Part II: Electron Energy

Introduction: Energy in electrochemistry and solar radiation

Electrochemistry allows to directly measure the exergy ("Gibbs Energy") available for electrochemical conversions. A good example is the reaction of hydrogen with oxygen forming water as used in fuel cells ¹. The energy released in this reaction can also be determined when burning hydrogen in oxygen atmosphere. Here the so-called "heat of combustion" is released. Performed under "**standard conditions**"², i.e. also constant pressure, the thermal energy released is the **standard enthalpy of reaction**,³, $H^0 = -285,8$ kJ mol⁻¹. If this energy would be Exergy, i.e. could fully be converted to electrical energy, a hydrogen/oxygen fuel cell should produce a voltage (the so-called "thermo neutral voltage" U^0_{th}) of 1.48 V ($U^0_{th} = H^0 / (n \cdot F)$). However, the exergy (or "thermodynamic free energy" $E^0_H = H^0 - (T \cdot S)$) contained in this total energy is only (under constant pressure) 237 kJ mol⁻¹ leading to a reversible cell voltage of $U^0 = E^0_H / (n \cdot F)$. So the Anergy content is 44 kJ mol⁻¹ or more than 15 %.

A similar maximum efficiency even under reversible conditions can be calculated from the entropy content in solar light. This also here leads to an anergy content of about 15 %, so that also a perfect (reversible, i.e. unreal) solar energy converter will never have an efficiency larger than 85 %.

Electron Energy

Electrical energy is considered to be pure exergy, i.e. it can fully (100 %) be converted to usable work. However, this is only the case if for the determination of it's amount a force driving charges in a circuit is taken as voltage, i.e. a potential difference in which both, the higher as well as the lower value can be reached experimentally: $E_{el} = U * Q$.

However, in solid state physics often the electrical potential relative to the so-called vacuum level is taken so that the product of Charge (the extensive "amount" of electrical energy) and the intensive force needed to move charges, the Electrical Potential is used: $E_{el} = Q * E_{el}$. If this electrical energy, calculated on the base of a reference zero point, which will never be reached e.g. in chemical reactions, would be taken to calculate energy input in a conversion process, again a large part of the electrical energy would be anergy with the same fundamental problem of calculating energy conversion efficiency as discussed above for the thermal energy. In principle this would also be the case at least for some reactions if the Electrochemical Potential had used to calculate energy content. Fortunately the term Electrical Energy was defined not based on a potential but as mentioned on a potential difference, the voltage. Thereby also the constant difference between Vacuum Level and Reference Potential (even independent on which reference electrode is used in a measurement) vanishes.

However, as for the other forms of energy, charges (in most cases the negative charges of electrons) move in potential differences. So the driving force is a potential difference, a voltage $U = E_2 - E_1$.

If in analogy to the thermal energy (where the driving force for an entropy flux is a temperature difference) an ambient electrical potential would be defined as lowest "available" potential (as for heat flux in "practical systems" the lowest thermal potential is the ambient temperature), also only a certain part of the electrical energy would be defined as exergy. This is also of some practical importance if "earth potential" is used as one potential by grounding one electrode.

¹ Wikipedia: "Polymer electrolyte membrane electrolysis", online: <u>http://en.wikipedia.org/wiki/Polymer electrolyte membrane electrolysis</u>, Feb. 12, 2014.

 ² Wikipedia: "Standard conditions for temperature and pressure", online: <u>http://en.wikipedia.org/wiki/Standard_condition</u>, Feb. 12, 2014.
³ Wikipedia: "Standard enthalpy of reaction", online: <u>http://en.wikipedia.org/wiki/Reaction_enthalpy</u>, Feb. 12, 2014.

There are still two important differences: The temperature scale has a physics-based absolute zero point (that of the Kelvin scale), whereas the electrical potential has not. In addition, alternating electrical currents are often used in practical devices whereas devices utilizing alternating heat fluxes do not exist; from a practical point of view there is no difference between the flux of negative and that of positive charges. Since in thermal systems we may in principle also speak about the flux of "cold", maybe one day also alternating heat fluxes may find practical applications.

Quantization of Energy

Quantum⁴ physics tells us that the energy of very small entities such as atoms, molecules or very small bodies (today therefore often called cluster or quantum dots) are quantized, i.e. can only take on certain discrete values of energy, the energy levels⁵. Electrons "occupy" certain energy levels being separated from other energy levels by a certain well-defined energy difference. In atoms these energy levels are those of the different atomic orbitals, in molecules those of the different molecular orbitals. Two electrons can occupy every such energy level, if they have different spins⁶.

The origin of these energy levels is the attraction of electrons by the core of the atoms consisting of protons (and neutrons) electrostatically binding the electron by Coulomb interaction, the attractive force of positive and negative charges. Therefore the neutrons do not change the binding energy of the electrons. The strong electron is bound to the atom (i.e. it's core), the lower the energy level is on an **electron energy scale**.

Although delocalized, the electron can be found with a defined probability in certain regions near the core of the atom called orbitals. Usual a 90 % probability to find the electron is shown as the form of the electron orbital⁷.

Electrons closest to the core (occupying the energy state of the innermost electron shell of the atom, the 1sorbital) have the lowest energy or "occupy the lowest energy level", electrons in orbitals further away from the core form energy levels of higher energy.

Energy Level Diagrams in Chemistry

Most common in Chemistry are energy diagrams of molecules depicting the total energy of the molecule, so-called Jablonski diagrams. It "illustrates the electronic states of a molecule and the transitions between them".



A Jablonski diagram showing Fig. 3: the excitation of molecule A to its singlet excited state $({}^{1}A^{*})$ followed by intersystem crossing to the triplet state (³A) that relaxes to the ground state by

The states are arranged vertically by energy and grouped horizontally by spin multiplicity. Nonradiative transitions are indicated by squiggly arrows and radiative transitions by straight arrows. The vibrational ground states of each electronic

state are indicated with thick lines, the higher vibrational states with thinner lines." 8 (fig. 3)

Electron energy level diagrams 9 (fig. 4), as used in chemistry, depict energy levels with respect to the strongest bound electrons, those in the lowest lying energy level (the energy level of the 1s-orbital), the innermost electron



Fig. 4: Energy scheme of the atomic orbitals model⁷⁸

- Wikipedia: "Energy levels", online: http://en.wikipedia.org/wiki/Energy_level, Nov. 30, 2014. 6
- Wikipedia: "Spin (physics)", online: http://en.wikipedia.org/wiki/Spin (physics), Feb. 22, 2015
- Wikipedia: "Atomic orbital", online: http://en.wikipedia.org/wiki/Atomic_orbital, Feb. 17, 2015
- Wikipedia: "Jablonski diagram", online: http://en.wikipedia.org/wiki/Jablonski_diagram, Nov. 29, 2014 9 Wikipedia: "Energieniveau", online: http://de.wikipedia.org/wiki/Energieniveau, Feb. 17, 2015

⁴ phosphorescence '' Wikipedia: "Quantum", online: <u>http://en.wikipedia.org/wiki/Quantum</u>, Feb. 17, 2015

orbital nearest to the nucleus. They are used to explain the energy quanta, which can be absorbed or emitted in optical spectroscopy. An atom¹⁰ can absorb only those distinct energies (quanta), which correspond exactly to the distance between the energy levels. Absorption here means that a photon of appropriate energy transfers this energy to an electron. This requires the availability of an unoccupied electron energy level (orbital) higher in energy by exactly this amount. This (by absorption of the photon) now excited electron is not in thermal equilibrium with the other electrons anymore, it is "hot". Also, the absorption has created an empty energy level at lower energy. The availability of this low energy state will allow an electrons of higher energy to release some of it's energy in the form of a photon (light quantum) and thereby occupy the lower laying (empty) energy level (orbital). The atom or molecule fluoresces¹¹ or, as shown in fig. 3, phosphoresces (after a non-radiative energy dissipation in e.g. an intersystem crossing).

In molecules, the orbitals of neighboring atoms interact with each other, i.e. energy levels of equal or similar energy split into a lower energy (stronger bound) binding and a higher energy (less strongly bound) ant-binding



Fig. 5: MO diagram of dihydrogen⁸¹ depicting also cross section sketches of the s-, σ and σ^* -orbitals

molecular orbital¹². Thereby a new energy scheme is formed which also can be analyzed quantitatively by absorption and/or photoelectron emission spectroscopy.

Transitions between occupied and empty electron energy levels allow the absorption of photons of the appropriate energy. Every absorption of light radiation requires such uptake of it's energy by electrons, which then become excited electrons, occupying an energy state situated at exactly the absorbed energy quantum higher than the level it had occupied before the absorption. An excited electron can relax into an unoccupied lower energy state by emitting the energy difference as a photon. The atom, molecule or cluster luminesces¹³.

The luminescence lines spectrum of atoms reveals the electronic structure of the atom, i.e. the energy diagram of the atom. If enough not-occupied energy levels exist in the absorbing material separated by smaller energy differences, electrons can also relax by transferring smaller energy packages to other electrons or lattice atoms inducing vibrations of atoms in the solid. Thermal relaxation can dissipate radiation energy to finally produce thermal energy at ambient temperature, i.e. anergy. Especially "hot" electrons occupying energy states higher energy states in energy "band" (see below) relax thermally very fast to the lowest empty energy level.

Energy Level Diagrams in Electrochemistry

Whereas electron energies are given in eV (i.e. the charge of one electron times the electrical potential E_{el}), electrical potentials in electrochemistry¹⁴ (electrode potentials¹⁵) are commonly given directly in Volt with respect to the used reference potential, the potential of a reference electrode. Still the potential difference (voltage) to a reference electrode¹⁶ is called "potential" as opposed to a potential difference or voltage determining the flux or flow of charges. A typical electrochemical cell¹⁷ as used in research consists of three electrode¹⁸ and is controlled by a potentiostat¹⁹. Thereby not only the voltage between an electrode (called "working electrode") and a second electrode, called "counter electrode" can be controlled as in conventional electric devices, but at the same time the potential difference between the working and a reference electrode is measured and thereby the

¹⁰ Wikipedia: "Atomic Orbital", online: <u>http://en.wikipedia.org/wiki/Atomic orbital</u>, Nov. 28, 2014; Wikipedia: "Electron Configuration", online: <u>http://en.wikipedia.org/wiki/Electron configuration</u>, Nov. 28, 2014; Wikipedia: "Energy Level", online: <u>http://en.wikipedia.org/wiki/Energy level</u>, Nov. 28, 2014;

¹¹ Wikipedia: "Fluorescence", online: <u>http://en.wikipedia.org/wiki/Fluorescence</u>, Nov. 30, 2014.

¹² Wikipedia: "Molecular orbital diagram", online: <u>http://en.wikipedia.org/wiki/Molecular orbital diagram</u>, Feb. 17, 2015

¹³ Wikipedia: "Luminescence", online: <u>http://en.wikipedia.org/wiki/Luminescence</u>, Feb. 17, 2015

¹⁴ Wikipedia: "Electrochemistry", online: <u>http://en.wikipedia.org/wiki/Electrochemistry</u>, Feb. 19, 2015

¹⁵ Wikipedia: "Electrode potential", online: <u>http://en.wikipedia.org/wiki/Electrode_potential</u>, Feb. 19, 2015

¹⁶ Wikipedia: "Reference electrode", online: <u>http://en.wikipedia.org/wiki/Reference_electrode</u>, Feb. 20, 2015

 ¹⁷ Wikipedia: "Electrochemical cell", online: <u>http://en.wikipedia.org/wiki/Electrochemical_cell</u>, Feb. 19, 2015
¹⁸ Wikipedia: "Voltammetry" online: <u>http://on_wikipedia.org/wiki//oltammetry</u> Ech. 19, 2015

 ¹⁸ Wikipedia: "Voltammetry", online: <u>http://en.wikipedia.org/wiki/Voltammetry</u>, Feb. 19, 2015
¹⁹ Wikipedia: "Potentiostat", online: <u>http://en.wikipedia.org/wiki/Potentiostat</u>, Feb. 19, 2015

electrochemical potential²⁰ of the working electrode. So in contrast to other potentials the electrochemical potential of an electrode can directly be controlled independently of currents flowing through this electrode: a potentiostatic set-up.

The standard reference potential E (*SHE*) is that of the "Standard Hydrogen Electrode", SHE²¹. With respect to this reference point the electrochemical potential (actually the voltage, U [*V*(*SHE*)]) can be positive or negative. This electrochemical reference (zero) point has been correlated to the zero-point used in solid state physics, the vacuum level, thereby defining the "absolute electrode potential" $E_{(abs)}$. The "absolute electrode potential is the difference in electronic energy between a point inside the metal (Fermi level²²) of an electrode and a point outside the electrolyte²³ in which the electrode is submerged (an electron at rest in vacuum). This potential is difficult to determine accurately. For this reason, standard hydrogen electrode is typically used for reference potential. The absolute potential of the SHE is 4.44 ± 0.02 V at 25 °C".²⁴

Thereby the electrochemical potential of every electrode at 25 °C can be recalculated:

$$E^{M}(abs) = E^{M}(SHE) + 4.44 \text{ V}$$

in which *E* is electrode potential, V is volt, *M* denotes the electrode made of metal M, (abs) denotes the absolute potential, (SHE) denotes the electrode potential relative to the standard hydrogen electrode.

Energy Level Diagrams in Solid State Physics

In a solid, atoms, ions or molecules form a highly ordered structure, a crystal lattice, in which they occupy with periodic positions. "The crystal lattice can be thought of as an array of 'small boxes' infinitely repeating in all three spatial directions. Such a unit cell is the smallest unit of volume that contains all of the structural and symmetry information to build-up the macroscopic structure of the lattice by translation."²⁵ In such a lattice the electronic orbitals especially of the outer (valence) electrons overlap and thereby interact (split up), forming bonds between nearest neighbors as described for molecules above. But are also the next neighbors and those further



Fig. 6: Fermi-function at 300 K for a Fermi level at 0.55 eV between 450 and 650 meV ⁹⁸ apart lead to further but smaller splitting of the energy states. Thereby the bonding and ant-bonding orbitals form so-called energy bands²⁶. Since every atom in a solid contributes energy states to the band, for an infinitely large crystal a band consists of an infinite number of energy states, a continuum of states. However, the bandwidth is limited, every band has an upper edge, the position of the highest electron energy state, and a lower edge. The density of states²⁷ starts at the band edge and in general has a maximum in the middle of the band. For crystals of limited size, especially if they become so-called quantum dots²⁸, only separate energy levels replace the "bands". The larger the solid becomes, the smaller the splitting of energy levels can be; the smaller the unit becomes, the larger these energy distances will be.

These energy states are filled with electrons up to the Fermi-level²⁹. **The Fermi-level is the energy, at which an energy state is or would be half filled.** At zero temperature (0 °K) this would be the border between completely filled energy states (below, grey) and completely empty states (above, white). However, since the ambient temperature thermally excites

²⁰ Wikipedia: "Electrode potential", online: <u>http://en.wikipedia.org/wiki/Electrode_potential</u>, Feb. 19, 2015

²¹ Wikipedia: "Standard hydrogen electrode", online: <u>http://en.wikipedia.org/wiki/Electrode_potential</u>, Feb. 19, 2015

²² Wikipedia: "Fermi level", online: <u>http://en.wikipedia.org/wiki/Fermi_level</u>, Feb.19.2015

²³ Wikipedia: "Electrolyte", online: <u>http://en.wikipedia.org/wiki/Electrolyte</u>, Feb. 20, 2015

²⁴ Wikipedia: "Absolute electrode potential", online: <u>http://en.wikipedia.org/wiki/Absolute_electrode_potential</u>, Feb. 20, 2015

²⁵ Wikipedia: "Crystal structure", online: <u>http://en.wikipedia.org/wiki/Crystal_structure</u>, Feb. 20, 2015

²⁶ Wikipedia: "Electronic band structure", online: <u>http://en.wikipedia.org/wiki/Electronic_band_structure</u>, Feb.20, 2015

²⁷ Wikipedia: "Density of states", online: <u>http://en.wikipedia.org/wiki/Density_of_states</u>, Feb. 20, 2015

²⁸ Wikipedia: "Quantum dot", online: <u>http://en.wikipedia.org/wiki/Quantum_dot</u>, Feb. 21, 2015

²⁹ Wikipedia: "Fermi level", online: <u>http://en.wikipedia.org/wiki/Fermi_level</u>, Feb. 20, 2015

electrons, there are unoccupied energy levels below the Fermi level and the same number of thermally excited electrons occupying energy states above the Fermi-level. The occupation of energy states above and below the Fermi level follows the Fermi function³⁰ (fig. 6) with an occupation of the energy states being 0.5 at he Fermi level. The white area (un-occupied states) below the Fermi level corresponds to the grey area (occupied states) above the Fermi level.

The Fermi level is the energy at which available energy states are (or would be, if there are no states here) half filled. As a thermodynamic function it is at the same time the electrochemical potential of electrons in the solid and very often used as reference (zero-) point in energy diagrams (compare e.g. fig. 6). Depending on the strength of interactions of atoms, ions or molecules in the solid the Fermi-level may be located within a continuum of states, i.e. a band or a region, where bands overlap, forming a metal³¹, or in a band gap as in semiconductors³² for band gaps up to about 3 eV or insulators³³ for band gaps larger than about 3 eV (compare fig. 7).

The energy levels in solids can directly be determined by a technique called photoelectron spectroscopy³⁴



Fig. 7: Filling of the electronic Density of states in various types of materials. Vertical axis is energy while the horizontal axis is the Density of states for a particular band in the material listed.⁹⁵

(PS), a technique similar to the absorption spectroscopy used in chemistry. Here, however, the electron is excited by very high-energy photons (X-rays in XPS³⁵with e.g. about 1500 eV or UV-light in UPS³⁶). The excitation here leads to electrons completely leaving the attraction of the nucleus. The well-defined photon energy absorbed by an electron is partly used to overcome the binding energy, i.e. the energetic difference between the electron energy of the orbital the electron occupied before light absorption and the vacuum level. This still leaves considerable kinetic energy for the electron, which is measured in ultra high vacuum using an electron energy analyzer.

The Semiconductor

A perfect semiconductor³⁷, i.e. it possesses a crystal without defects and impurities, is called intrinsic. It's Fermi level is located in the middle of the band gap (compare fig. 6). Thermal excitation across the band gap leads to an equal number of electrons in the conduction band³⁸ (the band originating from anti-binding states) and (missing or) "defect"-electrons or holes in the valence band³⁹ (originating from the bonding states). Recombination across the band gap leads to a stationary concentration of electrons and holes: $[e^-] = [h^+] = n_i$. The intrinsic charge carrier concentration n_i thereby becomes a material constant, since for a given semiconductor i always applies:

$$[e^{-}] * [h^{+}] = n_{i}^{2}$$
.

Intrinsic charge carrier concentrations n_i at room temperature (298 K)⁴⁰: Ge (Eg = 0.66 eV) 2 \cdot 10¹³ cm⁻³, Si (E_g =1,1 eV) 1 \cdot 10¹⁰ cm⁻³, InP (E_g = 1.34 eV) 1.3 10⁷ cm⁻³, GaAs (E_g = 1,4 eV) 2 \cdot 10⁶ cm⁻³, GaP (E_g = 2,26 eV) 2 cm⁻³, Diamond (E_g = 5,5 eV) ~10⁻²⁷ cm⁻³. The enormous variation results from the small thermal energy of kT

³⁰ Wikipedia: "Fermi-Dirac statistics", online: <u>http://en.wikipedia.org/wiki/Fermi-Dirac_statistics</u>, Feb. 20, 2015

³¹ Wikipedia: "Metal", online: <u>http://en.wikipedia.org/wiki/Metal</u>, Feb. 20, 2015

³² Wikipedia: Semiconductor", online: <u>http://en.wikipedia.org/wiki/Semiconductor</u>, Feb. 20, 2015

³³ Wikipedia: "Insulator", online: <u>http://en.wikipedia.org/wiki/Insulator_(electricity)</u>, Feb. 20, 2015

³⁴ Wikipedia: "Photoemission spectroscopy", online: <u>http://en.wikipedia.org/wiki/Photoemission_spectroscopy</u>, Feb. 16, 2015

³⁵ Wikipedia: "X-ray photoelectron spectroscopy", online: <u>http://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy</u>, Feb. 16, 2015

³⁶ Wikipedia: "Ultraviolet photoelectron spectroscopy", online: <u>http://en.wikipedia.org/wiki/Ultraviolet_photoelectron_spectroscopy</u>, Feb. 16, 2015

³⁷ Wikipedia: "Semiconductor", online: <u>http://en.wikipedia.org/wiki/Semiconductor</u>, Feb. 22, 2015; compare also: Wikipedia: "List of semiconductors", online: <u>http://en.wikipedia.org/wiki/List_of_semiconductor_materials</u>, Feb. 22, 2015

³⁸ Wikipedia: "Conduction band", online: <u>http://en.wikipedia.org/wiki/Conduction_band</u>, Feb. 20,2015

³⁹ Wikipedia: "Valence band", online: <u>http://en.wikipedia.org/wiki/Valence_band</u>, Feb. 20, 2015

⁴⁰ Ioffe-Institute: "Semiconductors on NSM", online: <u>http://www.ioffe.rssi.ru/SVA/NSM/Semicond/</u>, Feb. 21, 2015

being at room temperature only about 25 meV, so that a very large number of phonons⁴¹ need to come together to allow transitions of several eV.

In electronics mainly doped semiconductors are used, and the semiconductor in nearly all applications is Silicon⁴². Here the conductivity is controlled by a defined number of doping atoms added to the melt from which the silicon crystal is grown, or later diffused into the material from outside in a high-temperature process. Thereby the doping atoms mainly replace silicon atoms on their lattice positions. Most important in doping (for silicon phosphorus or arsenic is used for n and boron for p-type doping) is the introduction of new energy levels in the band gap close (i.e. within the range of thermal excitation by kT=25 meV at room temperature) to the band edges, when silicon is replaced by a doping atom. For n-type doping the anti-binding orbitals of the phosphorus-silicon bond are located close to the conduction band edge occupied by the additional electron the 5-valent phosphorus brings in. In p-type doping Boron introduces a bonding orbital, which due to the higher laying atomic orbitals of boron compared to silicon (the electrons in the group III-atom B are less strongly bound than in the group IV-atom Si as the P-atom binds electrons stronger than Si) is located at higher energies and thereby above (but close to) the valence band edge. It is occupied by only one electron from Si leaving a position for an electron unoccupied, since boron brings in one electron less. This unoccupied energy position is at room temperature partly (depending on the actual position of the Fermi-level) occupied by thermally excited valence band electrons, creating a negative charge in this energy state. By this thermal excitation they open up empty energy states in the valence band, (positively charged) holes, which are mobile and provide p-type conductivity. Electrons in the doping states in the band gap are not mobile since the distance to the next doping level is too far away. The same applies to the electron on phosphorus (-silicon anti-binding) energy state close to the conduction band edge, which after thermal excitation form mobile negative charges in the conduction band leaving a positively charged empty energy state in the valence band behind. The charges formed after thermal excitation on the doping levels are localized, immobile, but within the bulk of the semiconductor electrically compensated by the mobile charge carriers in the neighboring band (compare fig. 6). Only at contacts, when two materials with different Fermi levels are connected, mobile charge carriers will move to the contacting material with the lower electrochemical potential, i.e. electrons flow to the lower Fermi level material, holes to the one with the higher Fermi-level. Thereby the charged doping levels are not compensated anymore and form charged regions at the interface called space charge regions.

Since with doping also the concentration of electrons in the solid changes, the Fermi level changes position within the band gap from the middle of the band gap for the intrinsic material closer to the conduction band edge for n- and closer to the valence band edge for p-type doping. The energetic distance between the band edge and the Fermi level allows calculating the charge carrier concentration, which is (exponentially) higher for lower distance and lower for a smaller distance. As mentioned above, the product of electron- and hole-concentrations is constant (n_i^2). For silicon ($n_i^2 = 10^{20}$ cm⁻⁶) the mid-band position corresponds to electron- and hole-concentration of 10^{10} cm⁻³, whereas a Fermi-level at the band edge refers to a charge carrier concentration in the order of the number of energy states, i.e. about 10^{19} cm⁻³. This allows an easy estimation of Fermi level positions within the band gap. Since with the exponential increase with lower distance and an energetic distance of 550 meV from the mid of the band gap to the band edge this distance corresponds to 9 orders of magnitude, one order of magnitude in charge carrier concentration correspond to a shift of the Fermi level by 50 meV per decade of doping concentration. 50 meV closer to the valence band at the same time of course increase the hole concentration in the valence band and decreases the electron concentration in the conduction band, both by a factor of ten.

The Diode

A classical diode⁴³ is formed when a not too highly doped semiconductor (the doping concentration should be in the order of 10¹⁶ to 10¹⁷ cm⁻³) is brought in contact with a semiconductor or metal of appropriately different work function, i.e. a n-type semiconductor of small work function with a p-type semiconductor or metal of

⁴¹ Wikipedia: "Phonon", online: <u>http://de.wikipedia.org/wiki/Phonon</u>, Feb.21, 2015

⁴² Wikipedia: "Silicon", online: <u>http://en.wikipedia.org/wiki/Silicon</u>, Feb. 21, 2015

⁴³ Wikipedia: "Diode", online: <u>http://en.wikipedia.org/wiki/Diode</u>, Oct. 8, 2014

sufficiently larger work function (by more than about 300 meV) or a p-type semiconductor with a n-type semiconductor or metal of sufficiently smaller work function. Contact formation then leads to flow of majority carriers from the surface layer of the smaller work function material (i.e. the material with a Fermi level at higher electron energies, in which therefore the electrons have a higher electrochemical potential) to the material with the larger work function (the on the electron energy scale lower laying Fermi-level or smaller electrochemical potential of their electrons). Thereby thin layers in both semiconductors close to the interface are depleted of majority carriers, recombining after the described electron flux. So the layers on both sides of the interface between the semiconductors become charged by the now uncompensated charges localized on the binding energy states of doping atoms. These layers on both sides of the interface are depleted of mobile charge carriers down to a depth, sufficient to compensate the initial difference in work functions; the Fermi levels equilibrate. The necessary number of charges will be formed in a layer, which is thick for low and thin for high doping concentration. Space charge layers are formed.



Fig. 8: A p/n-junction between higher doped p and lower doped n-type silicon as (in the upper part) described in Wikipedia

The electric field between the charges on both sides of the interface compensates the initial difference in electrochemical potential difference between the electrons in the p- and those in the n-type semiconductors (i.e. the difference in Fermi levels). These charges are localized on the energy states in the band gap close to the respective band (electrons on binding states between the pdoping atoms and silicon close the valence band, and unoccupied anti-binding states between n-doping atoms like Phosphorus or Arsenic leaving one of the protons in the doping atom uncompensated by an electron (a localized positive charge on the doping atom). They are not anymore electrically compensated by oppositely charged mobile charge-carriers, which during junction formation had recombined with the majority carriers in the connected oppositely doped contact material. A p/n- or n/psemiconductor diode or a semiconductor/metal or "Schottky"-Junction is formed with space charge layers of a thickness determined by the total density of doping states, i.e. the doping concentration.

The thickness of the depletion layer formed thereby to compensate the initial difference in work functions (Fermi-levels) depends on the doping density. For a higher doping density (concentration of doping atoms) the necessary number of localized charges creating an electric field across the interface is reached already in a thin space charge layer (depleted from mobile charge carriers neutralizing the localized charges on energy levels formed by the doping atoms), lower doping concentrations lead to a thicker

space charge layer in the respective semiconductor and a larger potential drop within this semiconductor. For very highly doped semiconductors (above 10¹⁹ cm⁻³) the space charge region becomes so thin that charge carriers can tunnel through, for metals the potential drop occurs in the first atomic layers and therefore is not even shown in electron energy diagrams: metal/metal contacts exhibit no contact resistance. As for semiconductor/metal contact with an accumulation of majority carriers at the interface (doped n-type semiconductor in contact with a metal with a smaller work function, i.e. that the metal Fermi level is located above that of the n-type material, or a p-type semiconductor in contact with a metal of higher work function, i.e. the metal Fermi level is located below the Fermi level of the p-type material) the contact is called "Ohmic", i.e. the resistance of the bulk materials determine the current/voltage behavior. Back contacts of electronic devices are of this type.

The formation of a depletion layer and thereby of an electric field leads to a parallel bending of the vacuum level and all energy levels and their bands, in electron energy diagrams mostly drawn just as the lower edge of the

conduction band (E_c) and the upper edge of the valence band (E_v). Positive charges lower the energy of electron levels (lead to stronger bound, stabilized electrons), negative charges destabilize electrons and shift energy levels to higher energies. The Fermi-levels in equilibrium (which here means also without current flow) are the same, i.e. the electrochemical potential of electrons is the same in all parts of the device.

This band bending leads to the formation of energy barriers for mobile charge carriers, which can be overcome only by charge carriers thermally excited to higher levels within the band, their number decreasing exponentially with height ($e^{-E_B/kT}$). The same is true for the thermal excitation of charge carriers across the band gap.

These charge carriers determine the current when a voltage is applied to a rectifying junction, i.e. a junction forming the described depletion layer and thereby a barrier for majority charge carriers. A reverse bias applied to Ohmic contacts on the two outsides of the device - polarizing the side with band positions at lower energies (the n-type semiconductor in a n-/p- or a n-/metal Schottky-junction) even further down (in positive direction) - increases the band bending and thereby the barriers for the majority charge carriers. In reverse polarization only a very low (minority charge carrier) current (I₀) saturating at higher reverse voltages, generated by thermal excitation of charge carriers across the band gap, can flow. Otherwise the device is blocking the current. At zero voltage this thermally excited reverse current is compensated by a current thermally excited from the majority carriers at the band edges to the height of the barrier formed as described above.

Polarizing the diode in forward direction - i.e. applying a negative voltage to the n-type and/or a positive voltage to the p-type semiconductor - decreases the barrier for majority charge carriers. Their number at energies above the barrier increases exponentially with decreasing barrier height (e^{-EB/kT}) as already mentioned above, thereby leading to an exponential increase of the current in forward direction.

An ideal diode exhibits a very small saturation current in reverse direction reduced, at 0 V compensated and at voltages in forward direction outnumbered by an exponentially rising thermally activated forward current. In a real diode the forward current becomes at forward voltages already below the barrier height ($V_B=E_B/e$) limited by the resistance of the materials involved and thereby the exponential increase of the current approaches a linear (Ohmic) or square root (space charge limited current behavior. In reverse direction diodes tend to "break through", i.e. loose their rectifying behavior due to tunneling of charge carriers through the barrier, which for higher voltages becomes thinner, or other non-ideal processes.

The solar cell

A simple form of a solar cell is just an illuminated diode. In order to utilize solar light at least one of the Ohmic metal contacts to the diode needs to be made transparent, for most of the currently still used crystalline silicon solar cells with energy efficiencies (electrical power out divided by solar power in) between 12 and 16 %. This is obtained by doping the front side relatively high (in the order of 10^{18} cm⁻³) in order to achieve sufficient conductivity, and then printing thin metal stripes onto the front side to collect the current without reflecting too much light. The back side of these cells is generally fully metallized with the metal forming an Ohmic contact and also reflecting light which because of the low absorption coefficient of silicon still reaches the back side. The light is mainly absorbed in the about 200 µm thick about 10^{16} cm⁻³ p-doped wafer. The front side is n-doped overcompensating the p-doping (about 10^{17} cm⁻³), thereby however, increasing the recombination loss of photogenerated charge carriers in the surface. Strongly absorbed, mainly short wavelength light is thereby lost. To minimize these losses the n-type layer is relatively thin (less than 1 µm). This contact through it's band bending provides a barrier for holes, the majority carriers in the p-type absorber layer.

Upon illumination, electrons are excited from the valence into the conduction band. The number of such created holes in the valence band increases the number of mobile charge carriers at ambient temperature in the valence band of the p-doped absorber layer only slightly. The Fermi level remains basically unchanged it's distance from the valence band edge being a measure of the number of holes in this band. In contrast the electrons excited into the conduction band increases number of minority carriers considerably, so that the large

distance of the Fermi-level from the conduction band edge inside the absorber layer does not represent their number anymore. A second Fermi level called "Quasi-Fermi level" is needed to describe the number of minority carriers, here the electrons. More precise it of course represents the electrochemical potential of holes, the shift upon illumination representing the general logarithmic concentration dependence of the electrochemical potential. The opposite of course happens in the n-type contact layer, where the splitting of the Fermi level leads the one for the electrons basically unchanged while here the Quasi-Fermi level of holes appears considerably closer to the valence band. By now again (as before the contact formation) compensating more of the localized charges in the doping states the band bending decreases. The Quasi-Fermi levels of electrons and those of the holes equilibrate between the differently doped semiconductor layers, shifting those of the majority carriers reaching the metal contact recombine, reducing the Quasi-Fermi level splitting within a distance from the contact reflecting their diffusion length.

Under open circuit conditions, when no charge carriers can leave the device through the contacts, radiative recombination (luminescence) balances the absorption. It's intensity can be used directly to measure the Quasi-Fermi level splitting or photovoltage even without contacting the device.

In an ideal solar cell the photocurrent is only determined by the light intensity, independent of the voltage generated or applied. It's direction is that of the thermally generated saturation current I₀, opposite to that of the forward current. When the barrier height for majority carrier is reduced by the open circuit voltage, the forward and the photocurrent balance each other; at higher voltages applied the forward current dominates. The current/voltage curve therefore is still the simply exponentially increasing thermally activated forward current curve found in the diode, now however starting at strong reverse voltage from the voltage independent constant photocurrent, being directly proportional to the light intensity.

Other types of solar cells

The solar cell described above is basically the product of the electronic industry, where the growth of ultrapure silicon single crystals has been optimized and scaled up to a production size with very substantial cost reductions. Thereby this material with it's low absorption coefficient and therefore need for very thick single crystalline absorber layers allowing charge carriers to diffuse without recombination several hundred µm still dominates the market and may do so also in the future. Even the efficiency of the best laboratory cells has been risen close to that of the (in terms of absorption coefficient and appropriate (see below) band gap) much better suitable material GaAs, which had since the early 1980s held the efficiency record for single junction solar cells.

The GaAs solar cell

Thin film solar cells CdTe and CIGS (the second generation)

Organic solar cells

New inorganic materials CZTS and Perovskite

Photoelectrochemical solar cells

Semiconductor/liquid junctions

Rule of 70

Context

Understanding exponential (and to a lesser extend logarithmic) functions is essential for understanding natural or long-time processes. All "growth by percent" is exponential, which means it doubles (triples, quadruples, increases by a factor of ten, hundred etc.) in a constant number of years. Whereas it is difficult to grasp the meaning of "x-percent growth per year, it is much easier to se the consequences of something (money, number of people in a country or in the world, or CO2-concentration in the atmosphere) doubling every y number of years. Here the rule of 70" allows a quick (but rough) estimation to convert percent growth (or decrease) to doubling (or halving) time.

The rule of 70 is a "rule of thumb". It allows estimating the doubling time from the annual growth rate and vice versa:

Doubling Time = 70 / Annual Growth Rate , Annual Growth Rate = 70 / Doubling Time

or for a logarithmic decrease or decay the estimation of the halving time:

Halving Time = 70 / Annual Decrease in percent , Annual Decrease = 70 / Halving Time .

The Rule of 70:

Until very recently Wikipedia had a separate chapter on the rule of 70, now this is combined with other chapters in "Rule of 72"⁴⁴. This chapter discusses the origin (basically approximating ln 2 by 0.70) as well as different more precise approaches to estimate the above mentioned values. As shown in a direct comparison the number 72 gives slightly better results, is, however, more difficult to remember. Other more complicated formulas allow better estimates. However, 70 (or 72) is good enough to explain, that even a small growth of just say 4 % per year corresponds to a doubling of the growing value every (72/4=) 18 (or 79/4=17) years so that in a lifetime of just about 70 years the value would be 16 times larger (and another lifetime later already 16·16=256 times as large), be it a countries economy or the world population.

A precise calculation can be done using several online-calculators such as in ⁴⁵, a calculation of the deviation of the correct from the estimated value is given in ⁴⁶.

⁴⁴ Wikipedia: Rule of 72, online: <u>http://en.wikipedia.org/wiki/Rule_of_72</u>, May 4, 2014

⁴⁵ Moneychimp: Rule of 72, online: <u>http://www.moneychimp.com/features/rule72.htm</u>, May 4, 2014 ⁴⁶ MathWorld: Rule of 72, online: <u>http://mathworld.woffram.com/features/rule72.htm</u>, May 4, 2014

⁴⁶ MathWorld: Rule of 72, online: <u>http://mathworld.wolfram.com/Ruleof72.html</u>, May 4, 2014

Some other definitions

- **Boundary**: The real or imaginary surface delineating the thermodynamic system. The boundary separates the system from its environment. The boundary is an unambiguously defined surface. The boundary has zero thickness and zero volume.
- **Closed System**: A thermodynamic system whose boundary is not crossed by mass flow.
- **Cycle**: The special process in which the final state coincides with the initial state.
- **Environment**: The thermodynamic system external to the thermodynamic system.
- **Extensive Properties**: Properties whose values depend on the size of the system (e.g., mass, volume, energy, exergy, entropy).
- Intensive Properties: Properties whose values do not depend on the system size (e.g., pressure, temperature). The collection of all intensive properties constitutes the intensive state.
- **Open System:** A thermodynamic system whose boundary is permeable to mass and energy flow. Open systems (flow systems) have their own nomenclature: the thermodynamic system is usually referred to as the control volume, the boundary of the open system is the control surface, and the particular regions of the boundary that are crossed by mass flows are the inlet and outlet ports.
- **Phase**: The collection of all system elements that have the same intensive state (e.g., the liquid droplets dispersed in a liquid–vapor mixture have the same intensive state, that is, the same pressure, temperature, specific volume, specific entropy, etc.).
- **Process**: The change of state from one initial state to a final state. In addition to the end states, knowledge of the process implies knowledge of the interactions experienced by the system while in communication with its environment (e.g., work transfer, heat transfer, mass transfer, and entropy transfer). To know the process also means to know the path (the history, or the succession of states) followed by the system from the initial to the final state.
- State: The condition (the being) of a thermodynamic system at a particular point in time, as described by an ensemble of quantities called thermodynamic properties (e.g., pressure, volume, temperature, energy, enthalpy, entropy). Thermodynamic properties are only those quantities that do not depend on the "history" of the system between two different states. Quantities that depend on the system evolution (path) between states are not thermodynamic properties (examples of non-properties are the work, heat, and mass transfer; the entropy transfer; the entropy generation; and anergy, the destroyed exergy - see also the definition of process).

Thermodynamic System: The region or the collection of matter in space selected for analysis.

In this context important Wikipedia articles:

- Reliability of Wikipedia: http://en.wikipedia.org/wiki/Reliability of Wikipedia,
- Engineering notation: <u>http://en.wikipedia.org/wiki/Engineering_notation</u>,
- Metric prefix: <u>http://en.wikipedia.org/wiki/Metric_prefix</u>
- SI unit: http://en.wikipedia.org/wiki/SI unit,
- Exergy: <u>http://en.wikipedia.org/wiki/Exergy</u>,
- Thermodynamic free energy: http://en.wikipedia.org/wiki/Thermodynamic_free_energy,
- First law of thermodynamics: http://en.wikipedia.org/wiki/First law of thermodynamics,
- Second law of thermodynamics: http://en.wikipedia.org/wiki/Second_law_of_thermodynamics,
- Mass-energy equivalence: http://en.wikipedia.org/wiki/Mass-energy_equivalence,
- Energy: http://en.wikipedia.org/wiki/Energy,
- Outline of energy, http://en.wikipedia.org/wiki/Outline_of_energy,
- First law of thermodynamics: <u>http://en.wikipedia.org/wiki/First_law_of_thermodynamics</u>,
- Second law of thermodynamics: http://en.wikipedia.org/wiki/Second_law_of_thermodynamics,
- Internal Energy: http://en.wikipedia.org/wiki/Internal_energy,
- Forms of Energy: <u>http://en.wikipedia.org/wiki/Forms_of_energy</u>,
- Potential energy: http://en.wikipedia.org/wiki/Potential_energy,
- Gravitational potential energy: http://en.wikipedia.org/wiki/Gravitational_potential_energy,
- Elastic potential energy: <u>http://en.wikipedia.org/wiki/Elastic_potential_energy</u>,
- Nuclear potential energy: http://en.wikipedia.org/wiki/Nuclear_potential_energy,
- Kinetic energy: http://en.wikipedia.org/wiki/Kinetic_energy,
- Rotational energy: http://en.wikipedia.org/wiki/Rotational_energy,
- Electric energy: http://en.wikipedia.org/wiki/Electric_energy,
- Thermal energy: http://en.wikipedia.org/wiki/Thermal_energy,
- Magnetic energy: http://en.wikipedia.org/wiki/Magnetic_energy,
- Chemical energy: http://en.wikipedia.org/wiki/Chemical_energy,
- Radiant Energy: http://en.wikipedia.org/wiki/Forms_of_energy,
- Nuclear binding energy: http://en.wikipedia.org/wiki/Nuclear binding energy,
- Surface energy: http://en.wikipedia.org/wiki/Surface_energy,
- Standard enthalpy of reaction: <u>http://en.wikipedia.org/wiki/Reaction_enthalpy</u>,
- Standard conditions for temperature and pressure: http://en.wikipedia.org/wiki/Standard condition,