Upper Limit for the Conversion of Solar Energy

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Abstract—A semiconductor in the solar radiation field acts as a thermal electronic engine. It converts absorbed radiation heat into chemical energy of the excited electron–hole gas. In flow equilibrium, a homogeneous semiconductor gives off this chemical energy by radiative recombination to the surroundings. If provision is made, as by a p-n junction, to divert the excited electrons and holes, before they recombine, from their point of generation, their chemical energy may be converted into electrical energy. The ratio of this chemical energy current, which constitutes an upper limit for the obtainable electrical energy current, to the absorbed heat current is computed as a function of the value of the bandgap of the semiconductor. Under the assumption that the absorptivity of the electron–hole system of the semiconductor is unity for photon energies larger than the bandgap and zero for smaller photon energies, the conversion efficiency for unfocussed sunlight has a maximum of 30 percent for a bandgap of 1.3 eV.

I. INTRODUCTION

IN ANY SYSTEM that converts radiation heat into another form of energy, as, e.g., electrical energy, the first conversion step consists of the excitation of the absorbing system. By this step the radiation heat is converted partly into chemical energy of the absorbing system. In the case of solar-energy conversion by a semiconductor, the absorbing system is the electron–hole system of the semiconductor. It is this conversion of radiation heat into chemical energy that is subject to the limitation imposed by the second principle of thermodynamics.

The upper limit for the conversion of solar heat into chemical energy of the electron–hole system of a semiconductor follows from thermodynamical considerations of the state of flow equilibrium of the solar cell under exposure to the solar radiation. In this paper, in contrast to previous papers discussing the upper limit for the conversion of solar energy [1]-[7], the maximum chemical potential obtainable in a homogeneous semiconductor under solar irradiation is derived from the equilibrium condition of the excited electron–hole gas and the photon field generated by the excited electron–hole gas.[1]

Further conversion of the chemical energy of the excited electron–hole gas, as, e.g., into electrical energy or into other kinds of chemical energy as in photosynthesis, is not limited by the second principle. The situation is, in fact, similar to that in a power plant. There heat is converted into compression energy of steam. Only this conversion is governed by the second principle. The compression energy is further converted into rotatory kinetic energy of the turbine and eventually into electrical energy by an electrical generator. The efficiency of these further conversions is limited by irreversible processes such as friction losses, but not by the second principle.

We characterize the electron–hole gas of a semiconductor for our purpose by an absorptivity $a = 0$ for photon energies $\hbar\omega < \Delta\epsilon_g$, and $a = 1$ for $\hbar\omega \geqslant \Delta\epsilon_g$, with $\Delta\epsilon_g$ denoting the bandgap of the semiconductor. This is an idealization. For a real solar cell, the absorptivity a to be taken into account is that of a layer with a thickness equal to the diffusion length L of the minority charge carriers. a is connected with the absorption coefficient K and the diffusion length L by $a = 1 - \exp(-KL)$. If the absorption is due to direct transitions, as in GaAs, the step function which we use to describe the absorptivity is an excellent approximation for a. For indirect transitions, as in Si, this approximation is still reasonably good. Since the aim is to compute an upper limit for the conversion of solar energy, reflection losses are neglected by assuming $a = 1$ for $\hbar\omega \geqslant \Delta\epsilon_g$. Since the road we will take here presents a general thermodynamic method to obtain the efficiency for the conversion of radiation heat into chemical energy, it applies equally well to photosynthesis and photodecomposition of chemical compounds. In order to obtain numerical values for the upper conversion limit, the calculations given in this paper have to be adjusted to the absorptivity values appropriate for the particular system.

Absorption of photons from the solar radiation field results in the creation of electron–hole pairs. The electron–hole gas thermalizes to the lattice temperature T_0 by electron-phonon interaction. The free enthalpy per electron–hole pair at $T = T_0$, namely, the chemical potential of the excited electron–hole system, if not wasted by generating entropy via nonradiative recombination, may either be used for further conversion, e.g., in electrical energy, or may be emitted by radiative recombination of electrons and holes, thereby producing a radiation field of the temperature T_0. Since during thermalization neither additional electron–hole pairs are created nor do they recombine, their recombination lifetime being many orders of magnitude longer than their collision time, the rate of electron–hole pairs reaching $T = T_0$ is equal to the absorption rate of the incident photons. The energy transferred as heat to the lattice during the thermalization is wasted for further conversion. One may reduce this amount of wasted energy if the number of photons with $\hbar\omega \geqslant \Delta\epsilon_g$ is enhanced by absorption and reemission of an intermediate absorber. This possibility of enhancement of the conversion efficiency is discussed in a concomitant paper [8].

[1]A thermodynamic discussion of the entire photoelectrical solar-energy conversion, including a treatment of the thermodynamic fundamentals of the radiation field and of the electron–hole gas in a semiconductor, is given in a forthcoming book by these authors *Thermodynamics of Photoelectrical Solar Energy Conversion*.

II. THE ELECTRON-HOLE GAS AS THERMODYNAMIC SYSTEM

The electron-hole gas in a semiconductor is a homogeneous thermodynamic system. We limit ourselves to an intrinsic semiconductor. Thermodynamical homogeneity expresses that the extensive variables of the system are proportional to the number of particles of the system. The energy E is related to the absolute temperature T, the entropy S, the chemical potential μ, the number of electron-hole pairs N, the pressure p, and the volume V, for a homogeneous system by

$$E = TS + \mu N - pV. \tag{1}$$

We may note that the thermodynamical homogeneity relation (1) has nothing to do with spatial homogeneity of the electron-hole gas as the considered thermodynamical system. It holds as well for an inhomogeneously doped semiconductor, as a p-n junction, or a partly illuminated semiconductor. In this case the values of the quantities in (1) vary with distance in the semiconductor.

The chemical potential μ of the electron-hole pairs is equal to the difference of the electron and hole quasi-Fermi energies. Dividing the left and right side of (1) by N, and denoting the concentration of electron-hole pairs by n, we obtain for the energy per electron-hole pair ϵ, with σ being the entropy per electron-hole pair,

$$\epsilon = T\sigma + \mu - \frac{p}{n}. \tag{2}$$

We consider the case of a nondegenerate free-electron gas and hole gas, obeying Boltzmann statistics. Thus it is for an electron-hole pair

$$\epsilon = \Delta\epsilon_g + 3kT \tag{3}$$

and

$$p = 2nkT. \tag{4}$$

The contribution of the various terms in (2), as given by (3) and (4), are shown in Fig. 1 for an excited electron-hole gas with $\mu > 0$.

The chemical potential μ as a function of the concentration n of electron-hole pairs follows from

$$\mu = 2kT \ln \frac{n_{\mu=\mu}}{n_{\mu=0}} \tag{5}$$

the factor of 2 stemming from n denoting a concentration of pairs. The pair concentration $n_{\mu=0}$ is given by

$$n_{\mu=0} = N_{c,v} e^{-(\Delta\epsilon_g/2kT)} \tag{6}$$

with $N_{c,v}$ denoting the effective density of states of the conduction and valence band

$$N_{c,v} = 2\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}. \tag{7}$$

The effective masses m of the electrons at the conduction band edge and of the holes at the valence band edge have been assumed to be equal.

Equations (5) and (6) yield

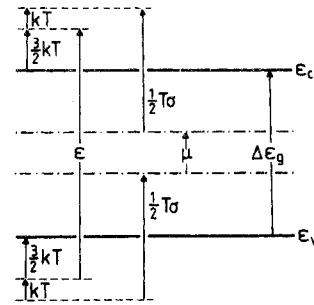$$\mu = \Delta\epsilon_g + 2kT \ln \frac{n}{N_c}. \tag{8}$$

Fig. 1. Terms contributing to the total energy per electron-hole pair ϵ of a nondegenerate intrinsic semiconductor at the temperature T, as given by (2)-(4). ϵ_c and ϵ_v denote the edges of the conduction and valence band, $\Delta\epsilon_g$ the band gap. σ is the entropy per electron-hole pair, μ its chemical potential. The dash-dotted lines are known as the quasi-Fermi levels for the conduction and the valence band, respectively.
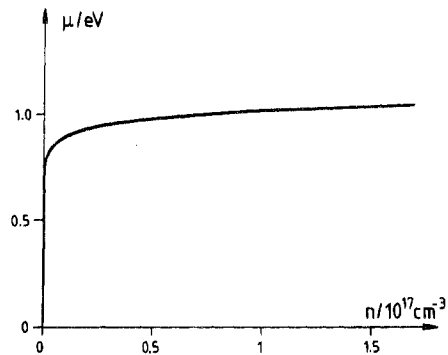

Fig. 2. Chemical potential μ of a nondegenerate electron-hole system of an intrinsic semiconductor at $T_0 = 300$ K as a function of the concentration n of electron-hole pairs. The bandgap is assumed to $\Delta\epsilon_g = 1.3$ eV, the effective density of states $N_{c,v} = 2.5 \times 10^{19}$ cm^{-3}. The value $\mu = 0$ is reached at a concentration of $n = 3.1 \times 10^8$/cm^3. The value of n in the open-circuit state of flow equilibrium is $n = 1.0 \times 10^{17}$/cm^3, in correspondance with the open-circuit chemical potential $\mu(\text{oc}) = 1.0$ eV, as computed from (12) and shown in Fig. 4.

This expression is plotted in Fig. 2. It shows the chemical potential of the excited electron-hole gas as a function of its concentration n. Since any state of flow equilibrium of the electron-hole system at the ambient temperature $T = T_0$ is characterized by a definite value of n, any state of flow equilibrium at $T = T_0$ is a point on the isotherm $\mu(T = T_0)$ in Fig. 2.

III. FLOW EQUILIBRIUM AT OPEN CIRCUIT

Which point on the isotherm $T = T_0 = 300$ K in Fig. 2 is that of flow equilibrium in the solar radiation field? In flow equilibrium electron-hole pairs are formed by solar photons and thermalize to the temperature T_0. In flow equilibrium, the same rate of electron-hole pairs that is generated by the solar radiation field of the temperature $T_S = 5800$ K, must disappear at $T = T_0$. Electron-hole pairs may disappear by being diverted from their point of origin for conversion into electrical energy or into chemical energy, as in photosynthesis. Further, they may disappear by either radiative or nonradiative recombination (Fig. 3). In flow equilibrium, the value of the chemical potential μ in Fig. 2 depends on the rates, and, therefore, on the processes, by which the electron-hole pairs disappear. The state of flow equilibrium with the maximum possible values of n and μ is that with zero electron-hole current flow into
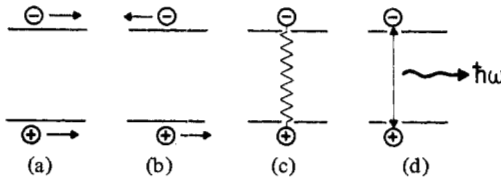
Fig. 3. In the state of flow equilibrium electron–hole pairs must disappear at the same rate as they are produced by the absorption of solar radiation. (a) Electrons and holes flowing away from their point of generation. The current flow is not connected with an electrical current flow. The chemical energy may be transferred by chemical reactions to other systems than that of the electron–hole pairs. (b) Electron–hole current flow connected with an electrical current, leading to the conversion of the chemical energy of the electron–hole gas into electrical energy. This current flow and energy conversion takes place in a p-n junction. (c) Nonradiative recombination of electron–hole pairs. The energy of the electron–hole pair is transferred to the lattice as heat. The process is irreversible since entropy is generated. (d) Radiative recombination of electron–hole pairs. In chemical equilibrium with the radiation field the chemical energy of the electron–hole pairs is equal to that of the emitted photons.

Fig. 4. Chemical potential $\mu(oc)$ of the electron–hole system of an intrinsic semiconductor in an open-circuit state of flow equilibrium as a function of the semiconductor bandgap $\Delta\epsilon_g$. The value of $\mu(oc)$ is computed from (10) and (12), using the values $T_S = 5800$ K, $T_0 = 300$ K, $\Omega_S = 6.8 \times 10^{-5}$.

further conversion and no nonradiative recombination. We will call this state the open-circuit state and characterize it by oc.

Flow equilibrium in the open-circuit state is determined by the fact that all electron–hole pairs that are generated by solar photons, disappear exclusively by radiative recombination. By radiative recombination at $T = T_0$ photons are emitted into a radiation field of $T = T_0$. In flow equilibrium, the electron–hole gas with the chemical potential $\mu(oc)$ is in chemical equilibrium, namely, in equilibrium with respect to the exchange of particles, with this radiation field of $T = T_0$. The reaction taking place is

$$e + h \rightleftharpoons photon. \tag{9}$$

The equilibrium of this chemical reaction requires equality of the chemical potentials of the reaction partners, namely, in the open-circuit state

$$\mu(oc) = \mu_{photon}(oc). \tag{10}$$

The spectral energy distribution of a radiation field with $\mu_{photon} > 0$ is derived in the Appendix.

The electron–hole gas receives the incident radiation from the sun under a solid angle Ω_{inc}. If the solar cell is exposed to the sun without concentrating optics, it is $\Omega_{inc} = \Omega_S = 6.8 \times 10^{-5}$. Using a focussing concentrator for the solar radiation, it becomes $\Omega_{inc} > \Omega_S$. The solar radiation field has the temperature $T_S = 5800$ K. The incident radiation is, therefore, an AM0 radiation. The electron–hole gas emits at $T_0 = 300$ K into a solid angle $\Omega = 4\pi$. We assume, as discussed in the introduction, an absorptivity a for the electron–hole gas

$$a = 0, \quad \text{for } \hbar\omega < \Delta\epsilon_g$$

$$a = 1, \quad \text{for } \hbar\omega \geqslant \Delta\epsilon_g. \tag{11}$$

The balance for the open-circuit state in flow equilibrium requires that the rate of photons absorbed from the sun with $T = T_S$ and from the surroundings with $T = T_0$ be equal to the rate of emitted photons. Neglecting the photons absorbed from the surroundings with $T = T_0$, and using the result derived in the Appendix, this balance reads for the absorptivity
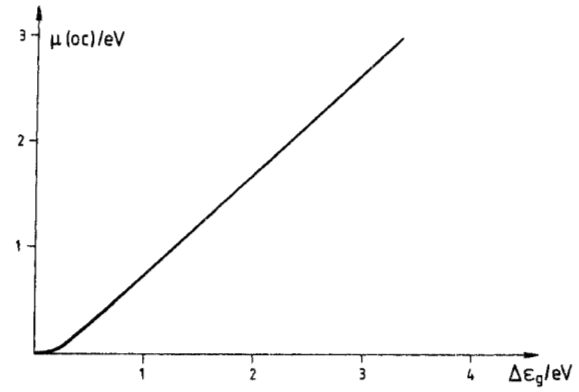
a given by (11)

$$\Omega_{inc} \int_{\Delta\epsilon_g}^{\infty} \frac{(\hbar\omega)^2}{e^{\hbar\omega/kT_S} - 1} \, d(\hbar\omega)$$

$$= 4\pi \int_{\Delta\epsilon_g}^{\infty} \frac{(\hbar\omega)^2}{e^{[\hbar\omega - \mu_{photon}(oc)]/kT_0} - 1} \, d(\hbar\omega). \tag{12}$$

This equation contains for known values of T_S, T_0, and Ω_{inc}, the chemical potential $\mu_{photon}(oc)$ of the radiation field at $T = T_0$ as a function of the bandgap $\Delta\epsilon_g$ of the semiconductor. According to (10), the value of $\mu_{photon}(oc)$ is equal to the chemical potential $\mu(oc)$ of the electron–hole gas in the open-circuit state of flow equilibrium. $\mu(oc)$ as a function of $\Delta\epsilon_g$, as computed from (10) and (12), is shown in Fig. 4.

For $\hbar\omega \gg kT_S$ and $\hbar\omega - \mu_{photon} \gg kT_0$, (12) simplifies to

$$\mu_{photon} = \Delta\epsilon_g \left(1 - \frac{T_0}{T_S}\right) + kT_0 \ln \frac{T_S}{T_0} + kT_0 \ln \frac{\Omega_{inc}}{4\pi}. \tag{13}$$

The last term in this expression exhibits the well-known logarithmic dependence of the chemical potential of the electron–hole gas on the light intensity. The inclusion of absorption of photons from the surroundings at $T = T_0$ into (12) and (13) would lead, as we shall not prove here, to $\mu_{photon} \to 0$ for the limit $\Omega_{inc} \to 0$.

It should be emphasized that the equilibrium with the radiation field at $T = T_0$, expressed by (12), enables us to determine the chemical potential $\mu(oc)$ of the electron–hole pairs in a semiconductor without having to know more about it than its absorptivity a.

IV. Flow Equilibrium with Electron-Hole Current Flow

If the chemical energy of the electron–hole system is to be converted further, the excited electrons and holes have to be diverted from their point of generation, as shown in Fig. 3(a) and (b). The density of this electron–hole current, which is either connected with an electrical current, as in Fig. 3(b), or is not, as in Fig. 3(a), is i. In any state of flow equilibrium, the current density i is the difference of the generation rate
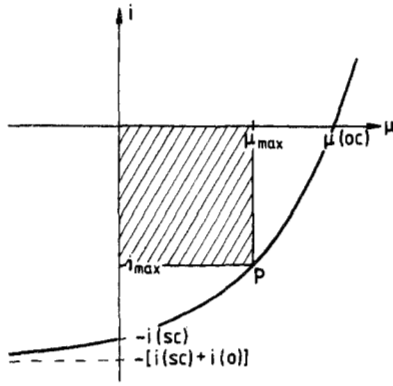
Fig. 5. Density of the chemical energy current i of the excited electron–hole gas as a function of the chemical potential μ of the excited electron–hole gas. The curve follows from Fig. 2 by interchanging ordinate and abscissa, and replacing n by i according to (17). While $i(\mathrm{sc})$ is due to solar radiation, the difference $i(0)$ between the asymptotic value of i for $\mu \to -\infty$ and $i(\mathrm{sc})$ is due to the surrounding radiation field at $T = T_0$. The hatched rectangle represents the chemical energy current density in the state P of flow equilibrium, that may be used for further conversion.

per volume G of electron–hole pairs within a penetration depth l of the absorbed solar photons, and the rate of recombination per volume R within the volume of depth l

$$i = -(G - R)l. \tag{14}$$

In this expression, the current is negative if it is accompanied by an energy current flowing out of the semiconductor. In the special case of the open-circuit state in flow equilibrium, it is $i(\mathrm{oc}) = 0$. It follows that

$$G = R(\mathrm{oc}). \tag{15}$$

If the chemical energy of the excited electron–hole system is further converted, it is $i \neq 0$.

The concentration of electron–hole pairs in the open-circuit state is related to the recombination rate $R(\mathrm{oc})$. Generally, the recombination rate for radiative recombination of electrons and holes is proportional to both the electron and the hole concentration

$$R \propto n^2. \tag{16}$$

It follows from (14) to (16) for the current density i

$$i = G\left(\frac{R}{G} - 1\right)l = Gl\left[\left(\frac{n}{n(\mathrm{oc})}\right)^2 - 1\right]. \tag{17}$$

Since n denotes the pair concentration in any state on the isotherm $\mu(T = T_0)$ in Fig. 2, it is according to (8)

$$\left(\frac{n}{n(\mathrm{oc})}\right)^2 = e^{[\mu - \mu(\mathrm{oc})]/kT_0}. \tag{18}$$

This expression inserted in (17) yields for the electron–hole current density (Fig. 5)

$$i = Gl(e^{[\mu - \mu(\mathrm{oc})]/kT_0} - 1). \tag{19}$$

This expression is the "current-chemical potential characteristic" for an intrinsic semiconductor. We note the close resemblance of this expression to the dependence of the electrical current density i_{el} on the electrical voltage U at $T = T_0$, as it

is commonly used in semiconductor photovoltaics, namely

$$i_{\mathrm{el}} = i_{\mathrm{el}}(0)\,(e^{(eU/kT_0)} - 1) - i_{\mathrm{el}}(\mathrm{sc}). \tag{20}$$

$i_{\mathrm{el}}(\mathrm{sc})$ denotes the density of the electrical short-circuit current that flows under illumination. $-i_{\mathrm{el}}(0)$ is the density of the saturated electrical dark current at $U \to -\infty$ across the rectifying photovoltaic junction. The resemblance of (20) and (19) is more clearly borne out, if analogously to $\mu(\mathrm{oc})$ in (19) the open-circuit voltage $U(\mathrm{oc})$ is introduced into (20). Since $U(\mathrm{oc})$ is U at $i_{\mathrm{el}} = 0$, it follows from (20) for $i_{\mathrm{el}} = 0$, that

$$U(\mathrm{oc}) = \frac{kT_0}{e} \ln\left[1 + \frac{i_{\mathrm{el}}(\mathrm{sc})}{i_{\mathrm{el}}(0)}\right]. \tag{21}$$

Using this expression, (20) may be written as

$$i_{\mathrm{el}} = [i_{\mathrm{el}}(0) + i_{\mathrm{el}}(\mathrm{sc})]\,(e^{[U - U(\mathrm{oc})]/kT_0} - 1). \tag{22}$$

The electrical current density $[i_{\mathrm{el}}(0) + i_{\mathrm{el}}(\mathrm{sc})]$ is due to a thermal generation rate $i_{\mathrm{el}}(0)/e$ of electron–hole pairs at $T = T_0$, and an optical generation rate $i_{\mathrm{el}}(\mathrm{sc})/e$ within the penetration depth of the exciting photons. In the same way, the generation rate G of electron–hole pairs in (19) includes contributions from both the solar radiation field and the surrounding black-body radiation field of $T = T_0$. It follows from (20) and (21) that

$$i_{\mathrm{el}}(\mathrm{sc}) = [i_{\mathrm{el}}(0) + i_{\mathrm{el}}(\mathrm{sc})]\,(1 - e^{-[eU(\mathrm{oc})]/kT_0}) \tag{23}$$

and

$$i_{\mathrm{el}}(0) = [i_{\mathrm{el}}(0) + i_{\mathrm{el}}(\mathrm{sc})]\,e^{-[eU(\mathrm{oc})]/kT_0}. \tag{24}$$

The corresponding contributions to the density of the total electron–hole current i are shown in Fig. 5. The contribution by the absorbed solar radiation in (19) is

$$i(\mathrm{sc}) = Gl(1 - e^{-[\mu(\mathrm{oc})]/kT_0}) \tag{25}$$

while the contribution from the surrounding black-body radiation field at the temperature $T = T_0$ of the electron–hole gas is

$$i(0) = Gl\,e^{-[\mu(\mathrm{oc})]/kT_0}. \tag{26}$$

V. CONVERSION EFFICIENCY FOR SOLAR HEAT INTO CHEMICAL ENERGY OF THE ELECTRON-HOLE GAS

The density of the chemical energy current that may be diverted from the point of excitation, is given according to (19) by

$$i\mu = Gl(e^{[\mu - \mu(\mathrm{oc})]/kT_0} - 1)\mu. \tag{27}$$

Since $i\mu$ vanishes for $\mu = \mu(\mathrm{oc})$ and for $\mu = 0$, it has a maximum value at some intermediate value $\mu = \mu_{\max}$. The energy current density $i\mu$ is shown as a rectangular area in Fig. 5. The differentiation of (27) yields

$$i_{\max} \cdot \mu_{\max} = f \cdot i(\mathrm{sc}) \cdot \mu(\mathrm{oc}). \tag{28}$$

f is commonly called the fill factor.

The ratio of the energy current (28) to the solar heat current incident on the semiconductor defines the efficiency η for the conversion of the solar heat into chemical energy of the excited electron–hole system of the semiconductor. It is
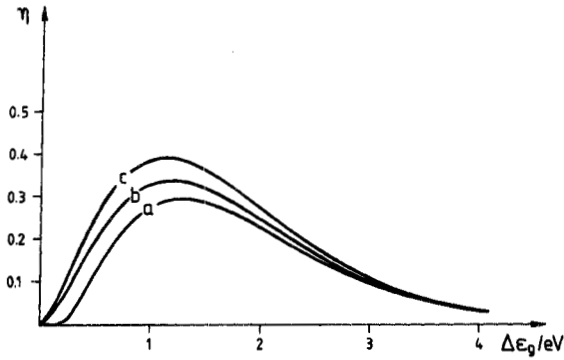
Fig. 6. Maximum efficiency η for conversion of solar radiation heat into chemical energy of the excited electron–hole system of an intrinsic semiconductor, for different solid angles Ω_{inc} of the incident solar radiation. Curve a: $\Omega_{inc} = \Omega_S = 6.8 \times 10^{-5}$ (no focussing). Curve b: $\Omega_{inc} = 0.01$. Curve c: $\Omega_{inc} = 4\pi$. The absorptivity of the electron–hole system is given by (11). Radiation from the surroundings at $T = T_0$ is included in the calculation. For $\Delta\epsilon_g \to 0$, all incident solar photons are absorbed but only a vanishing fraction of the energy of an absorbed photon is converted. For $\Delta\epsilon_g \to \infty$, a large amount of energy per absorbed photon may be converted but only a vanishing fraction of the incident photons is absorbed.

$$\eta = \frac{|i_{max} \cdot \mu_{max}|}{\text{incident solar energy current density}}. \quad (29)$$

Since according to (14) and (15) it is

$$R(\text{oc}) \cdot l = G \cdot l = \text{absorbed solar photon current density} \quad (30)$$

it follows from (25) and (28)–(30) that

$$\eta = \frac{\dfrac{\text{absorbed photon current density}}{\text{incident energy current density}} \cdot f \cdot (1 - e^{[\mu(\text{oc})]/kT_0}) \cdot \mu(\text{oc}). \quad (31)$$

For the absorptivity a, as given by (11), it is the ratio

$$\frac{\dfrac{\text{absorbed photon current density}}{\text{incident energy current density}}}{} = \frac{\displaystyle\int_{\Delta\epsilon_g}^{\infty} \frac{(\hbar\omega)^2}{(e^{\hbar\omega/kT_S} - 1)} d(\hbar\omega)}{\displaystyle\int_0^{\infty} \frac{(\hbar\omega)^3}{(e^{\hbar\omega/kT_S} - 1)} d(\hbar\omega)}. \quad (32)$$

For a given value of T_S, this expression is a function of $\Delta\epsilon_g$.

With (32) and $\mu_{oc} = \mu_{oc}(\Delta\epsilon_g)$, as it follows from (12) and is plotted in Fig. 4, $\eta = \eta(\Delta\epsilon_g)$ in (31) is completely determined. The result is shown in Fig. 6. The maximum conversion efficiency is obtained for a semiconductor with $\Delta\epsilon_g = 1.30$ eV, and is $\eta_{max} = 0.29$. This result represents an upper limit for the conversion of solar radiation incident on a single solar cell. It is based on the assumptions that all incident photons with $\hbar\omega \geqslant \Delta\epsilon_g$ generate free carriers and that their recombination is entirely radiative.

VI. THE CONVERSION OF CHEMICAL ENERGY OF THE ELECTRON–HOLE GAS INTO ELECTRICAL ENERGY

In order to convert chemical energy of the electron–hole gas into electrical energy, Fig. 3(b) shows that electrons and holes
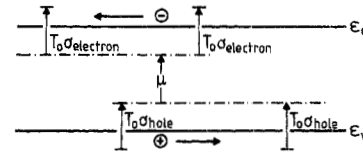

Fig. 7. For the conversion of the chemical energy of the electron–hole gas into electrical energy at $T = T_0$ the excited electron and hole have to be moved into opposite directions from their point of origin with $\mu > 0$ to points with $\mu = 0$. Since the motion has to be accomplished with as little increase of the entropy σ per particle as possible, it follows that the electrons have to be displaced into the n part, and the holes into the p part, of a p-n junction.
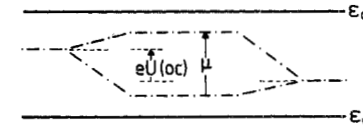

Fig. 8. Open-circuit state in flow equilibrium of an illuminated p-n junction. The condition $i_{el} = 0$ requires opposite sign for the slopes of the dash–dotted quasi-Fermi levels at any point. It follows that $eU(\text{oc}) < \mu$.

have to be drawn away from their point of generation in opposite directions. The conversion of chemical energy into electrical energy in a semiconductor is done isothermally at $T = T_0$. It may be effected as completely as the generation of entropy, the characteristic property of an irreversible process, may be avoided. The diversion of excited electrons and holes from their point of generation should, therefore, be effected subject to the condition that the entropy per particle stays as constant as possible. This condition requires, according to Fig. 1 for $T = \text{constant}$, that the dash–dotted quasi-Fermi levels are as parallel to the band edges as possible. For the chemical energy to be converted into electrical energy, the electrons and holes have to be displaced from their point of origin at which $\mu > 0$, to points in the circuit at which $\mu = 0$. As Fig. 7 shows, the device that accomplishes this task is a p-n junction.

The illuminated p-n junction of Fig. 7 is idealized. It is in contradiction with basic requirements for the divergence of the electrical current and the particle currents. Completing the energy diagram of Fig. 7 by joining the quasi-Fermi levels in the unilluminated regions outside the p-n junction, we obtain the diagram of Fig. 8 for the open-circuit situation. There is a gradient of the quasi-Fermi level for holes on the n-side, and for electrons on the p-side. In order for the electrical current to be zero at open circuit, the minority-carrier currents driven by these gradients must be compensated by currents of majority carriers, which need for their support nonzero gradients of the quasi-Fermi levels for holes on the p side and for electrons on the n side. It is, therefore, at open circuit

$$eU(\text{oc}) < \mu(\text{oc}). \quad (33)$$

The physical reason for this inequality lies in the fact that the minority and majority currents compensate each other in charge transport, but add up in the generation of Joule heat. Since this generation of entropy is not limited to open-circuit conditions, the conversion of solar radiation into chemical energy of the electron–hole system presents an upper limit to the subsequent conversion into electrical energy.

APPENDIX

ELECTRON-HOLE GAS IN CHEMICAL EQUILIBRIUM WITH A RADIATION FIELD AT $\mu = \mu_{\text{photon}} \neq 0$

We derive the chemical potential μ_{photon} of a photon gas that is in chemical equilibrium with an excited electron-hole system of $\mu \neq 0$. The free exchange of particles that constitutes the chemical equilibrium, consists of emission and absorption of photons by the electron-hole gas. We extend Einstein's derivation of Planck's law to the case $\mu_{\text{photon}} \neq 0$.

We represent the electron-hole system by two states of energy per particle ϵ_1 and $\epsilon_2 > \epsilon_1$. In order to include the case of states distributed in energy, as in the conduction and valence bands of a semiconductor, we refer to the concentration of states per volume as $D(\epsilon)d\epsilon$, with $D(\epsilon)$ being the concentration of states per volume and per energy per particle.

The chemical equilibrium is characterized according to Einstein by the rate equation

absorption rate = stimulated emission rate

$$\text{+ spontaneous emission rate.} \quad \text{(A1)}$$

Since we do not wish to limit ourselves to the concentrations of electrons at the levels ϵ_1 and ϵ_2 being small with respect to the concentration of states, we have to take into account the proportionality of the transition rates to the concentration of unoccupied final states as well. With $e_{\Omega, \hbar\omega}$ denoting the energy of the radiation field per volume, per solid angle, and per photon energy interval $d(\hbar\omega)$ at $\hbar\omega = \epsilon_2 - \epsilon_1$, we obtain for (A1)

$$B_{12} \cdot n_e(1) \cdot n_h(2) \cdot e_{\Omega, h\omega} \cdot 4\pi$$
$$= B_{21} \cdot n_e(2) \cdot n_h(1) \cdot e_{\Omega, h\omega} \cdot 4\pi$$
$$+ A_{21} \cdot n_e(2) \cdot n_h(1). \quad \text{(A2)}$$

A_{21} and $B_{21} = B_{12}$ denote the transition probabilities for spontaneous and stimulated transitions. For the description of the occupancy of level ϵ_1 we introduce a Fermi distribution $f_1(\epsilon_{F,v})$ with a quasi-Fermi level $\epsilon_{F,v}$, and correspondingly, for the occupancy of level ϵ_2 a Fermi function $f_2(\epsilon_{F,c})$ with a quasi-Fermi level $\epsilon_{F,c}$ (Fig. 9). It is

$$n_e(1) = D(\epsilon_1)d\epsilon \cdot f_1(\epsilon_{F,v}) = D(\epsilon_1)d\epsilon \cdot \frac{1}{e^{(\epsilon_1 - \epsilon_{F,v}/kT)} + 1}$$

$$n_e(2) = D(\epsilon_2)d\epsilon \cdot f_2(\epsilon_{F,c}) = D(\epsilon_2)d\epsilon \cdot \frac{1}{e^{(\epsilon_2 - \epsilon_{F,c}/kT)} + 1}$$

$$n_h(1) = D(\epsilon_1)d\epsilon - n_e(1) = D(\epsilon_1)d\epsilon \frac{1}{e^{-(\epsilon_1 - \epsilon_{F,v}/kT)} + 1}$$

$$n_h(2) = D(\epsilon_2)d\epsilon - n_e(2) = D(\epsilon_2)d\epsilon \frac{1}{e^{-(\epsilon_2 - \epsilon_{F,c}/kT)} + 1}.$$
$$\text{(A3)}$$

From (A2) follows, with $B_{12} = B_{21} = B$,

$$e_{\Omega, \hbar\omega} = \frac{1}{4\pi} \cdot \frac{A_{21}}{B} \cdot \frac{1}{\frac{n_e(1) \cdot n_h(2)}{n_e(2) \cdot n_h(1)} - 1}. \quad \text{(A4)}$$
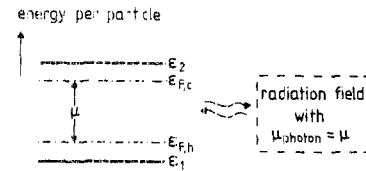

Fig. 9. A system with two energy levels ϵ_1 and ϵ_2 in chemical equilibrium with a radiation field. The occupancy of the upper level ϵ_2 is given by a quasi-Fermi level $\epsilon_{F,c}$, that of the lower level ϵ_1 by a quasi-Fermi level $\epsilon_{F,v}$. The chemical potential of the electron-hole system with the energy levels ϵ_1 and ϵ_2 is given by $\epsilon_{F,c} - \epsilon_{F,v} = \mu$. Chemical equilibrium between the electron-hole system and the radiation field is established by the free exchange of photons with $\hbar\omega = \epsilon_2 - \epsilon_1$. In chemical equilibrium, the chemical potentials μ_{photon} of the radiation field and μ of the electron-hole system have equal values.

It follows from (A3), using $\mu = \epsilon_{F,c} - \epsilon_{F,h}$, that

$$\frac{n_e(1) \cdot n_h(2)}{n_e(2) \cdot n_h(1)} = e^{(\epsilon_2 - \epsilon_1/kT)} \cdot e^{-(\epsilon_{F,c} - \epsilon_{F,v}/kT)} = e^{(\hbar\omega - \mu/kT)}.$$
$$\text{(A5)}$$

The comparison of (A4) and (A5) in the limiting case $\hbar\omega \to 0$, and for $\mu = 0$, with Rayleigh-Jeans's law is known to yield

$$\frac{1}{4\pi} \frac{A_{21}}{B} = \frac{\omega^3}{4\pi^3 c^3}. \quad \text{(A6)}$$

It results in

$$e_{\Omega, \hbar\omega} = \frac{1}{4\pi^3 \hbar^3 c^3} \cdot \frac{(\hbar\omega)^3}{e^{(\hbar\omega - \mu/kT)} - 1}. \quad \text{(A7)}$$

If this expression is applied to a semiconductor with an absorptivity a at $\mu \neq 0$, we obtain for the energy e_Ω and number n_Ω of photons per volume and per solid angle, in chemical equilibrium with the semiconductor

$$e_\Omega = \frac{1}{4\pi^3 \hbar^3 c^3} \int_0^\infty a \frac{(\hbar\omega)^3}{e^{(\hbar\omega - \mu/kT)} - 1} d(\hbar\omega) \quad \text{(A8)}$$

and

$$n_\Omega = \frac{1}{4\pi^3 \hbar^3 c^3} \int_0^\infty a \frac{(\hbar\omega)^2}{e^{(\hbar\omega - \mu/kT)} - 1} d(\hbar\omega). \quad \text{(A9)}$$

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