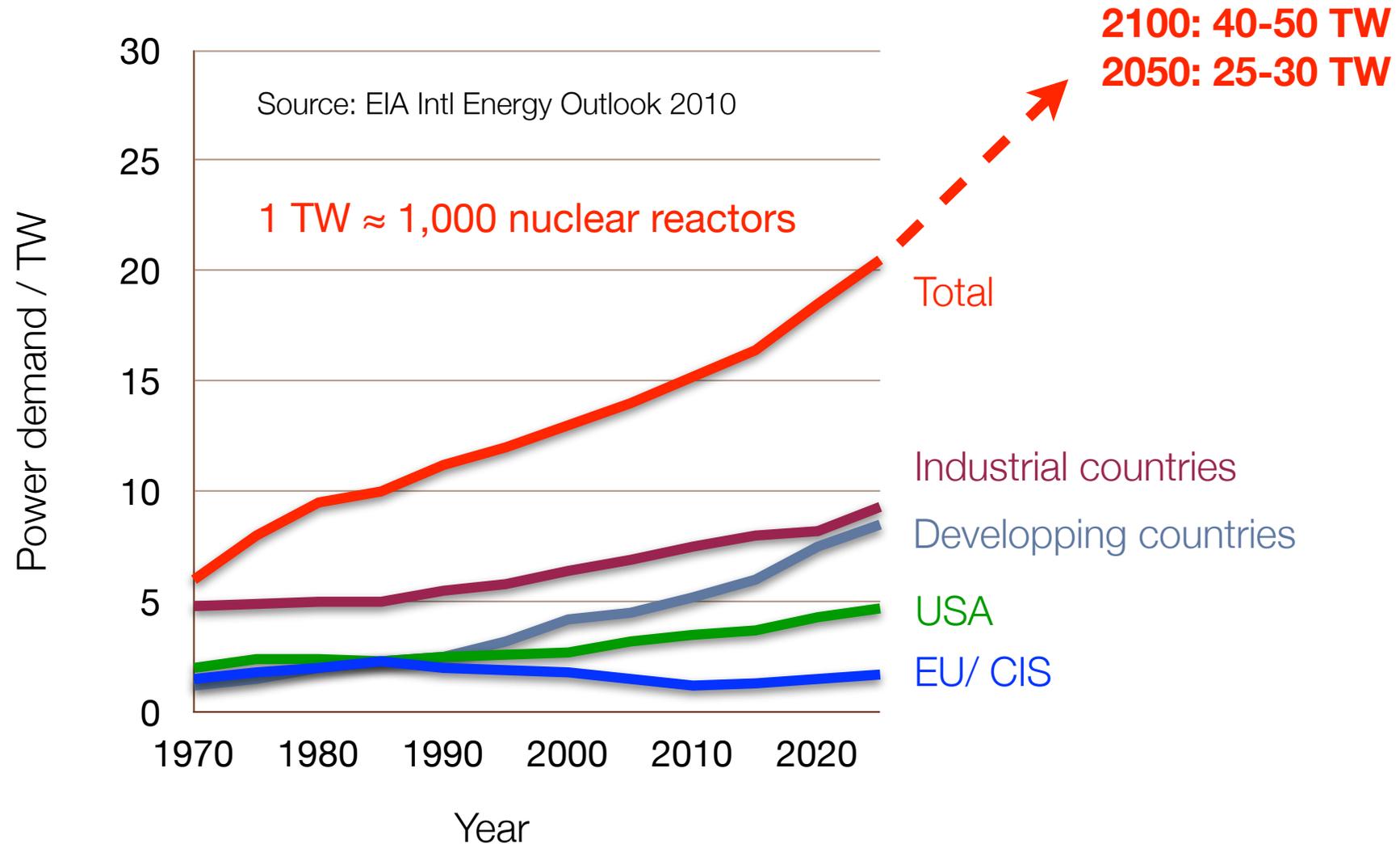


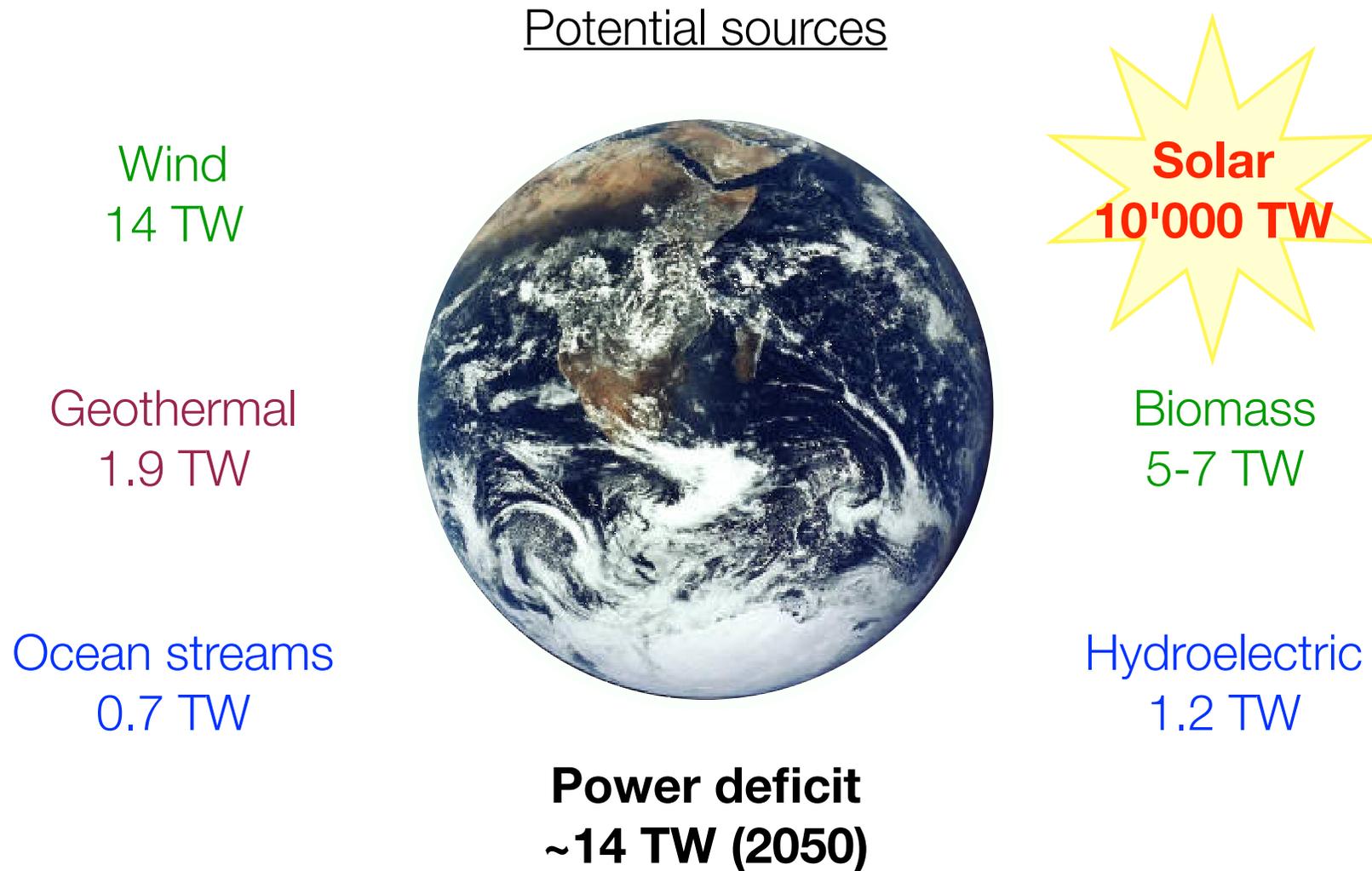
9. Solar energy conversion

9.1 Introduction

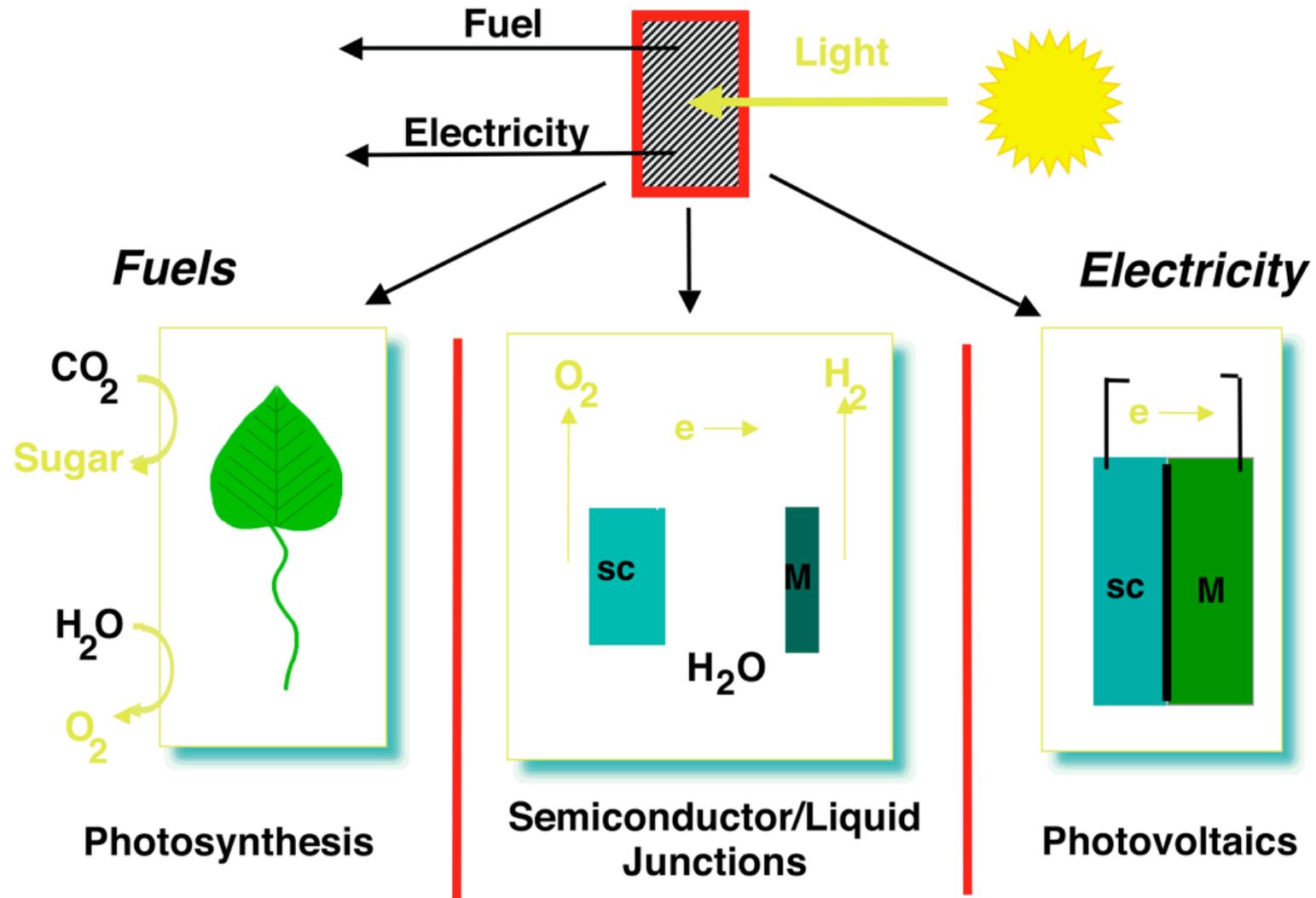
World energy demand outlook



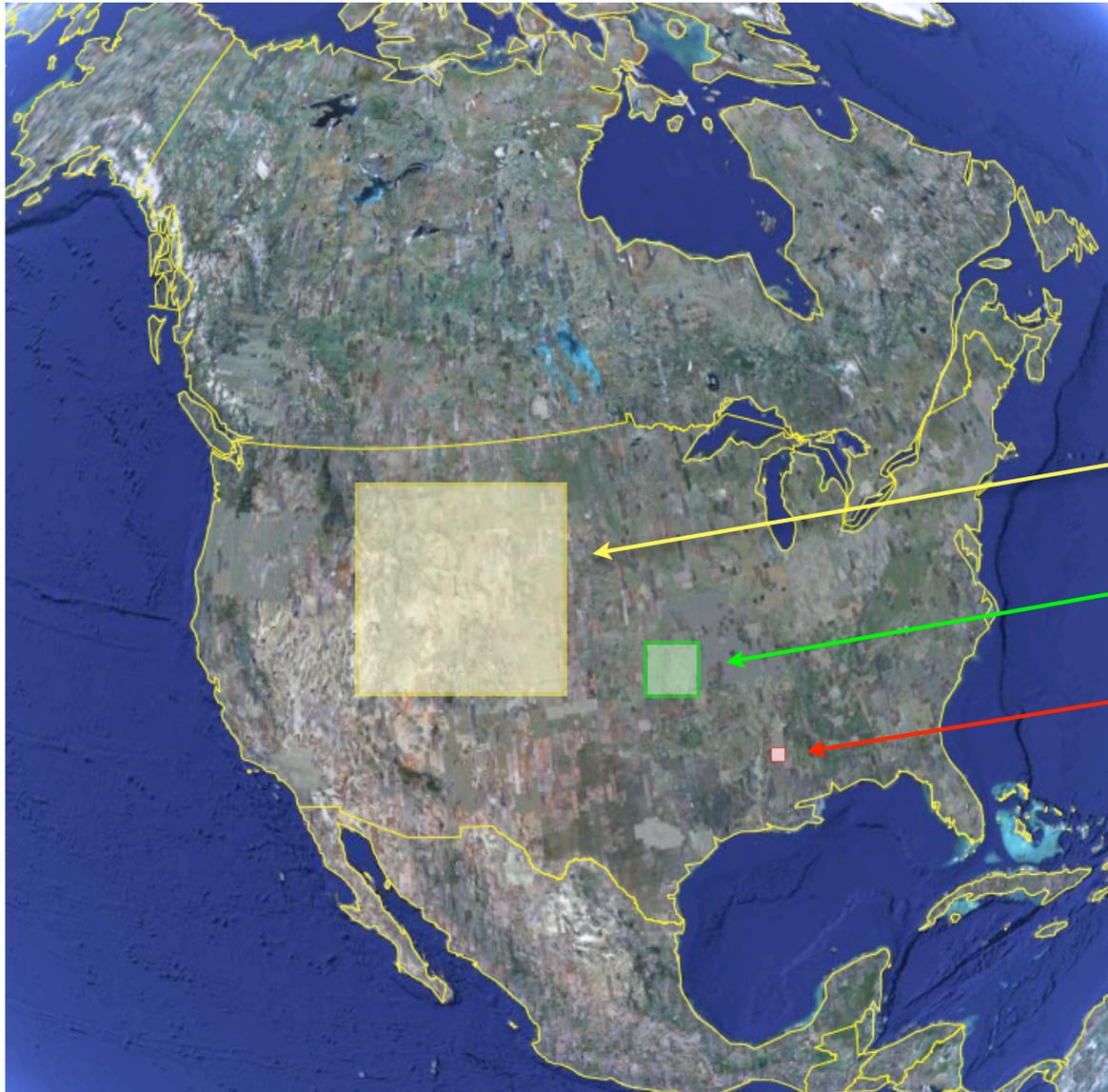
Renewable energy supply



Quantum conversion of solar energy



Bio-conversion of solar energy: Biofuels



Bio-ethanol
(from corn)

Optimized production of
cellulosis

Photovoltaics

Surface area that is required
for the production of energy
equivalent to 50% of the
annual automotive fuel
consumption in the US (year
2010)

9.2 Thermodynamic limitation of power conversion efficiency

Quantum solar energy conversion implies the transformation of the energy carried by the electromagnetic wave into a usable form of energy: work, electrical-, or chemical energy (not heat). The conversion efficiency η is thus defined as the ratio of the converted Gibbs energy ΔG_c ('free energy') over the Gibbs energy associated to the incident radiation ΔG_R :

$$\eta = \frac{\Delta G_c}{\Delta G_R}$$

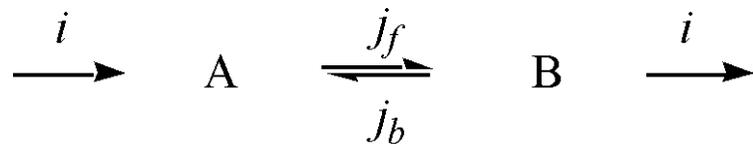
Free energy losses can occur during the conversion, due to the irreversibility of the thermodynamic transformation (2nd principle of thermodynamics). The origin of such irreversibility in the solar energy conversion is threefold:

- Non-equilibrium conditions due to power extraction
- Entropy of light (Carnot thermodynamic limitation)
- Free energy waste under polychromatic radiation

For a single-bandgap absorber, the maximum conversion efficiency, called the **Shockley-Queisser limit**, is typically $\eta = 31 \%$.

Non-equilibrium conditions due to power extraction

Consider a transformation in which the system A with an associated free energy ΔG_A is converted into a system B at the free energy ΔG_B . The rate of storage of energy in the converted system B is $J \cdot \Delta G_B$, where the flux $J = -d[A]/dt = d[B]/dt$.



If A and B are in equilibrium the net flux to the system B is $J = j_f - j_b = 0$. Under non-equilibrium conditions, due for instance to power extraction ($i > 0$), there is a net loss of free energy ΔG_I :

$$\Delta G_I = \Delta G_B - \Delta G_A$$

If K is the equilibrium constant for the conversion $A \rightleftharpoons B$ in ideal conditions, van't Hoff's isotherm yields:

$$\Delta G_I = \Delta G_B - \Delta G_A = -RT \ln K + RT \ln ([B]/[A]), \text{ and}$$

$$\Delta G_I = RT \ln (1 - \varphi) \quad \text{where } \varphi = J / j_f.$$

Non-equilibrium conditions due to power extraction

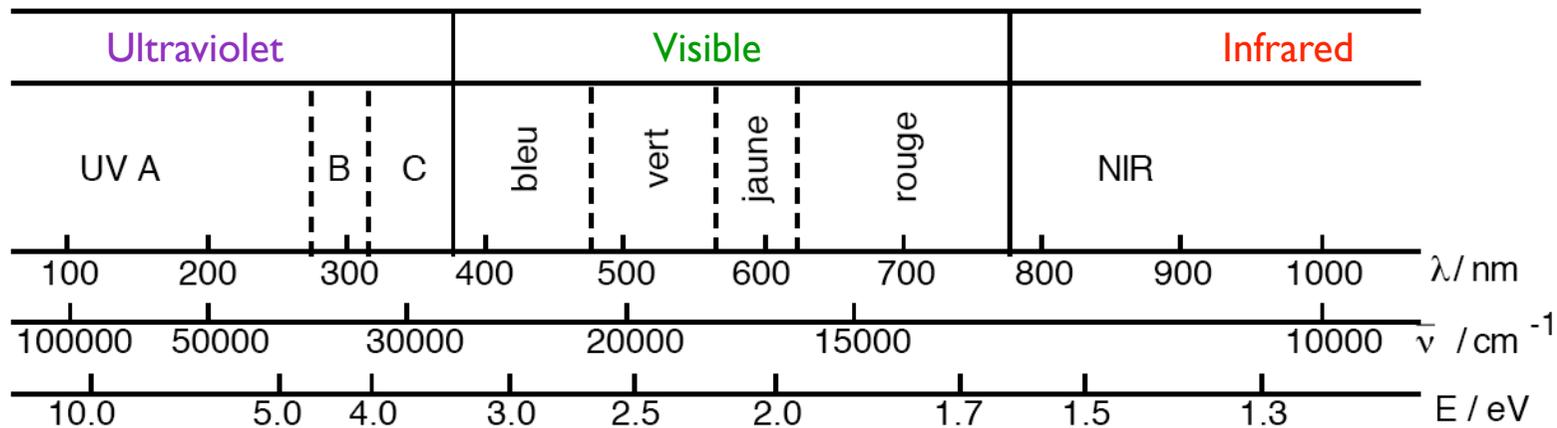
The conversion power P of the transformation is given by $P = J \cdot \Delta G_B = J \cdot (\Delta G_A + \Delta G_I)$. At maximum power, the conversion flux is:

$$\frac{\varphi}{1 - \varphi} - \ln(1 - \varphi) = \frac{G_A}{R T}$$

The free energy conversion efficiency is finally expressed by: $\eta_p = \frac{\Delta G_A + \Delta G_I}{\Delta G_A}$

The amount of free energy converted in a photochemical or photovoltaic process implying visible light is typically 1-2 eV. If $\Delta G_A = 1$ eV, one calculates from the latter equations:

$$\varphi = 0.972, \quad \Delta G_I = -0.093 \text{ eV}, \quad \text{and} \quad \eta_p = 0.91.$$



Entropy of light - Carnot conversion yield

Consider a monochromatic radiation at wavelength λ . Its total energy is $\Delta U_R [\text{J} \cdot \text{Einstein}^{-1}] = N_A \cdot hc / \lambda$, where N_A is Avogadro's number, c the speed of light and h Planck's constant.

The absolute entropy associated with it is $S_R = \Delta U_R / T_R$. T_R being the effective **temperature of the monochromatic radiation**.

The entropy of the radiation S_R at T_R is lost when the light disappears in the absorption process. An equivalent amount of entropy must then be created in the absorber at ambient temperature T_A . As a result, part of the free energy is lost and the maximum free energy available at temperature T_A is given by Maxell's equation:

$$\Delta G_{\max} = -S_R \cdot \Delta T = U_R \cdot \frac{T_R - T_A}{T_R}$$

The maximum Gibbs energy conversion efficiency is then expressed by the following expression, that is the Carnot formula applied to radiation:

$$\eta_R = \frac{\Delta G_{\max}}{\Delta U_R} = \frac{T_R - T_A}{T_R}$$

It remains that T_R has still to be estimated.

Radiation temperature - Plank's law

The temperature $T_R(\lambda)$ of a monochromatic radiation of wavelength λ and of a given spectral irradiance B_λ is defined as being the temperature of a blackbody giving rise to the same irradiance at the wavelength λ . The radiation temperature is then expressed by Plank's law:

$$T_R = \frac{hc}{k_B \lambda} \cdot \frac{1}{\ln \left(1 + \frac{2 hc^2 \Omega}{\lambda^5 B_\lambda} \right)}$$

The spectral irradiance or “brightness” B_λ with units $[\text{J s}^{-1} \text{ m}^{-2} \text{ ster}^{-1} \text{ Hz}^{-1}]$ represents the radiation energy per unit time per unit area per solid angle per frequency interval. Ω is the solid angle subtended by the radiation source at the observer, including any optical concentrator. We should note that if the radiation source is a blackbody, T_R does not depend upon λ .

Conversion of the radiation energy implies necessarily absorption of light. During this process, the directionality of the radiation beam is lost. The **effective absorbed radiation temperature** T_{Ra} is therefore equivalent to that of diffuse light scattered in all directions with $\Omega = 4\pi$:

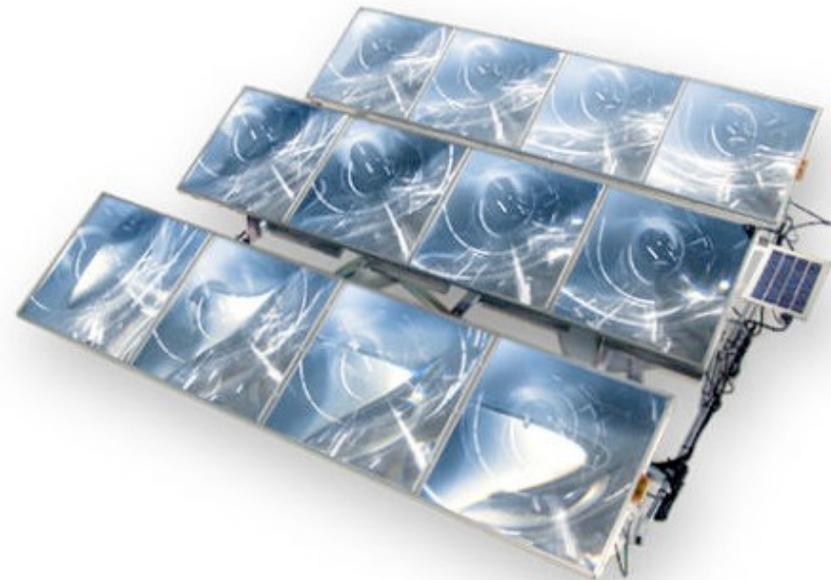
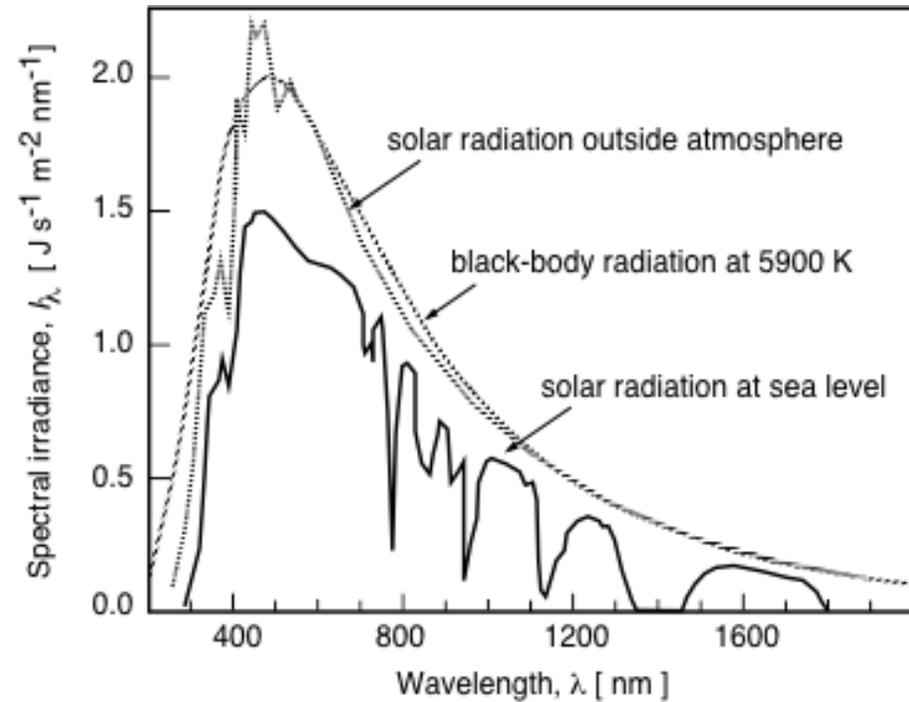
$$T_{Ra} = T_{R,scattered} = \frac{hc}{k \lambda} \cdot \frac{1}{\ln \left(1 + \frac{8\pi hc^2}{\lambda^5 B_\lambda} \right)}$$

Radiation temperature - Plank's law

The sun delivers a spectral irradiance at the earth surface (without concentrator) of $1.16 \text{ W m}^{-2} \text{ nm}^{-1}$ at $\lambda = 700 \text{ nm}$. The solid angle represented by the Sun seen from Earth is $\Omega = 6.8 \times 10^{-5} \text{ ster}$. From previous equations, one then calculates: $T_R = 5'500 \text{ K}$ and $T_{R,a} = 1'297 \text{ K}$.

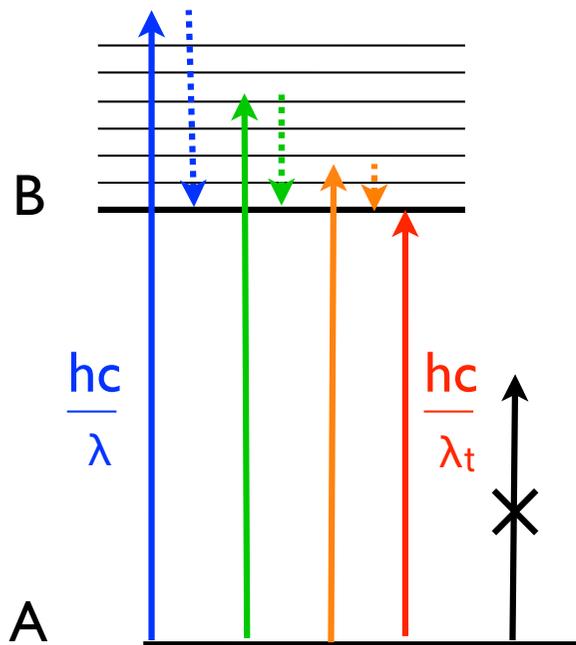
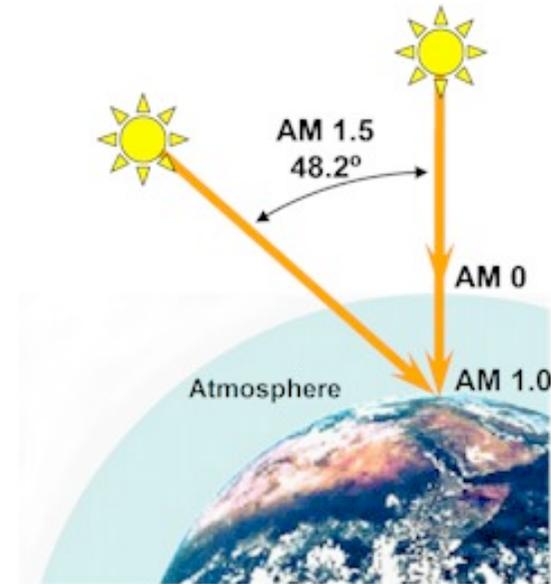
If $T_A = 298 \text{ K}$, the Carnot formula yields a maximum free energy conversion efficiency $\eta_{R,a} = 0.77$.

Solar light can be concentrated by using parabolic mirrors or Fresnel lenses. In the same conditions, **concentration of the incident radiation** by a factor of 10, for example, translates into an increase of the irradiance and thus of the radiation temperature from 1297 K to 1517 K and a rise of the maximum conversion efficiency from 0.77 to **0.80**.



Energy waste under polychromatic light irradiation

The **airmass** AM is defined as the path length that light from a celestial object takes through Earth's atmosphere relative to the length at the zenith. AM = 1 at the zenith (AM 1.0), AM = 1.5 at an angle of 48.2° (AM 1.5) and roughly AM = 2 at 60° (AM 2.0). AM obviously depends on geographical latitude, time and season. At our latitude, in Summer, at noon, AM = 1.5.



For a **monochromatic** radiation at $\lambda = 700 \text{ nm}$ and AM 1.0 solar irradiance, $\Delta G_{R,a} = 1.36 \text{ eV}$, the Gibbs energy conversion efficiency is

$$\eta_g = \eta_p \cdot \eta_{R,a} = 0.91 \cdot 0.77 = 0.71.$$

So far, we assumed that the free energy acquired by the absorber during the absorption process was equal to that of the absorbed photon. This is generally not true for polychromatic radiation when a single gap absorber is used.

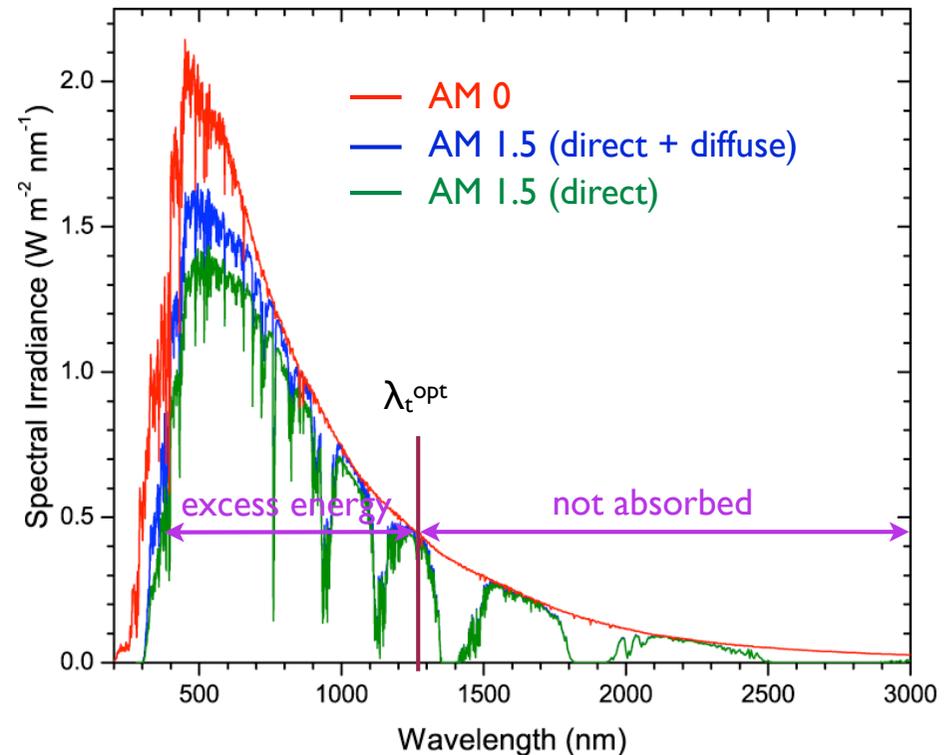
Energy waste under polychromatic light irradiation

Assuming that no reaction can take place from hot vibronic states, all absorbed photons after degradation of excess energy, give rise to the same excitation energy $\Delta E = hc / \lambda$. At each wavelength $\lambda < \lambda_t$, the usable fraction of the absorbed photon energy is:

$$\theta = \frac{hc}{\lambda_t} / \frac{hc}{\lambda} = \frac{\lambda}{\lambda_t}$$

It follows that the fraction θ of the energy absorbed from a polychromatic source which is finally available in the conversion process is given by :

$$\theta = \frac{\int_0^{\lambda_t} F_\lambda \frac{\lambda}{\lambda_t} d\lambda}{\int_0^{\infty} F_\lambda d\lambda}$$



The optimal threshold wavelength λ_t for a given irradiance spectrum may be determined from the latter equation. For a Planckian radiation with $T_R = 5'200$ K (direct solar light at AM 1.5), the optimal wavelength is $\lambda_t^{\text{opt}} = 1'273$ nm (0.97 eV) and accordingly $\theta^{\text{opt}} = 0.44$.

Thermodynamic limitation of power conversion efficiency (summary)

- Non-reversible conditions at maximum power extraction

$$\eta_p = 0.91$$

- Entropy of light (Carnot thermodynamic conversion limitation)

$$T_R = 5'500 \text{ K} \Rightarrow T_{R,a} = 1'297 \text{ K (without concentrator)} \Rightarrow \eta_e = 1 - T_{R,a} / T_a = 0.77$$

- Polychromaticity of solar light

For monochromatic radiation:

$$\eta = \eta_p \times \eta_e = 0.91 \times 0.77 = 0.71$$

For typical AM 1.5 solar spectrum:

$$\lambda_{\text{opt}} = 1'273 \text{ nm (0.97 eV)} \Rightarrow \theta_{\text{opt}} = 0.44$$

$$\eta = \eta_p \times \eta_e \times \theta = 0.91 \times 0.77 \times 0.44$$

$$\eta = 0.31 \quad \text{Shockley-Queisser limit}$$

Dye sensitizers used in solar cells have a typical absorption threshold of $\lambda_t = 750 \text{ nm}$ (1.6 eV). For AM 1.5 radiation, one calculates $\theta = 0.38$ and an overall maximum theoretical efficiency $\eta = 0.28$.

