

Thermodynamics and electrochemistry

Introduction

Thermodynamics was originally developed along with heat machines like the steam engine. The central point was that there are limits as to which extend thermal energy can be converted to work. Today thermodynamics has found use in practically all technical disciplines and involves much more than thermal engines.

In this context, thermodynamics is relevant for

- power generation from thermal energy sources.
- quantification of the energy content of a fuel available for a given application.
- the understanding of electrochemical cells for conversion and storage of energy.
- calculation of theoretical cell voltages.

Electrochemistry is the bridge between chemistry and electricity. It is a fundamental feature of chemistry that it is governed by the electrons in the molecules and atoms. Chemical reactions often involve transfer of electrons, i.e., oxidation and reduction and by means of electrodes. The energy of the electrons in transfer can be manipulated externally. One might say that electrochemistry provides a tool for our direct interference with the chemical systems. This is very useful in the broad field of energy technologies as we can extract chemical energy directly as electrical energy in batteries and fuel cells. Likewise, we can store electrical energy in chemical systems by means of rechargeable batteries and electrolyzers.

Thermodynamics is about energy, especially thermal and chemical energy, which are both disordered (uncoordinated, without a common direction of possible action). Ordered energy as macroscopic mechanical energy, electrical energy and work play a role too, but the relevance of thermodynamics lies in its ability to describe the interplay between disordered and ordered energy. Thermodynamics is also an abstraction treating the extreme cases, which are the ultimate limits for energy transfer. The term reversibility is central despite it is never realized in real systems. Argumentations are often supported by so called “thermodynamic machines” which are combinations of different ideal unit operations without friction or any other imperfections not given by thermodynamics; imperfection that in theory can be minimized as much as we like approaching zero.

Recap of basic thermodynamics

Definitions

Different textbooks use either capital letter symbols or small cap symbols for the thermodynamic functions and other physical quantities. There seem to be no general agreement. Here capitals are used for absolute quantities (external quantities, depending on the size of the system) and small cap symbols for molar or mass based quantities (internal quantities). As an example, in this text “ U ” is used for internal energy (with the unit Joule, J) while “ u ” is used for molar or mass specific internal energy (J mol^{-1} or J kg^{-1} , respectively). Likewise “ C_V ” is the absolute constant volume heat capacity (J K^{-1}) and “ c_v ” the molar or mass specific constant volume heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$ or $\text{J kg}^{-1} \text{K}^{-1}$).

The thermodynamic system

The “thing” we look at and assign quantities to is the *system* or the *thermodynamic system*. It constitutes a fixed volume, a fixed amount of substance, the interior of a box or something else with a well-defined boundary. If the system is defined by walls, these walls may be included or excluded in the system. Everything outside the system (the rest of the universe) is called the surroundings. In thermodynamics, we look at changes in the system caused by exchange of energy or matter between the surroundings and the system. If energy enters the system, it is counted as positive, if it leaves, it is counted negative. Everything is from the perspective of the system. See Figure 1. This is rather trivial, but yet important to note.

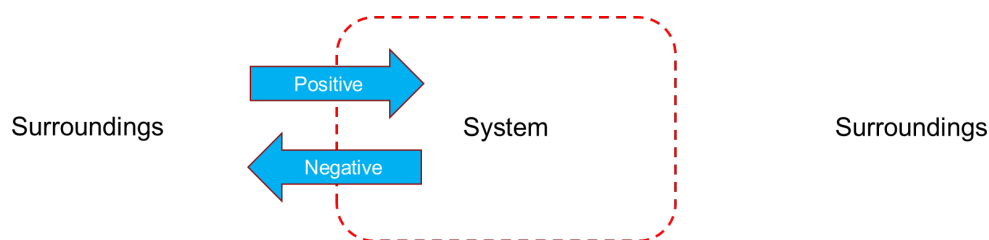


Figure 1. The thermodynamic system and its surroundings. The arrows represent flow of energy or matter.

Some more definitions and terms

An *isolated* system is a system that does not exchange heat with the surroundings.

A *closed* system does not exchange matter with the surroundings.

An *adiabatic* process is a process with no exchange of heat with the surroundings.

An *isothermal* process is a process carried out at a constant temperature.

An *isobaric* process is a process carried out at constant pressure.

An *isochoric* process is a process carried out at constant volume.

An *exothermic* (or *exothermal*) process is a process that evolves heat. The opposite is an *endothermic* (or *endothermal*) process.

Heat and work

The most common way the system interacts with its surroundings is by exchange of *heat* and *work*. Heat and work are both energy in transition i.e., energy that is transferred.

If the system is heated with energy from the surroundings, we say that heat enters the system or that heat is transferred to the system. The temperature increases as the system accumulates more energy. We say that the system increases its thermal energy, i.e., energy in the form of molecular motion and vibrations. It does not contain the transferred heat; it contains thermal energy that was transferred as heat. Heat as well as thermal energy are disordered forms of energy as the energy does not act in a specific direction.

The other form of energy in transition is *work*. In contrast to heat, it is directional and ordered. If the system is compressed from the outside, work is exerted on it. This is called compression work and is often visualized by a piston moving in one direction. The definition of work is that it is *movement against an opposing force*. In the moving piston case, the opposing force is that of the pressure in front of the piston. After compression, the system has increased its energy because the molecules in the system have been accelerated by the piston. The system now contains the compression energy as an increase in thermal energy. It does not contain the work applied to it. Moreover, one cannot tell from the system if the increase of thermal energy was caused by a flow of heat or by work. Examples of other forms of work are stirring motion (locally ordered to begin with) and electrical energy in a wire (also directional).

The thermodynamic state functions

The fundamental thermodynamic energy functions are the *internal energy*, the *enthalpy*, the *Gibbs free energy* and the *Helmholtz free energy*. The last fundamental thermodynamic function is the *entropy*. This is not an energy function since it has another dimension (another unit), but it is defined by the state of the system. In the following, the thermodynamic functions will be summarized. Heat and work are not state functions since they are not defined by the state of the system. One could say that they are immediately “forgotten”.

Internal energy

The internal energy, U , is in principle all the energy the system contains, regardless the form. It includes thermal energy, chemical energy, any kinetic or potential energy and even nuclear energy. We cannot easily determine the total internal energy of a system, but that is not a problem either, because we are only interested in the changes, and changes can be accounted for with high accuracy. These changes are changes in thermal energy brought about by heat and work and in some cases by chemical reactions evolving or consuming heat¹. So, practically in thermodynamics, the internal energy is the thermal energy of the system, which is contained by the molecules and atoms by their motion, vibrations and repulsive and attractive interaction (kinetic and potential energies). Again, this is called *heat* in colloquial language, but not in thermodynamics. In thermodynamics, thermal motion of the molecules in the system is indeed *thermal energy*.

¹ The use of the term *heat* here is justified by the fact that heat from the chemical reaction is added to the thermal energy pool of the system (or consumed by the chemical reaction)

For a system that is only changed by flows of heat or by work and no chemical reactions take place, we need not consider the chemical energy of the system, since it doesn't change.

The definition of a perfect or ideal gas

For calculations involving a gas, the gas is often assumed to be a *perfect gas* or an *ideal gas*. These terms assume that there is no interaction between the gas molecules apart from fully elastic collisions. There is no attractive or repulsive forces and thus the molecule don't feel each other. Moreover, the molecules don't occupy any space. This simplification is a reasonable approximation at high temperature or low pressure when the intermolecular distance is large. It makes many calculations simpler since the gas can be described by the ideal gas equation (1).

$$pV = nRT \quad (1)$$

With the pressure, p , the volume, V , the number of mole gas, n , the gas constant R and the absolute temperature T (in Kelvin). It follows that if there are no interactions between the molecules, the distance between them has no effect on the energy they contain. Consequently, the internal energy of a perfect gas does not depend on the pressure.

Enthalpy

The enthalpy, H , is a slightly modified form of internal energy. By definition, it is the internal energy with the addition the product of the volume and the pressure of the system.

$$H \equiv U + pV \quad (2)$$

Enthalpy is more practical to use than internal energy in systems of constant pressure. When the internal energy changes, the system volume will change too to maintain constant pressure. This implies exchange of pressure-volume work with the surrounding and thus an accompanying additional change of internal energy, which complicates calculations. When using enthalpies, the exchange of work with the surrounding the volume change implied is exactly compensated by the change in the pV term of the enthalpy. In other words, the pV term is a buffer keeping track of the work balance at all times. Like for internal energy, we are only interested in the changes and absolute values are irrelevant. The absolute values found in tables are based on a given definition of the starting point of the scale, just like for temperature, which can be quantified in centigrade and Kelvin with the only difference being the zero of the scales. A simplified, yet useful statement is that enthalpy is the practical internal energy at constant pressure. Like the internal energy, the enthalpy of a perfect gas is independent of pressure.

Entropy

Entropy, S , is referred to as the degree of disorder in the system, but more correctly, it is a measure of the spreading of energy and matter. It is first of all a statistical phenomenon. The case where thermal energy is spread among all molecules present is more likely than a case where it is concentrated in one area or among a small number of molecules. Likewise, it is much more likely that molecules in a gas are spread over the entire volume available than they are accumulated in certain locations.

Entropy is easily created in a process, but it cannot be destroyed. This is the key to the importance of entropy in relation to energy technologies. No single process can make the energy less disordered or

spread, only the opposite. A system can indeed change state to a less disordered one (i.e., with lower entropy), but only if the process of change is coupled to another process elsewhere leading to a gain of entropy of at least the same magnitude.

The *second law of thermodynamics* is also called the entropy law. It states that entropy cannot be destroyed.

Entropy is defined statistically by Boltzmann's entropy formula (not included here) and thermodynamically by Clausius' inequality

$$dS \geq \frac{dQ}{T} \quad (3)$$

Where S is the entropy of the system, Q is a quantity of heat transferred into the system and T is the temperature of the system. The entropy of the system can change due to the entropy a flow the heat carries (the spread of the energy in the heat flow). Then entropy is only transferred, and no new entropy is generated. The heat transfer is then reversible. It is the case when heat is transferred without a temperature difference (an infinitively slow thermodynamic extreme, since the driving force for heat transfer is a temperature difference). If heat is transferred over a temperature difference, as in the real world, the entropy increases additionally by generation of entropy as the concentrated energy of the inflowing heat is dissipated among the molecules of the system which are originally at a lower temperature and thus a lower thermal energy level.

Entropy is not an energy function. It can be seen from (2) that the unit of entropy is J K^{-1} for absolute quantities or $\text{J K}^{-1} \text{mol}^{-1}$ for molar quantities.

It is a good rule of thumb that with a fixed amount of matter, the entropy of a gas phase is much higher than that of a condensed phase (a liquid or a solid) because the gas molecules spread over the entire volume available while condensed matter only occupies its own specific volume. A liquid has higher entropy than a crystalline solid since the latter has a correspondingly limited number of fixed positions in the lattice. This is all about spatial entropy, i.e., spreading in space. The thermal entropy is more similar for the three phases. The total entropy is ranked in the following order:

$$S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}} \quad (4)$$

If a chemical process leads to a net increase of gaseous molecules, one can be very certain that the entropy change of the reaction is positive. Likewise, if there is a net reduction in the number of gaseous molecules, entropy diminished. This is not allowed, but the process might still be possible if it generates heat. When calculating the change of thermodynamic functions in a reaction, constant temperature is assumed. This means that a heat evolving reaction (an exothermic reaction) supplies heat to the surroundings in order to maintain a constant temperature. This heat flow carries entropy and since the thermal energy of the flow is generated by the process, the entropy of it is generated too. This generated thermal entropy is often much higher than the lost spatial entropy of the reaction and thus the second law is not violated. This balancing principle is the basis for concept of Gibbs free energy.

Gibbs free energy

The ultimate indicator deciding whether a process will happen or not is the total (universal) change of entropy resulting from it (including all other coupled processes). A common coupled process is the transfer of heat to the surroundings from an exothermic (heat evolving) process, which could be the combustion of a fuel. If the fuel is hydrogen the reaction



leads to a net loss of 1.5 moles of gas molecules per mole of reaction. The spatial entropy is thus reduced. At the same time, heat is transferred to the surrounding since the process is highly exothermal. The thermodynamic driver of the process is the total entropy balance, not what is given by the change of entropy with all species at the same temperature. The thermal entropy generated and carried out by the heat flow can be determined by eq. (2). In the ideal case, the heat is transferred at constant temperature (with zero temperature difference) and no additional entropy is generated in the transport process. With no entropy generation, this process is by definition reversible, and we can replace “ \geq ” with “ $=$ ” in eq. (2) and since the temperature is constant, it integrates to

$$\Delta S = \frac{Q_{\text{rev,min}}}{T} \quad (6)$$

Where $Q_{\text{rev,min}}$ is the minimum flow of heat to the surrounding needed to just match the change of entropy of the reaction ΔS_r .

The reaction heat is the enthalpy change of the reaction, ΔH_r is the total energy liberated by the reaction. If the fuel is combusted for the purpose of power generation, then as much as possible should not be discarded to the surrounding but converted to power (i.e., work, ordered energy with zero entropy) and now we can determine how much of the combustion enthalpy is at our disposal for generating work. The ideal reversible case with no additional entropy generation is when the entropy change of the reaction is exactly matched by the entropy carried by a part of the reaction enthalpy (= $Q_{\text{rev,min}}$) flowing as heat to the surroundings.

$$\Delta S_r = \frac{Q_{\text{rev,min}}}{T} \quad \text{or} \quad Q_{\text{rev,min}} = T\Delta S_r \quad (7)$$

The rest of the reaction enthalpy we can use freely without any restriction from the second law. We call that the Gibbs free energy of the reaction, ΔG_r (after the American scientist Josiah Willard Gibbs).

$$\Delta G_r = \Delta H_r - T\Delta S_r \quad (8)$$

Eq. (7) is valid for all processes, not only chemical reactions

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

Note that energies leaving the system are signed negative. This means that work or heat delivered by the system are signed negative. An exothermic reaction has a negative value of ΔH_r and if it is capable of producing work the value of ΔG_r is also negative. Consequently, a negative change of entropy of the reaction causes a less negative value of ΔG_r and less work can be delivered by the system.

If the process results in a net increase of entropy (at constant temperature) the capability to deliver work exceed the enthalpy of reaction. This is possible, but to observe energy conversion, only if heat can be absorbed from elsewhere.

Helmholtz free energy is similar to Gibbs free energy but defined at constant volume instead of constant pressure. It relates to internal energy as Gibbs free energy relates to enthalpy.

Thermal engines

The Carnot limitation

Any heat engine, i.e., a heat driven machine that produces work from a flow of heat, is ultimately limited in conversion efficiency by Carnot's principle stating that the efficiency, η_{\max} , of the conversion process depends on the temperature of the heat source, T_h , and the temperature at which unutilized heat is liberated from the system, T_c .

$$\eta_{\max} = \frac{T_h - T_c}{T_h} \quad (10)$$

The Carnot limit is restricting any process in which heat is converted to work. Examples are internal combustion engines, thermal power plants, steam engines, jet engines and Stirling engines. Real engines have even lower efficiency, due to various imperfections (e.g., heat loss, friction and unideal combustion) and by reducing the imperfections, the Carnot limit can be approached but never met and certainly not passed. Fuel cells, which operate by a more direct conversion process without converting the chemical energy into heat first, are not limited by Carnot's principle, but still limited by the change in Gibbs free energy of the process.

Carnot's principle can be justified by considering the entropy balance of the conversion process. See Figure 1. A flow of heat from high temperature to low temperature without generation of work is spontaneous because the cold heat sink gains more entropy than the hot heat source loses. In both ends $\Delta S = Q/T$, in the ideal case, so with same heat flow, a low temperature gives the highest entropy. Thus overall, entropy increases. If part of the heat energy is converted into work (we don't care how) there can still be a net increase in entropy. The limiting case is when the entropy is just kept constant with balanced entropy flows out of the source and into the sink.

More intuitively, when work is generated from heat, it is done by thermal expansion of a medium and in order to close the cycle the medium must be contracted again before it can be re-expanded. This contraction is driven by heat liberation at a lower temperature, T_{low} .

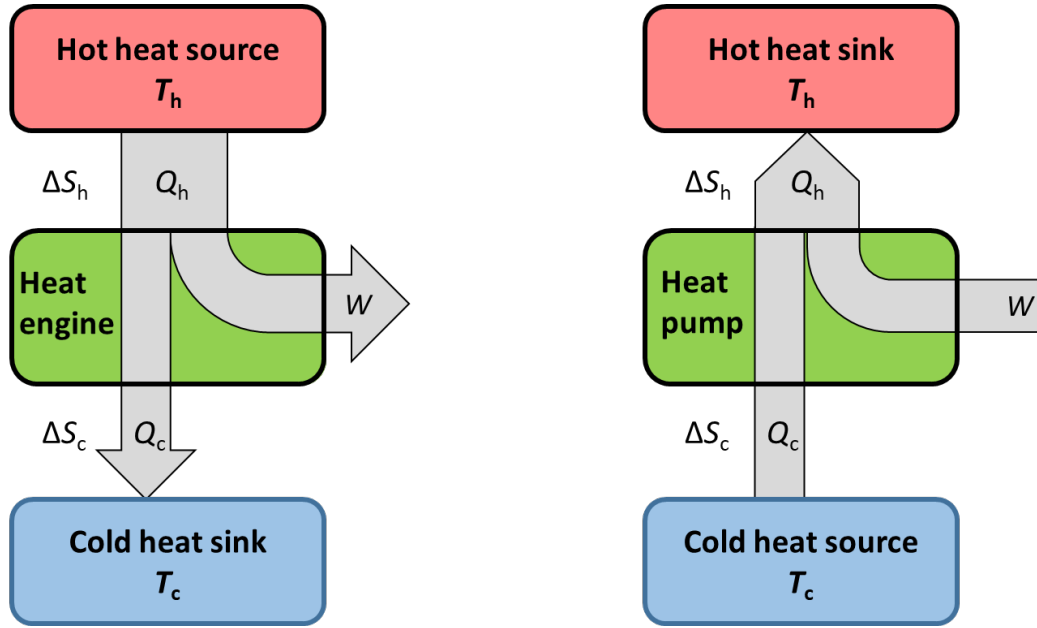


Figure 2. Thermodynamic principles of a heat engine and a heat pump.

The work extracted equals the heat energy consumed

$$W = Q_h - Q_c \quad (11)$$

The entropy balance with maximum work generation is (without signing)

$$\Delta S_h = \Delta S_c \quad \text{or} \quad \frac{Q_h}{T_h} = \frac{Q_c}{T_c} \quad (12)$$

Rearranging (11) and insertion into (10) gives

$$W_{\max} = \left(1 - \frac{T_c}{T_h}\right) Q_h \quad (13)$$

Which corresponds to (9). The value in the brackets is the Carnot factor or Carnot efficiency, η_{\max} .

$$W_{\max} = \eta_{\max} Q_h \quad \text{with} \quad \eta_{\max} = 1 - \frac{T_c}{T_h} = \frac{T_h - T_c}{T_h} \quad (14)$$

One may also look at it this way: if efficiency is “what you get” divided by “what you pay”, the temperature difference, $T_h - T_c$, in the numerator of the last term of (13) is kind of a measure of the energy extracted from the flow (the work obtained, what you get) and T_h in the denominator is a similar measure of all the high quality energy supplied from the hot source (the energy spend, what you pay).

Heat pumps

A heat pump is a device that upgrades heat to a higher temperature. It is mostly used for domestic heating but can just as well be used in industrial processes. The idea is to utilize a low-grade heat source for heating something already being at a higher temperature. This process is not spontaneous but can be forced by work.

In a thermodynamic sense, a heat pump is the reverse of a heat engine. See Figure 1. Even in the ideal case described in the previous part, the efficiency of a heat engine is always below one, so we can expect that the efficiency defined similarly for the reverse process is then above one. The missing entropy in the flow into the hot sink is generated from the work applied to the device. Again, in the ideal case the entropies of the two heat flows are just balancing. The work contains no entropy but generates entropy in the device. As we often see in thermodynamics, it is not important how such a heat pump is constructed, we only set the limits that thermodynamics dictates.

A real physical heat pump can be constructed in different ways, but the usual way is shown in Figure 2. A liquid with a suitable boiling point is evaporated by low grade heat from the low temperature heat source. It is then compressed (this is where work is applied) and the compression work results in a heating of the vapour (remember, the energy added as heat is contained as thermal energy. It is not contained in the pressure). Due to the increased pressure, the vapour condenses in the condenser and the latent heat (condensation heat) heats up the fluid further and the heat, or part of it, is released at the high temperature. After releasing heat, the fluid, now in liquid form, passes a nozzle after which the pressure is much lower and it evaporates again. This time the latent heat leads to a cooling of the fluid it meets the low temperature heat source and the circle is completed.

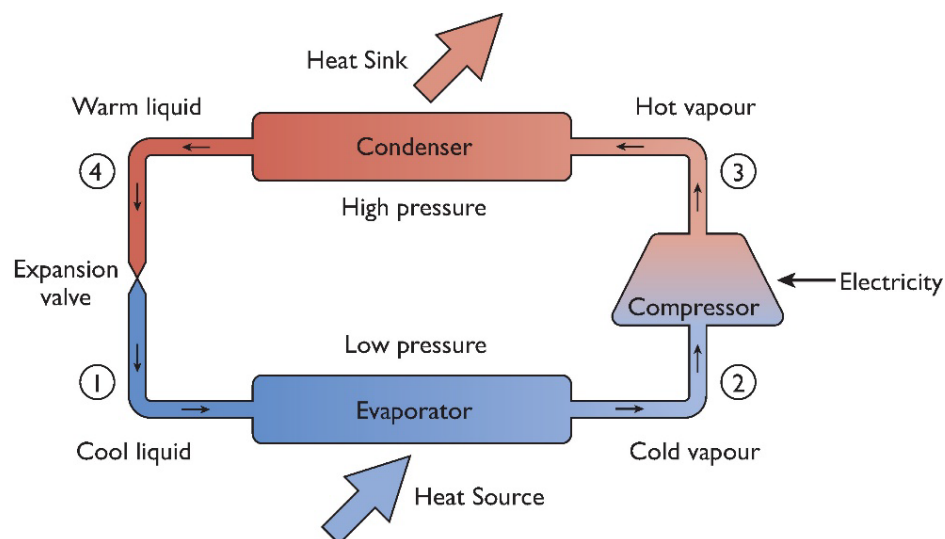


Figure 3. The usual working principle of a heat pump.

When used for domestic heating, the low-grade heat source can be the air outside or underground pipes with a circulating heat transfer liquid. With efficiencies above one, heat pumps are normally not described by the term efficiency but by the term *Coefficient of Performance* (COP).

$$\text{COP} = \frac{\dot{Q}_h}{\dot{W}_{\text{comp}}} = \frac{P_h}{P_{\text{el}}} \quad (15)$$

Where \dot{Q}_h is the heating heat flow, \dot{W}_{comp} the compressor work flow, P_h the heating power and P_{el} the electrical power used for the compressor. COP depends on the heat pump, the mode of operation and on the temperatures of the heat source and sink. Therefore, a heat pump cannot be labelled a specific COP, but is characterized by charts with different conditions. However, common COP values are 2-4.

The ultimate idealized COP is

$$\text{COP}_{\text{max}} = \frac{Q_h}{W_{\text{min}}} \quad (16)$$

and can be found from Carnot's formula (9) slightly rearranged now with W_{min} instead of W_{max} . This is the same value for work, the limiting case.

$$W_{\text{min}} = \frac{T_h - T_c}{T_h} Q_h \quad (17)$$

Inserting (16) into (15) gives

$$\text{COP}_{\text{max}} = \frac{T_h}{T_h - T_c} \quad (18)$$

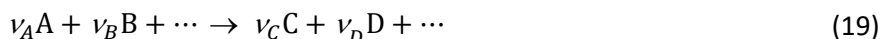
Thermodynamic functions of chemical reactions

When a chemical reaction takes place, thermal energy is either liberated or consumed as a result of the energy balance between chemical bonds formed and chemical bonds broken. The energy of a chemical bond is negative in the sense that when two atoms form a bond, they commonly attain a lower energy level than before. As energy cannot vanish it is liberated as thermal energy. In a total chemical reaction, some bonds are broken, and others are formed. If the chemical energy is lowered by the process, the liberated energy is concentrated among the product molecules as thermal energy. If the energy would remain with the product molecules as kinetic energy in velocity and vibrations, the process could easily reverse regenerating the reactant molecules, because the necessary energy would still be close by ready to be consumed again. However, the highly concentrated energy will shortly after be dissipated among other molecules and thus be less available to a reverse reaction. This spreading of the reaction energy increases the entropy of the system, and the likelihood of the reverse reaction is small.

It is very useful to determine the change in the thermodynamic functions as consequences of chemical reactions. In tables it is always deemed that the final temperature is the same as the initial temperature,

very often 298.15 K, and that the pressure of all reactants and all products is the standard pressure, 1 bar. Any thermal energy generated is thus assumed transferred out of the system. This is the heat of reaction. If thermal energy is consumed by the process, the equivalent amount is assumed transferred to the system.

The change in any of the thermodynamic functions is then the sum of the respective values of the products (what is gained) minus that of the reactants (what is consumed or lost). In (15), x is the molar thermodynamic function of interest. Δx_r is the molar change of thermodynamic function of the reaction and x_i and x_j are the thermodynamic functions of the reacting and formed species. ν_i and ν_j are the stoichiometric coefficients, i.e., the numbers in the chemical equation stating the number of moles of each molecule. (x should not be confused with molar fractions)



$$\Delta x_r = \sum_{prod.} \nu_i x_i - \sum_{reac.} \nu_j x_j \quad (20)$$

This is the general principle used for both enthalpy, entropy and free energy of reaction and now we only need decide which molar values can be assigned to the involved species.

As stated above, we cannot easily (practically) determine absolute values of the enthalpy of a system or a substance, just as we cannot for the internal energy, but suitable definitions have been made. One valid way is just to decide on one arbitrary state as basis for the zero point of the scale for enthalpy, entropy and Gibbs free energy. This is an approach similar to the Celsius scale starting at the melting point of ice. It works since we are only interested in the changes, but a smarter and well adapted way is to use enthalpies of formation and free energies of formation. For the entropy scale, so called third law entropies are used. This is all explained in the following paragraphs.

Standard enthalpy of formation

Molar standard enthalpy of formation, Δh_f^0 , is defined as the enthalpy of formation of the compound by chemical reactions from the constituting elements in their stable states, i.e., at 1 bar and typically at 298.15 K. The “0” indicates that standard conditions apply. Taking water as an example, the stable state at these conditions is liquid, not gas or solid. This is trivial, but many solids can exist in different structures and then the one with the lowest energy is considered the stable form. The enthalpy of formation is then the enthalpy change of the reaction forming liquid water at 298.15 K from hydrogen gas and oxygen gas each at 1 bar and 298.15 K. By this definition, the standard enthalpy of formation thus becomes zero for all elements in their stable state at 1 bar and 298.15 K, and then the problem of defining absolute enthalpies is surpassed. Any compound can be assigned a standard enthalpy of formation and the enthalpy change of any chemical reaction can subsequently be calculated as the difference between the formed and the consumed species. Since the enthalpy of the elements as well as the final compound are state functions, it doesn't matter through which chemical routes formation for the final compound happens.

For the general reaction



the molar standard enthalpy change of reaction, Δh_r^0 , is

$$\Delta h_r^0 = \nu_C \Delta h_{f,C}^0 + \nu_D \Delta h_{f,D}^0 - \nu_A \Delta h_{f,A}^0 - \nu_B \Delta h_{f,B}^0 \quad (22)$$

and in the general case

$$\Delta h_r^0 = \sum_{\text{prod.}} \nu_i \Delta h_{f,i}^0 - \sum_{\text{react.}} \nu_j \Delta h_{f,j}^0 \quad (23)$$

Again, the standard enthalpy of formation of any element is zero, because formation of an element from itself involves no change at all.

Standard free energy of formation

Molar standard Gibbs free energy change of reaction, Δg_r^0 , is defined the same way as enthalpy of formation, just with free energy values. It follows that calculation of molar standard Gibbs free energy of reaction is done by the general formula

$$\Delta g_r^0 = \sum_{\text{prod.}} \nu_i \Delta g_{f,i}^0 - \sum_{\text{react.}} \nu_j \Delta g_{f,j}^0 \quad (24)$$

Like the standard enthalpy of formation, the standard Gibbs free energy of formation of any element is zero.

Standard third law entropies

In contrast to the functions internal energy and enthalpy, a point of zero has been defined for entropy. It is done by the third law of thermodynamics stating that the entropy of any perfect crystal at the absolute zero of the temperature scale (0 K) has zero entropy. From that, the entropy content can be calculated at any other temperature and form by rewriting (2) a little and integration it from $T = 0$ K to the temperature of interest. If the pressure is maintained as the standard pressure, 1 bar, the value is the standard entropy and again, tabulated values are typically given for $T = 298.15$ K and the expression becomes

$$s^0 = \int_{T=0 \text{ K}}^{T=298.15 \text{ K}} \frac{c_p(T)}{T} dT \quad (25)$$

Entropy changes from phase changes (melting, boiling and structural changes) in the way must be included by adding the entropy from the latent heat via (2). The calculation requires knowledge of how the heat capacity changes with temperature and it is not a common activity to perform. Instead, already tabulated values can be used.

The molar standard entropy change of reaction is then

$$\Delta s_r^0 = \sum_{\text{prod.}} \nu_i \Delta s_i^0 - \sum_{\text{react.}} \nu_j \Delta s_j^0 \quad (26)$$

Enthalpy of combustion

The main descriptor of a fuel is its *heating value* or *calorific value*, which is the amount of heat that is liberated on combustion with oxygen. Fuels as we know them are all made from hydrogen, carbon, oxygen and nitrogen. In the combustion process, hydrogen and oxygen atoms are converted to water, carbon atoms to CO₂ and nitrogen atoms into dinitrogen molecules, N₂. The latter is the ideal case and depending on the combustion process, various nitrogen oxides (NOX) may be formed to some extent.

Gasoline is a complicated mixture of hydrocarbons, but is often illustrated by octane, C₈H₁₈, for simplicity. The combustion process is as follows



The standard enthalpy of combustion, Δh_c^0 , is the standard enthalpy of the combustion reaction calculated by equation (18) as:

$$\Delta h_{c,\text{C}_8\text{H}_{18}}^0 = \Delta h_r^0 = 8\Delta h_{f,\text{CO}_2}^0 + 9\Delta h_{f,\text{H}_2\text{O}(\text{l})}^0 - \Delta h_{f,\text{C}_8\text{H}_{18}}^0 - 12.5\Delta h_{f,\text{O}_2}^0 \quad (28)$$

With the table values $\Delta h_{f,\text{CO}_2}^0 = -393.51 \text{ kJ mol}^{-1}$, $\Delta h_{f,\text{H}_2\text{O}(\text{l})}^0 = -285.83 \text{ kJ mol}^{-1}$, $\Delta h_{f,\text{C}_8\text{H}_{18}}^0 = -249.9 \text{ kJ mol}^{-1}$, $\Delta h_{f,\text{O}_2}^0 = 0.0 \text{ kJ mol}^{-1}$, the standard enthalpy of combustion, Δh_c^0 , becomes $-5479.65 \text{ kJ mol}^{-1}$.

As stated above, the term “standard” states that all species are at standard pressure, i.e., 1 bar, and in their stable states at the given temperature, which is 298.15 K according to normal practice. This means that water is liquid (H₂O(l)). Δh_c^0 is negative since heat is liberated from the system. Had it been positive, the substance of our attention would not be a fuel since it is a key property of a fuel that it liberates energy on combustion.

Higher and lower heating value

$-\Delta h_c^0$ (the enthalpy of combustion signed positive) is the same as the *higher heating value* (HHV) of the fuel. An equivalent *lower heating value* (LHV) is defined the same way, only with water in the vapour (gas) state (H₂O(g)) having a slightly lower enthalpy of formation. The difference is equal to the enthalpy change between liquid and vapour, the enthalpy of vaporization. Other names for higher and lower heating value are *gross calorific value* (GCV) and *net calorific value* (NCV), respectively.

Maximum heat and work of a fuel

The maximum heat obtainable from a fuel equals $-\Delta h_c^0$, its higher heating value. The maximum work obtainable from the same fuel is given by the equivalent free energy of combustion with opposite signing $-\Delta g_c^0$ (again, in thermodynamics the signing is defined from the systems point of view, but heat

or work obtainable is from the spectators point of view, i.e. from the surroundings, thus with the opposite signing). The maximum work obtainable from reaction (22) is

$$\Delta g_{c,C8H18}^0 = \Delta g_r^0 = 8\Delta g_{f,CO2}^0 + 9\Delta g_{f,H2O(l)}^0 - \Delta g_{f,C8H18}^0 - 12.5\Delta g_{f,O2}^0 \quad (29)$$

Again, with opposite signing of $\Delta g_{c,C8H18}^0$.

Electrochemical cells

Electrochemical cells are composed of electrodes and an electrolyte. The electrodes are electron conductors, and the electrochemical processes take place on the surface of them. The electrolyte is the substance between the electrodes which contains and conducts ions (charged molecules) generated or consumed in the electrochemical processes. Electrolytes are often liquid, perhaps an aqueous solution of ions, or they can be solid in the form of polymeric or ceramic membranes designed with ion conducting properties. The electrochemical processes at the electrodes either generate or consume electrons and these have to be conducted away from (or to) the surface where the reaction takes place. Likewise, ions formed or consumed at the surface of the electrodes, are transported to or from the electrode electrolyte interface by the ion conducting electrolyte.

Electrical current (electronic current) is passed through the electrodes. The electrochemical process at one electrode converts the electronic current into an ionic current which is then carried by ions in the electrolyte across to the other electrode where it is converted back to the electronic form. With an external circuit, the current circle is closed as it always has to be. The only difference to a normal electrical circuit is that in part of the circle, the current is carried by ions instead of electrons. See Figure 4

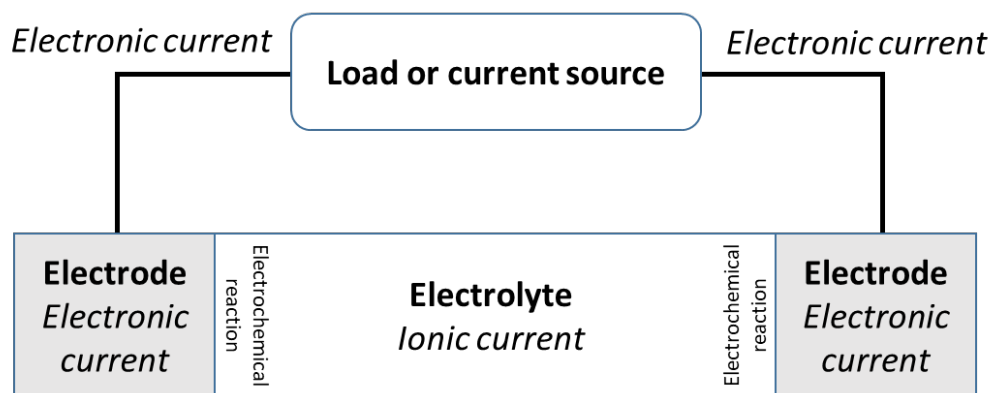


Figure 4. The electrical circuit within an electrochemical cell.

Electrical potential, current and energy

An overview of the energy aspects of electrochemistry could start with a link between potential, current and energy. Electrical potentials are defined in a rather abstract manner. The electrical potential at a location is the work per charge necessary to bring a small charge from a place free of any electrical interaction/forces (could be outer space) and all the way to the location of interest. This is not very practical and is only meant as an illustration. We cannot practically measure absolute potentials, but it doesn't matter since absolute potentials are not relevant. Like with the thermodynamic energy functions, we are only interested in potential differences, and these can be measured in many cases. An electrical potential difference represents a driving force for moving a charge. When a charge moves between two potentials, it either loses or gains energy (potential energy) depending on the direction. The energy (work, W) absorbed or liberated by the charge is the product of the charge, Q , and the potential difference travelled, ΔE .

$$W = Q\Delta E \quad (30)$$

The charge passing pr. time unit, t , is the current, I .

$$Q = It \quad (31)$$

The current in a wire is also movement of charge over a potential difference, i.e., a field in the wire. Combining the two gives

$$W = I\Delta Et \quad (32)$$

And since power, P , is energy per time, then

$$P = I\Delta E \quad (33)$$

If the medium that the charge passes through has a resistance, R (this is practically always the case with the exceptions of superconductors and absolute vacuum), the charge is "taxed" and loses some of the energy it gained from the potential differences. If the resistance is constant and independent of the current, the energy loss can be described as a voltage loss (potential loss) by Ohms law

$$\Delta E = RI \quad (34)$$

The charge and discharge of a battery are sketched in Figure 3. The energy delivered during discharge is $I\Delta Et$ or EQ and must be absorbed by the external load, which is a lightbulb, \otimes , in the figure. The current is controlled by the voltage of the battery and the resistance of the load. If the battery is fit for the task, it maintains the rated voltage and all the energy is consumed by the load (and a small fraction in the wire) and converted to light and mostly heat in the light bulb. If the resistance of the load is small, the current become large and perhaps larger than what the battery can deliver. Then the voltage of the battery decreases and so does the current until a situation is reached where the battery can keep up. The extreme case is a shortcut where the load is practically bypassed or has zero resistance. Even in this case all the energy delivered by the battery has to go somewhere (first law) and current and voltage will again adjust to the negligible, but non-zero, resistance of the wire.

When the battery is charged, current is forced in the opposite direction and the energy EIt is stored in the battery by means of chemical changes inside. The battery behaves like a resistor, but is changing the resistance somewhat during the charging. Some batteries show that they are fully charged by a steep increase of resistance, others don't.

Coming back to the situation when the battery is discharged through a load with a too small resistance, a question is, what happens in the battery when the voltage has to be reduced? The chemical system inside has stored the energy $E_{high}Q$ and is now discharging the energy $E_{low}Q$, where Q is of the same value since it is given by the same chemical process. The answer for now is that the processes inside the battery has a resistance too. The missing energy can be found as heat evolved inside the battery. During charging, some heat is actually also evolved, but the heat should only be large when the battery is fast-charged, fast-discharged, over-charged or over-discharged (i.e., beyond the endpoint).

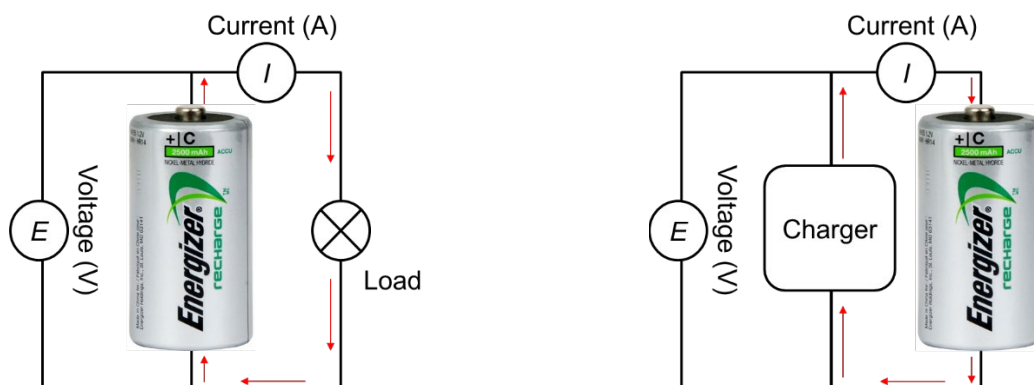


Figure 5. Discharge (left) and charge (right) of a battery.

Electrochemical reactions

There are many different kinds of electrode processes. They can be divided into two main kinds, the faradaic and the non-faradaic. A faradaic process (or reaction) involves electron transfer between the electrolyte and the electrode. It causes an oxidation or a reduction of something (i.e., increase or decrease of the oxidation state of the species involved). A non-faradaic process does not involve electron transfer, but it still affects the electrode potential. The way this is possible is that charged species in the electrolyte accumulate near the electrode surface and are balanced by a similar accumulation of charge of the opposite signing in the electrode. This is called *double layer charging*, and the electrode-electrolyte interface behaves like a capacitor. We shall not deal further with non-faradaic processes; only note that they exist and are important for some diagnostics techniques (electrochemical impedance spectroscopy).

A faradaic reaction is written like any other chemical reaction, only, in addition to molecules and ions, it involves electrons, e^- . Note that the charge balance across the reaction arrow must include the charge of the free electrons(s). See (30) and (31).

Anode and cathode

In electrochemistry, the terms *anode* and *cathode* are frequently used. The definition is as follows:

The *anode* is the electrode where an oxidation takes place. Something is oxidized and increases its oxidation state at the anode and electrons are liberated to the anode. An anodic process is an oxidation process, and an anodic current is the electron current generated from an anodic process. A simple anodic process is the oxidation hydrogen to protons



The *cathode* is the electrode where reduction takes place. Something is reduced at the cathode and electrons are consumed from the cathode. A cathodic process is a reduction process, and a cathodic current is the current generated from a cathodic process. The equivalent cathodic process of the one in (30) is the reduction of protons to molecular hydrogen



The implication on fuel cells and electrolyzers is slightly inconvenient. For the fuel cell, the anode is the fuel (hydrogen) electrode because hydrogen is oxidized to positive hydrogen ions and the cathode is the oxygen electrode where oxygen is reduced. So far, no problems, but when we repeat the logic with the electrolyzer, we define the anode as the oxygen electrode, because oxygen is now oxidized into oxygen molecules. Likewise, the cathode is now the hydrogen electrode. When fuel cell people meet electrolyzer people, this can lead to some confusion. For rechargeable batteries, it is even worse. Here the same cell changes the electrode naming when the mode is changed from charge to discharge. It is in both cases common to refer to the electrodes as the *positive* and the *negative* electrode since that does not change. For fuel cells and electrolyzers, the terms *hydrogen electrode* and *oxygen (or air) electrode* are commonly used.

From thermodynamics to electrochemistry

We have established that the free energy of a reaction quantifies the maximum work we can obtain from a chemical process (an electrochemical process is no different). We don't need to know how to extract this work, only that it not prevented by thermodynamics. The following derivation is based on one mole of the reaction of interest.

$$w_{\max} = -\Delta g_r \quad (37)$$

Where w_{\max} is the maximum molar work obtainable (from outside). We also know that the maximum work we can obtain from a charge moved through an electrical field, or between two electrical potentials, is the product of the charge and the potential difference

$$w_{max} = q\Delta E \quad (38)$$

Current is ordered and carries no entropy, only maximum quality energy, and can be converted completely to work. In an electrochemical cell, the potential difference is the cell voltage, E_{cell} (This holds in all cases, not only at equilibrium)

$$qE_{cell} = -\Delta g_r \quad (39)$$

The charge transferred while carrying out one mole of the reaction is the charge of one mole electrons, which is given by Faradays constant, F , ($F = 96485 \text{ C mol}^{-1}$) multiplied by the number of electrons in the reaction, n (in (30) and (31), $n = 2$), and the (34) can be rearranged into

$$E_{cell} = \frac{-\Delta g_r}{nF} \quad (40)$$

This is the ideal reversible cell voltage of a cell with index “r” referring to the *reactions* inside the cell. If the free energy of reaction is negative, the cell voltage becomes positive. In case of a battery, this is the discharging process. If we look at the charging process, the electrochemical reaction is reversed and consequently, Δg_r changes signing (but keeps its numerical value) and the cell voltage become negative, other things being equal. This makes little sense since the wires are still connected plus to plus and minus to minus. A solution could be to say that if everything is strictly signed, the charge transferred, which actually changes direction, should change signing. However, the usual practice is to refer to the fact that energy is added to the system during charging and a positive Δg_r (i.e., without the minus) is used.

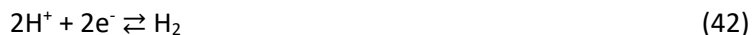
Standard potentials

Electrochemical cells always involve both an anodic and a cathodic reaction, i.e., an oxidation and a reduction process. Each of the two processes are called *half-cell reactions* and examples are the reactions (30) and (31), although these two examples will not make much sense in the same cell. Ions produced at one electrode, others are consumed at the other and a charge balance is maintained by movement of ions – the ionic current in the electrolyte. With only one electrode and thus only one half-cell reaction (oxidation or reduction), charge will accumulate at the electrode (as electrons) and in the electrolyte as ions. After a very short while the process will stop due to the generated charge imbalance. Despite that half-cell reactions always appear in pairs and that the potential of one electrode cannot be measured individually, it is convenient to assign a potential to each of them in a way that makes the potential difference between them equal to the difference in the values of the individual half-cell reactions.

$$E_{cell} = E_{halfcell2} - E_{halfcell1} \quad (41)$$

Since such a potential will likely depend on concentration, pressure and temperature, it is also convenient to define a standard state for the involved species. This standard state is defined similarly to that in general thermodynamics, namely by standard temperature² and pressure³, and the potential is the standard potential is then E^0 .

The problem of measurement of half-cell potentials is circumvented by defining one electrode reaction as reference and measure all the rest with respect to this reference. For this, the hydrogen electrode is chosen, or more exact the standard hydrogen electrode (SHE). The electrode reaction is



and all species must be in the standard state having activity 1 and the solvent must be water. Activity 1 is established with minor approximation with 1 molar H^+ ($\text{pH} = 0$) and 1 bar hydrogen⁴. This definition is valid at any temperature.

A note on activity, a :

Activity is a concept in thermodynamics used to quantify substances instead of using partial pressure of gasses or concentration species in a solution. Pressure and concentration are more intuitive but suffer from the fact that their actual chemical impact is somewhat different from what it should be at a given pressure or concentration. This is due to non-ideal behaviour and shielding effects of other molecules. It may be that the chemical equilibrium established in a real system is slightly different from what it should be with the given concentrations and/or pressures because some species are “seen” as if the concentration is lower than it is. Activity mitigates that by taking the value that makes equilibrium and concentration (or pressure) fit. Activity is then linked to concentration or pressure by activity coefficients that can be estimated by different more or less complicated tricks. The activity of pure condensed phases (liquids and solids) are by definition 1.

Thus, accurate calculation can be complicated and it is common practice simply to replace activities with partial pressures or concentrations. The error is often quite small and acceptable.

A nice feature of activity is that it is dimensionless. This is convenient when it is used in the Nernst equation, which is introduced later.

After this reference has been defined, the electrode potential of any other electrode reaction can be measured. If all involved species of the second electrode system are at unit activity like in the SHE then the potentials are standard potentials. A good approximation to unit activity is 1 bar for gasses, pure condensed phases for liquids and solids, and 1 molar concentration for dissolved species. Table 1

² Strictly speaking there is no standard temperature, but 25 °C is nearly always used as stated in the tables.

³ Standard pressure is generally 1 bar, but since many accurate tables were generated based on the previous standard pressure 1 atm (1.01325 bar), this is still valid for standard potentials.

⁴ 1 atm is still widely accepted (1.01325 bar), and the difference is in most cases negligible.

contains a limited selection of standard potentials. Note that the standard potential in general vary with temperature. It is only the value for SHE that is fixed for all temperatures by definition.

Table 1. Standard potential for a small selection of electrode processes at 25 °C.

Reaction	E° (V)	Reaction	E° (V)
$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}$	-3.01	$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.0000
$\text{Ca}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ca}$	-2.84	$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$	0.34
$\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na}$	-2.71	$\text{Cu}^+ + \text{e}^- \rightleftharpoons \text{Cu}$	0.52
$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}$	-2.84	$\text{Hg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Hg}$	0.80
$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}$	-1.66	$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	0.80
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-0.76	$\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	1.07
$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$	-0.44	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 4\text{H}_2\text{O}$	1.23
$\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}$	-0.40	$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	1.36
$\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni}$	-0.23	$\text{F}_2 + 2\text{e}^- \rightleftharpoons 2\text{F}^-$	2.87

The standard cell voltage of an electrochemical cell can be calculated as the difference of the standard potentials of the reactions taking place on the two electrodes. If a battery was to be constructed from the Zn reaction and the Ag reaction from Table 1, then the standard cell voltage would be

$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	0.80 V
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-0.76 V
Total	1.56 V

For an acidic hydrogen fuel cell or a water electrolyzer at 25 °C the calculation is

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	1.23 V
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.00 V
Total	1.23 V

This holds at 25 °C and as long as all activities are 1, which is true for the two metals as they are pure condensed phases. The ions and gasses will need to have unit activities (~1 M and ~1 bar). For other activities, refer to the Nernst equation, which is introduced below. For other temperatures, the standard potentials need to be corrected (apart from that of hydrogen).

Standard cell potentials from reactions

The standard cell voltage of an electrochemical cell can be calculated from the standard Gibbs free energy of the total reaction by (35), and the standard Gibbs free energy of reaction can be found by (19).

Standard half-cell potentials can be calculated similarly, but require free energies of the involved ions, which is beyond the scope here.

Variation of voltage with pressure, concentration and temperature

The Nernst equation – variation with pressure and concentration

The standard potential of an electrochemical cell only applies if all reacting species and products are at unit activity, or with good approximation at 1 bar or 1 molar concentration. This is rarely the case and the tool to calculate electrode potentials with the reactants at other pressures and concentration is the *Nernst equation*. Equilibrium is still assumed. The basic idea is to add a compensating term to the standard Gibbs free energy that is the basis for the voltage calculation.

$$\Delta g_r = \Delta g_r^0 + \text{compensation} \quad (43)$$

The compensating term is a logarithmic function of the product of the activities, a , (or pressures or concentrations) of all produced species, each to the power of their respective stoichiometric coefficients, ν , divided by the product of the reactant activities treated the same way

$$\Delta g_r = \Delta g_r^0 + RT \ln \frac{\prod_{Prod.} a_i^{\nu_i}}{\prod_{React.} a_i^{\nu_i}} \quad (44)$$

Π means the product of a series like Σ is a sum. The derivation of (39) is based on the dependence of the free energy on activity for each involved species, but it is omitted here. An intuitive interpretation is that if the activity of the products is increased, the logarithmic compensation term becomes larger and consequently Δg_r less negative and the process less favoured. Similarly, increased activity of reactants promotes the process towards the products.

For an electrochemical reaction, a similar expression for the cell potential can be obtained by division with the charge transferred according to the reaction scheme, nF , like in (35). This brings up the issue of signing of the cell voltage again. With a spontaneous process (e.g., for a fuel cell) Δg_r^0 is negative and the cell voltage becomes negative too. Normally cell voltages are considered positive, and the equation is divided by -1. For non-spontaneous processes Δg_r^0 is positive and there is no signing problem.

We then get the *Nernst equation* in a generalized form in the two cases

$$\text{For negative } \Delta g_r^0: \quad E_{cell} = E_{r,cell}^0 - \frac{RT}{nF} \ln \frac{\prod_{Prod.} a_i^{\nu_i}}{\prod_{React.} a_i^{\nu_i}} \quad (45)$$

$$\text{For positive } \Delta g_r^0: \quad E_{cell} = E_{r,cell}^0 + \frac{RT}{nF} \ln \frac{\prod_{Prod.} a_i^{\nu_i}}{\prod_{React.} a_i^{\nu_i}} \quad (46)$$

Memory rule: A change is final state minus initial state or final divided by initial, i.e., *products over reactants*. For signing, the sign between the terms *follows the signing of Δg_r^0* .

The final step is to convert activities to pressures or concentrations for all phases that are not pure and condensed. Here it is shown for the fuel cell reaction, which as negative Δg_r^0 :



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \frac{a_{\text{H}_2\text{O}}^2}{a_{\text{O}_2} a_{\text{H}_2}^2} \quad (48)$$

With $a_{\text{H}_2\text{O}} = 1$, $a_{\text{O}_2} = \frac{p_{\text{O}_2}}{p^0}$ and $a_{\text{H}_2} = \frac{p_{\text{H}_2}}{p^0}$ (division with standard pressure to eliminate the pressure unit):

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \frac{1}{\frac{p_{\text{O}_2} p_{\text{H}_2}^2}{(p^0)^3}} \quad (49)$$

The expression can also be simplified (with the logarithm term reciprocated and changed signing between the terms) as

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{RT}{nF} \ln \frac{p_{\text{O}_2} p_{\text{H}_2}^2}{(p^0)^3} \quad (50)$$

(49) also works for electrolysis. If constructed the same way, signing will be different in the beginning, but product and reactants are also swapped. Consequently, we end the same place. It actually has to be so because the Nernst equation describes the equilibrium voltage, and this is independent on the direction of the reaction when the cell is operated (fuel cell or electrolyzer).

When setting up Nernst, it is a good idea always to check if a change of a reactant or a product leads to a reasonable direction of change of the cell voltage. It can be seen that increasing partial pressures of oxygen or hydrogen leads to a slightly increased cell voltage in accordance with intuition (more impact of the reactants)

Variation with temperature

Temperature is part of the Nernst equation, but one cannot just calculate the temperature dependence by simply varying T . The reason is that the standard Gibbs free energies on which the standard potentials are based, also vary with temperature. The entropy, that the Gibbs free energy depends on, depends strongly on temperature. Such calculations are more complicated, and it is recommended to use tabulated values of either the standard free energy or the standard potentials at other temperatures, if possible.

Thermodynamics versus kinetics

Finally, a short note on thermodynamics versus kinetics. Kinetics is the science of the rate of reaction. Reaction rates can be affected by catalysts, which are other molecules or surfaces that take part in the reactions without being consumed. An example is a platinum surface on which hydrogen oxidation and reduction take place fast. Hydrogen binds to the surface during the reaction but renders it unaffected afterwards. A good catalyst can accelerate the reaction very much, but it doesn't change the thermodynamics and the chemical or electrochemical equilibrium, it only leads to a faster establishment of the same equilibrium.

In brief, thermodynamics decides the maximum available energy, but not the rate of conversion. Kinetics sets the rate of conversion, i.e., the power in energy systems. Nevertheless, poor kinetics leads to imperfections and losses and the reality that not all of the maximum available energy given by thermodynamics are utilized in real systems. Charging a battery requires somewhat more energy than what can be reclaimed during discharge, and the difference in energy is wasted as heat. Thermodynamics does not foresee that and cannot prevent it either.

Overvoltage

The additional voltage needed to charge a battery and the similar lowering of the voltage during discharge are commonly called *overvoltages*. It does not matter if this leads to higher or lower voltages (we do not talk about *undervoltages*). What matters is that the voltage is shifted away from what is expected from idealized thermodynamics, which only treats equilibria and reversible processes. A reversible process is infinitively slow and since we cannot wait for that in practical applications, we change the potential a bit to force the process during charging and we accept a slightly lower cell voltage during discharge. A common principle is that the overvoltages are always working against the purpose of the electrochemical cell (with a few exceptions that are irrelevant in this context). When we want to drive a process by electrical energy, we need to apply a higher voltage and when we like the cell to generate electrical energy, we pay a penalty via a lower voltage.

The physical origin of overvoltages are

- Voltage loss due to the ohmic resistance in the electrolyte and in cables and connections. This loss is purely ohmic, i.e., it follows Ohms law, which dictates that the voltage loss is proportional to the current.
- Electrochemical losses at the electrodes. The charge transfer process can be slow and by polarizing the electrode (changing its potential) electron transfer in one direction is favored and the process is accelerated. This contribution is not at all ohmic but follows a logarithmic like characteristic with current. This overvoltage is referred to as *charge transfer overvoltage*, *kinetic overvoltage* or simply *anodic or cathodic overvoltage*. At high currents, transport of species to and from the reaction sites on the electrodes can be a limiting factor. This may in some cases result in *transport overvoltages*, which are also called *concentration overvoltages*.

Overvoltages are also called *overpotentials*. They apply to batteries, fuel cells and electrolyzers the same way.

Electrocatalysts

The efficiency or rate of electrochemical processes depends heavily on the quality of the reaction sites on the electrode. In most cases an electrocatalyst is applied there. An electrocatalyst is a material that is optimized for promoting the charge transfer reaction. Like other catalysts it takes part in the process but is left unchanged afterwards and thus not consumed. A proper choice of catalyst is often more effective than a high polarization, but both catalyst and some degree of polarization are mandatory in practical electrochemical cells for conversion of energy. Typical catalyst materials are metallic nanoparticles, possibly noble metals, and a variety of metal oxides.