

## История электрохимии. 2. Растворы электролитов

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

Раздельный транспорт ионов 1853..... Гитторф, Кольрауш

Обобщения Аррениуса и Оствальда

Активность как термодинамическая величина (Льюис)

Первая физическая модель (Борн)

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

**Фарадей:**  
законы  
электролиза

ПРИКЛАДНАЯ ЭЛЕКТРОХИМИЯ



1800-1803

1833-1834

1805

1857

1874

1887

1894

**Гротгус:**  
механизм протекания  
тока через растворы

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

**Концепция  
Аррениуса**

**Растворы:**

1853-59, Гитторф:  
числа переноса

1865, Фик:  
законы диффузии

**Кольрауш,  
Гейдвайлер:**  
Ионное произ-  
ведение воды

**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  
a l'Aide de l'Electricite 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.**

## Электрохимически инициированное осаждение

### 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.

## XXIV

**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.

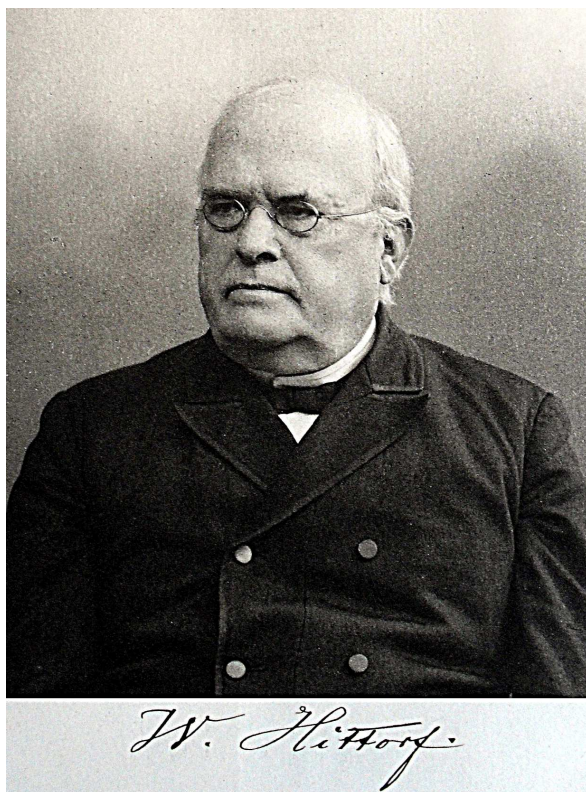


“Über die chemische Wirksamkeit des Lichtes und der Elektrizität”, *Jahres Verhandlungen der Kurländischen Gesellschaft für Literatur und Kunst*, **1819**, 1, 119-184

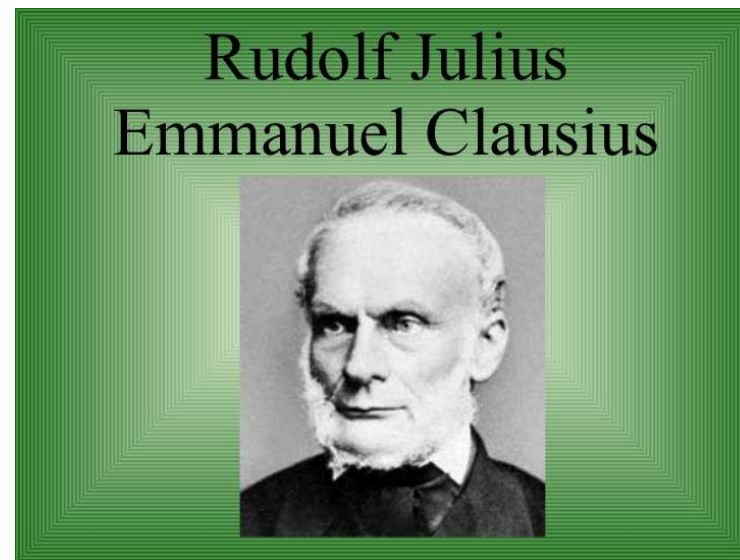
...in solution **even without electrical current** there is a **continuous exchange between molecules and their elementary parts**.



**Тепловое движение** и возможность  
спонтанной диссоциации,  
Poggendorff's Annalen 101 (1857) 338



Poggendorff's Annalen, 89, 177, **1853**



А. С. Савельев, **1953**  
«О гальванической  
проводимости жидкостей»

Числа переноса



Скорости  
механического  
движения



Электрические  
подвижности

Методика измерения  
электропроводности:  
платинированная платина

7. *Ueber platinirte Electroden und Widerstandsbestimmung; von Friedrich Kohlrausch.*

1. Bei der Platinirung von Electroden zum Zwecke von Widerstandsbestimmungen, welche ich mit den Herren Holborn und Dieselhorst ausführte, gebrauchten wir die von den Herren Lummer und Kurlbaum für ihre bolometrischen Zwecke ausgemittelte Lösung. Dieselbe besteht aus 1 Platinchlorid und 0,008 Bleiacetat in 30 Wasser.

Die Anwendung dieser Lösung ist nicht nur wegen der Sicherheit, mit welcher der Niederschlag als matter, tief schwarzer Platinmohr entsteht, angenehm, sondern es fiel uns an den so behandelten Electroden das, trotz ihrer durch den Zweck gebotenen geringen Oberfläche besonders gute Tonminimum bei der telephonischen Widerstandsmessung auf. Die Erscheinung hängt offenbar mit der Aggregatform des Platinmohrs zusammen, welche unter der Mitwirkung des gelösten Bleies entsteht. Die bekannte räthselhafte Verschiedenheit, mit welcher die eine Platinchloridlösung schlecht, eine andere regelmäßig gut platinirt, darf man nun wohl sicher darauf zurückführen, dass die letztere die geeignete Verunreinigung durch ein anderes Metall (Zink, Kupfer, Blei) enthielt.

Die weitere Verfolgung des Gegenstandes führte zu Ergebnissen, welche als ein wesentlicher Fortschritt der Wechselstrommethode bei der Messung electrolytischer Widerstände bezeichnet werden dürfen.

Letzteres wird sofort einleuchtend, wenn ich einige Erfahrungen mittheile. Die 10 cm<sup>2</sup> grossen Electroden in einem Fläschchen, wie ein solches für Widerstandsbestimmung von Wasser oder dergl. gebraucht zu werden pflegt, wurden mit der L.-E.'schen Lösung kräftig platinirt, angewässert und nun dieses Gefäss mit einem anderen von etwa 15facher Widerstandscapazität, welches mit der gleichen Flüssigkeit gefüllt wurde wie jenes, in der Brücke mit dem Telephon verglichen, indem die Widerstände beider auf einen Rheostaten zurückgeführt wurden. Die beiden Gefässe standen in demselben Bade. Selbst bei Fällung mit normaler NaCl-Lösung entstand ein zur Einstellung noch brauchbares Minimum, obwohl der Flüssigkeits-



Friedrich Wilhelm Georg Kohlrausch

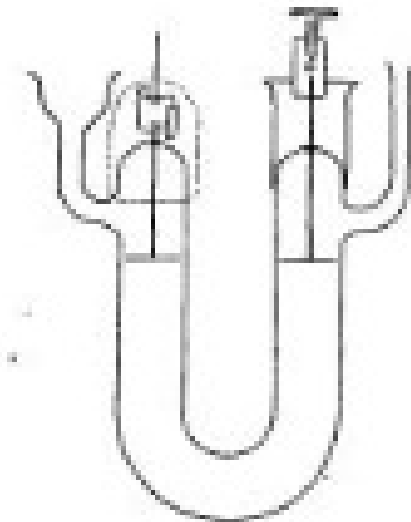


Fig. 1.  
U<sub>2</sub> mit Gefäss.

Annalen der Physik und Chem  
60 (1897) 315- 322

**Электролитическая  
диссоциация**



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



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



**Вильгельм Оствальд**  
(1853 - 1932)



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

HARPER'S SCIENTIFIC MEMOIRS

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IV.

THE MODERN

THEORY OF SOLUTION

MEMOIRS BY PFEFFER, VANT 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 эбулио- и криоскопии  
 Из данных по электропроводности

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.

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

### Gilbert Newton Lewis

Proc Amer Acad Arts and Sciences, 43 (1907) 259-293



..... 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

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

$$\downarrow$$

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

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

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

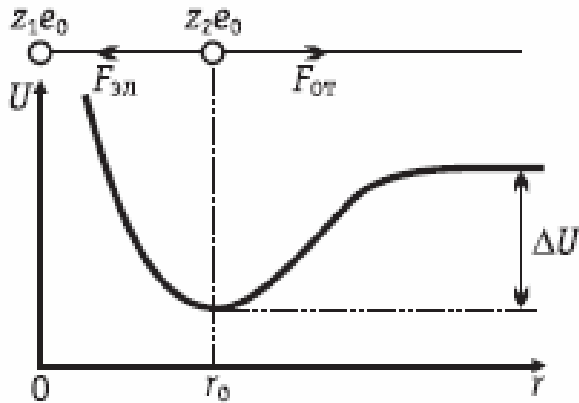
## Первая модель

# 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

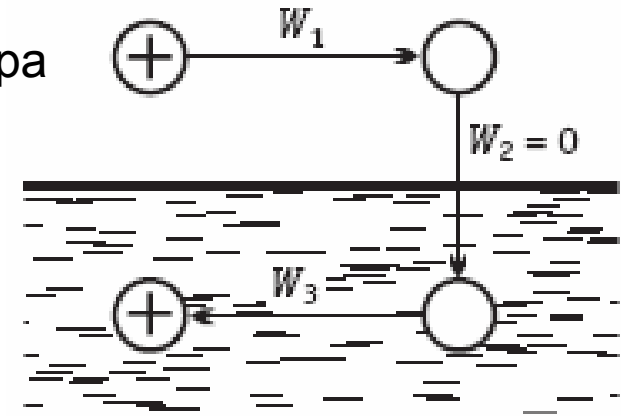
из данных по  
сжимаемости



**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

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

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

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

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