ネルンスト式とは何か

(京大院工　垣内　隆)

意外にわからないネルンスト式

ネルンスト式は自明か？

1. $$E = E^{0\prime} + \frac{RT}{nF} \ln \frac{[\mathrm{Rd}_1][\mathrm{Ox}_2]}{[\mathrm{Ox}_1][\mathrm{Rd}_2]}$$

2. $$E = E^{0\prime} + \frac{RT}{nF} \ln \frac{[\mathrm{Ox}]}{[\mathrm{Rd}]}$$

3. $$\Delta_{\mathrm{S}}^{\mathrm{M}}\phi = \text{ const. } + \frac{RT}{nF} \ln \frac{[\mathrm{Ox}]}{[\mathrm{Rd}]}$$

1.

$$Rd_1 + Ox_2 = Ox_1 + Rd_2$$

$$M_1 \,|\, S_1(Ox_1/Rd_1) \,\vdots\, S_2(Ox_2/Rd_2) \,|\, M_2 \,|\, M_1'$$

$$E = E^{0\prime} + \frac{RT}{nF} \ln \frac{[Rd_1][Ox_2]}{[Ox_1][Rd_2]}$$

E は電池の端子間電圧

2.

$$E = E_R - E_L$$

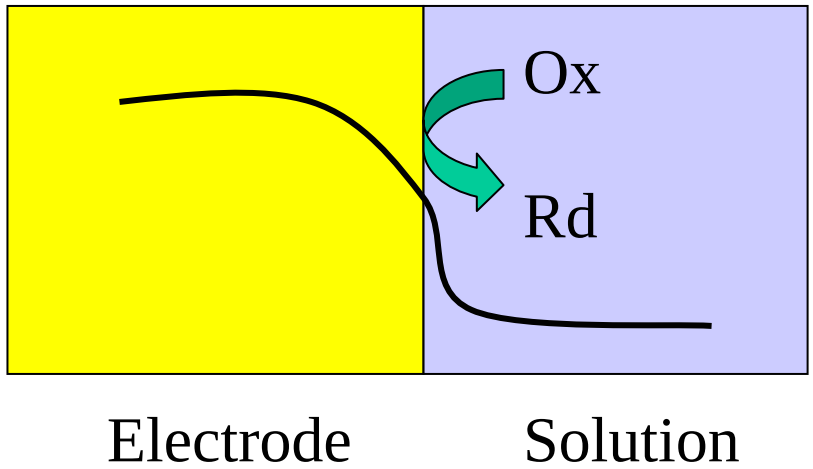
$$E_L = E_L^{0\prime} + \frac{RT}{nF} \ln \frac{[Ox_1]}{[Rd_1]}$$

$$E_R = E_R^{0\prime} + \frac{RT}{nF} \ln \frac{[Ox_2]}{[Rd_2]}$$

$$Ox + ne^- = Rd$$

電池の端子間電圧 E を分割してそれぞれを右側と左側の電極の電極電位とする

3.



$$\Delta_{\mathrm{S}}^{\mathrm{M}}\phi = \text{ const. } + \frac{RT}{nF}\ln\frac{[\mathrm{Ox}]}{[\mathrm{Rd}]}$$

$$\Delta_{\mathrm{S}}^{\mathrm{M}}\phi = \phi^{\mathrm{M}} - \phi^{\mathrm{S}}$$

どれが正しいネルンスト式？

1. 電池の起電力とΔG

$$E = -\frac{\Delta G}{nF}$$

$$\Delta G = \Delta G^0 + RT \ln \frac{[\mathrm{Rd}_1][\mathrm{Ox}_2]}{[\mathrm{Ox}_1][\mathrm{Rd}_2]}$$

熱力学の関係式

W. Nernst, “Die elektromotorische Wirksamkeit der Ionen,” *Z. phys. Chem.*, **4**, 129-181 (1889).

電池の熱力学はすでに確立されていた。

H. Helmholtz, “Ueber galvanischen Ströme, verursacht durch Concentrationsuntershiede; Folgerungen aus der mechanishen Wärmetheorie,” *Ann. Phys. Chem.*, **3**, 201-216 (1878).

J. W. Gibbs, “On the Equilibrium of Heterogeneous Substances,” in *The scientific papers of J. Willard Gibbs*, Dover, New York (1961) Chapter 3.

Trans. Conn. Acad. Arts and Sci., **3**, 108-248 (1875-1876); 343-524 (1877-1878).

Gibbs が発表した雑誌

TRANSACTIONS

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1873.

CONTENTS OF VOL. II, PART 2.

電池の起電力についての Gibbsの 功績

Favre のデータを詳細に解析

Cd | HCl | H_2, Pt

P. A. Favre, *Compt. Rend.*, **68**, 1305 (1869).

M. Dole, *Principles of experimental and theoretical Electrochemistry*, McGraw Hill, New York (1935) Chap. 16.

and sometimes cold is produced.* When neither is produced, of course the electromotive force of the cell is exactly equal to its diminution of energy per unit of electricity transmitted. But such a coincidence is far less significant than the fact that an absorption of heat has been observed. With acid containing about seven equivalents of water $(HNO_6+7HO)\,[HNO_3+3\frac{1}{2}H_2O]$, M. Favre has found

$$(V''-V')\Delta e=46781^{\text{cal.}},\quad \Delta\epsilon=-41824^{\text{cal.}},\quad \Delta Q=4957^{\text{cal.}};$$

and with acid containing about one equivalent of water

$$(HNO_6+HO)\,[HNO_3+\tfrac{1}{2}H_2O],$$

$$(V''-V')\Delta e=49847^{\text{cal.}},\quad \Delta\epsilon=-52714^{\text{cal.}},\quad \Delta Q=-2867^{\text{cal.}}.$$

In the first example, it will be observed that the quantity of heat absorbed in the cell is not small, and that the electromotive force is nearly one-eighth greater than can be accounted for by the diminution of energy in the cell.

This absorption of heat in the cell he has observed in other cases, in which the chemical processes are much more simple.

For electrodes of cadmium and platinum in hydrochloric acid his experiments give†

$$(V''-V')\Delta e=9256^{\text{cal.}},\qquad \Delta\epsilon=-8258^{\text{cal.}},$$
$$\Delta W_P=-290^{\text{cal.}},\qquad \Delta Q=1288^{\text{cal.}}.$$

In this case the electromotive force is nearly one-sixth greater than can be accounted for by the diminution of energy in the cell with the work done against the pressure of the atmosphere.

For electrodes of zinc and platinum in the same acid one series of experiments gives‡

$$(V''-V')\Delta e=16950^{\text{cal.}},\qquad \Delta\epsilon=-16189^{\text{cal.}},$$
$$\Delta W_P=-290^{\text{cal.}},\qquad \Delta Q=1051^{\text{cal.}};$$

and a later series,§

$$(V''-V')\Delta e=16738^{\text{cal.}},\qquad \Delta\epsilon=-17702^{\text{cal.}},$$
$$\Delta W_P=-290^{\text{cal.}},\qquad \Delta Q=-674^{\text{cal.}}.$$

In the electrolysis of hydrochloric acid in a cell with a porous partition, he has found‖

$$(V'-V'')\Delta e=34825^{\text{cal.}}\qquad \Delta Q=2113^{\text{cal.}},$$

* *Mém Savants Étrang.*, loc. cit., p. 93; or *Comptes Rendus*, t. lxix, p. 37, and t. lxxiii, p. 893.

† *Comptes Rendus*, t. lxviii, p. 1305. The total heat obtained in the whole circuit (including the cell) when all the electromotive work is turned into heat, was ascertained by direct experiment. This quantity, 7968 calories, is evidently represented by $(V''-V')\Delta e-\Delta Q$, also by $-\Delta\epsilon+\Delta W_P$. (See (691).) The value of $(V''-V')\Delta e$ is obtained by adding ΔQ, and that of $-\Delta\epsilon$ by adding $-\Delta W_P$, which is easily estimated, being determined by the evolution of one kilogramme of hydrogen.

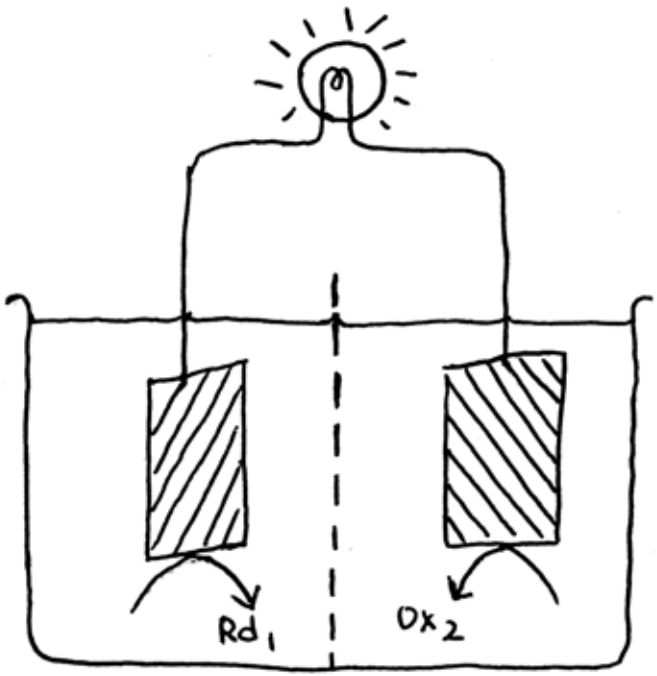
‡ *Ibid.*

§ *Mém. Savants Étrang.*, loc. cit., p. 145.

‖ *Ibid.*, p. 142.

ネルンストが考えたこと

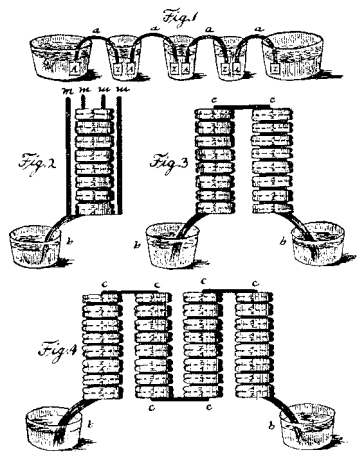
電池の起電力はどこで発生しているか？
電位差はどこにあるのか？



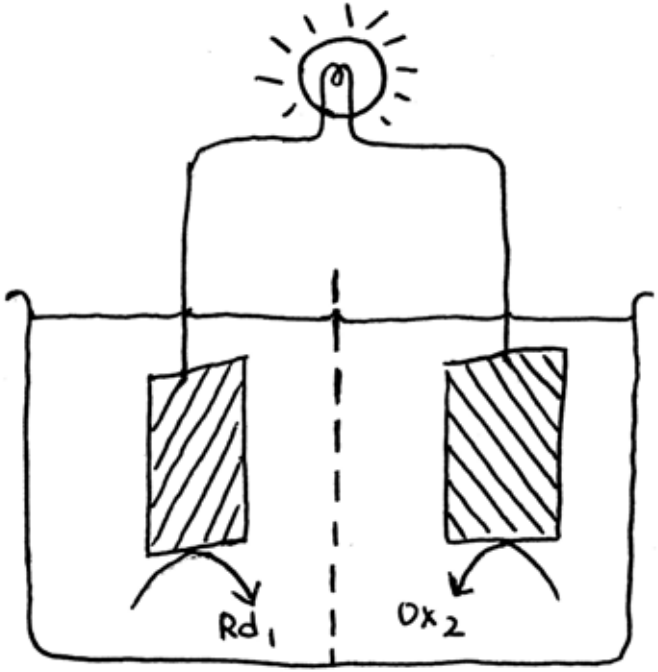
Volta

Fabroni

Kelvin



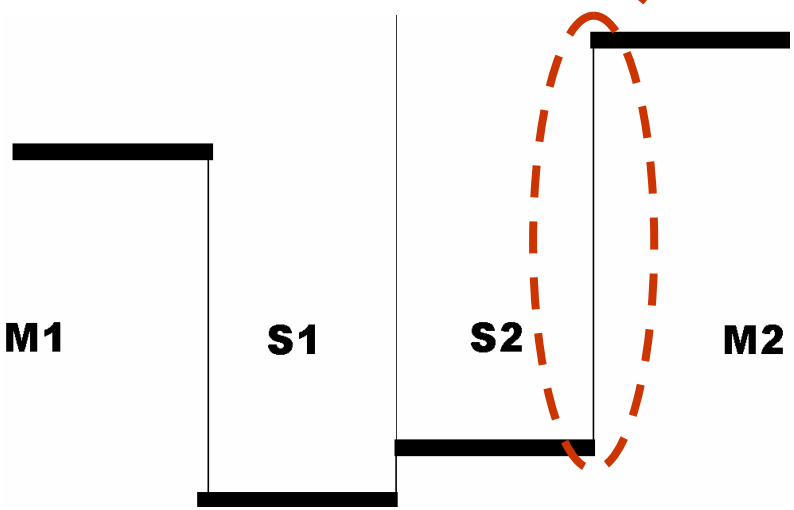
J. A. V. Butler, *Electrocapillarity*, Methuen, London (1940), Chap. 1 .



W. Nernst, "Die elektromotorische Wirksamkeit der Ionen," *Z. phys. Chem.*, 4, 129-181 (1889).

$$E = 0.860T \ln \frac{P}{p} \times 10^{-4} \text{ Volt}$$

"Es sei nun *E* die Potentialdifferenz zwischen Metall und Elektrolyt und *p* der osmotische Partialdruck der Ionen dieses Metalls im Elektrolyt"



この E は電極電位ではない！

"der elektrolytischen Loesungstension *P*"

「電離溶解圧」

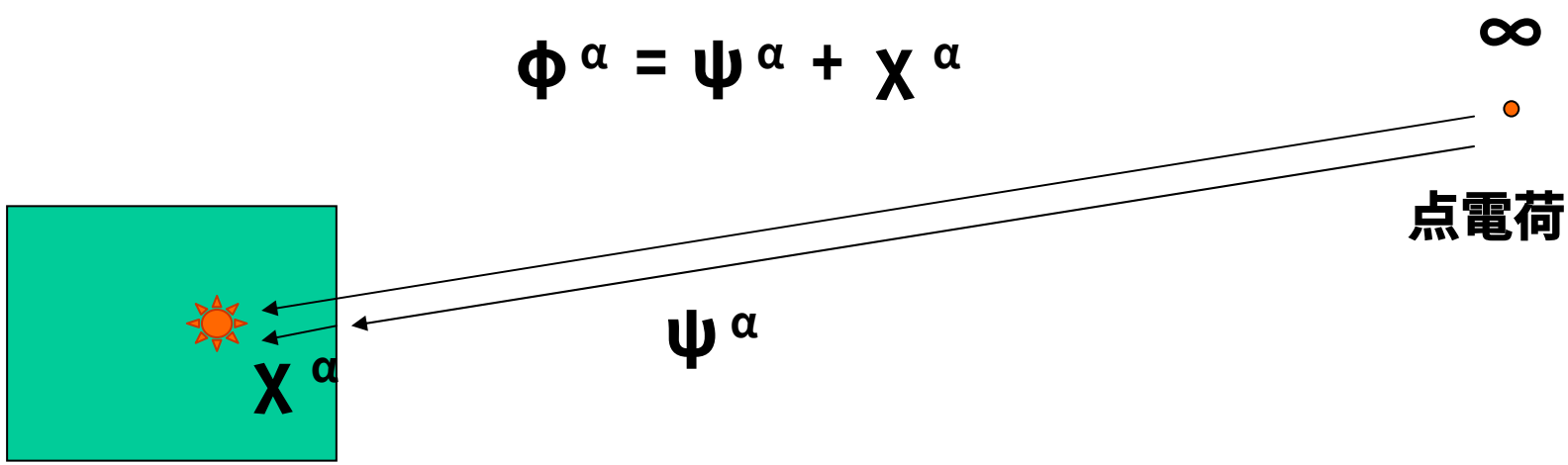
ネルンストは相間電位差を考えていた

相間電位差
Phase-boundary potential

<u>電位差、電位</u>？？？

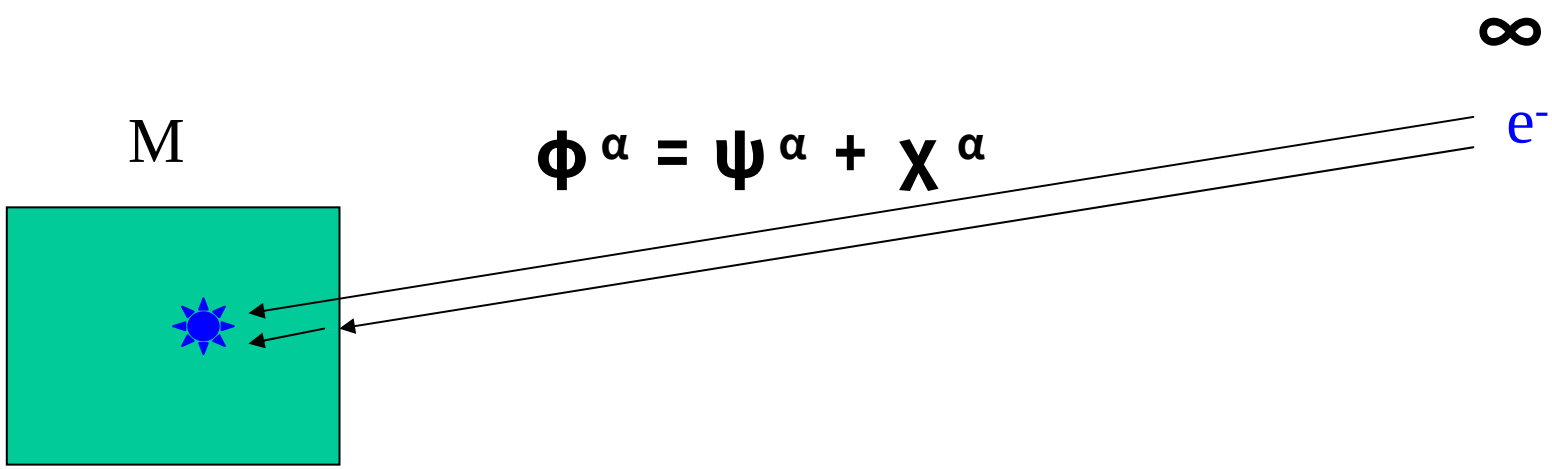
相 α の Inner potential (**内部電位**) ϕ^{α}

$$\phi^{\alpha} = \psi^{\alpha} + \chi^{\alpha}$$



ψ: Outer potential (外部電位)
χ： Surface potential (表面電位)

相M中での電子の化学ポテンシャル



$$\tilde{\mu}_{\mathrm{e}}^{\mathrm{M}} = \mu_{\mathrm{e}}^{0,\mathrm{M}} - F\phi^{\mathrm{M}}$$

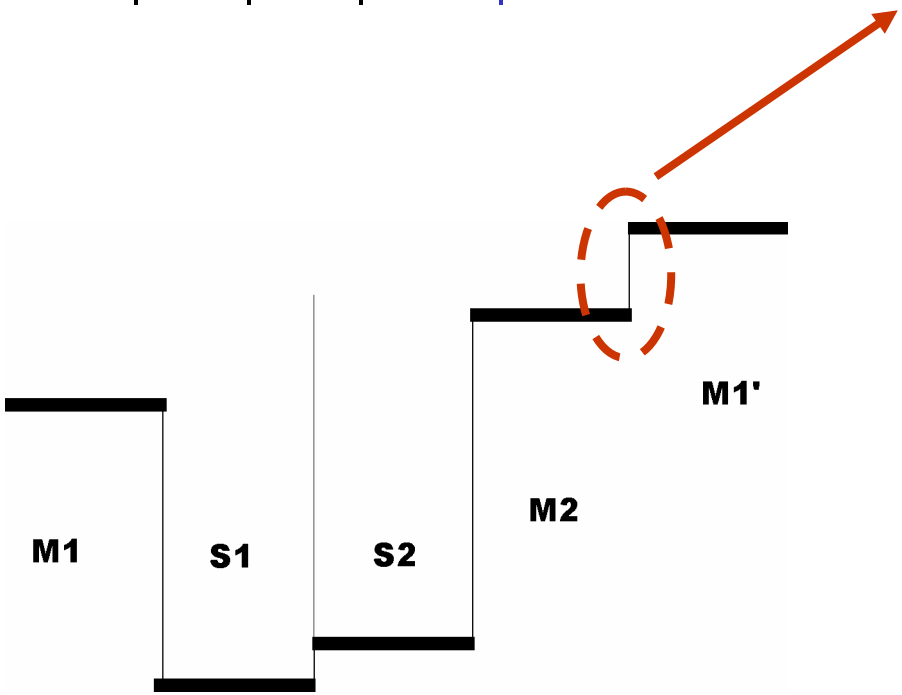
化学的相互作用 ＋ 静電的相互作用 (考え方)

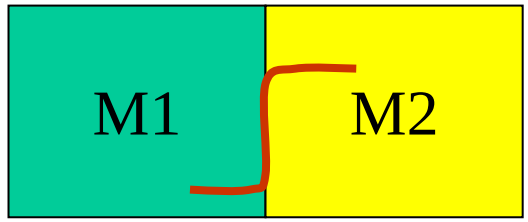
$$\alpha_{\mathrm{e}}^{\mathrm{M}} = \mu_{\mathrm{e}}^{0,\mathrm{M}} - F\chi^{\mathrm{M}} = -\Delta\Phi_{\mathrm{e}}$$

Real potential (実電位) = - 電子の仕事関数

電池の両端の金属 (導体) は同一の物質であるべし

M1 | S1 | S2 | M2 | M1’





電位差が発生

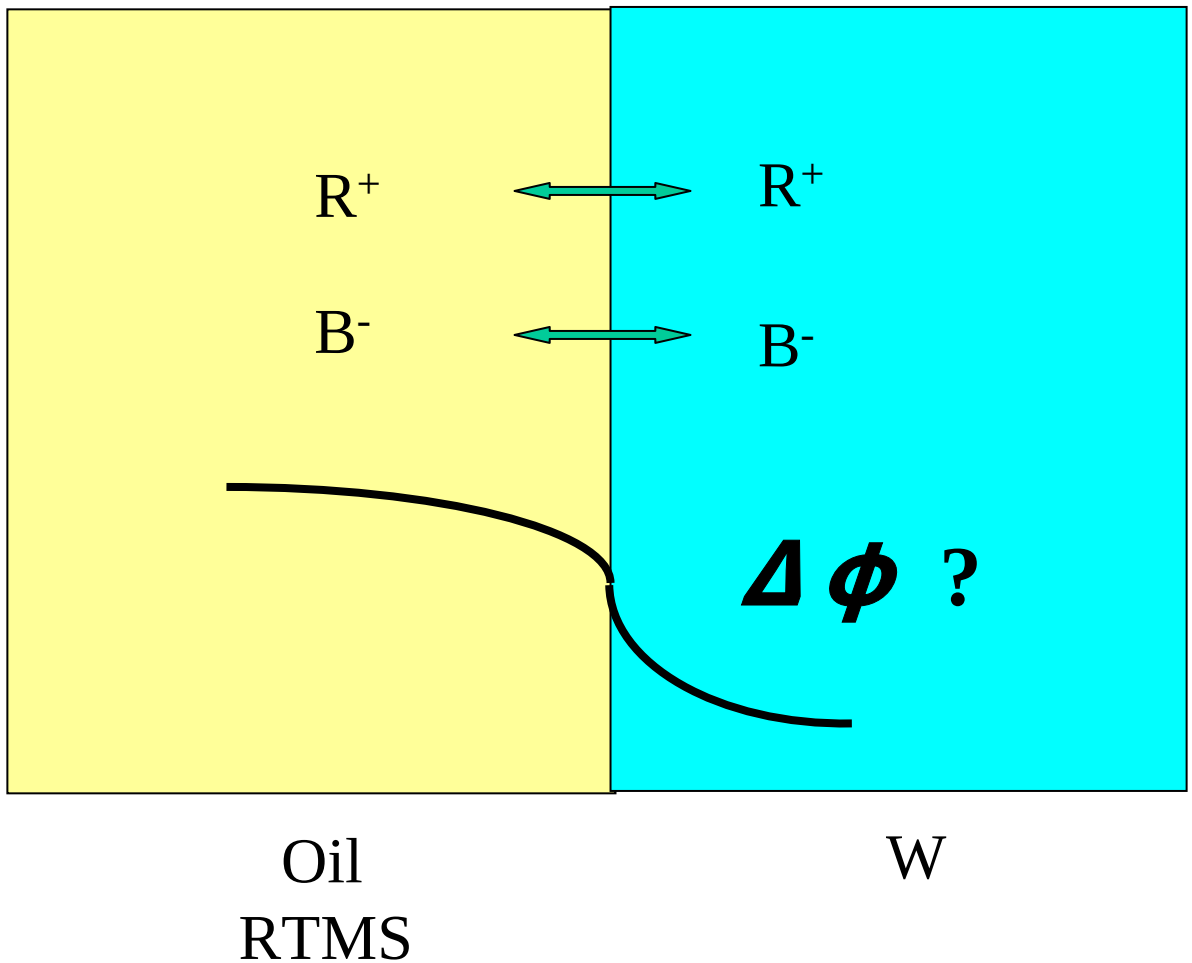
$$E = \frac{p_0}{w}\ln\frac{P}{p} + \frac{p_0}{w'}\ln\frac{P'}{p'} + A$$

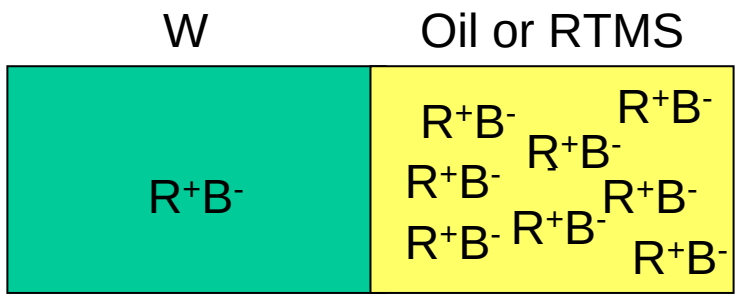
“Das Zusatzglied *A* soll einer etwaigen Elektromotorischen Wirksamkeit der Beruehrungsflaeche der beiden Elektrodenmetalle Rechnung tragen.”

“Wahrscheinlich ist dieselbe Null oder wenigstens sehr klein.”

もう一つのネルンスト式

Phase-boundary potential?





$$\tilde{\mu}_i^{W} = \tilde{\mu}_i^{O}$$

$$\boxed{\Delta_O^W \phi = \Delta_O^W \phi_{R^+}^0 + \frac{RT}{F} \ln \frac{a_{R^+}^O}{a_{R^+}^W}}$$

Nernst 式

where

$$\Delta_O^W \phi_{R^+}^0 = -\frac{1}{zF}(\mu^{0,W} - \mu^{0,O})$$

Standard ion-transfer potential

$$\Delta_{\mathrm{O}}^{\mathrm{W}}\phi = \Delta_{\mathrm{O}}^{\mathrm{W}}\phi_{\mathrm{R}^+}^{0} + \frac{RT}{F}\ln\frac{a_{\mathrm{R}^+}^{\mathrm{O}}}{a_{\mathrm{R}^+}^{\mathrm{W}}}$$

W. Nernst, “Ueber die Loeslichkeit von Mischkrystallen,”
Z. phys. Chem., **9**, 137-142 (1982).

「イオンが分配すると界面電位差ができ、電気二重層が生じる」

この場合は（も）明確に相間電位差を意識している。

分配電位差のより詳しい取り扱いは

R. Luther, “Elektromotorische Kraft und Verteilungsgleichgewicht,”
Z. phys. Chem., **19**, 529-571 (1896).

Nernst は、液ー液界面の電位差も電極ー溶液界面の電位差も基本的には同じメカニズムで説明できると考えていた。

$$E = 0.860T \ln \frac{P}{p} \times 10^{-4} \text{ Volt}$$

$$\Delta_{\mathrm{S}}^{\mathrm{M}}\phi = \text{const.} + \frac{RT}{nF} \ln \frac{[\mathrm{Ox}]}{[\mathrm{Rd}]}$$

Nernst 式 と呼ぶにふさわしいのは 3.

1.

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{[\mathrm{Rd}_1][\mathrm{Ox}_2]}{[\mathrm{Ox}_1][\mathrm{Rd}_2]}$$

は、まずいのか？

- Nernst の功績を正しく評価していない。

"Nernst's theory of the origin of the potential difference at the junction of metals and their salt solutions, which, though it did not touch the question of the metal contanct, served to focus attention more closely on the electrodes as the more important part of the Galvanic cell."
J. A. V. Butler, "*Electrocapillarity*," Methuen, London (1940), p.6.

- 界面電位差に関するトータルな見方
  （電極｜溶液、液｜液界面） に欠ける。

- 片方に注目する（して良い）というネルンスト式の（実用的な）利点が見えない。

まずい！

2. $$E = E^{0\prime} + \frac{RT}{nF}\ln\frac{[\mathrm{Ox}]}{[\mathrm{Rd}]}$$ は、どうか？

- Nernst の功績を正しく評価していない。
- 界面電位差に関するトータルな見方
  （電極｜溶液、液｜液界面） に欠ける。

1. と同じく
まずい！

- しかし、片方に注目する（して良い）というネルンスト式の（実用的な）利点はとらえられている。

$E^{0\prime}$ を標準電極電位と理解する限り
実用的には問題ない。

- それに $\Delta\left(\frac{RT}{nF}\ln\frac{[\mathrm{Ox}]}{[\mathrm{Rd}]}\right) = \Delta(\Delta\phi) = \Delta(E) \simeq \Delta(E_1)$

まあいいか？

しかし、それにしても

どうしてこうなるのか？

伝言ゲーム

土台の劣化

ネルンスト式に限らない。
科学の退化、退廃？？？

一例： Henderson-Hasselbalch **式**

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

or

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{c_{\mathrm{A}^-}}{c_\mathrm{HA}}$$

?

Henderson-Hasselbalch Equation

The central equation for buffers is the **Henderson-Hasselbalch equation**, which is merely a rearranged form of the K_a equilibrium expression.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\log K_a = \log\frac{[H^+][A^-]}{[HA]} = \log[H^+] + \log\frac{[A^-]}{[HA]}$$

$$\underbrace{-\log[H^+]}_{pH} = \underbrace{-\log K_a}_{pK_a} + \log\frac{[A^-]}{[HA]}$$

Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[A^-]}{[HA]} \qquad (10\text{-}16)$$

D. C. Harris, "Quantitative Chemical Analysis," 6th ed., (2003), p.190.

clearly related to the degree of disorder of the chain *(4)*. Furthermore, as Nash says, "partial straightening of chain segments is an ordering process reflected in an entropy decrease" *(5)*. Lambert has not included this point when citing the same reference. I do agree that energy is more "spread out" in relaxed than in stretched rubber chains; however, this leads to an increase in the molecular disorder in the relaxed state.

The Gibbs free energy, ΔG, was selected in the rubber band activity *(6)* in lieu of the Helmholtz free energy, ΔA, since general chemistry texts do not ordinarily mention the latter. It was noted that the assumption of constant pressure was an approximation. I agree that using ΔA is more rigorous. However, even in applying the Helmholtz equation, the assumption of constant volume is not necessarily true, especially if one notes that rubber bands contract laterally when stretched *(4)*. Regardless of which form of free energy is used, it is clear from the activity that the temperature in the $T\Delta S$ term is not perfectly constant so that this term is also approximate. Nevertheless, in my view, making these approximations does not invalidate the conclusions the student obtains from performing the activity.

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The Henderson–Hasselbalch Equation: Its History and Limitations

In 1864 Guldberg and Waage first formulated the mass action law *(1)* and refined it to its final, present form in 1879 *(2)*. This law is one of the basic laws of chemical equilibrium and was crucial to the subsequent development of both physical and analytical chemistry. All three early Nobel laureates recently featured in this *Journal (3–5)*, van't Hoff, Arrhenius, and Ostwald, specifically mentioned Guldberg and his work in their Nobel acceptance speeches *(6)*. Guldberg, its longer-surviving author, died in 1902, a century ago; his law remains one of the foundations of modern chemistry and is an essential part of all chemistry curricula.

Unfortunately, the names of Guldberg and Waage have all but disappeared from U. S. chemistry textbooks and have been replaced by those of Henderson and Hasselbalch. Henderson *(7, 8)* contributed an approximate result, useful over a limited range of conditions for a single buffer mixture of a monoprotic acid and its conjugate base, but it is unfortunate that his name (and that of Hasselbalch, whose contribution is even more peripheral) is now replacing those of Guldberg and Waage. Regrettably, a recent paper in this *Journal (9)* perpetuates this misconception and the associated confusion.

Henderson never claimed to have formulated the mass action law. At the time of his papers on buffer action *(7, 8)*, this law was well-established and, by 1908, had already found its way into both U.S. textbooks *(10)* and history books *(11)*. Moreover, ten years before his papers on buffer action, Henderson had reported on an *application* of the mass action law *(12)*, which already at that time needed no more reference.

In view of the above it is regrettable to read that "The Henderson–Hasselbalch equation is, of course, the mass action expression cast in logarithmic format" *(9)*. It isn't. Instead, the Henderson *approximation*, a term he used himself in this context *(8)*, is an expression that, by replacing actual concentrations by their total analytical equivalents, retains the form of the mass action law but with an entirely different meaning and of a much more restricted applicability *(13)*.

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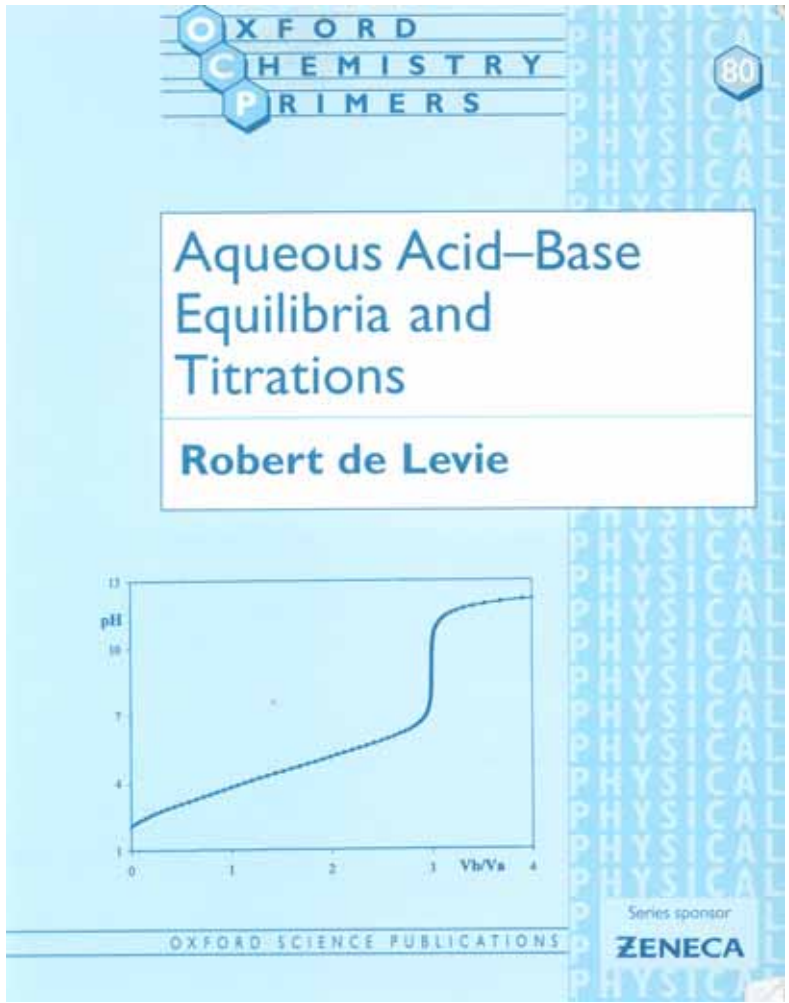
ついでながらお薦めの一冊



他にも似たような話. . . . .

Nicolsky 式

vs.

Nicolsky – Eisenman 式

いわゆる「絶対電極電位」 or 「単極電位」

ところで、ネルンストの問題提起（問題意識）はどう解決されたのか？

1．電位差はどこにあるのか？

2．それを右と左に（ユニークに）分割することはできるか？

R. Parsons, “The single electrode potential: its significance and calculation,” in *Standard Potentials in Aqueous Solution*, A. L. Bard, R. Parsons, and J. Jordan eds., Dekker, New York, (1985), Chapter 2.

M1 | S1 | S2 | M2 | M1’

$$\Delta_{\mathrm{S1}}^{\mathrm{M1}}\phi + \Delta_{\mathrm{S2}}^{\mathrm{S1}}\phi + \Delta_{\mathrm{M2}}^{\mathrm{S2}}\phi \neq E$$

右端にM1を追加する
(同じ種類の金属 (導体) の間の内部電位差は測定可能)

$$\phi^{\mathrm{M1}} - \phi^{\mathrm{M1}'} = \Delta_{\mathrm{S1}}^{\mathrm{M1}}\phi - \Delta_{\mathrm{S1}}^{\mathrm{S2}}\phi - \Delta_{\mathrm{S2}}^{\mathrm{M2}}\phi - \Delta_{\mathrm{M2}}^{\mathrm{M1}'}\phi$$

$$\Delta_{\mathrm{M2}}^{\mathrm{M1}'}\phi \simeq \Delta\Phi_{\mathrm{M2}} - \Delta\Phi_{\mathrm{M1}}$$ **は数ボルトある。**

$$\phi^{\mathrm{M1}} - \phi^{\mathrm{M1'}} = \Delta_{\mathrm{S1}}^{\mathrm{M1}}\phi - \Delta_{\mathrm{S1}}^{\mathrm{S2}}\phi - \Delta_{\mathrm{S2}}^{\mathrm{M2}}\phi - \Delta_{\mathrm{M2}}^{\mathrm{M1'}}\phi$$

いま、簡単のために液間電位差を無視すると

$$\phi^{\mathrm{M1}} - \phi^{\mathrm{M1'}} = \Delta_{\mathrm{S}}^{\mathrm{M1}}\phi - \Delta_{\mathrm{S}}^{\mathrm{M2}}\phi - \Delta_{\mathrm{M2}}^{\mathrm{M1'}}\phi$$

したがって

$$E_{\mathrm{emf}} \neq \Delta_{\mathrm{S}}^{\mathrm{M1}}\phi + \Delta_{\mathrm{S}}^{\mathrm{M2}}\phi$$

つまり、右と左の電極｜溶液間の内部電位差の和とすることは出来ない。

では、左右の「寄与」に分けてしまうことは不可能か？

$$E_{\mathrm{emf}} = (\Delta_{\mathrm{S}}^{\mathrm{M1}}\phi - \mu_{\mathrm{e}}^{\mathrm{M1}}/F) - (\Delta_{\mathrm{S}}^{\mathrm{M2}}\phi - \mu_{\mathrm{e}}^{\mathrm{M2}}/F)$$

こうすると、分割は出来る。

「単極電位」は

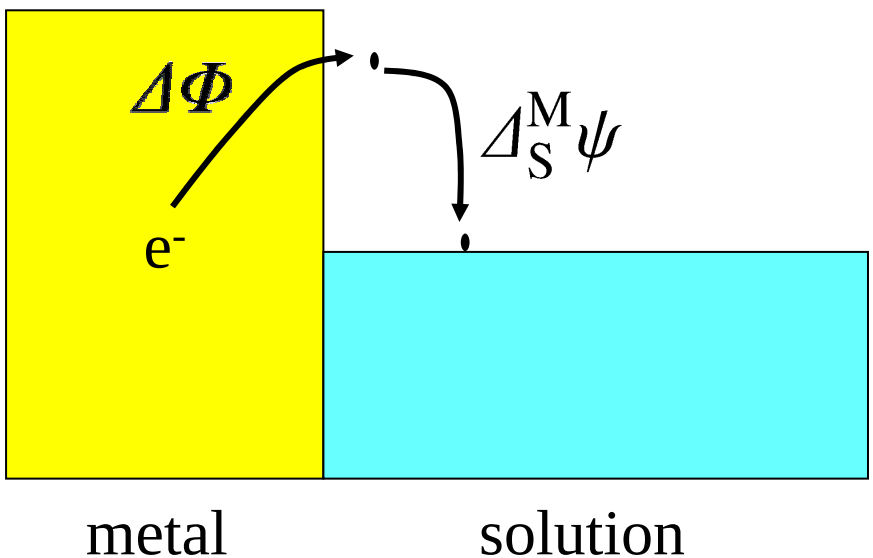
$$\boxed{{}_{\mathrm{r}}E^{\mathrm{M}} = (\Delta_{\mathrm{S}}^{\mathrm{M}}\phi - \mu_{\mathrm{e}}^{\mathrm{M}}/F)}$$

しかし、これは測定可能な量ではない。

Kanevski の考え方

$$
\begin{aligned}
{}_{\mathrm{K}}E^{\mathrm{M}} &= {}_{\mathrm{r}}E^{\mathrm{M}} + \chi^{\mathrm{S}} \\
&= \Delta_{\mathrm{S}}^{\mathrm{M}}\phi - \mu_{\mathrm{e}}^{\mathrm{M}}/F + \chi^{\mathrm{S}} \\
&= \Delta_{\mathrm{S}}^{\mathrm{M}}\psi - \mu_{\mathrm{e}}^{\mathrm{M}}/F + \chi^{\mathrm{M}} \\
&= \Delta_{\mathrm{S}}^{\mathrm{M}}\psi - \alpha_{\mathrm{e}}^{\mathrm{M}}/F \\
&= \Delta_{\mathrm{S}}^{\mathrm{M}}\psi + \Delta\Phi_{\mathrm{M}}
\end{aligned}
$$

この物理的意味



水素電極の場合

$$\mathrm{H^+} + \mathrm{e^-} \Rightarrow \frac{1}{2}\mathrm{H_2}$$

$$\tilde{\mu}^{\mathrm{S}}_{\mathrm{H^+}} + \tilde{\mu}^{\mathrm{M}}_{\mathrm{e^-}} = \frac{1}{2}\mu^{\mathrm{G}}_{\mathrm{H_2}}$$

これより

$$_{\mathrm{r}}E^{\mathrm{H}} = (\alpha^{\mathrm{S}}_{\mathrm{H^+}} - \frac{1}{2}\mu^{\mathrm{G}}_{\mathrm{H_2}})/F$$

測定可

$$\alpha^{S}_{H^+} = -11.276 \text{ eV}$$

J. Farrell and P. McTigue, *J. Electroanal. Chem.*, **139**, 37-56 (1982).

$$H^+(g) + e^-(g) \Rightarrow H(g) \qquad -13.613 \text{ eV}$$

$$H(g) \Rightarrow \frac{1}{2}H_2(g) \qquad -2.107 \text{ eV}$$

$$_{r}E^{H} = 4.44 \text{ V}$$

しかしまた、M 中の電子と溶液中の電子との（仮想的な）平衡を考えれば、

$$ {}_{\mathrm{r}}E^{\mathrm{M}} = -\alpha^{\mathrm{S}}_{\mathrm{e}^-} / F $$

この基準の取り方に依れば、金属中の電子と溶液中の電子の準位を（真空基準で）比較することが出来る。

結論

- 「何事にも先達はあらまほしきことなり」
- ネルンスト式の「相関距離」
- 「なしくずし」の流行る世の中ではあるが、
  角が立っても．．．．．