

Historical burdens on physics

18 Electrochemical cells

Subject:

Apart from electric generators, electrochemical cells are the most important electric energy sources. Historically they were the first technical electric energy sources. There is not doubt that they should be treated in the secondary physics education.

Deficiencies:

They are not found in the physics curriculum. Why? The opinion of the physics teachers may be: "There is not much to understand. All there is to do is to learn by heart the various reactions occurring at the electrodes. These are different according to the type of the cell. Thus, it is a subject typical for the chemistry class."

The impression one gets when consulting the chemistry text book seems to confirm this conclusion. One is lavished with so many details and technical terms that at the end one is unable to notice that the question has remained unanswered – a procedure, that we scientists often reproach to the humanists. The quantity, that would allow for an explanation which is independent of the details and the peculiarities of a particular reaction, i.e. the chemical potential is even not introduced – neither in the physics nor in the chemistry lessons.

Moreover, the subject does not belong exclusively into chemistry. It belongs also to physics, because the electrochemical cell can be explained with methods, which are typical for physics and second, because in general the details of a particular reaction do not matter.

A comparison with the treatment of another class of electric energy sources is advisable. We treat the generator by showing the basic principle by means of a simple model experiment. In this way, the effect which is the base of all electric generators can be understood. The many variants of realistic technical generators are at best betoken. We should proceed in a similar way when treating electrochemical cells. The general working principle should be in the foreground.

Origin:

The fact that the chemical potential is not used.

Gibbs's fundamental equation

$$dE = TdS - pdV + \mathbf{v}d\mathbf{p} + \mu dn + \phi dQ - \dots$$

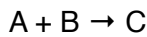
tells us which physical quantities are needed to describe energy exchanges: the thermodynamical quantities temperature T , entropy S , pressure p and volume V , the mechanical quantities velocity \mathbf{v} , and momentum \mathbf{p} , the chemical quantities chemical potential μ and amount of substance n , the electrical quantities electric potential ϕ and electric charge Q , etc. It happens that two of these quantities are almost not in use, just as if they were off-limits: entropy and chemical potential. For that a high price has to be paid: Either one helps himself with cumbersome surrogates – as for instance the enthalpy (instead of the entropy) as a measure for heat, that

suits not really well, or the energy devaluation in order to describe entropy production –, or one simply eliminates those subjects from the curriculum, that could be explained by using these quantities, – as in the case of the electrochemical cell.

Disposal:

Who is not afraid of the chemical potential explains the electrochemical cell in the following way:

The substances A and B can react to C:



The reaction is driven by the chemical potential difference

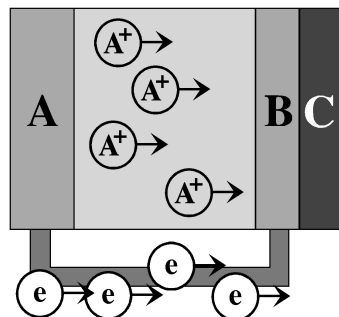
$$\Delta \mu = (\mu_A + \mu_B) - \mu_C.$$

The chemical potentials of the various substances are tabulated. When the reaction extent is ξ , the energy

$$E = \Delta \mu \cdot \xi$$

is released as electric energy. How does the cell work?

As long as the reactants A and B are separated in space one from the other, they cannot react. The reaction has an infinite *reaction resistance*, just as no electric current flows between two bodies with different electric potentials, as long as there is no conductor between them. If A is a gas and we connect the containers with a pipe, A can flow to B and the reaction can begin. In this case, however, the whole energy, that is released will be used, or misused, for the production of heat. We now establish a connection of a particular kind, see the Figure.



A and B are not joined by one connection but by two. One of them – a salt solution (the so called electrolyte) – is permeable or is a conductor only for A^+ ions, but not for electrons e . The other one – a copper wire – is a conductor for electrons and a non-conductor for A^+ ions. Now, A can proceed to B only by separating into A^+ and e . A^+ goes through the A^+ -conductor and e through the e -conductor. When arrived at B, they can react with B to C. For the moment, all the released energy would again only serve to produce heat. However, we now have the possibility to use one of the two currents to drive something. It is more comfortable to choose the electron current. In this way all of the released energy can be tapped.

The out-coming energy can be expressed by means of the voltage $\Delta \phi$ and the electric charge Q . We have:

$$\Delta \phi \cdot Q = \Delta \mu \cdot \xi.$$

Since $Q = z \cdot F \cdot \xi$ (z is a small integer, depending on the nature of the reaction, and F is the Faraday constant), we get the voltage of the cell:

$$\Delta\phi = \frac{\Delta\mu}{z \cdot F}.$$

Summarizing: The electric charge has to go up-hill within the cell, i.e. against its own natural tendency. In order to do so the charge carriers need another driving force. This is the chemical potential difference. Thus the charge carriers go within the cell up-hill the electric potential mountain and down-hill the chemical potential mountain.

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