

# CHEMICAL POTENTIAL – A QUANTITY IN SEARCH OF RECOGNITION

## Measuring the Chemical Potential with an Electrochemical Cell

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How can the values of the chemical potential be determined? In order to keep the explanations concrete let us consider a fuel cell. The general significance of the arguments will be seen at the end.

Fig. 1 shows the cell symbolically: A flow of chemical energy, or power

$$P_{\text{chem}} = (\mu_A - \mu_B) \cdot J_{\xi}$$

is entering the cell from the left and an electric energy flow

$$P_{\text{el}} = (\varphi_1 - \varphi_2) \cdot J_Q$$

is leaving it toward the right.

Here,  $\mu_A$  is the total chemical potential of the reactants and  $\mu_B$  the total chemical potential of the reaction products.  $J_{\xi}$  is the reaction rate, i.e. the reaction extent per time and  $J_Q$  is the electric current, i.e. the charge flow per time.

Since the fuel cell works reversibly, the entering chemical energy flow must be equal to the outgoing electrical energy flow:

$$(\mu_A - \mu_B) \cdot J_{\xi} = (\varphi_1 - \varphi_2) \cdot J_Q. \quad (1)$$

This equation has a suggestive form: The reactants enter the fuel cell at a high chemical potential  $\mu_A$ . They then transform into other substances with a lower chemical potential  $\mu_B$ . Thereby, they “lift” the electric charge from the lower electric potential  $\varphi_2$  to the higher potential  $\varphi_1$ . Thus, the decline or drop of the chemical potential is used to lift or raise the electric charge to a higher electric potential.

The cell could also be used in the opposite way: electric energy at the entrance and

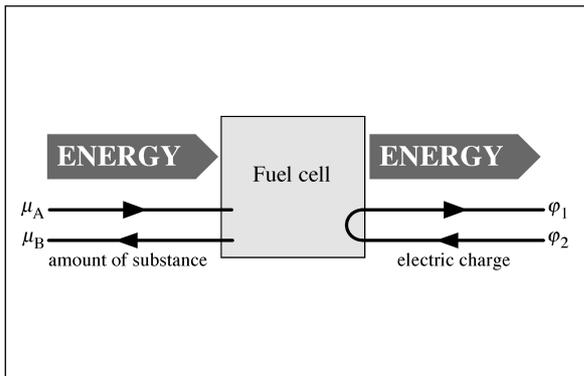


Fig. 1. Flow chart of the fuel cell. While amount of substance goes from high to low chemical potential, electric charge is lifted from low to high electric potential.

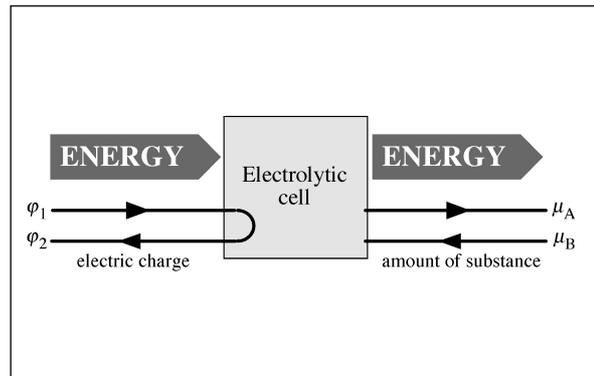


Fig. 2. Flow chart of the electrolytic cell. While electric charge goes from high to low electric potential, amount of substance is lifted from low to high chemical potential.

chemical energy at the exit, Fig. 2. Electric charge is going from high to low electric potential, thereby lifting substances from low to high chemical potential. Let us mention that this kind of device has several analogs. In an electric water pump, electric charge goes from high to low electric potential and water goes from low to high pressure. The opposite happens in a hydroelectric power plant: water goes from high to low pressure and raises electric charge from low to high potential. And yet another example: in a thermal power plant, entropy goes from high to low temperature (high to low “thermal potential”), thereby raising electric charge from low to high electric potential. The opposite is an electric heat pump, where electric charge goes down and entropy goes up.

Back to the measurement of the chemical potential.

With Eq. (1), we have a means to measure differences of chemical potentials:

$$\mu_A - \mu_B = \frac{(\varphi_1 - \varphi_2) \cdot J_Q}{J_\xi}$$

The method is as follows: Measure the electric energy flow (or power)  $P_{el} = (\varphi_1 - \varphi_2) \cdot J_Q$  and divide by the reaction rate  $J_\xi$  [1]. Actually, the procedure is even more simple. The electric current and the reaction rate are related:

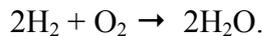
$$J_Q = z \cdot F \cdot J_\xi$$

Here,  $z$  is a small integer, whose value depends on the considered reaction, and  $F$  is the Faraday constant. We get:

$$\mu_A - \mu_B = z \cdot F \cdot (\varphi_1 - \varphi_2).$$

Thus, the chemical potential difference can directly be calculated from the open-circuit voltage of the corresponding electro-chemical cell.

As an example, let us consider the hydrogen fuel cell. The net reaction is



Since the hydrogen is ionized, for each 2 moles of hydrogen we have 4 moles of electrons:



and thus  $z = 4$ . We give a simple explanation of how the fuel cell works by introducing a wire as an electron conductor and ion insulator, and an electrolyte as the inverse: an ion conductor and electron insulator.

The observed electric potential difference is 1.23 V. With  $F = 9.65 \cdot 10^4$  C/mol, we get:

$$\begin{aligned} \mu_A - \mu_B &= 2\mu(\text{H}_2) + \mu(\text{O}_2) - 2\mu(\text{H}_2\text{O}) = z \cdot F \cdot (\varphi_2 - \varphi_1) \\ &= 4 \cdot 9.65 \cdot 10^4 \text{ C/mol} \cdot 1.23 \text{ V} = 474.8 \text{ kG}. \end{aligned}$$

Since the chemical potentials of  $\text{H}_2$  and of  $\text{O}_2$  are zero by definition, the chemical potential of water turns out to be:

$$\mu(\text{H}_2\text{O}) = -237 \text{ kG}.$$

In principle, every chemical reaction can be run reversibly and electrochemically. Starting from the chemical elements, whose potential values are arbitrarily chosen to be zero for norm conditions, in principle the potential of any other substance can be measured.

Actually, the practical measurement of chemical potentials is not necessarily done in this way. When we need a practical way to measure some quantity, in general we do not go back to the definition of this quantity. What we do is to look for a way which is technically simple and inexpensive. For a measurement of the quantity  $X$ , any effect which depends on the values of  $X$  is applicable. In general, we do not measure a temperature by directly using the thermodynamic definition of the temperature. Instead we use thermocouples, resistance thermometers or mercury thermometers. The same holds true for the measurement of chemical potentials. Here, the number of possible effects that are appropriate for a measurement is even larger than for temperature, given the great number of different substances and the great number of phenomena that are related to the chemical potential.