



Photovoltaic Effect: An Introduction to Solar Cells

Text Book: Sections 4.1.5 & 4.2.3

References:

The physics of Solar Cells by *Jenny Nelson*, *Imperial College Press*, 2003.

Solar Cells by *Martin A. Green*, *The University of New South Wales*, 1998.

Silicon Solar Cells by *Martin A. Green*, *The University of New South Wales*, 1995.

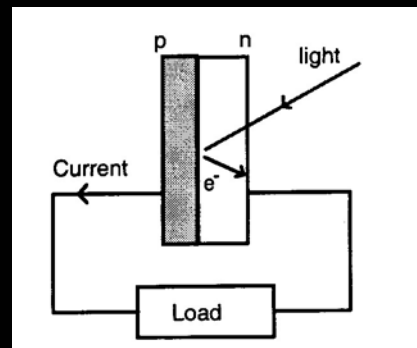
Direct Energy Conversion by *Stanley W. Angrist*, *Allyn and Beacon*, 1982.



Photovoltaic Effect

Solar photovoltaic energy conversion: Converting sunlight directly into electricity.

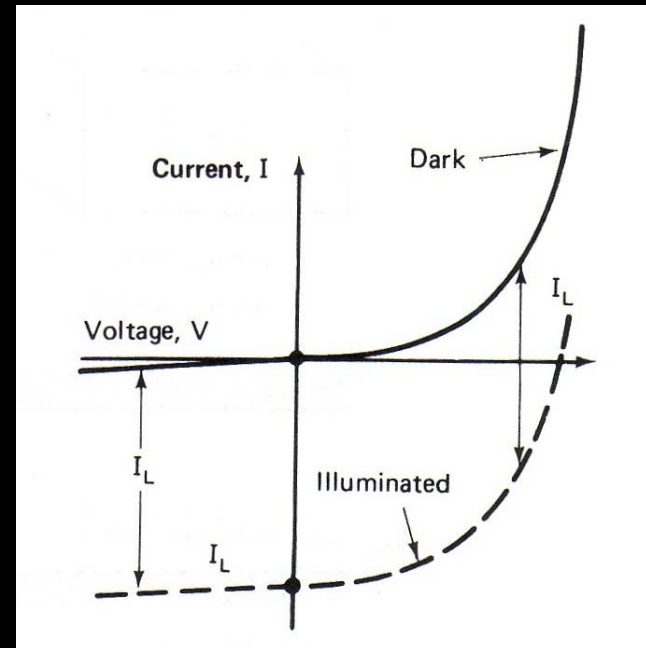
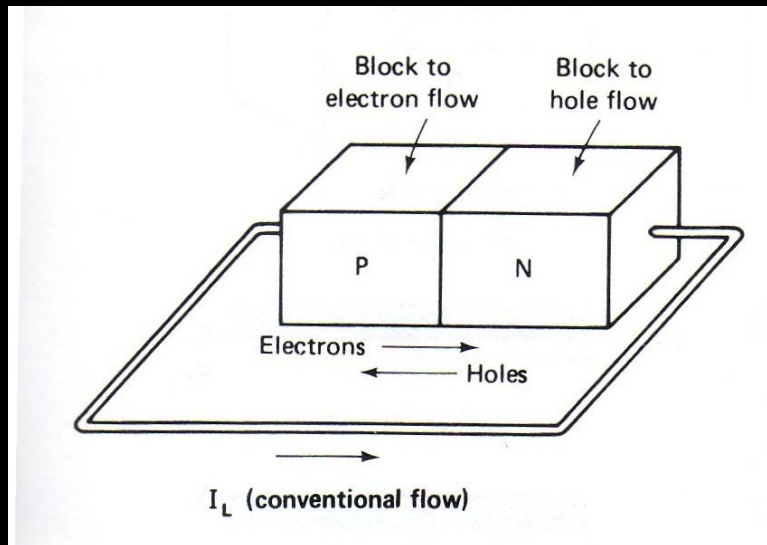
When light is absorbed by matter, photons are given up to excite electrons to higher energy states within the material (the *energy difference* between the initial and final states is given by $h\nu$). Particularly, this occurs when the energy of the photons making up the light is larger than the forbidden band gap of the semiconductor. But the excited electrons relax back quickly to their original or ground state. In a photovoltaic device, there is a built-in asymmetry (due to doping) which pulls the excited electrons away before they can relax, and feeds them to an external circuit. The extra energy of the excited electrons generates a potential difference or electron motive force (e.m.f.). This force drives the electrons through a load in the external circuit to do electrical work.





Pn-Junction Diode

The solar cell is the basic building block of solar photovoltaics. The cell can be considered as a two terminal device which conducts like a diode in the dark and generates a photovoltage when charged by the sun.



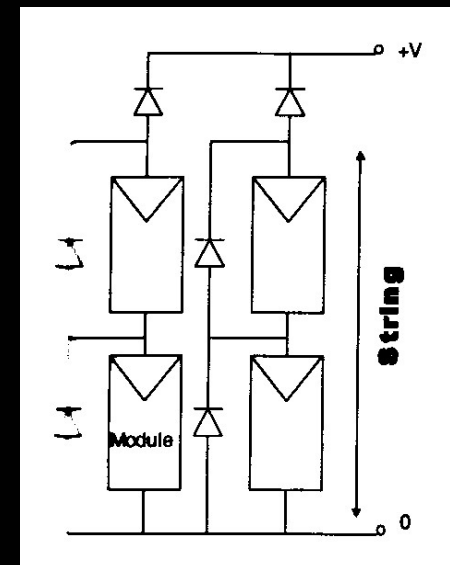
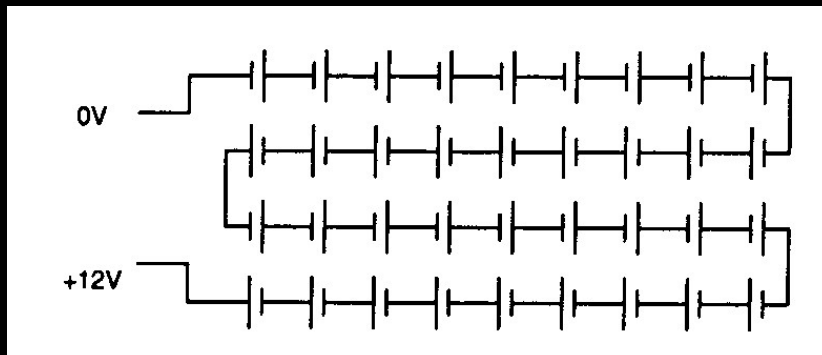
When the junction is illuminated, a net current flow takes place in an external lead connecting the p-type and n-type regions.

The light generated current is superimposed upon the normal rectifying current-voltage characteristics of the diode. The power can be extracted from the device in a region shown in the fourth quadrant.



Solar Cell

The solar cell is the basic building block of solar photovoltaics. When charged by the sun, this basic unit generates a dc photovoltage of 0.5 to 1.0V and, in short circuit, a photocurrent of some tens of mA/cm^2 . Since the voltage is too small for most applications, to produce a useful voltage, the cells are connected in series into *modules*, typically containing about 28 to 36 cells in series to generate a dc output of 12 V. To avoid the complete loss of power when one of the cells in the series fails, a blocking diode is integrated into the module. Modules within arrays are similarly protected to form a photovoltaic generator that is designed to generate power at a certain current and a voltage which is a multiple of 12 V.





Solar Cell - Definitions

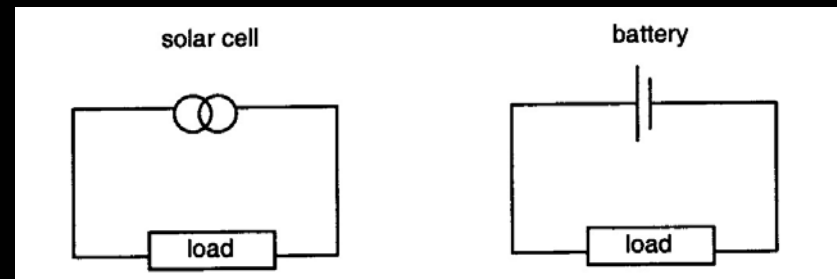
Open circuit voltage V_{oc} : When light hits a solar cell, it develops a voltage, analogous to the e.m.f. of a battery in a circuit. The voltage developed when the terminals are isolated (infinite load resistance) is called the open circuit voltage.

Short circuit current I_{sc} : The current drawn when the terminals are connected together is the short circuit current.

For any intermediate load resistance R_L the cell develops a voltage V between 0 and V_{oc} and delivers a current I such that $V = IR_L$, and $I(V)$ is determined by the *Current-voltage characteristic* of the cell under that illumination.

Both I and V are determined by the illumination as well as the load.

The current is approximately proportional to the illumination area, the *short circuit current density*, J_{sc} is a useful quantity for comparison.





Photocurrent and Quantum Efficiency

The photocurrent density, J_{sc} , generated by a solar cell under illumination at short circuit is dependent on the incident light spectrum.

Quantum efficiency (QE): It is the probability that an incident photon of energy E will deliver one electron to the external circuit.

$$J_{sc} = q \int b_s(E) QE(E) dE$$

Where $b_s(E)$ is the incident spectral photon flux density, the number of photons of energy in the range E to $E+dE$ which are incident on unit area in unit time and q is the electronic charge.

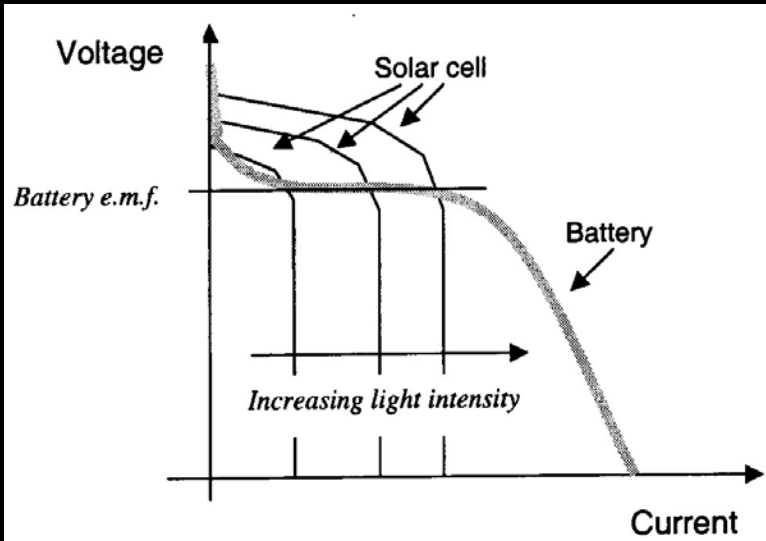
$$E = \frac{hc}{\lambda} = \frac{1240}{\lambda}$$

QE depends on the solar cell material and electronic characteristics, but does not depend on the incident spectrum.



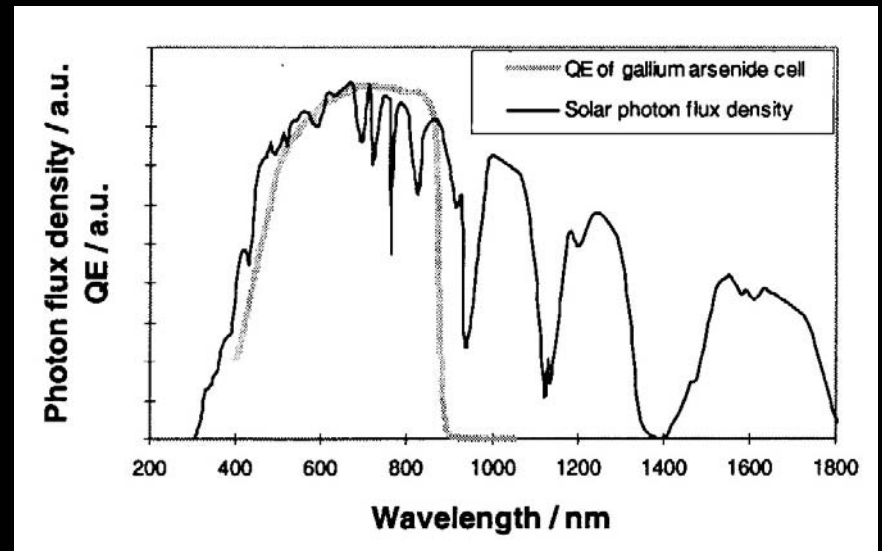


Photocurrent and Quantum Efficiency



A battery normally delivers a constant e.m.f. at different levels of current and will deteriorate when it is heavily discharged. The solar cell delivers a constant current for any given illumination level while the voltage is determined largely by the load resistance.

The short circuit photocurrent is obtained by integrating the product of the photon flux density and QE over photon energy. It is desirable to have a high QE at wavelengths where the solar flux density is high.





Photon Flux

Consider a beam of red light with a wavelength $\lambda = 6000 \text{ \AA}$. Its energy in electron volts is

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{6000 \times 10^{-10}} = 2.08 eV$$
$$eV = 1.6 \times 10^{-19} \text{ joule}$$

The *photon flux* is a quantity useful in solar cell calculations: it is defined as the number of photons crossing a unit area perpendicular to the light beam per second. If we let F denote the intensity of the light in w/cm^2 then we have

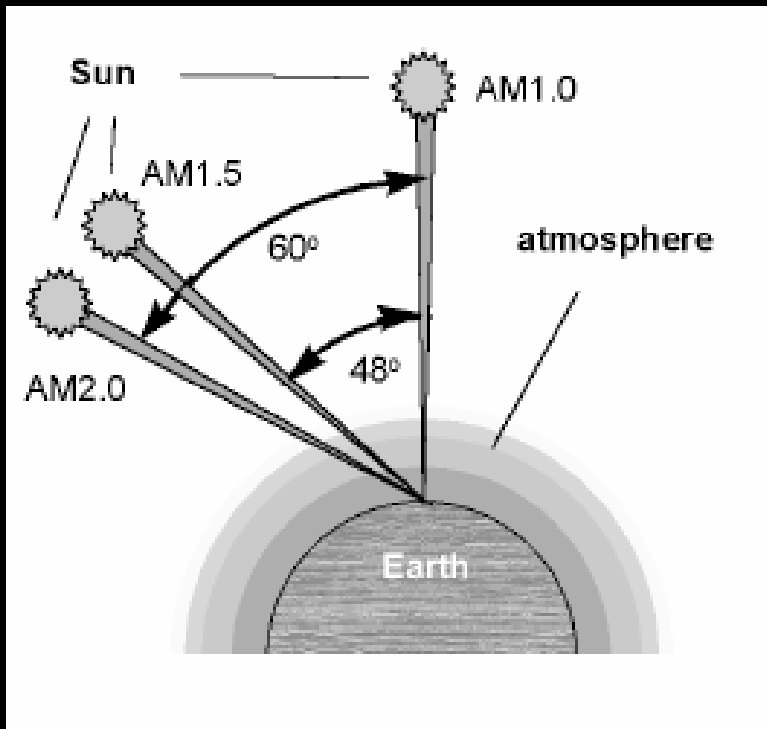
$$\Phi = N_{ph} E = \frac{N_{ph} hc}{\lambda_{av}}$$

where N_{ph} is the number of photons carrying the energy.





Solar Radiation



The path length of the solar radiation through the Earth's atmosphere in units of Air Mass (AM) increases with the angle from the zenith. The AM 1.5 spectrum is the preferred standard spectrum for solar cell efficiency measurements.

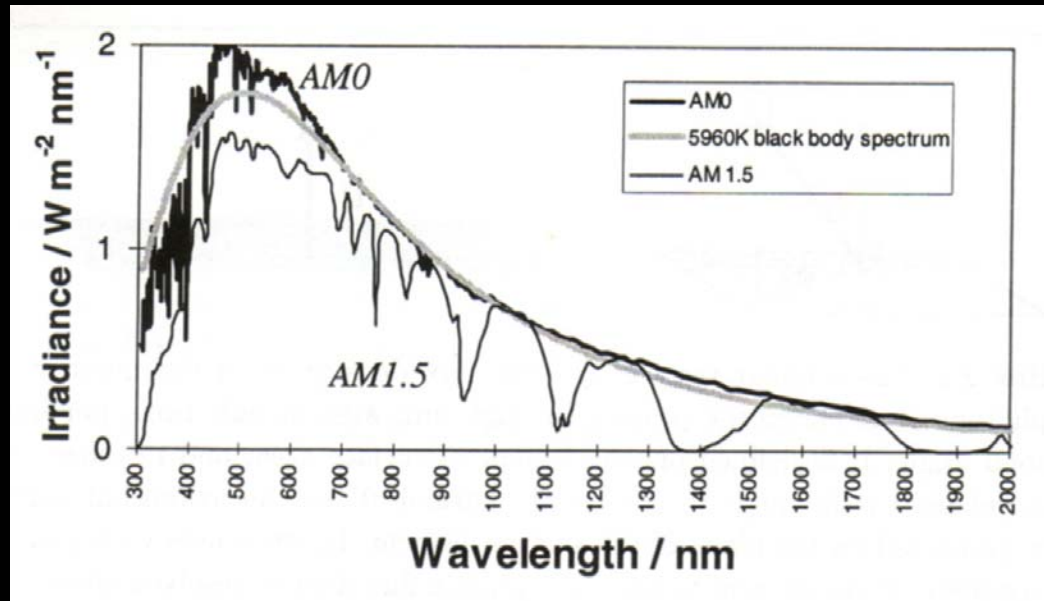
The easiest way to estimate the air mass in practice is to measure the length of the shadow s cast by a vertical structure of height h using

$$AM = \sqrt{1 + \left(\frac{s}{h}\right)^2}$$



Solar Irradiance

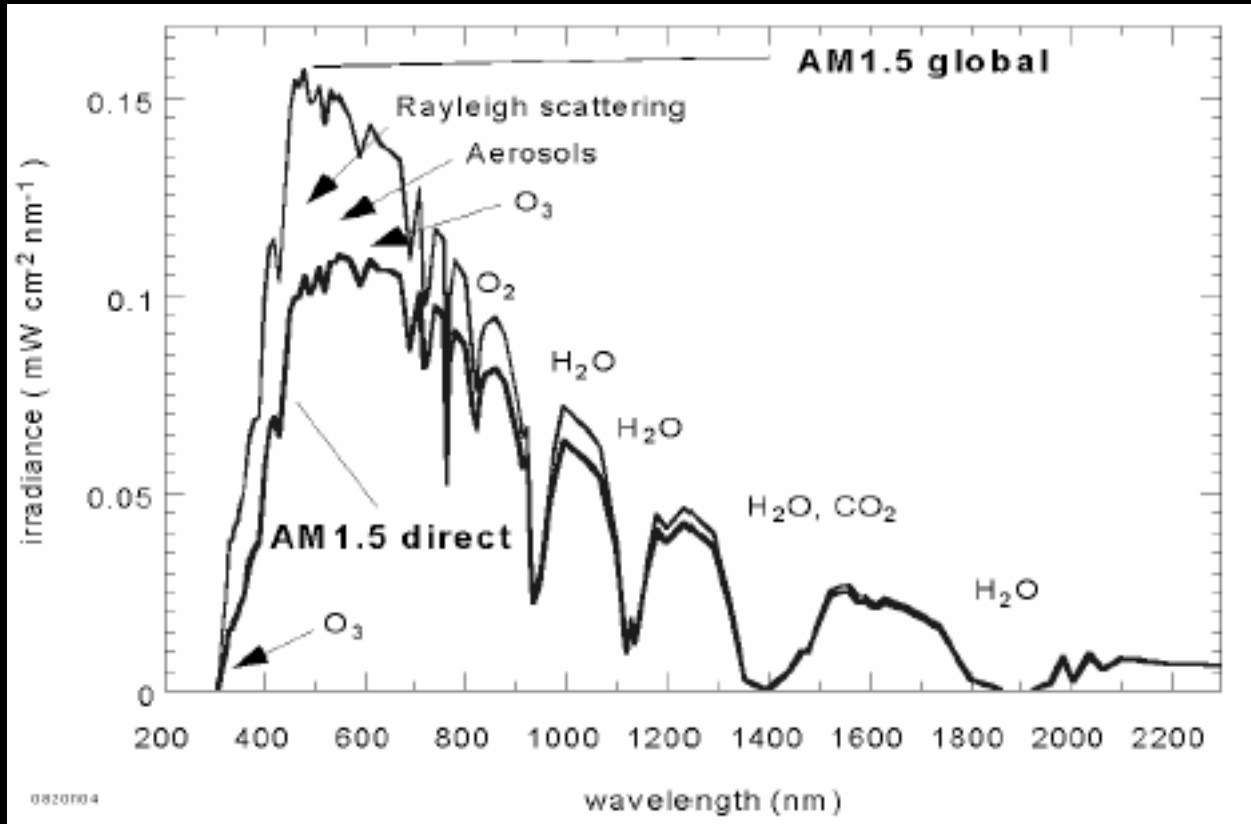
Solar irradiance: The amount of radiant energy received from the Sun per unit area per unit time. It is a function of wavelength at a point outside the Earth's atmosphere. Solar irradiance is greatest at wavelengths, 300-800 nm.



The extraterrestrial spectrum resembles the spectrum of a *black body* radiation at 5760 K. The black body emits photons with a distribution of energies determined by its surface temperature.



Solar Radiation Spectrum



The global spectrum comprises the direct plus the diffused light.



AM 1.5d Spectrum Energy Distribution

(eV) :	4.1	3.5	3.1	2.8	2.5	2.3	2.1	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.24	1.18	1.13	1.08	1.03	0.99	0.95	0.69	0.62	0.5
(nm):	300	350	400	450	500	550	600	650	700	750	800	850	900	950	1000	1050	1100	1150	1200	1250	1300	1800	2000	2500
300	0	0.7	2.9	7.6	14	21	28	35	42	48	54	59	64	67	70	74	77	79	81	84	86	96	96	100
350		0	2.2	6.9	14	21	28	35	41	47	53	58	63	66	69	73	77	78	80	83	85	95	96	99
400			0	4.7	11	18	25	33	39	45	51	56	61	64	67	71	74	76	78	81	83	93	93	97
450				0	6.7	14	21	28	34	40	46	51	56	59	62	66	70	71	73	76	78	88	89	92
500					0	7.0	14	21	28	34	39	44	50	52	56	60	63	64	67	69	72	81	82	86
550						0	7.1	14	21	27	32	37	42	45	49	53	56	57	60	62	65	74	75	79
600							0	7.1	14	20	25	30	35	38	42	46	49	50	52	55	58	67	68	72
650								0	6.5	13	18	23	28	31	35	39	42	43	45	48	51	60	61	65
700									0	6.1	12	17	22	25	28	32	35	37	39	42	44	54	54	58
750										0	5.6	11	16	19	22	26	29	30	33	35	38	48	48	52
800											0	5.1	10	13	16	20	24	25	27	30	32	42	43	46
850												0	5.1	8.0	11	15	19	20	22	25	27	37	37	41
900													0	2.9	6.3	10	13	15	17	20	22	32	32	36
950														0	3.3	7.3	11	12	14	17	19	29	29	33
1000															0	3.9	7.2	8.4	11	13	16	26	26	30
1050																0	3.2	4.5	6.8	9.5	12	22	22	26
1100																	0	1.2	3.5	6.2	8.7	18	19	23
1150																		0	2.3	5.0	7.5	17	18	21
1200																			0	2.7	5.2	15	15	19
1250																				0	2.5	12	13	16
1300																					0	10	10	14
1800																						0	0.5	4.3
2000																							0	3.8
2500																								0

Silicon solar cells with a bandgap of 1.13eV can maximally absorb 77% of the terrestrial solar energy.





Irradiance

The emitted energy flux density or irradiance, $L(E)$ is related to the photon flux density through

$$L(E) = E b_s(E)$$

Integrating over E gives the total emitted power density, $\sigma_s T_s$, where σ_s is Stefan's constant that is given by

$$\sigma_s = \frac{2\pi^5 k^4}{15c^2 h^3}$$

At the sun's surface, the power density is 62 MW/m²

Outside the Earth's atmosphere, the power density is 1353 W/m²

Solar Constant





Photon Flux Calculation

Let Φ denote intensity of the light in W/cm^2 and the number of photons carrying that energy N_{ph} is computed from the expression

$$\Phi = N_{ph} E = N_{ph} h \nu_{av} = \frac{N_{ph} hc}{\lambda_{av}}$$

For example, if outside the atmosphere the solar spectrum has an intensity of $0.135 W/cm^2$ and each photon carries on the average 1.48 eV, then the photon flux is

$$N_{ph} = \frac{0.135 W/cm^2}{1.48 eV} \frac{eV}{1.60 \times 10^{-19} joule} \frac{joule}{W - sec} = 5.8 \times 10^{17} \frac{1}{cm^2 - sec}$$

<i>m</i>	<i>w</i>	<i>Comments</i>	Φ (W/cm^2)	ξ_{av} (eV)	N_{ph} (No./sec- cm^2)
0	0	Outside atmosphere	0.135	1.48	5.8×10^{17}
1	0	Sea level, sun at zenith	0.106	1.32	5.0×10^{17}
2	0	Sea level, sun at 60 deg from zenith	0.088	1.28	4.3×10^{17}
3	0	Sea level, sun at 70.5 deg from zenith	0.075	1.21	3.9×10^{17}
1	2	About 50% relative humidity	0.103	1.25	4.8×10^{17}
3	5	Extreme condition	0.059	1.18	3.2×10^{17}
1	0	Cloudy day (7000°K Black Body)	0.012	1.44	5.2×10^{16}

$$m = 1/\cos\theta$$

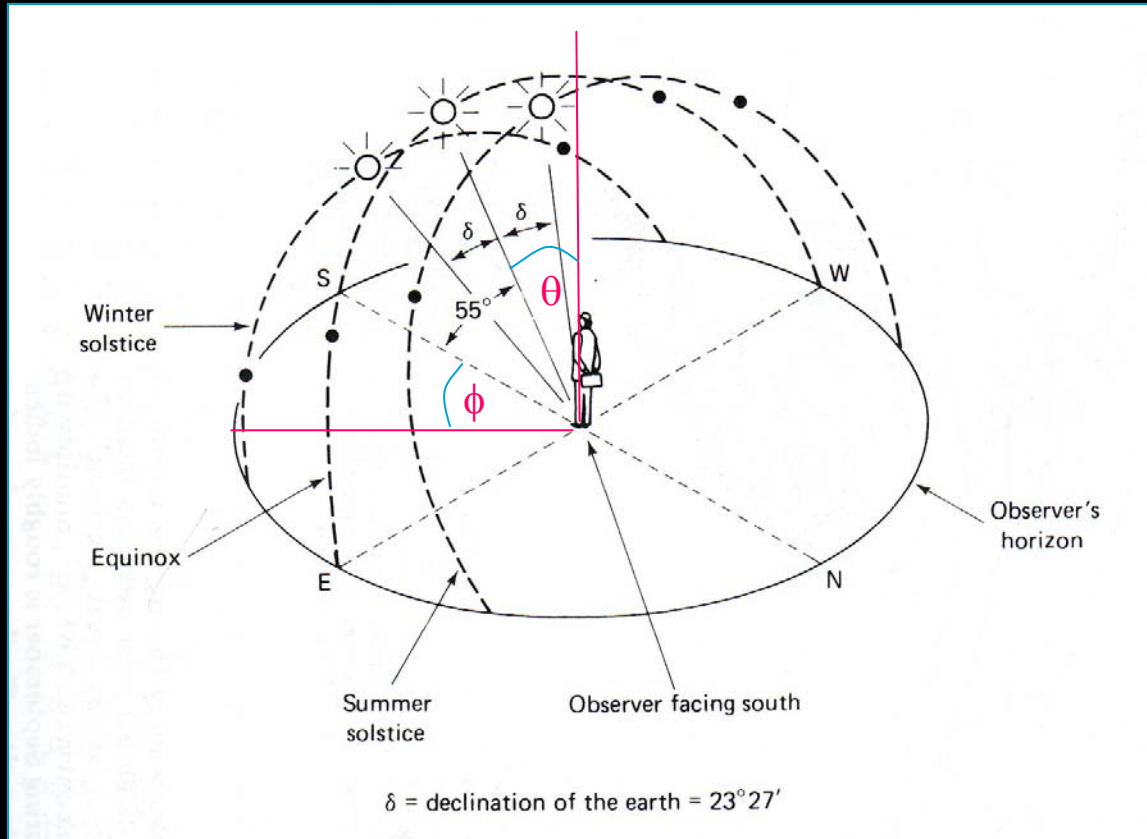
w = number of *cm* of perceptible water vapor

Note: N_{ph} is computed by summing the number of photons in the energy range from 0 up to 4 eV found in the solar spectrum





Motion of the Sun



Apparent motion of the sun relative to a fixed observer at latitude 35° in the northern hemisphere. The position of the sun is shown at solar noon and shaded circles represent the sun's position 3 h before and after solar noon.



Spectral Photon Flux Density

The *spectral photon flux* $\beta(E, \mathbf{s}, \theta, \phi)$ - number of photons of given energy passing through unit area in unit time per unit solid angle. It is defined on an element of surface area with its direction is defined by the angle to the surface normal, θ , and an azimuthal angle, ϕ , projected on the plane of the surface element. The photon flux density resolved along the normal to the surface is denoted by b , which is obtained by integrating the components of β normal to the surface over solid angle.

β is given by

$$\beta_s d\Omega ds dE = \frac{2}{h^3 c^2} \left(\frac{E^2}{e^{\frac{E}{k_B T_s}} - 1} \right) d\Omega ds dE$$

$$b_s ds dE = \int_{\Omega} \beta_s(E, \mathbf{s}, \theta, \phi) \cdot \cos \theta d\Omega ds dE$$

$$b_s ds dE = \frac{2F_s}{h^3 c^2} \left(\frac{E^2}{e^{\frac{E}{k_B T_s}} - 1} \right) ds dE$$



$$F_s = \pi \sin^2 \theta_{\text{sun}}$$

Where θ_{sun} is the half angle subtended by the radiating body to the point of the flux measurement. For the sun as seen from the Earth $\theta_{\text{sun}} = 26^\circ$



Current Density at Ambient Temperature

The spectral photon flux at a point s on the surface of a solar cell at ambient temperature, T_a is

$$\beta_a d\Omega ds dE = \frac{2}{h^3 c^2} \left(\frac{E^2}{e^{k_B T_a} - 1} \right) d\Omega ds dE$$

With appropriate integration of the above expression, we obtain the incident flux of thermal photons normal to the surface of a flat solar cell as

$$b_a(E) = \frac{2F_a}{h^3 c^2} \left(\frac{E^2}{e^{k_B T_a} - 1} \right)$$

Where $F_a = \pi$ for the ambient radiation received over a hemisphere. The equivalent current density absorbed from the ambient is

$$j_{abs} = q(1 - R(E))a(E)b_a(E)$$

Where $a(E)$ (known as the absorbance that is determined by the absorption coefficient of the material and by the optical path length through the device) is the probability of absorption of a photon of energy E and $R(E)$ is the probability of photon reflection. $J_{abs}(E)$ is the electron current density equivalent to the absorbed photon flux if each photon of energy E generates one electron.





Current Density Under Illumination

Under illumination by a solar photon flux $b_s(E)$, the cell absorbs solar photons of energy E at a rate

$$(1 - R(E))a(E)b_s(E)$$

The current density for photon emission is given by

$$j_{rad} = q(1 - R(E))a(E)b_e(E)$$

The net equivalent current density or *radiative recombination current density* is then given by

$$j_{abs} - j_{rad} = q((1 - R(E))a(E)(b_e(E) - b_a(E)))$$

The output is determined by a balance between light absorption, current generation and recombination. Generation is an electronic excitation event which increases the number of free carriers available to carry charge, which requires an input of energy. Recombination is an electronic relaxation event which reduces the number of free carriers and releases energy. For every generation process there is an equivalent recombination processes.

Generation, by the absorption of a photon, is the promotion of an electron from valance to conduction band, which creates an electron-hole pair. Recombination is the loss of an electron or hole through the decay of an electron to a lower energy state.

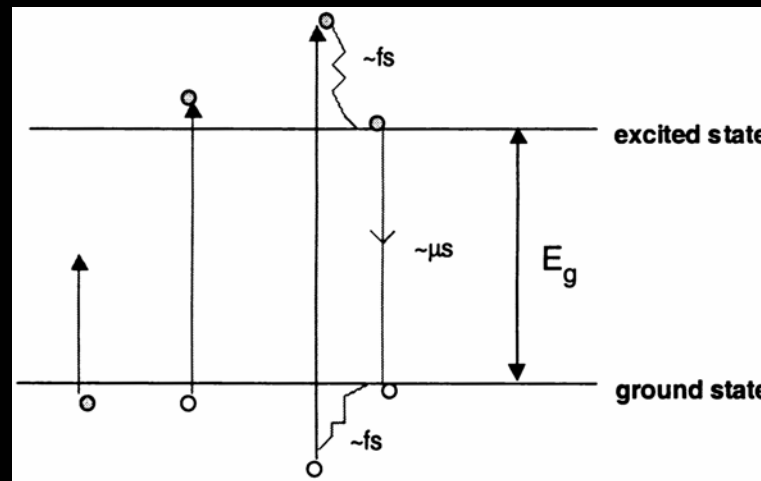




Photocurrent

Consider a two band system: the ground state is initially full and the excited state empty

Band gap, E_g : The bands are separated by a band gap



Photons with energy $E < E_g$ can not promote an electron to the excited state. Photons with $E \geq E_g$ can raise the electron but any excess energy is quickly lost as heat as the carriers relax to the band edges. We will assume that electrons in each band are in quasi thermal equilibrium at the ambient temperature T_a and the chemical potential for that band is μ_i . An absorbed photon with $E \gg E_g$ achieves the same result as as the photon with $E = E_g$. Hence it is the **photon flux** and not the photon energy density which determines the photo generation. Once excited, the electrons remain in the excited state for a relatively long time.

Photocurrent

For the case of the most efficient solar cell we have perfectly absorbing, non reflecting material so that all incident photons of energy $E > E_g$ are absorbed to promote exactly one electron to the upper band. We also have perfect charge separation so that all electrons which survive radiative recombination are collected by the negative terminal of the cell and delivered to the external circuit. This gives maximum photocurrent for that band gap. Then

$$QE(E) = \begin{cases} 1 & E \geq E_g \\ 0 & E < E_g \end{cases}$$

and

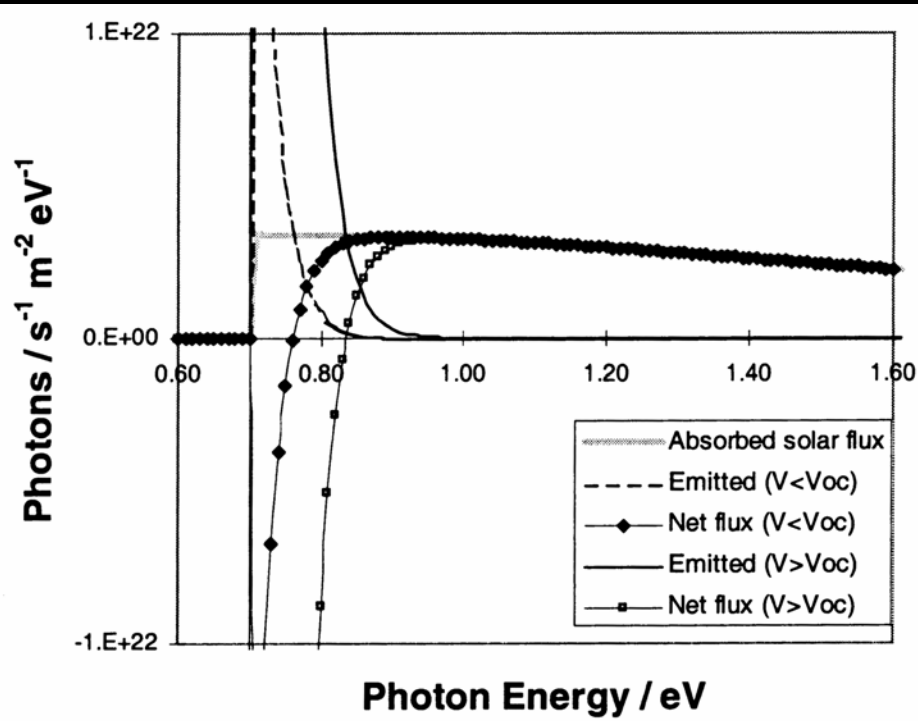
$$J_{sc} = q \int_{E_g}^{\infty} b_s(E) dE$$

Photocurrent is then a function of only of the band gap and the incident spectrum. Lower the E_g the greater will be J_{sc}





Net Electron Current



The net electron current is due to the difference between the two photon flux densities: the absorbed flux, which is distributed over a wide range of photon energies above the threshold E_g , and the emitted flux, which is concentrated on photon energies near E_g . As V increases, the emitted flux increases and the net current decreases. At V_{oc} the total emitted flux exactly balances the total absorbed flux and net current is zero.



Dark Current and Open Circuit Voltage

When load is present, a potential difference develops between terminal and it generates a current which acts in the opposite direction to the photocurrent. Therefore the net current is reduced from its short circuit value. The reverse current is called the **dark current** $I_{dark}(V)$ which flows across the device under an applied voltage or **bias voltage**, V in the dark.

Most solar cells behave like a diode in the dark, admitting much larger current under forward bias ($V > 0$) than under reverse bias ($V < 0$). This rectifying behavior is a feature of photo voltaic devices, since an asymmetric junction is needed to achieve charge separation. For an ideal diode the dark current density is given by

$$J_{dark}(V) = J_0 \left(e^{\frac{qV}{k_B T}} - 1 \right)$$

Where J_0 is a constant, k_B is Boltzmann's constant and T is temperature in K.





Superposition Approximation

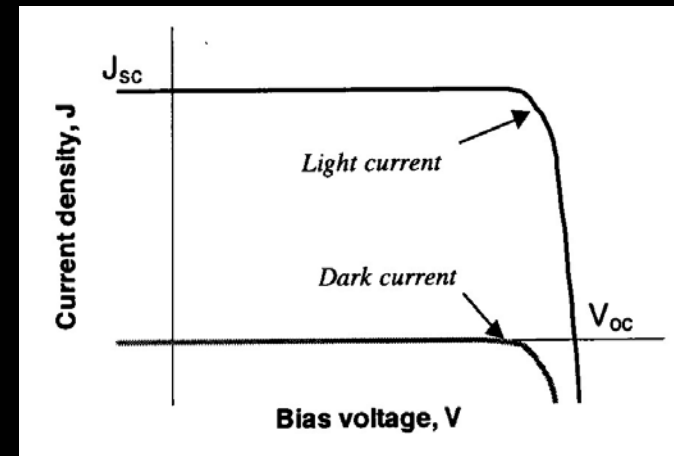
The overall current voltage response of the cell, its *current-voltage characteristic*, can be approximated as the sum of short circuit photocurrent (positive) and the dark current.

The overall current voltage response of the cell, its *current-voltage characteristic*, can be approximated as the sum of short circuit photocurrent and the dark current. The net current density in the cell is

$$J(V) = J_{sc} - J_{dark}(V)$$

For an ideal diode,

$$J = J_{sc} - J_0 \left(e^{\frac{qV}{k_B T}} - 1 \right)$$

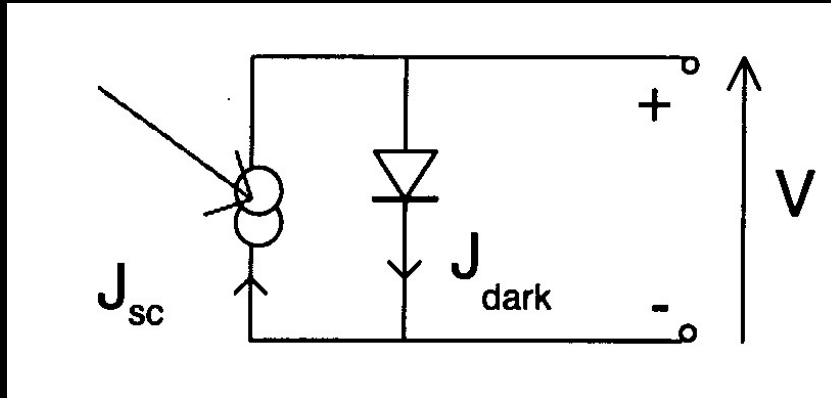


When the dark current and short circuit photocurrent exactly cancel out, we have for the ideal diode (forward bias $V > 0$)

$$V_{oc} = \frac{kT}{q} \ln \left(\frac{J_{sc}}{J_0} + 1 \right)$$



Equivalent Circuit of Ideal Solar Cell



When the current-voltage product is positive and the voltage is between 0 and V_{oc} , the cell generates power. At $V > V_{oc}$ the device consumes power and it is the regime where light emitting diodes operate. At $V < 0$, the illuminated device acts as a photodetector, consuming power to generate a photocurrent.

When illuminated, the ideal cell produces a photocurrent to the light intensity. That photocurrent is divided between the variable resistance of the diode and the load, in a ratio which depends on the resistance of the load and illumination level. For higher resistances, more of the photocurrent flows through the diode, resulting in higher potential difference between the cell terminals but a smaller current through the load. The diode thus provides the photo voltage. Without the diode, there is nothing to drive the photocurrent through the load.

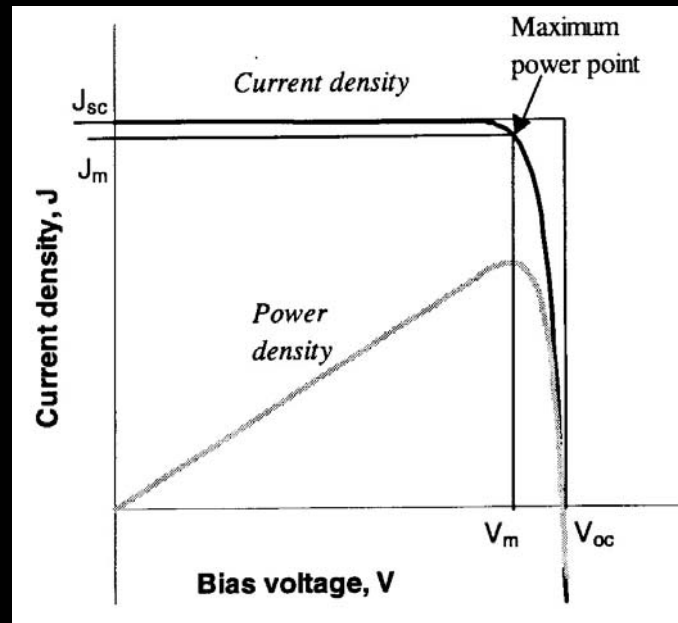


Efficiency

The *cell power density* is given by

$$P = JV$$

P reaches maximum at the cell's operating point or *maximum power point (MPP)*.



The fill factor is defined as

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}}$$





Efficiency

The efficiency η of the cell is the power density delivered at the operating point as a fraction of the incident light power density, P_s

$$\eta = \frac{J_m V_m}{P_s} = \frac{J_{oc} V_{oc} FF}{P_s}$$

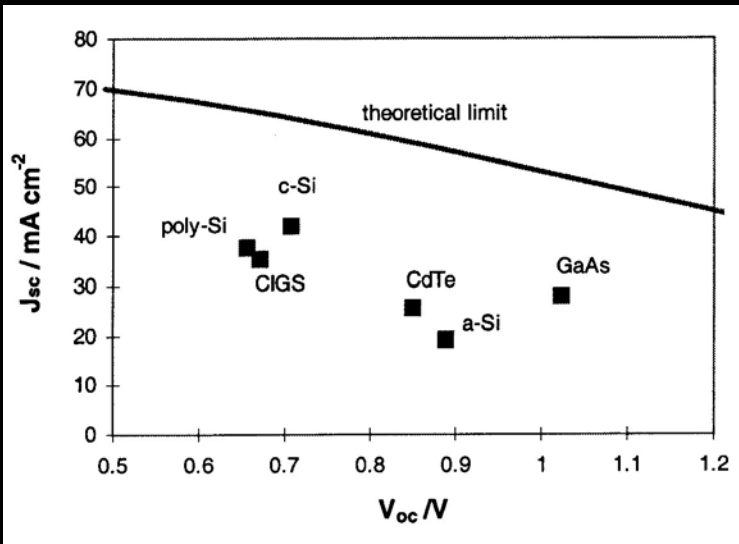
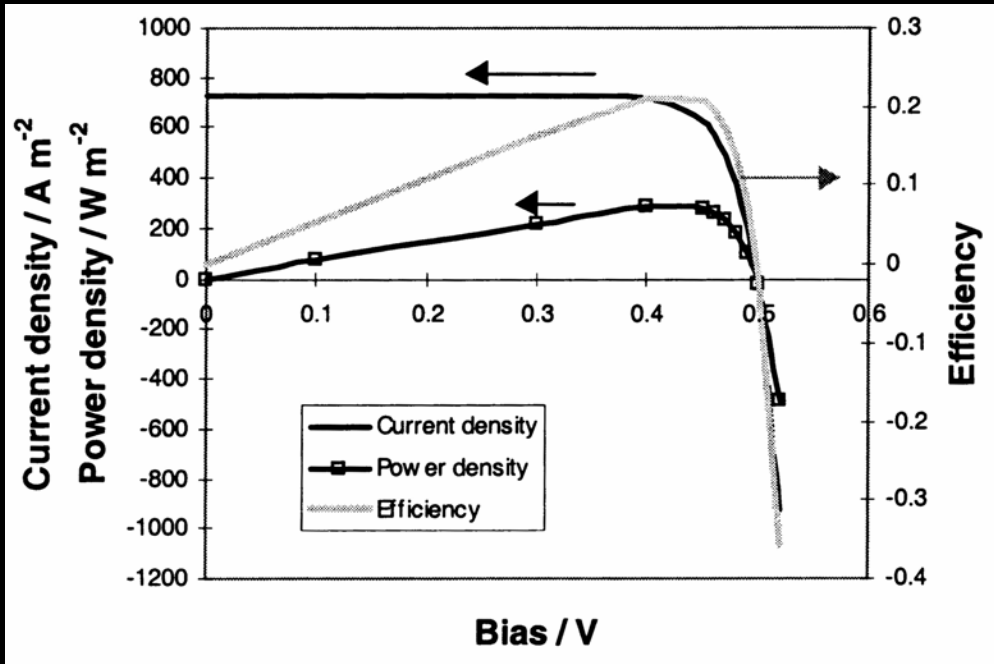


Table 1.1. Performance of some types of PV cell [Green *et al.*, 2001].

Cell Type	Area (cm ²)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	Efficiency (%)
crystalline Si	4.0	0.706	42.2	82.8	24.7
crystalline GaAs	3.9	1.022	28.2	87.1	25.1
poly-Si	1.1	0.654	38.1	79.5	19.8
a-Si	1.0	0.887	19.4	74.1	12.7
CuInGaSe ₂	1.0	0.669	35.7	77.0	18.4
CdTe	1.1	0.848	25.9	74.5	16.4



Current Density and Efficiency



The current density is calculated from the multiplication of q and integrated net photon flux.

The power conversion efficiency is calculated from the incident and extracted power from photon fluxes. The incident power density is obtained from

$$P_s = \int_0^{\infty} E b_s(E_s) dE$$

The extracted power density is given by

$$P = VJ(V)$$

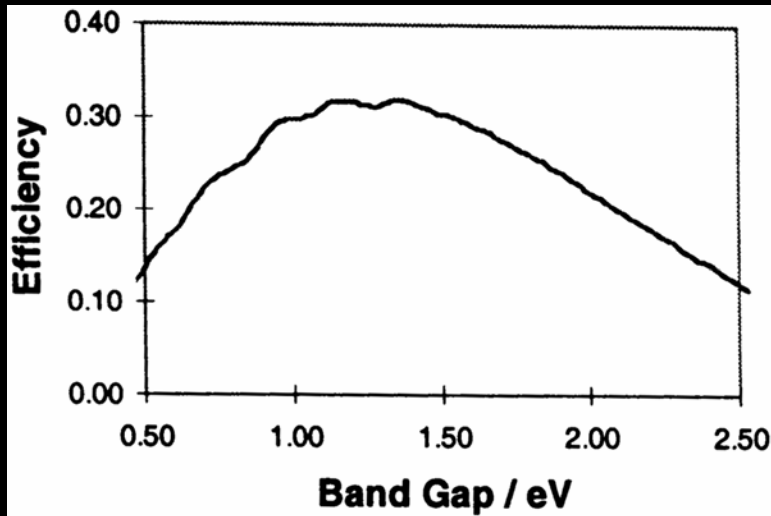
The power conversion efficiency:

$$\eta = \frac{VJ(V)}{P_s}$$

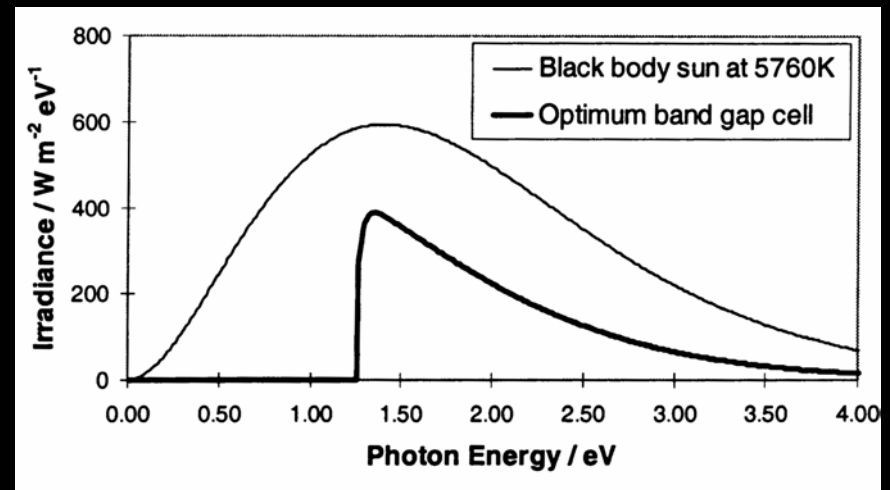


Band Gap Effect

The *power conversion efficiency* of the ideal two band photoconverter is a function only of E_g and the *incident spectrum*. If the incident spectrum is fixed, then efficiency depends only on the band gap.



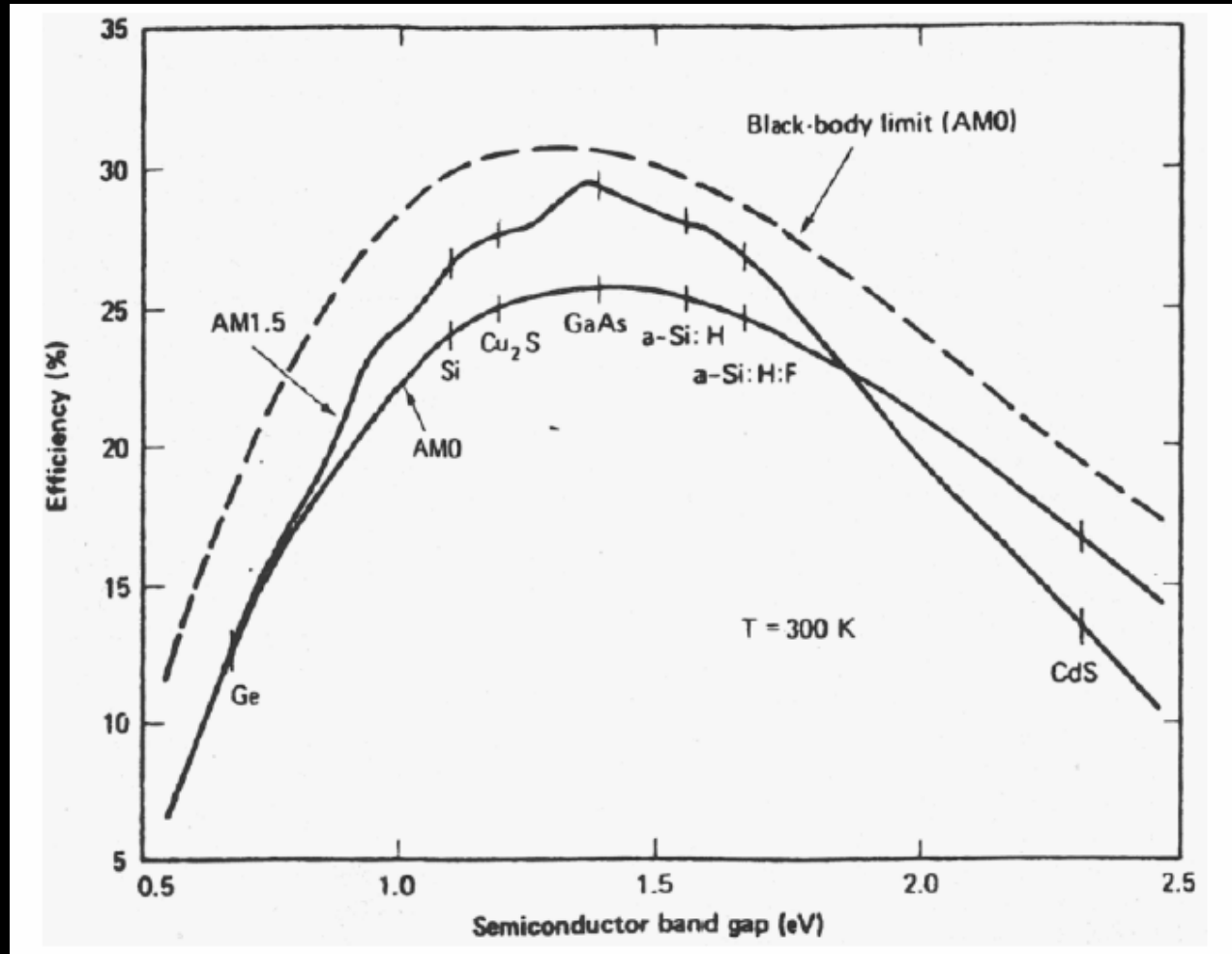
Limiting efficiency for single band gap solar cell in AM 1.5. The maximum efficiency for a standard solar spectrum is around 33% at a band gap of 1.4 eV.



The available power spectrum for an optimum band gap cell at maximum power point is compared with incident power from a black body sun.



Power conversion efficiency limits





Parasitic Resistances

Real cells: Resistance of the contacts and leakage currents around the sides of the device

Series resistance: it arises from the resistance of the cell material to current flow, particularly through the front surface to the contacts and from resistive contacts. It is a particular problem at high current densities, i.e. under concentrated light.

Shunt resistance: It arises from the leakage of the current through the cell around the edges of the device and between contacts of different polarity. It is a problem with poorly rectifying devices.

The diode equation becomes

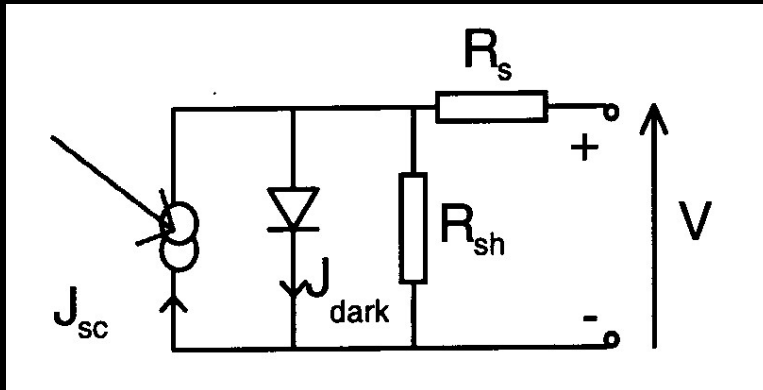
$$J = J_{sc} - J_0 \left(e^{q \left(\frac{V + JAR_s}{kT} \right)} - 1 \right) - \frac{V + JAR_s}{R_{sh}}$$

Where A is the cell area

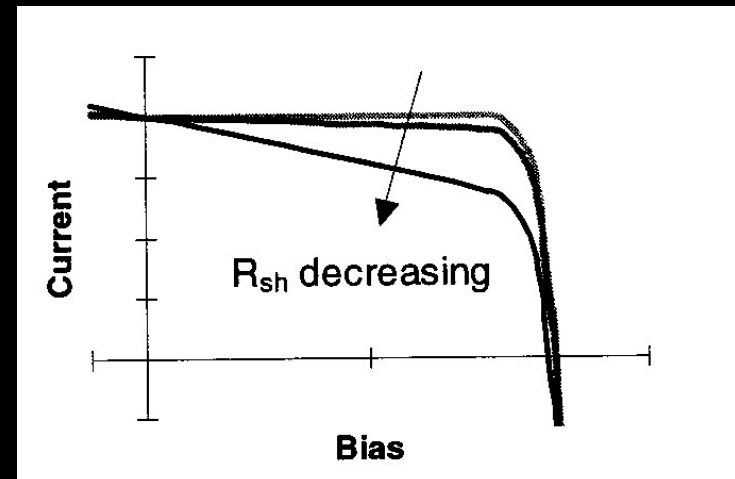
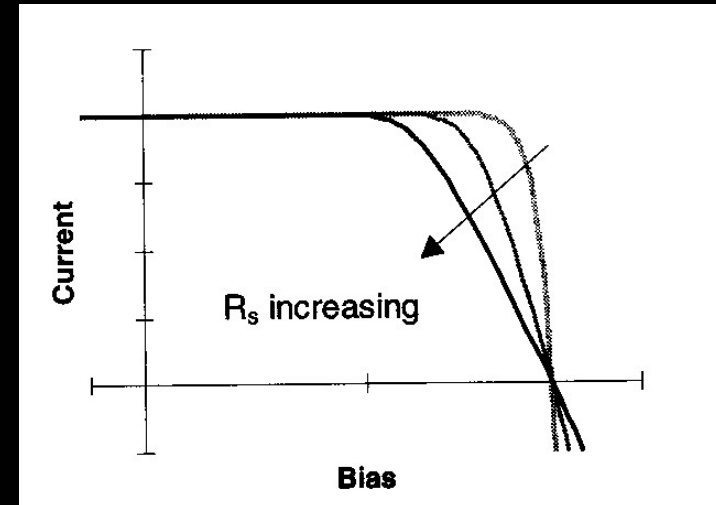




Parasitic Resistances

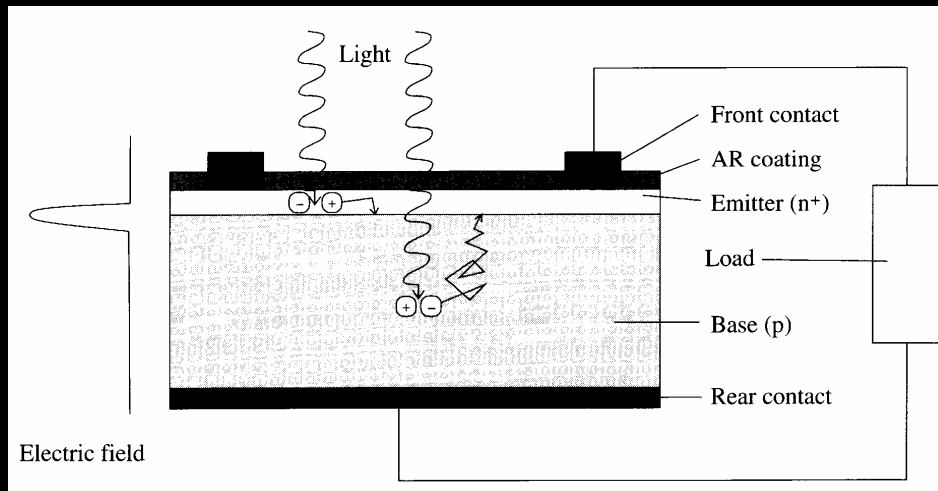


The effect of resistances is to reduce the area of the maximum power rectangle compared to $J_{sc} \times V_{oc}$.





Solar cell



The bulk of the energy converter is composed of p-type material. Only a front surface layer of the wafer has n-type conductivity. The n-layer is called the emitter and the p-region is called the base. When forming such a so called pn-junction diode structure, electrons from the emitter diffuse instantaneously into the base, and holes from the p-region diffuse into the emitter. This is due to the fact that emitter contains a very high concentration of electrons compared to the base, where as the base is rich in holes. This diffusion of charge carriers leads to the build up of an electric field, resulting internal voltage in the vicinity of the pn-junction. Under equilibrium conditions, the electrical forces due to this field compensate the forces driving the diffusion -thus no electric current flows.



Real Solar Cells

The real solar cells do not achieve ideal performance due to following reasons:

1. Incomplete absorption of the incident light. Photons are reflected from the front surface or pass through the cell without being absorbed. This reduces the photocurrent.
2. Non-radiative recombination of photogenerated carriers. Excited charges are trapped at defect sites and subsequently recombine before being collected. This happens, for example, near junctions. It reduces both the photocurrent, through the probability of carrier collection and the voltage by increasing the dark current.
3. Voltage drop due to series resistance between the point of photogeneration and the external circuit. This reduces the available power.





Summary

1. The current size generated by the cell in short circuit depends upon the incident light intensity and the energy spectrum.
2. The photocurrent is related to incident spectrum by the quantum efficiency of the cell.
3. When a load is present, a potential difference is created between the terminals of the cell and this drives a current, dark current, in the opposite direction to photocurrent. As the load resistance is increased the potential difference increases and the net current decreases until the photocurrent and dark current exactly cancel out. The potential difference at this point is called the open circuit voltage.
4. At some point before the open circuit voltage is reached the current voltage product is maximum. The cell should be operated with a load resistance which corresponds to this point.
5. In real cells, the current-voltage characteristic behavior is degraded by the presence of series and parallel or shunt resistances.





Homework

Due: October 18, 2005

The design of a photovoltaic converter

We wish to design a solar power plant that produces 1000 watts. The energy of the photons and their density are given as

$$\Phi = 0.059 \text{ W/cm}^2 ; \varepsilon_{av} = 1.25 \text{ eV}; N_{ph} = 4.8 \times 10^{17} \text{ No./sec-cm}^2.$$

Assume that the converter units are p-n junctions made from silicon with the following properties:

$\varepsilon_g = 1.11 \text{ eV}$, $\mu_p = 400 \text{ cm}^2/\text{volt-sec}$, $\mu_n = 1000 \text{ cm}^2/\text{volt-sec}$, $\tau_p^* = 10^{-5} \text{ sec}$, $\tau_n^* = 10^{-7} \text{ sec}$, $N_a = 10^{19} \text{ cm}^{-3}$ acceptors in the p-layer, $N_d = 10^{17} \text{ cm}^{-3}$ donors in the n-layer and $T = 300 \text{ K}$.

Use the following reference for the necessary material.

Ref: Direct Energy conversion by Stanley W. Angrist, Ch 5.



Direct Energy Conversion: Thermoelectric Conversion

References:

Section 4.1.3 in the text Book

Direct Energy Conversion by Stanley W. Angrist, Allyn and Beacon, 1982.

Direct Energy Conversion by Reiner Decher, Oxford University press, 1997.



Direct Energy Conversion

The best achievable thermal efficiency for electricity generation with conventional methods is about 50%.

In general when a process can occur directly rather than passing through several intermediate steps, it is reasonable to expect that it may take place more efficiently.

Fuel cells (a mode of direct energy conversion) have already demonstrated a capability of producing small quantities of electrical energy with considerable efficiency.

The ability to convert primary energy directly into the required form at its point of use would be of great use in many systems (space exploration, satellites, remote weather stations etc.).



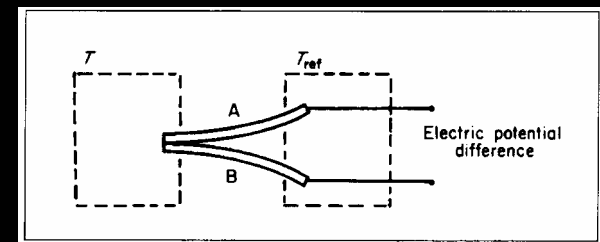
Thermoelectric Effect

One of the ways to directly convert the thermal power to electric power is through thermoelectric generators.

In metals and semiconductors, electrons are free to move in the conduction band. They respond to electric fields, which establish a flux of charges or current. These electrons can also respond to a gradient of temperature so as to accommodate a flow of heat.

The motion of the electrons transports both their charge and their energy. At junctions of dissimilar materials the electrons flow across a discontinuity in the energy levels of the conduction bands. If the spectrum of electron quantum states is different in the two materials, the crossing of negatively charged electrons or positively charged holes will not preserve the statistical distribution of electrons around the Fermi level.

$$f(E) = \frac{1}{e^{\frac{E - \mu_i}{kT}} + 1}$$



Where E is the electron energy and k is the Boltzmann's constant. The maintenance of the current may require addition or removal of heat (thermoelectric generator) or heating the junction will increase or decrease the electric current.

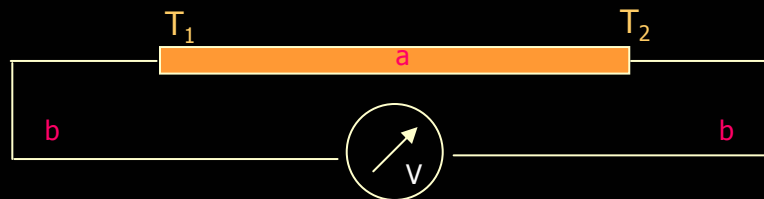


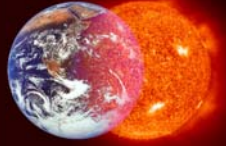
Seebeck Experiment

Seebeck Coefficient: When two ends of a conductor of material **a** are maintained at different temperatures, say $\Delta T = T_1 - T_2$, Seebeck observed in 1822 that a voltage V (varies with ΔT) can be measured when the current is zero. The *Seebeck coefficient* is then defined as

$$\alpha_{ab} \equiv \lim_{\Delta T \rightarrow 0} \frac{\Delta V}{\Delta T}$$
$$V = \int_{T_1}^{T_2} \alpha_{ab} dT$$

This equation can be interpreted as that the electrons will acquire an electric potential as they are transported from region of varying thermal energies. Energies are measured by their temperatures.





Seebeck Coefficient

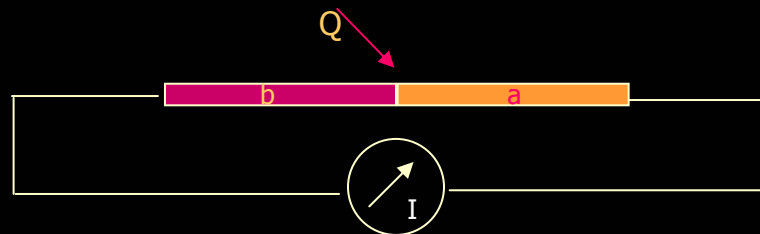
Material	α ($\mu\text{V}/\text{K}$)
Al	-0.2
Constantan	-47.0
Cu	+3.5
Fe	+13.6
Pt	-5.2
Ge	+375.0
Si	-455.0



Peltier Experiment

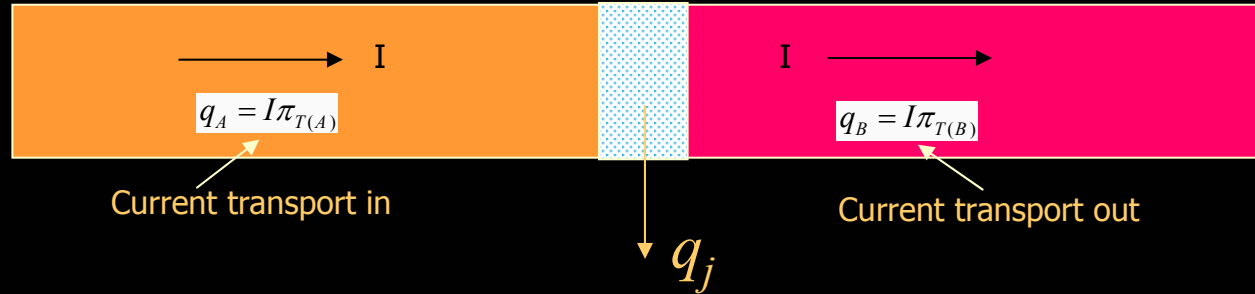
Peltier Coefficient: Consider two bars of material *a* and *b* that are joined with a current source as shown in the figure below. Peltier observed in 1844 that the current flow results in the evolution of heat in an amount proportional to the current and the heat is absorbed when the current is reversed, known as *Peltier effect*. It is quantified through a proportionality constant associated with a particular junction of materials. The Peltier coefficient is defined as the ratio of heat evolved to current flowing:

$$\pi_{ab} = \frac{Q}{I}$$





Junction of two Dissimilar Materials



The rate at which heat must be removed from the junction in order to maintain the temperature constant:

$$q_j = I^2 R_j + I(\pi_{T(A)} - \pi_{T(B)}) \text{ watts}$$

$$q_j = I^2 R_j + IT(\alpha_A - \alpha_B) \text{ watts}$$

The rate at which electrical work is done on the junction with resistance R_j is the current times the potential drop across the junction

$$IV_{A,B} = I^2 R_j$$



Thomson Experiment

Thomson Effect: Lord Kelvin (William Thomson) in 1854 realized that a relation between Seebeck and Peltier effects should exist and derived a relationship from thermodynamic arguments. This third thermoelectric effect, now known as Thomson effect is a lateral heating or cooling effect that takes place in a homogeneous conductor when an electric current passes in the direction of a temperature gradient.

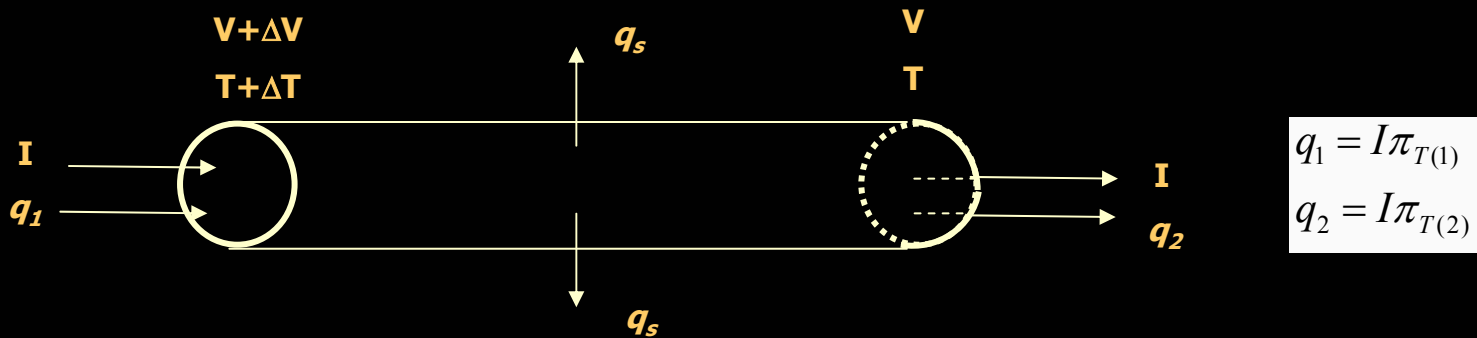
A unit length of bar with temperature gradient evolves heat in excess of joule dissipation (I^2R) when current flows as represented in the figure below. The Thomson coefficient is given by

$$\gamma \equiv \lim_{\Delta T \rightarrow 0} \frac{1}{I} \frac{\Delta Q}{\Delta T}$$
$$Q = \int_{T_1}^{T_2} \gamma dT$$





Thomson Heat



Heat developed is greater or less than I^2R depending upon the magnitude and direction of the current.

The rate at which heat must flow out the sides of the rod in order for the temperature at every point in the rod to be maintained constant:

$$q_s = I\Delta V + I\pi_{T(1)} - I\pi_{T(2)} = I[\Delta V + (T + \Delta T)\alpha_1 - T\alpha_2]$$

Since

$$\alpha_1 = \alpha_2 + \frac{d\alpha}{dT}\Delta T$$

$$q_s = I\left(\Delta V + T\frac{d\alpha}{dT}\Delta T + \alpha\Delta T\right)$$

Since the voltage drop across the rod is $\Delta V = IR - \alpha\Delta T$

$$q_s = I^2R + I\left(T\frac{d\alpha}{dT}\Delta T\right)$$

Thomson heat





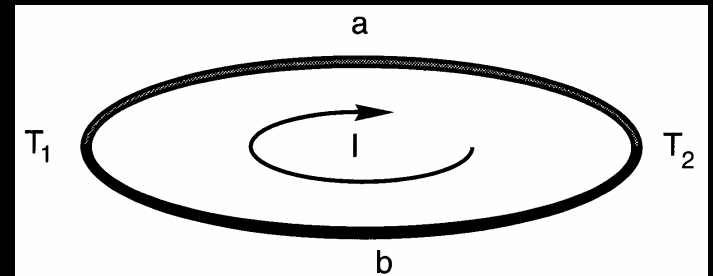
Thermoelectric Interactions

The three effects and the constants that describe them are related through energy balance that must apply around a circuit. The balance states that the electrical power generated as a result of temperature difference maintained cross a junction equals to the heat dissipated at the two junctions and through the two bars.

$$\int_{T_1}^{T_2} \alpha_{ab} IdT = (\pi_{ab_2} - \pi_{ab_1})I + \int_{T_1}^{T_2} (\gamma_a - \gamma_b) IdT$$

or

$$\alpha_{ab} = \frac{d\pi_{ab}}{dT} + (\gamma_a - \gamma_b)$$



The entropy generated at the two junctions, where the temperatures differ, gives

$$\Delta S = \left(\frac{\pi_{ab_2}}{T_2} - \frac{\pi_{ab_1}}{T_1} \right) I$$

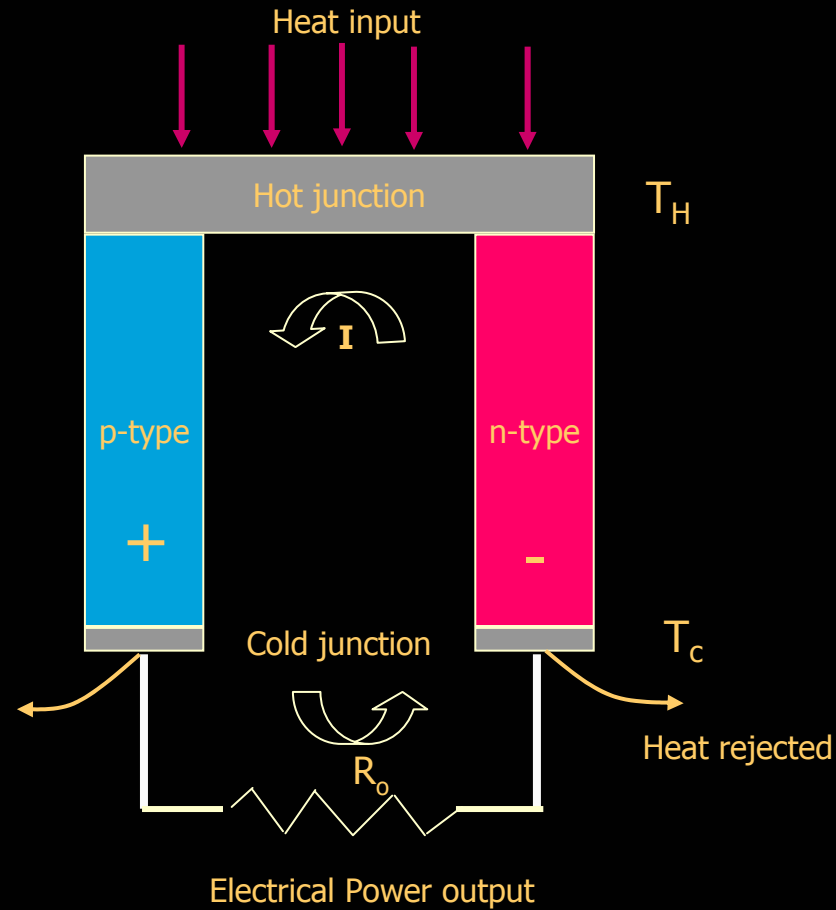
$$\int_{T_1}^{T_2} Id \left(\frac{\pi_{ab}}{T} \right) + \int_{T_1}^{T_2} I \frac{(\gamma_a - \gamma_b)}{T} dT = 0$$

$$\frac{d\pi_{ab}}{dT} - \frac{\pi_{ab}}{T} + (\gamma_a - \gamma_b) = 0$$

$$\frac{\pi_{ab}}{T} = \alpha_{ab}$$



Thermoelectric Generator

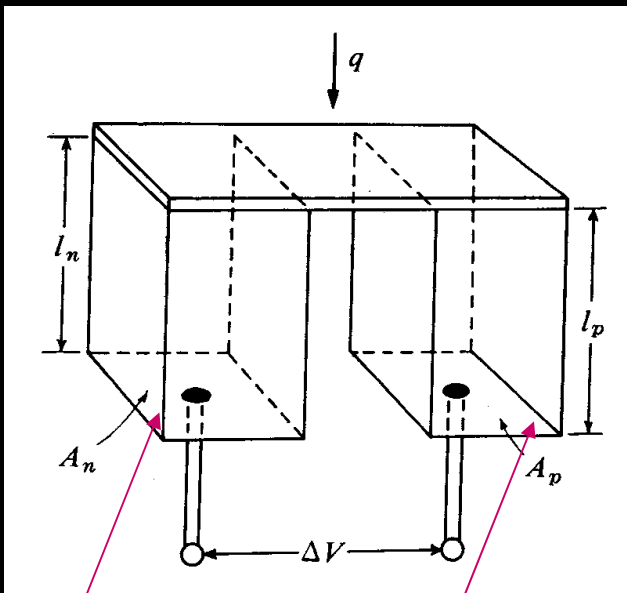




Thermoelectric Generator

Thermoelectric generators are useful devices for converting heat energy directly into electrical energy.

In a thermoelectric generator a heat flux induces a potential difference across a junction of dissimilar materials.



Negative Seebeck Coefficient

Positive Seebeck Coefficient

The output voltage ΔV , and input heat flux, q is given by

$$\Delta V = \alpha \frac{\Delta T}{T} - R I$$

$$q = C \frac{\Delta T}{T} + \alpha I$$

Where ΔT is the temperature drop through the device in the direction of the heat flux q , ΔV is the potential rise through the device in the direction of I , α , R and C are interaction, resistance and conductance coefficients respectively.

Ref: *Direct Energy Conversion* by S.W. Angrist, 1976.



Thermoelectric Generator

The p and n legs have thermal and electrical conductivities k_i and σ_i respectively (i refers to either p or n). The conductance k of a bar of length l and cross sectional area A is given by

$$K_i = k_i \frac{A_i}{l_i}$$

The electrical resistance R of a bar of length l and cross sectional area A is given by

$$R_i = \sigma_i \frac{l_i}{A_i}$$





Thermoelectric Generator

The first equation indicates that the voltage difference measured across the terminals of the device is proportional to the internal resistance and to the temperature difference applied to the generator. In the second equation we see that the heat flux is proportional to the temperature difference and to the current through the device. Thus under open circuit conditions with zero current the ratio C/T represents the internal thermal conductance (the thermal conductivity $\lambda = ql/(A\Delta T)$ of the generator K :

$$K = \frac{C}{T} = \frac{\lambda_n A_n}{l_n} + \frac{\lambda_p A_p}{l_p} \quad (\text{watts/}^\circ\text{K})$$

and

$$R = \frac{\rho_n l_n}{A_n} + \frac{\rho_p l_p}{A_p} \quad (\text{ohms})$$

$$\text{where, } \rho = A \frac{\Delta V}{I}$$

In addition, we define α to be the *Peltier coefficient*, π_T the heat transfer per unit current for the particular combination of materials that make up the generator.

$$\pi_T = \pi_{T_n} + \pi_{T_p} \quad (\text{watts/amp})$$

and

$$\alpha_1 = \frac{\alpha}{T} = \frac{\alpha_n + \alpha_p}{T} \quad (\text{volts/degree})$$





Thermal Efficiency

Where α_1 is defined as the *Seebeck Coefficient*, the voltage rise per unit of temperature for a particular combination of materials for the device.

The dissipation (the difference between the maximum possible work rate and the actual work rate) for the device is given by

$$D = C \left(\frac{\Delta T}{T} \right)^2 + RI^2$$

The dissipation can also be represented as the product of the entropy generation times the absolute temperature.

The thermal efficiency is defined as the ratio of the electrical power output P_o to the thermal input q_H to the hot junction

$$\eta_t = \frac{P_o}{q_H}$$





Thermal Efficiency

The thermal input to the hot junction is given by

$$q_H = K\Delta T + \alpha_1 T_H I - \frac{1}{2} I^2 R$$

and

$$P_o = I^2 R_o$$

where R_o is the load resistance. The open circuit voltage is $\alpha\Delta T$, so the electric current drawn from the generator is

$$I = \frac{\alpha_1 \Delta T}{R + R_o}$$

The thermal efficiency may be computed from

$$\eta_t = \frac{I^2 R_o}{K\Delta T + \alpha_1 T_H I - \frac{1}{2} I^2 R}$$



Figure of Merit

Good thermoelectric materials should possess large Seebeck coefficients, high electrical conductivity and low thermal conductivity. A high electrical conductivity is necessary to minimize Joule heating, whilst a low thermal conductivity helps to retain heat at the junctions and maintain a large temperature gradient. These three properties were later embodied in the so-called figure-of-merit, Z . Since Z varies with temperature, a useful dimensionless figure-of-merit can be defined as ZT

The figure-of-merit of a thermoelectric material is defined as :

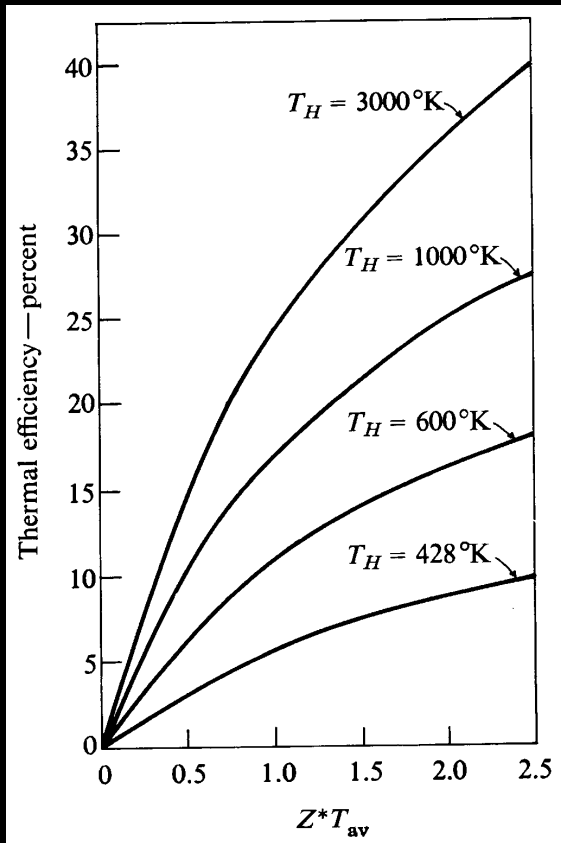
$$Z = \frac{\alpha^2 \sigma}{\lambda}$$

Where α is the Seebeck coefficient of the material (measured in microvolt/K), σ is the electrical conductivity of the material and λ is the total thermal conductivity of the material.





Thermoelectric Generator



Introduce the ratio of load resistance to the internal resistance m' , in the previous equation

$$m' = \frac{R_o}{R}$$

and after some manipulation result in the following

$$\eta_t = \frac{m' \left(\frac{\Delta T}{T_H} \right)}{\frac{(1+m')^2}{Z^* T_H} + (1+m') - \frac{1}{2} \frac{\Delta T}{T_H}}$$

where

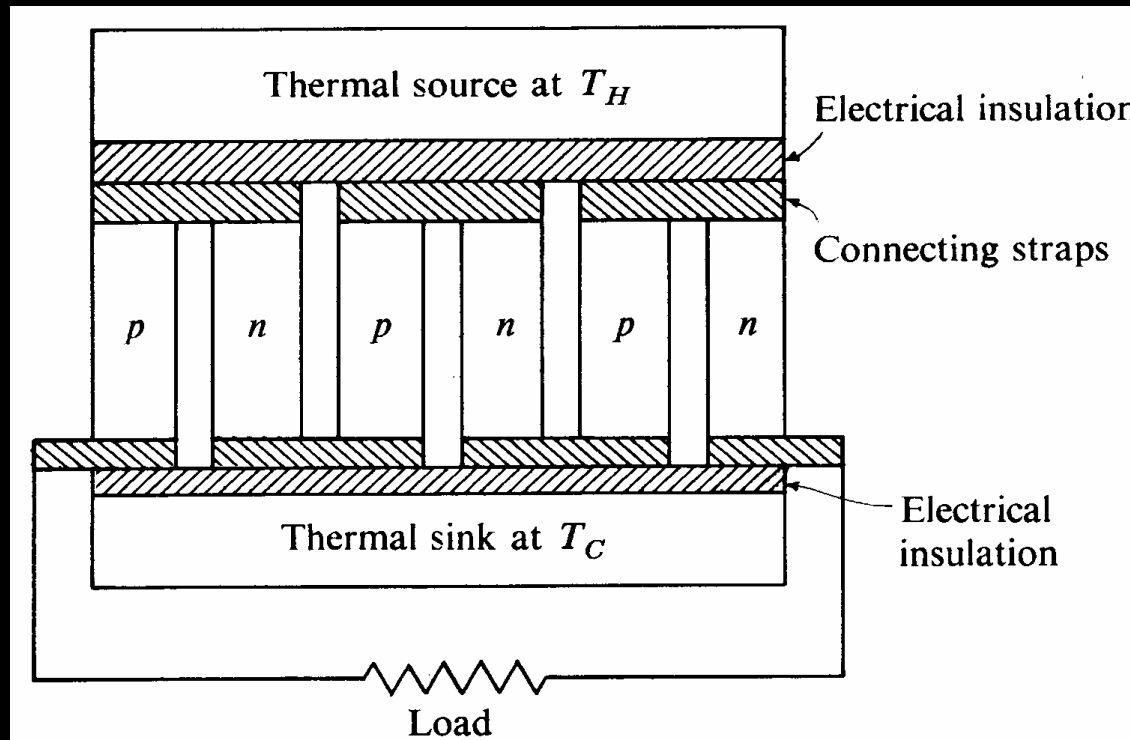
$$Z^* = \frac{(\alpha_{1n} + |\alpha_{1p}|)^2}{\left[(\rho_n \lambda_n)^{\frac{1}{2}} + (\rho_p \lambda_p)^{\frac{1}{2}} \right]^2}$$

$$T_{av} = \frac{T_c + T_H}{2}$$



Thermoelectric Generator

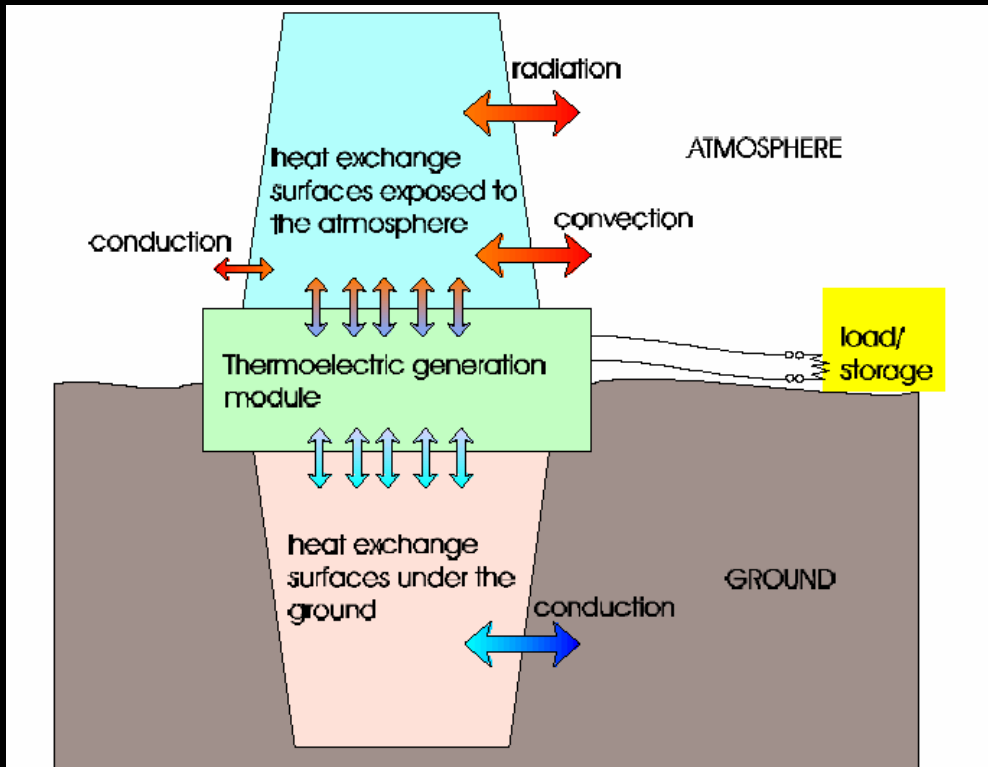
Multistage generators



The output voltage for N couples is simply N times the voltage of a single couple, where as the current is the same as for a single couple. The optimal load resistance is n times the optimal load resistance of a single stage device, whereas the electrical power output and thermal input increase linearly with N . thus the thermal efficiency is independent of the number of couples.



Ground Source Thermoelectric Generator

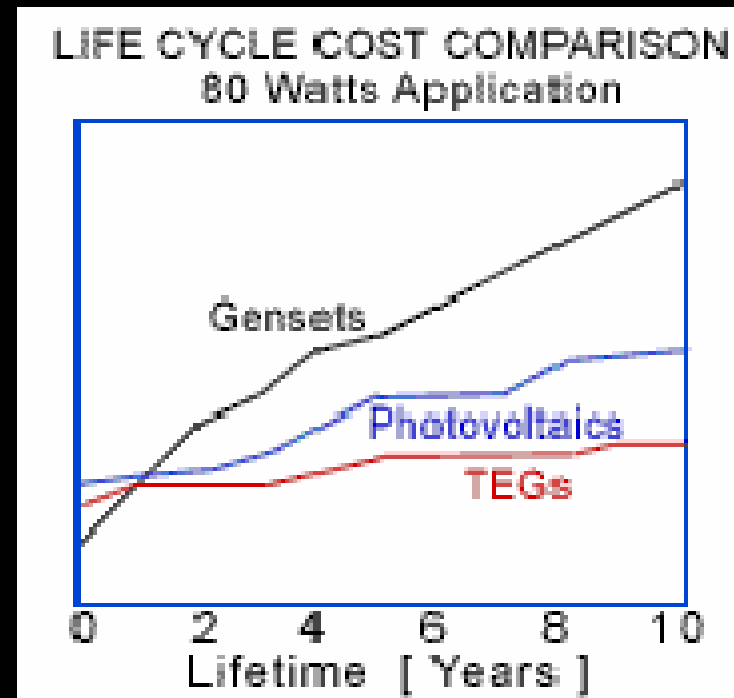
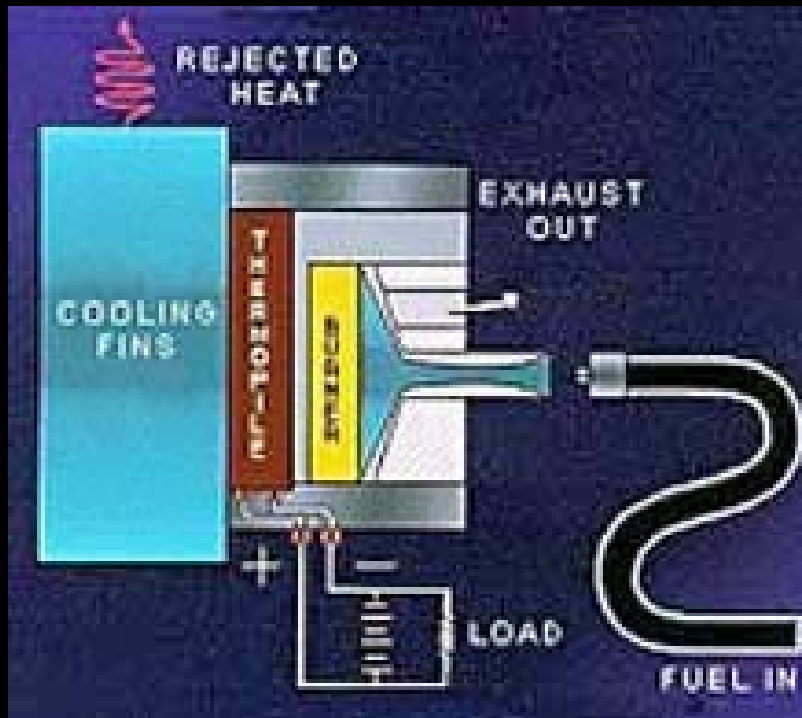


$$\Delta T \sim 20^{\circ} - 30^{\circ}\text{F}$$

$$\eta_{\text{TEG}} = 0.15 \eta_{\text{Carnot}}$$



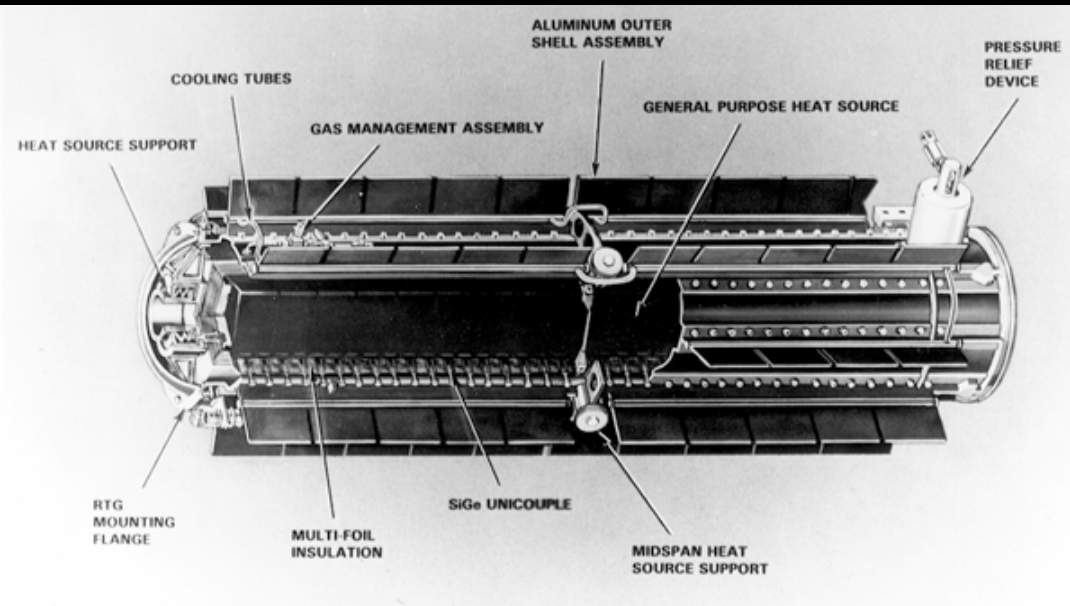
Thermoelectric Generator



Thermopile: A thermopile is made of thermocouple junction pairs connected electrically in series.



Radioisotope Thermoelectric Generators



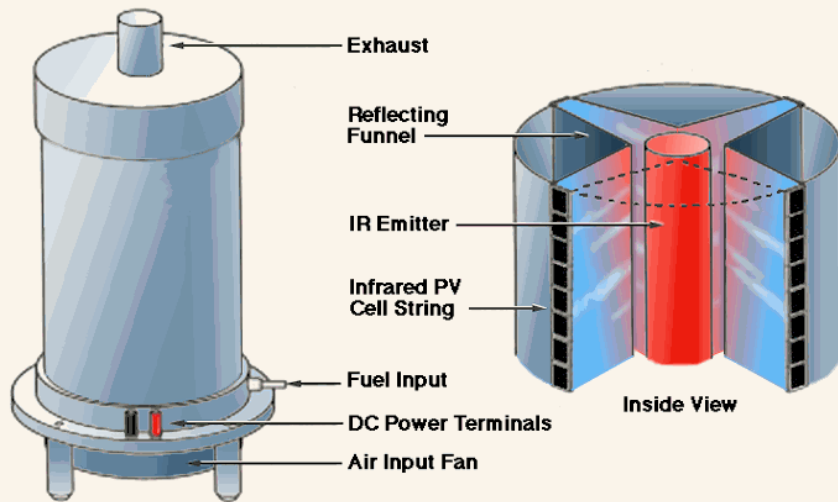
An RTG basically consists of two parts: a source of heat and a system for converting the heat to electricity. The heat source contains a radioisotope, such as plutonium-238, that becomes physically hot from its own radioactivity decay. This heat is converted to electricity by a thermoelectric converter which uses the Seebeck effect. An electromotive force, or voltage, is produced from the diffusion of electrons across the junction of two different materials (e.g., metals or semiconductors) that have been joined together to form a circuit when the junctions are at different temperatures.

Doping semiconductor materials such as silicon-germanium with small amounts of impurities such as boron or phosphorus produces an excess or deficiency of electrons, and therefore makes the semiconductor a more efficient power converter than metals. The joining of these thermoelectric materials with hot radioisotopes produces a reliable source of power with no moving parts. The temperature difference between the hot and cold junctions is about 700 K (800 deg F).



Thermophotovoltaic Generator

Thermophotovoltaic (TPV) Generator



To generate power, fuel is continuously burned in a ceramic tube which glows red-hot. The photovoltaic cells which surround the tube receive the infrared (IR) photons from this emitter and convert them to electric power. In effect, "solar" cells are used with a small manmade "sun" created by burning methane. However, because this "sun" is only 1" away from the cell, IR power intensities at the cell are one thousand times higher than the sunlight on the roof of a car. Unlike an internal combustion engine, fuel is burned continuously without periodic explosions. Combustion is complete and clean.

Thermoelectric Generator

Homework Problem:

Design a thermoelectric generator to operate between 30°C and 350°C . Consider both a maximum efficiency and maximum power design. In addition to finding the power output and thermal efficiency of the device, find its voltage, current and the required heat input.

Go to the reference books to get the necessary material.





Direct Energy Conversion: Thermionic Conversion

References:

Section 4.1.3 in the text Book

Direct Energy Conversion by Stanley W. Angrist, Allyn and Beacon, 1982.

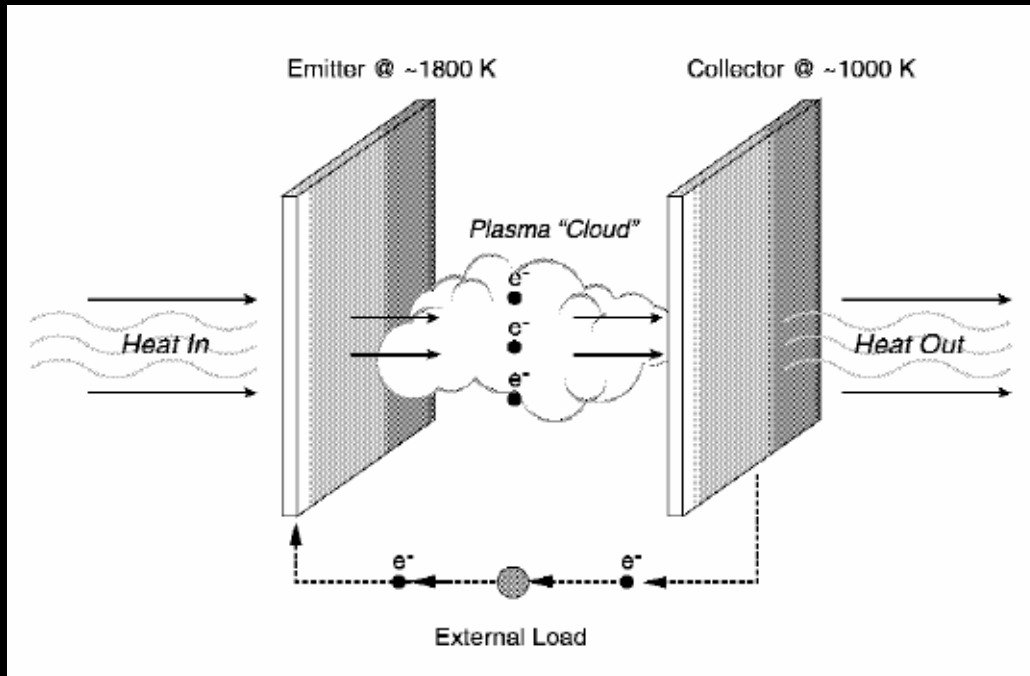
Direct Energy Conversion by Reiner Decher, Oxford University press, 1997.





Thermionic Energy Conversion

A thermionic converter is a static device that converts heat into electricity by releasing electrons from a hot emitter surface ($\sim 1800\text{K}$) across a small inter electrode ($< 500\ \mu\text{m}$) to a cooler collector surface. Since it is a form of heat engine, its efficiency is determined by Carnot efficiency.



Process that converts heat directly into electrical power. Two metal electrodes separated by a narrow gap. The binding energies of the emitter and collector surfaces that act on electrons are known as the work functions of the electrode surfaces. The electrons absorbed by the collector produce a usable electrical current as they return to the emitter through an external circuit. Electrical power is produced by virtue of the potential difference between the emitter and collector.



Operating Regime

Emitter Temperature: 1600 -2000 K

Collector Temperature: 800-1100 K

Electrode efficiency: 20%

Power Density: 1-10 W/cm²

Space charge effect that limits the flow of electrons

Thermal energy losses to the environment

Problem to overcome: Find a material with high enough emission

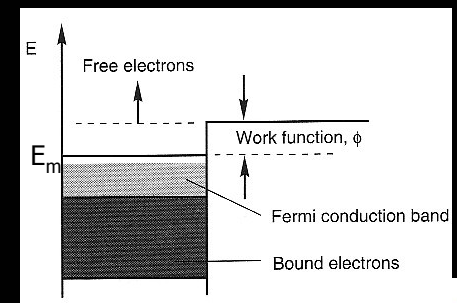


Work Function

An electrode surface can be thought of as atoms arranged in some orderly geometrical fashion in a lattice structure. The electrons that move in the outermost orbits of the atom are held to their respective atom by a very weak force. Hence they may leave their own orbit to enter another orbit around some other nucleus. Thus the electrons in the outermost orbits so not belong to specific atoms and are generally given the name of free electrons. For example copper has about one free electron to every atom while a semiconductor has typically one free electron to about every one million atoms.

The mobile electrons in the electrode lies in the conduction band where the energy is lower than the free or unbound state. At absolute zero, the kinetic energy of the free electrons would occupy quantum states (energy levels) from zero up to a maximum value called the Fermi level. These energy levels are separated from one another by very small but discrete amounts of energy. Each quantum level contains a limited number of free electrons. At temperatures other than absolute zero, some electrons start to have energies greater than the Fermi level.

Free electrons are retained in the metal by the forces of attraction between two unlike charges. The energy required to overcome this force is called the surface work or *work function*, ϕ , expressed in electron volts. We note that the work required to lift the electron to some energy level is $\phi + E_f$, where E_f is the Fermi level.



Work Function

The **work function** of a material is defined as the amount of energy required for an electron with a certain energy to overcome and escape the binding attractive charge, or surface potential, of a material's surface

The electrodes in a thermionic energy converter have different Fermi levels; the *emitter* has *low Fermi level* where as the *collector* has a relatively *high Fermi level*. Thus the emitter work function is greater than the collector work function.

When sufficient heat is supplied from a high temperature source to the emitter, some of the high energy free electrons at the Fermi level will obtain enough energy to escape from the emitter surface, i.e they gain energy equals to the emitter work function with additional kinetic energy. In the ideal case, when the electrons strike the collector, they will give up their kinetic energy plus energy equal to the collector work function.

Once the electron has reached the Fermi energy level of the collector, it is still at higher energy than the electron at the Fermi energy level of the emitter. Its higher potential may now be utilized to cause it pass through some external load.

Efficient operation of a thermionic converter requires an emitter surface with a relatively low work function of 3 electron volts or less and even lower collector **work function** of 1.5 electron volts or less. The converter must also have the right charge transport conditions in the inter electrode gap, the area between the emitter and collector surfaces, to allow electrons to flow from the emitter to the collector.





Richardson-Dushman Equation

In order for an electron to escape the surface it must have sufficient energy to move it from the Fermi surface to a point outside the metal. That energy, per unit charge, is called the work function ϕ . We designate the work function of the emitter (cathode) as ϕ_E and that for the collector (anode) as ϕ_C .

$$V = \phi_E - \phi_C$$

For an ideal diode the Richardson-Dushman equation states as

$$J \left(\frac{\text{amps}}{\text{cm}^2} \right) = A T_E^2 e^{-\left(\frac{\phi_E}{k T_E} \right)}$$

Where A depends on material and ranges from 3-100 amps/(cm² K²).

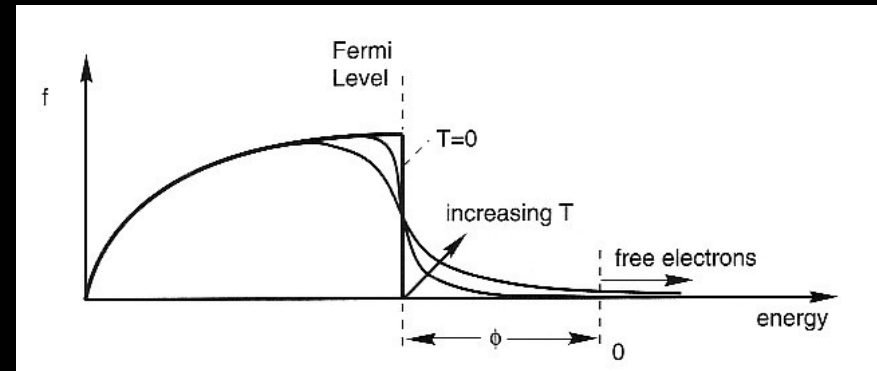




Energy Distribution Function

The energy distribution function gives the number of electrons per unit volume $f(E)$ with energy in a range between E and $E+dE$. The number density of electrons, n_c is then given by

$$n_c = \int_0^{\infty} f(E) dE$$



The resulting current density is given by Richardson-Dushman equation

$$j = AT^2 e^{-\left(\frac{\phi}{kT}\right)}$$

Material Properties

Material	Work function	A constant
	ϕ (eV)	(10^6 A/m ² K ²)
Cs	1.89	0.50
C	3.96	0.46
Mo	4.2	0.55
Ni	4.61	0.30
Pt	5.32	0.32
Pt	5.40	1.70
Ta	4.19	0.55
W	4.52	0.60
W	4.54	0.46
W+Ba	1.6	0.015
W+Th	2.7	0.04
BaO	1.5	0.001
SrO	2.2	1.00
ZrC	3.94	1.20
Theoretical value	—	1.23

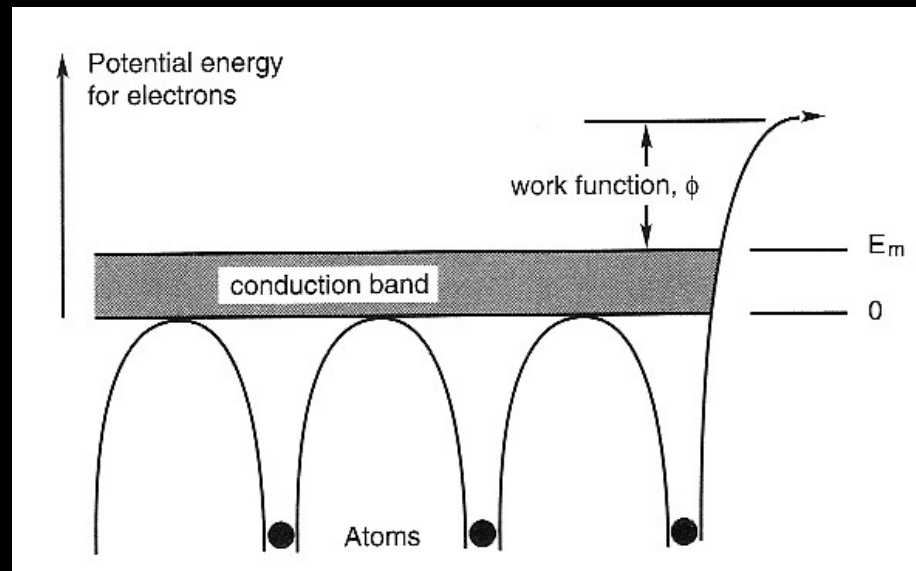
Richardson's
constant

$$A = \frac{emk_B^2}{2\pi^2\hbar^3}$$

Emission Heat Transport

As the electrons leave the surface, they carry with the energy supplied by the metal. The energy flux is calculated from the particle flux (j/e ; e is the electron charge) times the energy per particle. Then the heat transferred per unit mass heat flux is given by

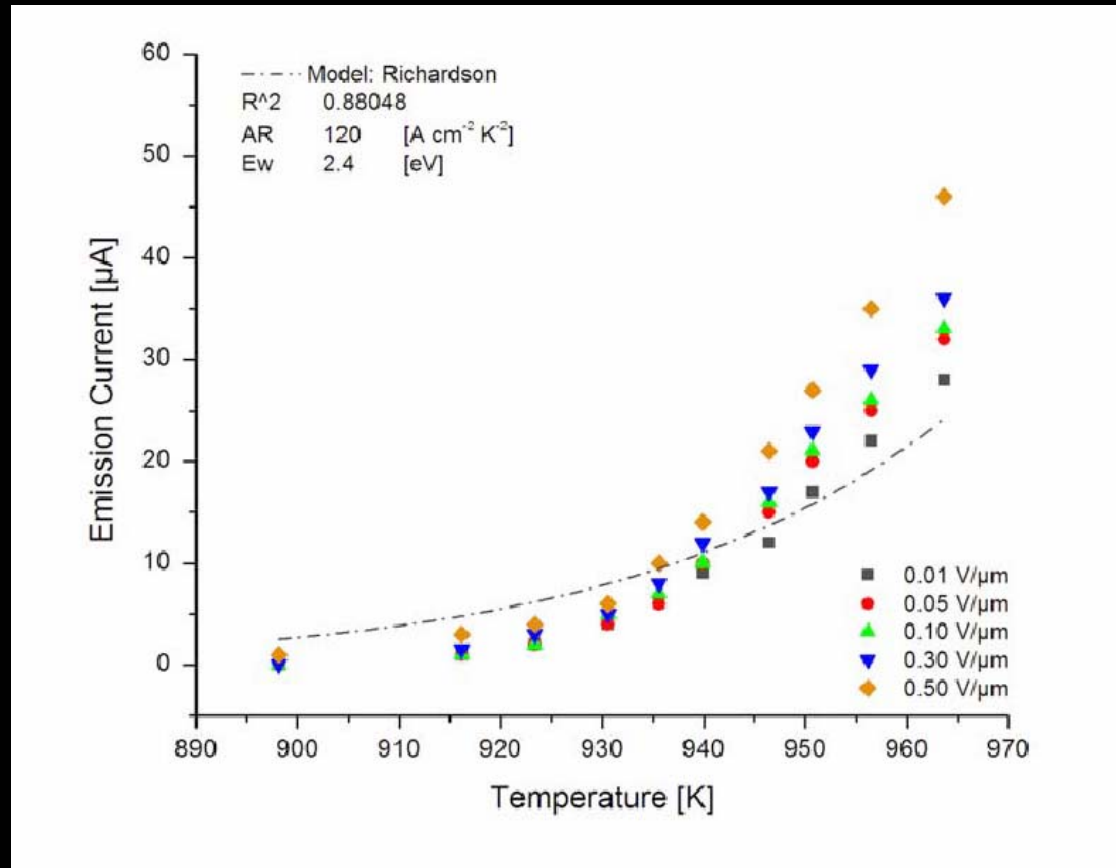
$$q = \frac{j}{e} [2kT + E_m + e\phi]$$





Emission Characterization

Thermionic electron emission from a nitrogen doped diamond film as a function of temperature and applied electric field. The dotted curve shows a fit to the Richardson-Dushman equation.





Open Circuit Voltage

The current from the two electrodes are given by

$$j_c = AT_c^2 e^{-\left(\frac{e\phi_c}{kT_c}\right)}$$

$$j_e = AT_e^2 e^{-\left(\frac{e\phi_e}{kT_e}\right)}$$

The net current in a cell where these surfaces face one another is

$$j = J_c - j_a$$

At open circuit, net current j must be zero. The cathode potential at open circuit is therefore given by (for $V_c = V_{oc}$, V_c is the potential cathode-emitted electrons must overcome to escape and balance the anode current)

$$j = AT_c^2 e^{-\left(\frac{eV_c}{kT_c}\right)} - AT_e^2 e^{-\left(\frac{e\phi_e}{kT_e}\right)} = 0$$

The open circuit voltage is given by

$$V_{oc} = V_c - \phi_e = \phi_e \left(\frac{T_c}{T_e} - 1 \right) + 2 \frac{kT_c}{e} \ln \left(\frac{T_c}{T_e} \right)$$

The cell output voltage V_o is then equal to

$$V_o = V_c - \phi_e$$





Saturation Current

The maximum possible current density from the cathode at a given temperature is given by

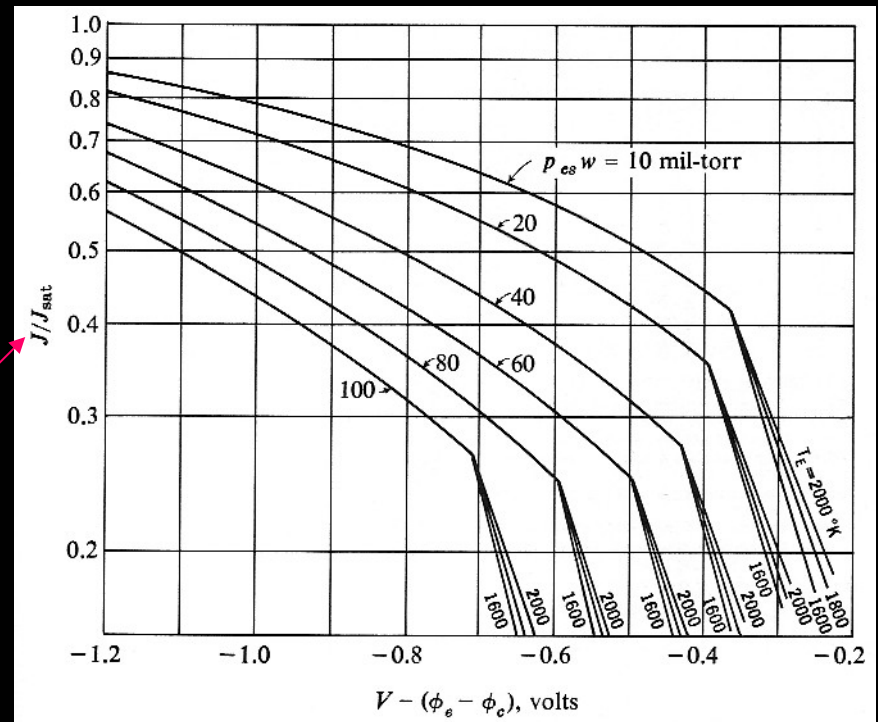
$$j_c = AT_c^2 e^{-\left(\frac{e\phi_c}{kT_c}\right)} \equiv J_{sat}$$

In the absence of any space-charge effects and negligible anode emission current, the net current is approximately equal to the cathode emission current.

p_{es} : interelectrode pressure

w : spacing between electrodes

Actual current density to the saturation current density





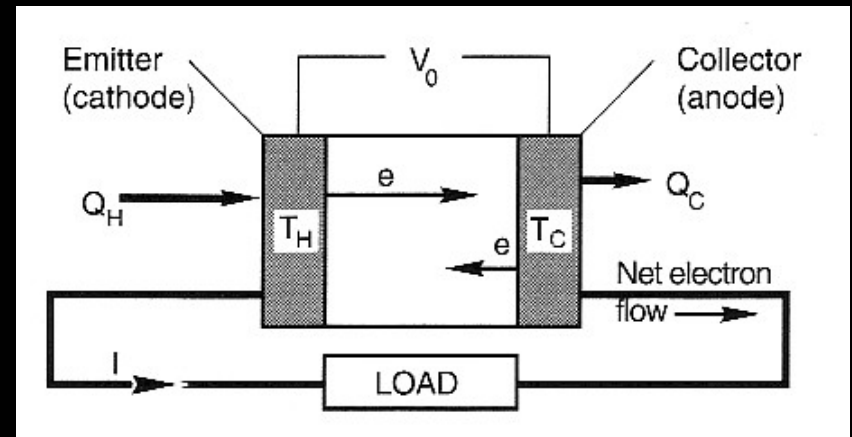
Thermal Efficiency

The thermal efficiency may now be calculated by dividing the output power by the heat supplied to give

$$\eta_t = \frac{V(J_e - J_c)}{q}$$

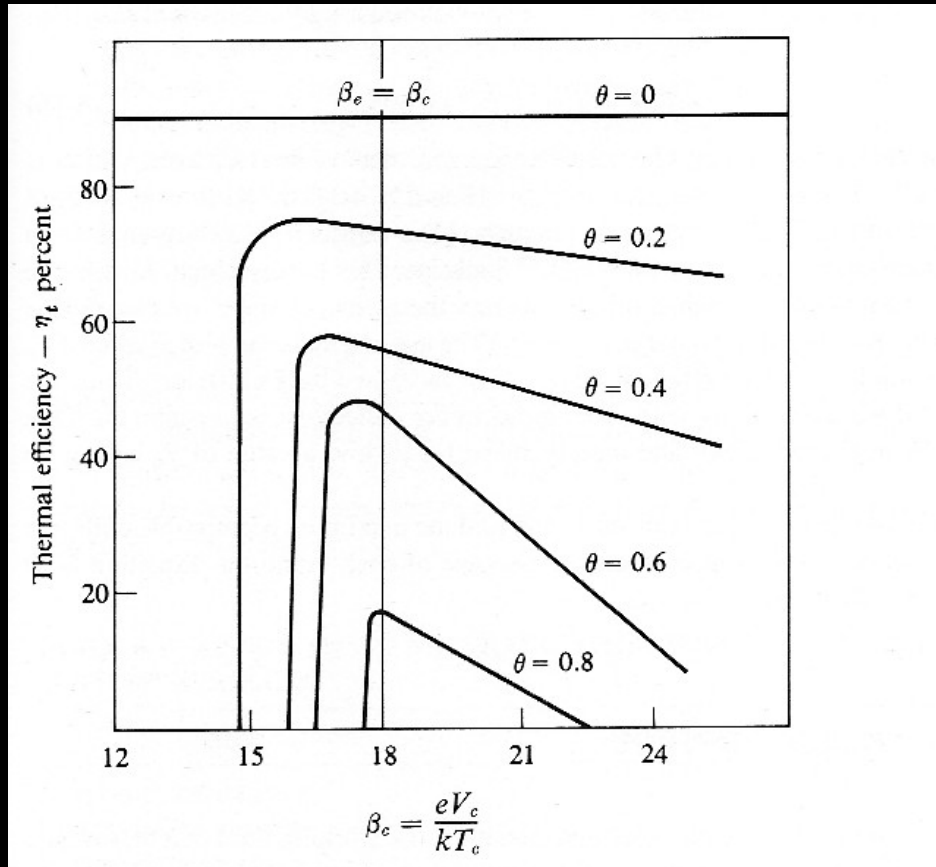
Where V is the output voltage given by

$$V = V_e - V_c = \frac{1}{e}(E_{f_c} - E_{f_e})$$





Thermal Efficiency

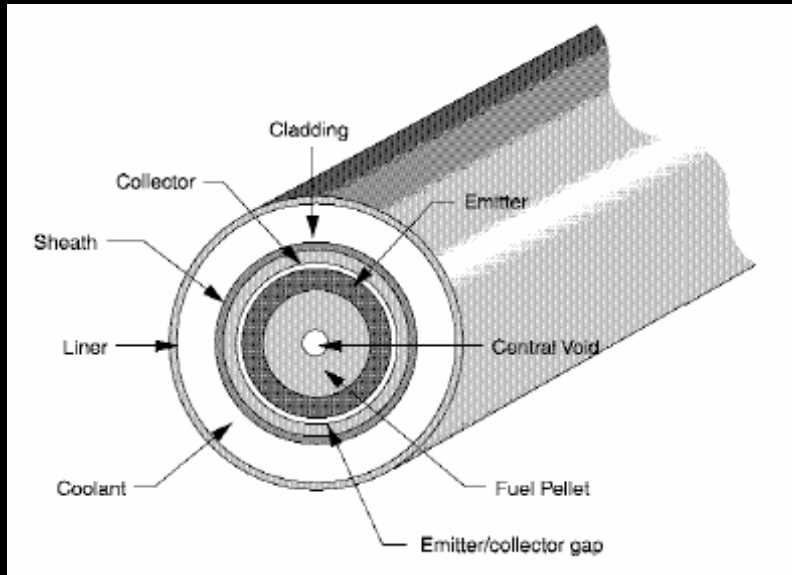


$$\theta = \frac{T_c}{T_e}$$

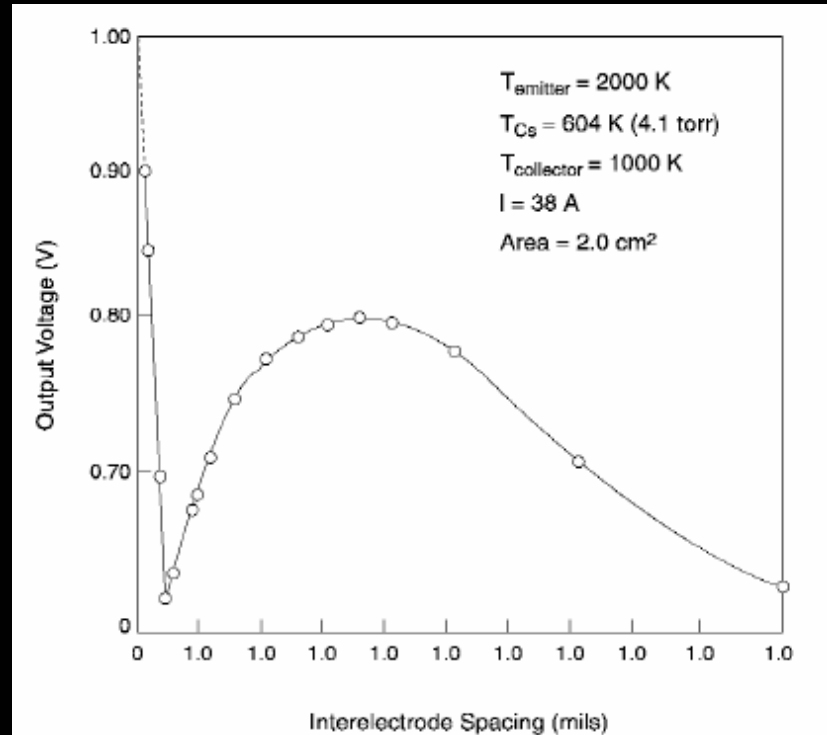
$$\beta = \frac{eV}{kT}$$



Thermionic Energy Conversion



A cross sectional view of a thermionic fuel element (TFE). The nuclear fuel is located in the middle of TFE and heat radiates outward.



Solar thermionic output voltage based on emitter-collector spacing. JPL-1967