio of the actual molecular conductivity of the solution to the maximum limiting value which the molecular conductivity of the same solution approaches with increasing dilution. This obtains for solutions which are not too concentrated (i. e., for solutions in which disturbing conditions, such as internal friction, etc., can be disregarded).

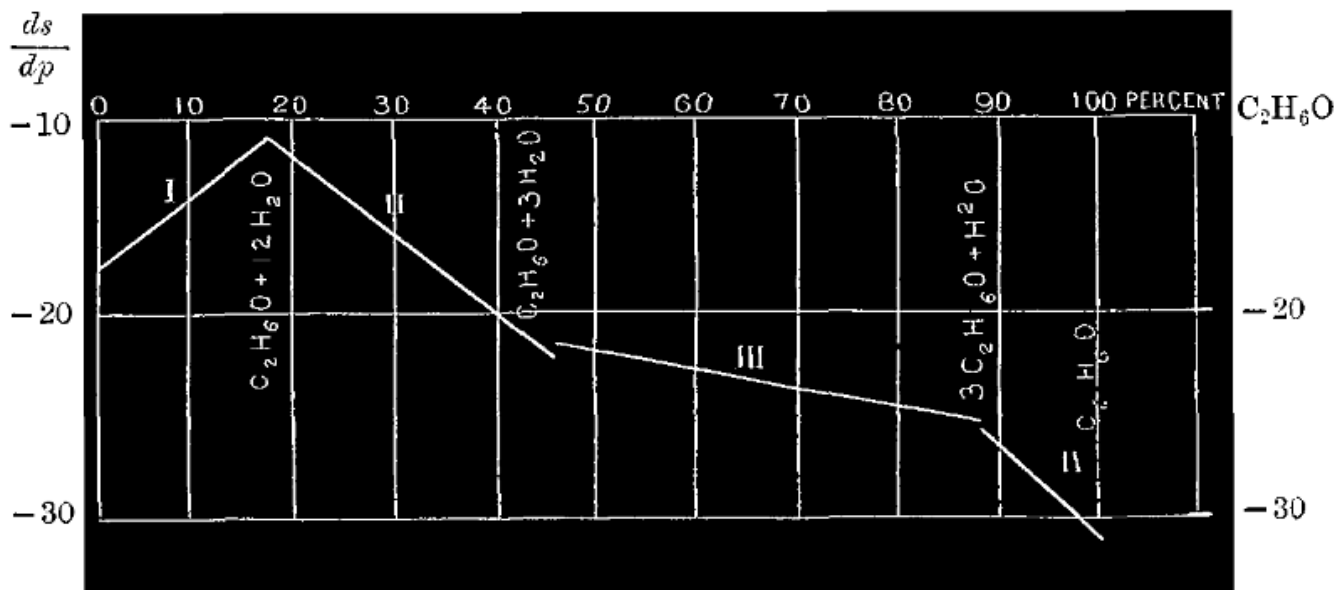
Из данных по эбулиометрии и криоскопии

Из данных по электропроводности

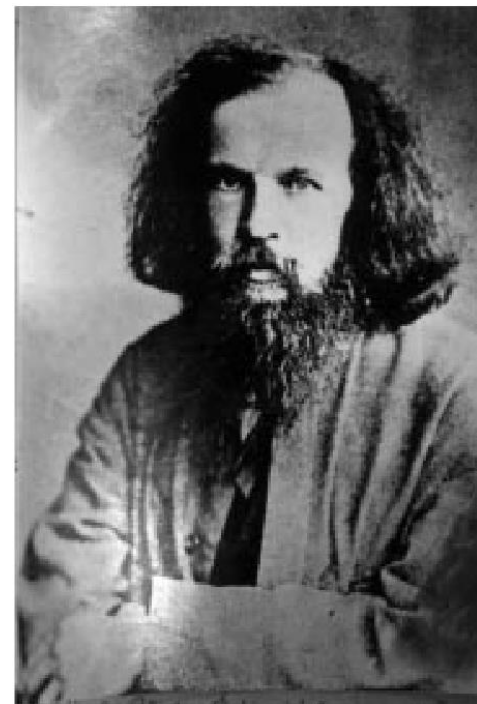
LXXVIII.—*The Compounds of Ethyl Alcohol with Water.*

By D. MENDELÉEFF.

J. Chem. Soc. Trans. 51 (1887) 778-782



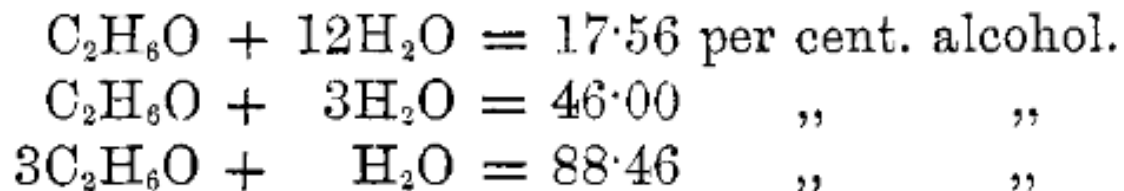
(производная плотности по концентрации)



Д.И. Менделеев  
в 1878

«гидратная теория  
растворов»

Applying this method to the solution of  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_6\text{O}$ , three definite combinations are found to exist, namely—





## Gilbert Newton Lewis (1875 – 1946)

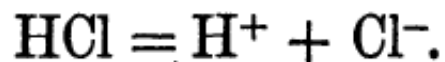
Proc. Amer. Acad. Arts & Sci., 43 (1907) 259-293

Likewise we shall find it desirable to introduce besides the fugacity, which has the dimensions of pressure, another quantity which has the dimensions of concentration.

$$\text{активность} \rightarrow \xi = \frac{\psi}{RT} \leftarrow \text{фугитивность}$$



..... It is probable that no one of these laws is ever strictly true. **As approximations to the truth they have been of the greatest service.** But now that their utility has been demonstrated, the attention of a progressive science cannot rest upon their acknowledged triumphs, but must turn to the investigation of their inaccuracies and their limitations. From the study of the deviations from the simple gas laws has grown one of the most interesting chapters of chemistry. **So from a study of the deviations** from such a law as the mass law we may expect results of the highest value.



According to the ordinary mass law,

Переход от концентрационных констант к термодинамическим

$$\frac{C_{\text{H}}C_{\text{Cl}}}{C_{\text{HCl}}} = K.$$



$$\frac{\xi_{\text{H}}\xi_{\text{Cl}}}{\xi_{\text{HCl}}} = K.$$

If therefore the mass law is false, it must be because the activity is not simply proportional to the concentration for one or more of these three substances. The problem, therefore, is to determine how the activity of the undissociated substance and the activity of the ions vary with the concentrations of both. It seems that all the facts which are at present

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$$\frac{\xi_{\text{O}}^{\text{O}} \xi_{\text{P}}^{\text{P}} \dots}{\xi_{\text{A}}^{\text{A}} \xi_{\text{B}}^{\text{B}} \dots} = K \text{ (a constant)} \quad \text{- в общем виде для константы равновесия.}$$

И для ЭДС цепи: 
$$E = \frac{RT}{mF} \ln K - \frac{RT}{mF} \ln \frac{\xi_{\text{O}}^{\text{O}} \xi_{\text{P}}^{\text{P}}}{\xi_{\text{A}}^{\text{A}} \xi_{\text{B}}^{\text{B}}}$$

**Термин «ионная сила» возник из анализа корреляций между коэффициентами активности:**

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

**THE ACTIVITY COEFFICIENT OF STRONG ELECTROLYTES.<sup>1</sup>**

BY GILBERT N. LEWIS AND MERLE RANDALL.

J. Amer. Chem. Soc.  
43 (1921) 1112-1154

Received March 10, 1921.

In any solution of strong electrolytes let us multiply the stoichiometrical molality of each ion by the square of its valence (or charge). The sum of these quantities, divided by two (since we have included both positive and negative ions), we shall call the ionic strength, and designate by  $\mu$ . Thus in pure solutions of potassium chloride, magnesium sulfate and barium chloride, all at 0.01 M, we have, respectively,  $\mu = 0.01$ ,  $\mu = 0.04$ , and  $\mu = [(4 \times 0.01) - 0.02]/2 = 0.03$ . We may now state our general principle: *In dilute solutions the activity coefficient of a given same ionic strength.*

В сильно разбавленных растворах была зависимость только от заряда иона; при более высоких концентрациях явно появлялась зависимость еще и от размера иона.

TABLE XXIV.

Activity Coefficients of Individual Ions at Various Values of the Ionic Strength.

$\mu =$	0.001	0.002	0.005	0.01	0.02	0.05	0.1
H <sup>+</sup>	0.98	0.97	0.95	0.92	0.90	0.88	0.84
OH <sup>-</sup>	0.98	0.97	0.95	0.92	0.89	0.85	0.81
Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup>	0.98	0.97	0.95	0.92	0.89	0.84	0.79
Li <sup>+</sup>	0.98	0.97	0.95	0.92	0.89	0.85	0.81
Na <sup>+</sup>	0.98	0.97	0.95	0.92	0.89	0.84	0.80
K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup>	0.98	0.97	0.95	0.92	0.89	0.84	0.79
Ag <sup>+</sup>	0.97	0.96	0.93	0.90	0.85	0.80	0.77
Tl <sup>+</sup>	0.97	0.96	0.93	0.90	0.85	0.75	0.64
NO <sub>3</sub> <sup>-</sup>	0.97	0.96	0.94	0.91	0.87	0.77	0.68
ClO <sub>3</sub> <sup>-</sup> , BrO <sub>3</sub> <sup>-</sup> , IO <sub>3</sub> <sup>-</sup>	0.95	0.93	0.89	0.85	0.79	0.70	0.61
Me <sup>++</sup> <sup>a</sup>	0.78	0.74	0.66	0.60	0.53	0.43	0.34
SO <sub>4</sub> <sup>-</sup>	0.7	0.71	0.63	0.56	0.47	0.35	0.26
La <sup>+++</sup> , Fe(CN) <sub>6</sub> <sup>-</sup>	0.73	0.66	0.55	0.47	0.37	0.28	0.21

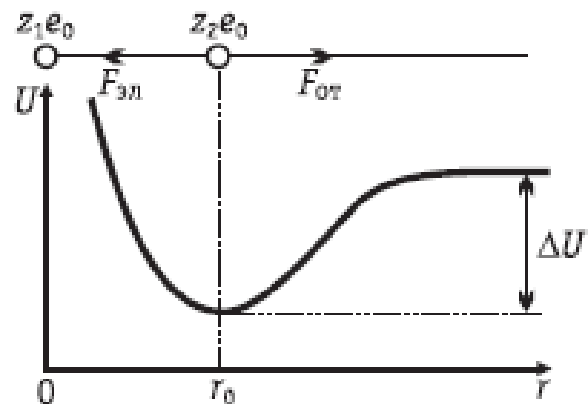
<sup>a</sup> Under Me<sup>++</sup> we include Mg<sup>++</sup>, Ca<sup>++</sup>, Sr<sup>++</sup>, Ba<sup>++</sup>, Cu<sup>++</sup>, Zn<sup>++</sup>, Cd<sup>++</sup>, except that for Cd<sup>++</sup> the value is not to be used for obtaining the activity coefficient of a halide.

# Энергия кристаллической решетки

(определение: работа по превращению кристалла в ионный пар)

М. Борн, 1919: ионный кристалл, заряды ионов  $z_1$  и  $z_2$

$$F_{\text{притяжения}} = -\frac{z_1 z_2 e_0^2}{4\pi\epsilon_0 r^2} \quad F_{\text{отталкивания}} = \frac{B}{r^{n+1}}, \quad n > 1$$



$$\Sigma F = -\frac{dU}{dr}; \quad \Sigma F(r_0) = 0$$

$$\Delta G_{\text{кр}} = N_A A \frac{z_1 z_2 e_0^2}{4\pi\epsilon_0 r_0} \left( 1 - \frac{1}{n} \right)$$

Константа Моделунга

Равновесное межионное расстояние

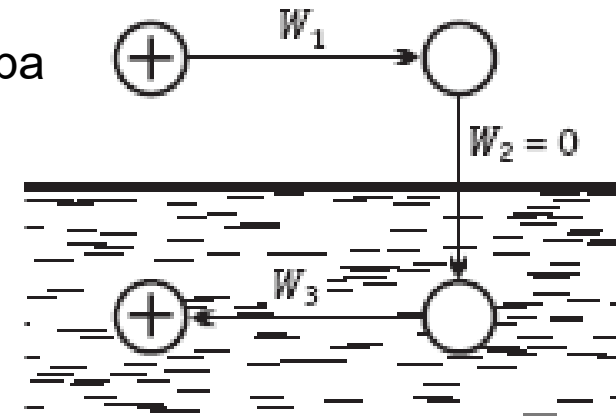
из данных по сжимаемости



**Макс Борн  
(1882 – 1970)**

Метод циклов  $\longrightarrow$  Цикл Борна-Габера

М.Борн, *Z. Phys.* 1(1920)45



*Ион – сфера*

*Среда – континуум,  $\epsilon$*

*Работа переноса незаряженной сферы из вакуума в среду – 0*

*Поддержание электронейтральности*

$$\Delta G_A = N_A (W_1 + W_3)$$

$$\varphi = \frac{z_i e_0}{4\pi\epsilon\epsilon_0 r_i}$$

$$W = \int_0^{z_i e_0} \varphi dq = \frac{(z_i e_0)^2}{8\pi\epsilon\epsilon_0 r_i}$$

$$-\Delta G_s = N_A \frac{(z_i e_0)^2}{8\pi\epsilon_0 r_i} \left( 1 - \frac{1}{\epsilon} \right)$$