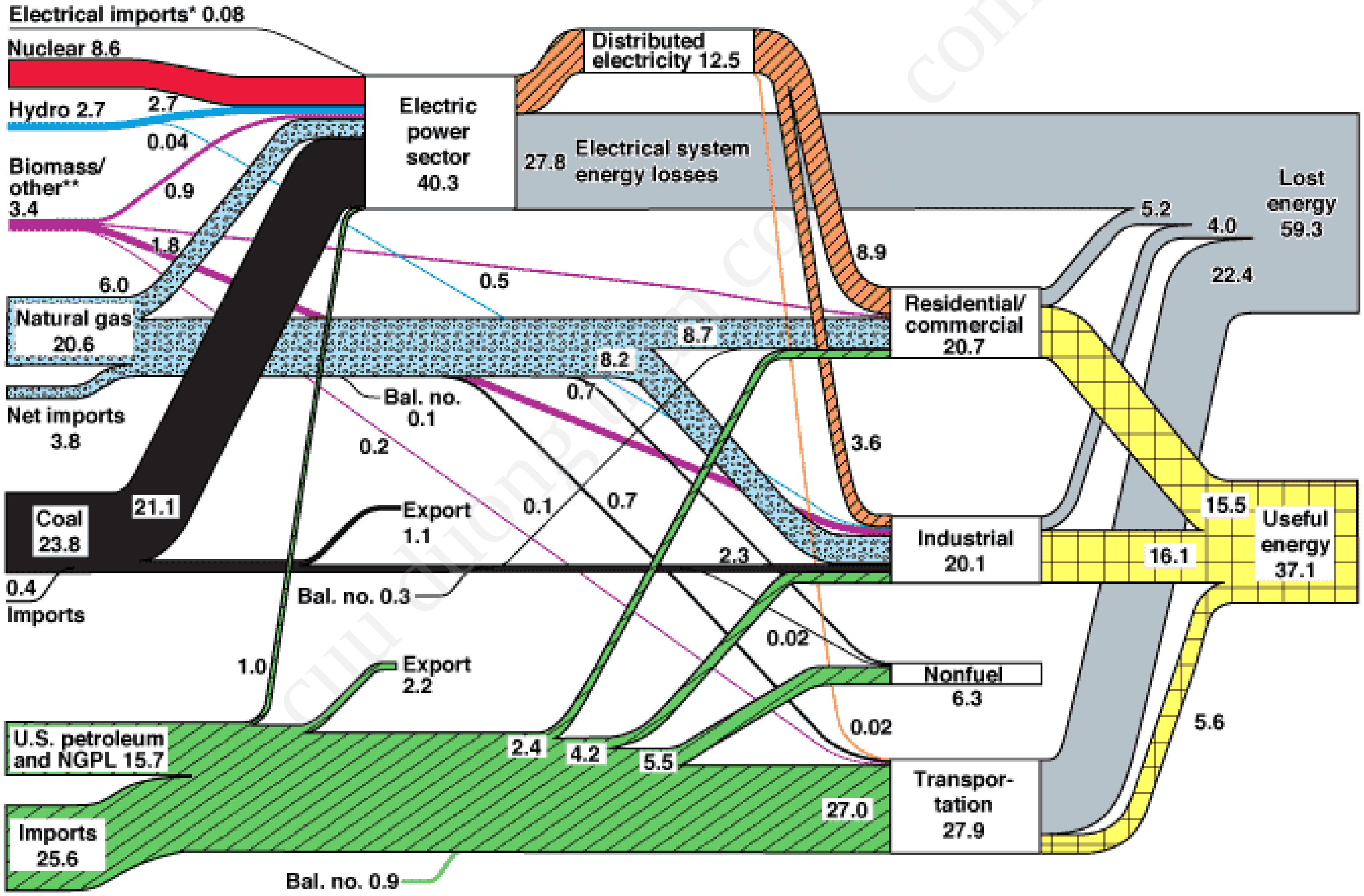
Sustainability

http://thermoelectrics.matsci.northwestern.edu/index.html

Heat in Energy Use

Heat plays a major role in global energy consumption. Heat itself may the be final use of energy (e.g. residental heating). Heat is also a waste product in the transformation of energy, for example in electric power generation or transportation.

U.S. Energy Flow Trends – 2002
Net Primary Resource Consumption ~103 Exajoules

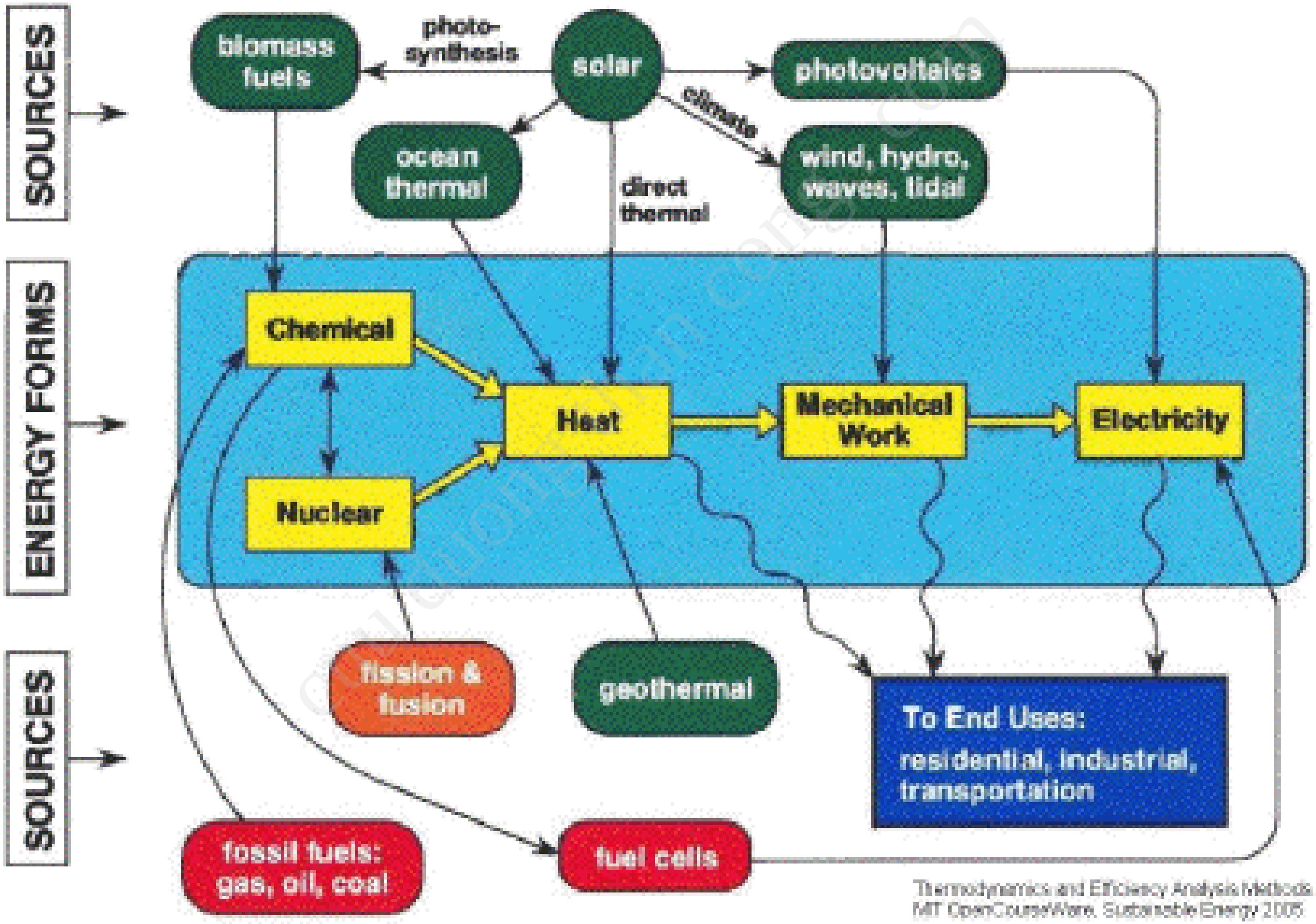


Source: Production and end-use data from Energy Information Administration, *Annual Energy Review 2002*.
*Net fossil-fuel electrical imports.
**Biomass/other includes wood, waste, alcohol, geothermal, solar, and wind.

June 2004
Lawrence Livermore
National Laboratory
http://eed.llnl.gov/flow

More than 60% of the energy produced in the U.S. is never utilized, most of it in the form of waste heat. Thermoelectric materials allow the direct conversion between thermal and electrical energy, and can therefore recover some of this lost energy. From the above chart, a major contributor to waste heat is in the transportation sector where only 20% of the fuel's energy ends up as useful energy.

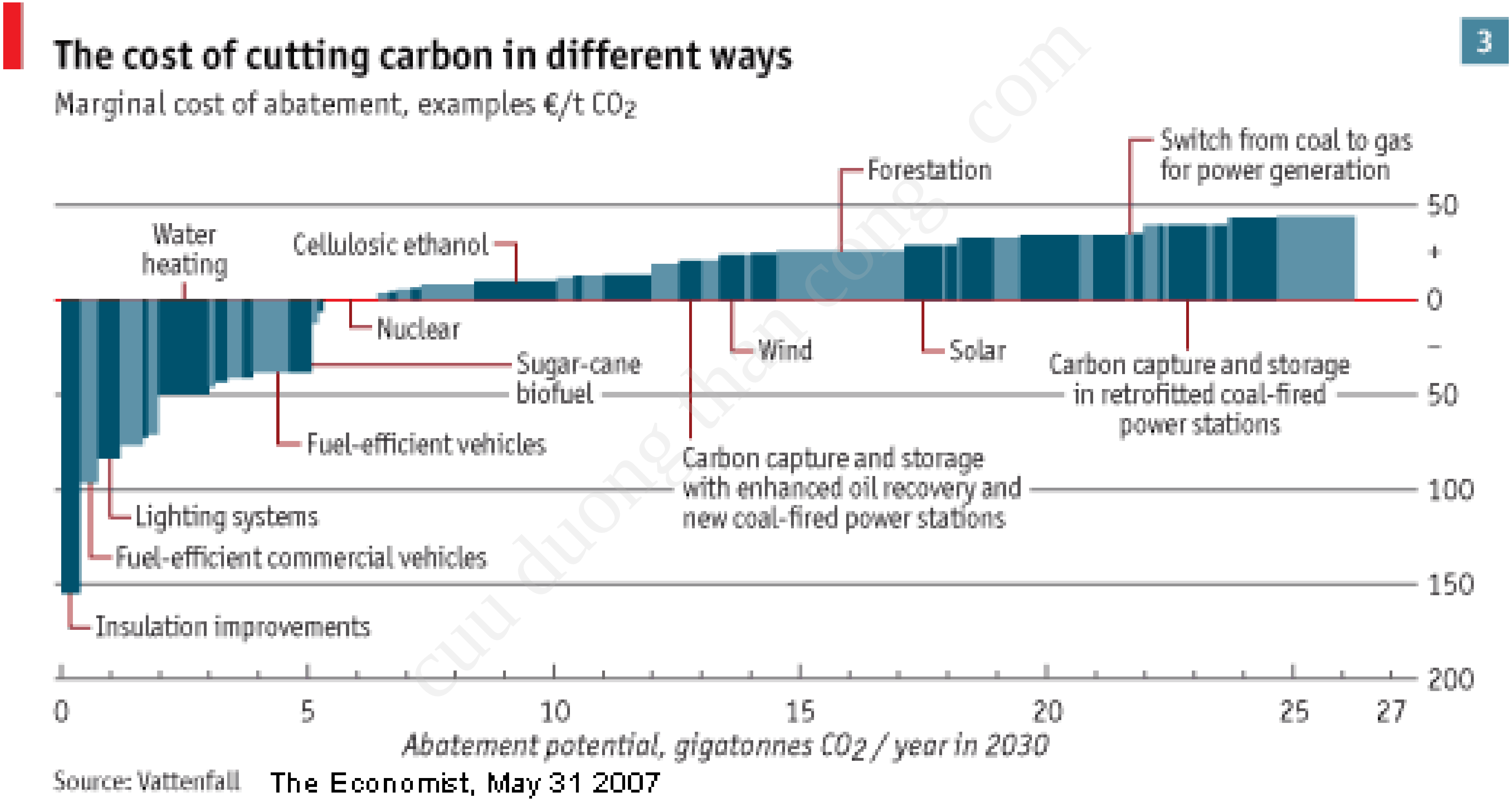
Thermal energy (heat) is a common link between many forms of energy. This means that improving the net heat to electricity efficiency, or bypassing the thermal energy step altogether (as in fuel cells), will improve energy utilization.



Thermodynamics and Efficiency Analysis Methods - J. Tester
MIT OpenCourseWare. Sustainable Energy 2005

Improving thermal efficiency should be a major activity to reduce carbon dioxide emissions because its implementation will, in many instances, actually save money (figure below).

Insulation improvements and efficient water heating will reduce carbon emissions and, over the long term, save more in energy costs than the cost of the improvements even without a carbon tax.

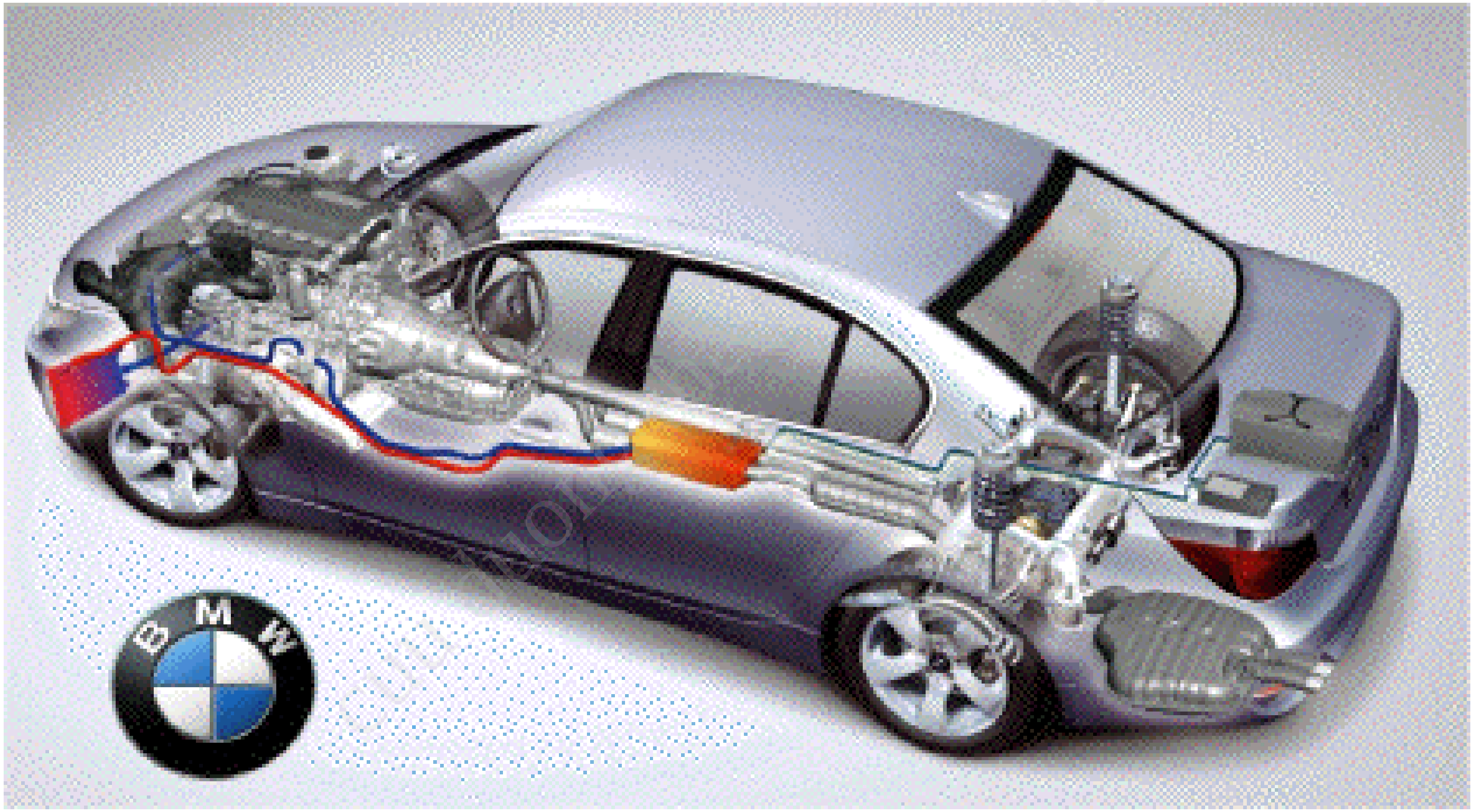


The Economist, May 31 2007

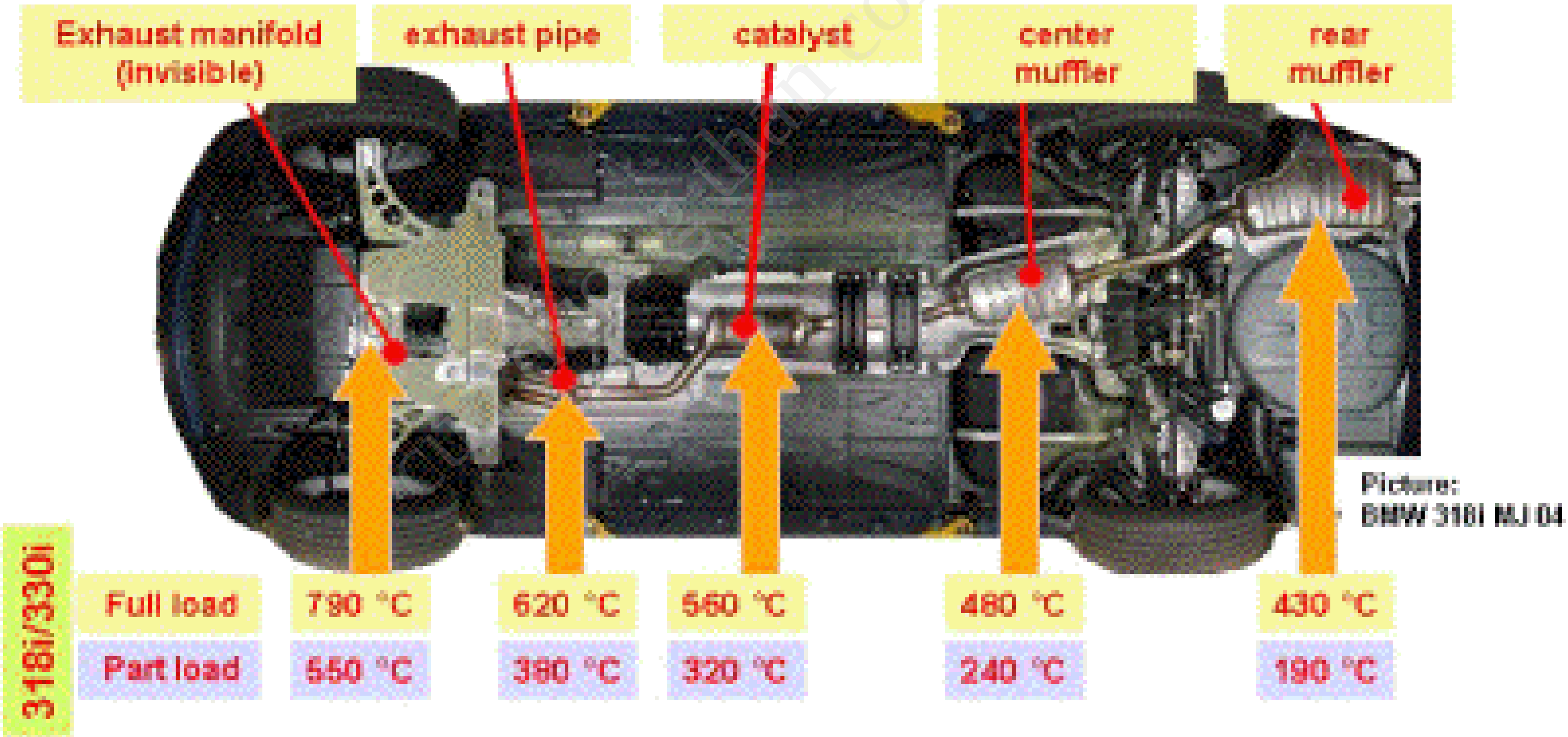
Waste Heat Recovery

Automobiles are an example of high energy usage with low efficiency. Roughly 75% of the energy produced during combustion is lost in the exhaust or engine coolant in the form of heat.

By utilizing a portion of the lost thermal energy to charge the battery instead of using an alternator (adds drag on the engine) the overall fuel economy can be increased by about 10%.


BMW

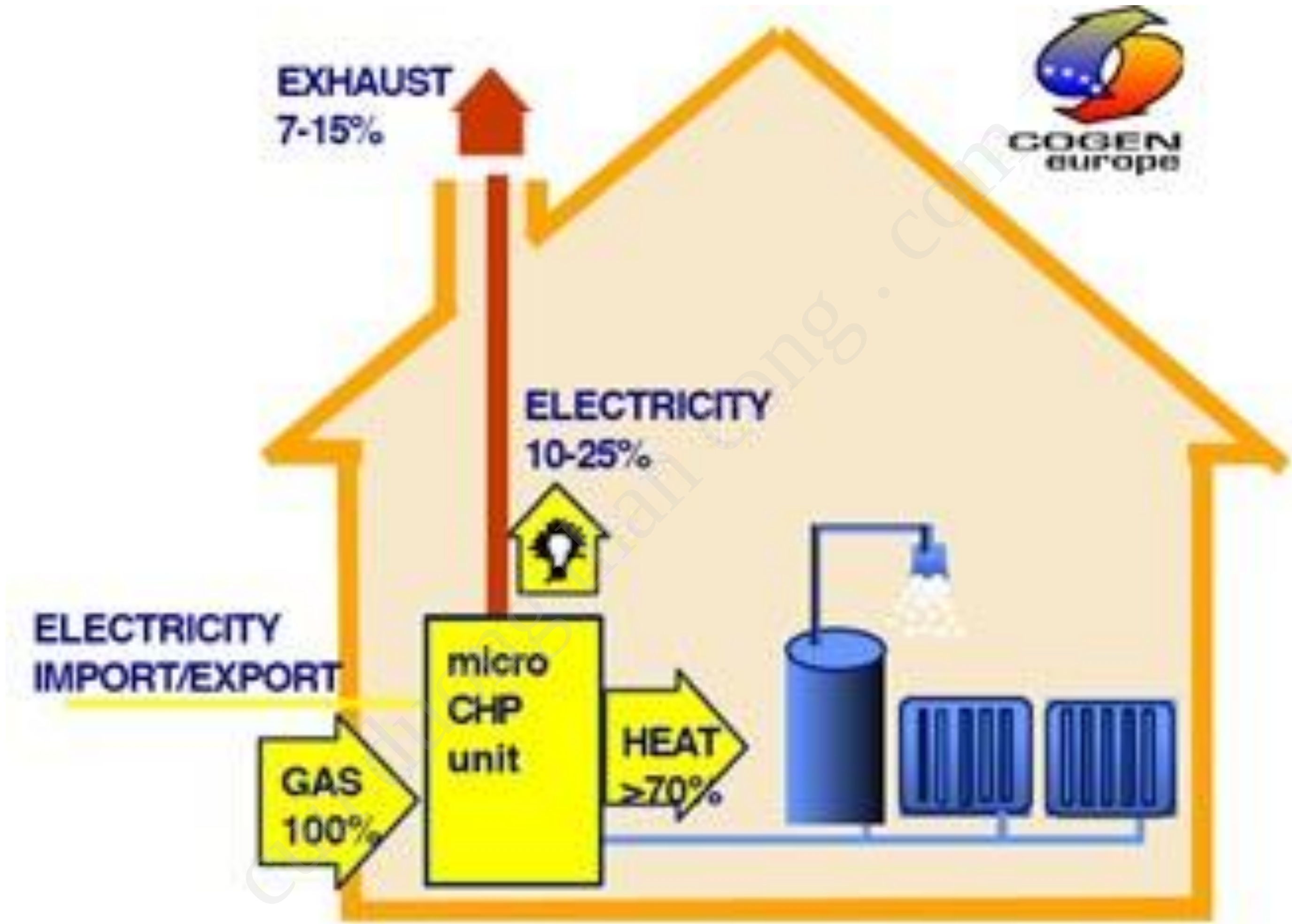
Depending on the engine load the exhaust temperatures after the catalytic converter reach about 300-500 degrees Centigrade. Thermoelectric generators are ideal for such applications as they are small, with no moving parts, and relatively efficient at these temperatures.



Cogeneration of Heat and Electricity

Because most electricity is produced by a heat engine, which is limited by Carnot efficiency, much of the energy is lost in the heat rejected. A typical steam power plant is only 40% efficient. The remaining heat is wasted, unless this rejected heat can be used for heating. The use of this heat then can add to the energy utility.

Conversely, any time a fuel is burned to make low temperature heat (such as in a home) the ability to produce useful work or electricty from that heat is wasted. A small cogeneration plant in the home would produce electricty whenever the heat is needed. The added fuel consumed to produce the electricity has essentially the same energy content as the electricity produced. Thus in terms of energy untilization the efficiency of electricity generation approaches 90% compared to the 40% in a typical power plant.



Thermoeletric systems are ideal for small (e.g. single family home) cogeneration because they could be small and silent. Even with their lower thermal to electric efficiency compared to dynamic heat engines, the electricity would be produced with high efficiency (electric power/extra fuel consumed) because the heat rejected will not be wasted.

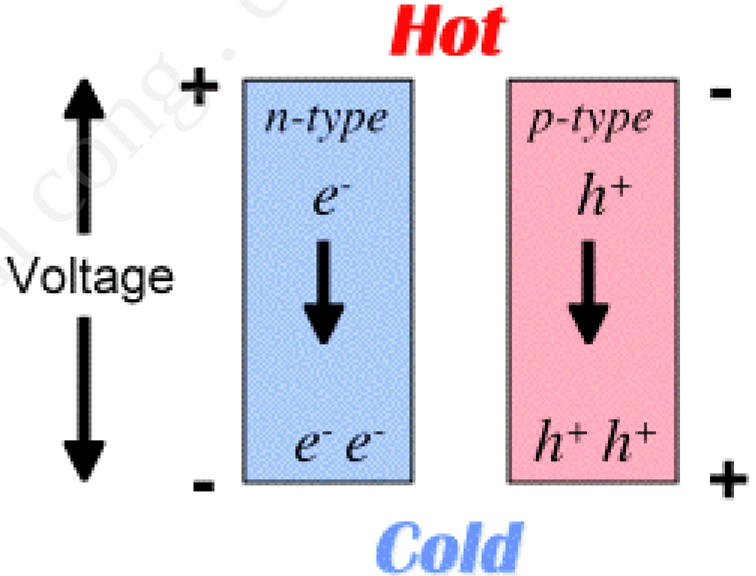
The Science of Thermoelectric Materials

$$V = \alpha \Delta T$$

V = Voltage

α = Seebeck coefficient

ΔT = Temperature difference



The Seebeck Effect

In a thermoelectric material there are free electrons or holes which carry both charge and heat.

The electrons and holes in a thermoelectric semiconductor behave like a gas of charged particles.

If a normal (uncharged) gas is placed in a box within a temperature gradient, where one side is cold and the other is hot, the gas molecules at the hot end will move faster than those at the cold end.

The faster hot molecules will diffuse further than the cold molecules and so there will be a net build up of molecules (higher density) at the cold end. The density gradient will drive the molecules to diffuse back to the hot end.

The Seebeck Effect

In the steady state, the effect of the density gradient will exactly counteract the effect of the temperature gradient so there is no net flow of molecules.

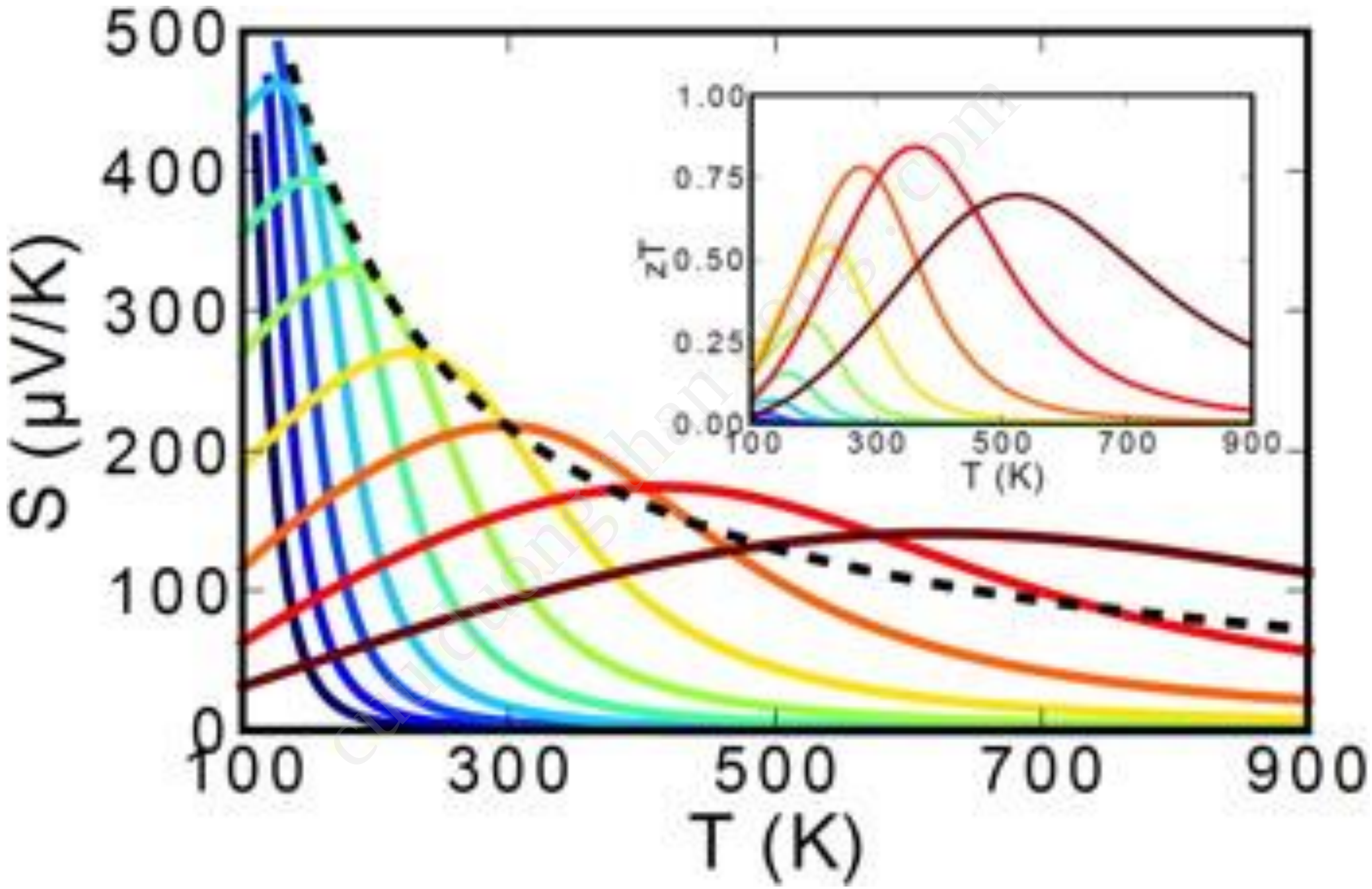
If the molecules are charged, the buildup of charge at the cold end will also produce a repulsive electrostatic force (and therefore electric potential) to push the charges back to the hot end. The electric potential (Voltage) produced by a temperature difference is known as the Seebeck effect and the proportionality constant is called the Seebeck coefficient.

If the free charges are positive (the material is p-type), positive charge will build up on the cold which will have a positive potential. Similarly, negative free charges (n-type material) will produce a negative potential at the cold end.

Thermopower Peak and Band Gap

In a semiconductor at high enough temperature electrons will have high enough energy to excite across the band gap. When that happens there will be both n-type carriers in the conduction band and p-type carriers in the valence band such that the resultant *thermopower* (absolute value of Seebeck coefficient) will be *compensated* (reduced) because the two contributions subtract.

In a heavily doped semiconductor, where the dopants produce many *majority carriers* (could be either n-type or p-type) the thermopower will be reduced at high temperature due to the excitation of *minority carriers* of opposite sign. Although there are fewer minority carriers than majority carriers, they have a larger thermopower. This leads to a peak in the thermopower as a function of temperature.



The Figure above shows how the Seebeck coefficient changes when the doping changes from lightly doped (blue) to heavily doped (red).

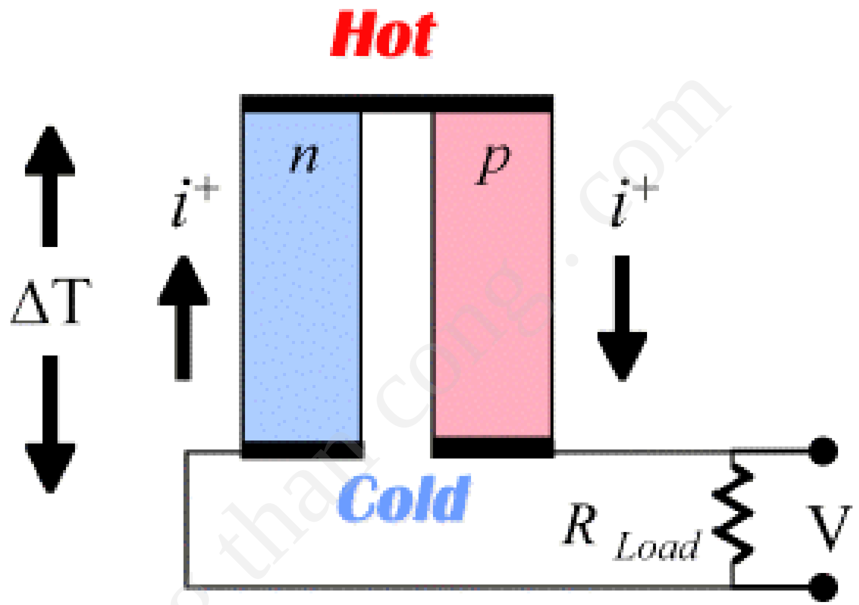
The Temperature at which the thermopower peaks, T_{max}, and the thermopower (absolute value of Seebeck coefficient) of the peak, $|S|_{max}$, can be used to estimate the semiconducting band gap, E_g

$$E_g = 2e|S|_{max}T_{max}$$

Thermoelectric Power Generation

If the hot ends of the n-type and p-type material are electrically connected, and a load connected across the cold ends, the voltage produced by the Seebeck effect will cause current to flow through the load, generating electrical power. The electrical power produced is the product of the voltage and electrical current across the load. The temperature difference provides the voltage but it is the heat flow which enables the current.

A thermoelectric generator behaves much like an ideal voltage soure with an internal resistance due largely to the resistance of the thermoelectric materials themselves. The voltage at the load is reduced from the open circuit voltage by the Ohm's law ($V = IR$) voltage drop due to this internal resistance. Maximum efficiency is reached when the load and internal resistances are nearly equal because this is close to the maximum power achieved from load matching.



$V = \alpha \Delta T - IR_{TE}$

V = Voltage across Load

I = Electrical current

R = Resistance of generator

α = Seebeck coefficient

ΔT = Temperature difference

$P = IV$

$P = \eta Q$

Q = Heat input (Watt)

η = Efficiency

V = Voltage across Load

I = Electrical current

The resistance of the thermoelectric elements depend on the electrical resistivity as well as the length and cross sectional area.

$$R_i = \rho_i \frac{l}{A_i}$$

R_i = Resistance of element i

ρ_i = Resistivity

l = Length of elements

A_i = Cross - sectional area

$$K_i = \kappa_i \frac{A_i}{l}$$

K_i = Thermal Conductance of element i

κ_i = Thermal conductivity

l = Length of elements

A_i = Cross - sectional area

Just as the power in a resistor is V^2/R the power produced in a thermoelectric generator depends on the square of the voltage (Seebeck coefficient and temperature difference) divided by the resistivity. Notice also that the power per area can be arbitrarily adjusted with l (length)

$$P \approx \Delta T^2 \frac{\alpha^2}{\rho} \frac{A_{TE}}{l}$$

$$A_{TE} = \text{Area of TE elements}$$

The efficiency of a generator depends not just on the power produced but also how much heat is provided at the hot end. The heat input is needed for the thermoelectric process (Peltier effect) as well as normal thermal conduction (Fourier's law) and is offset by the Joule heating in the device. The Fourier's law thermal conduction of the thermoelectric materials add a thermal path from hot to cold that consumes some heat and reduces the efficiency.

It can be shown that the maximum efficiency of a thermoelectric material depends on two terms. The first is the Carnot efficiency, for all heat engines can not exceed Carnot efficiency. The second is a term that depends on the thermoelectric properties, Seebeck coefficient, electrical resistivity and thermal conductivity. These material properties all appear together and thus form a new material property which we call zT, the Thermoelectric Figure of Merit. For small temperature difference this efficiency is given by:

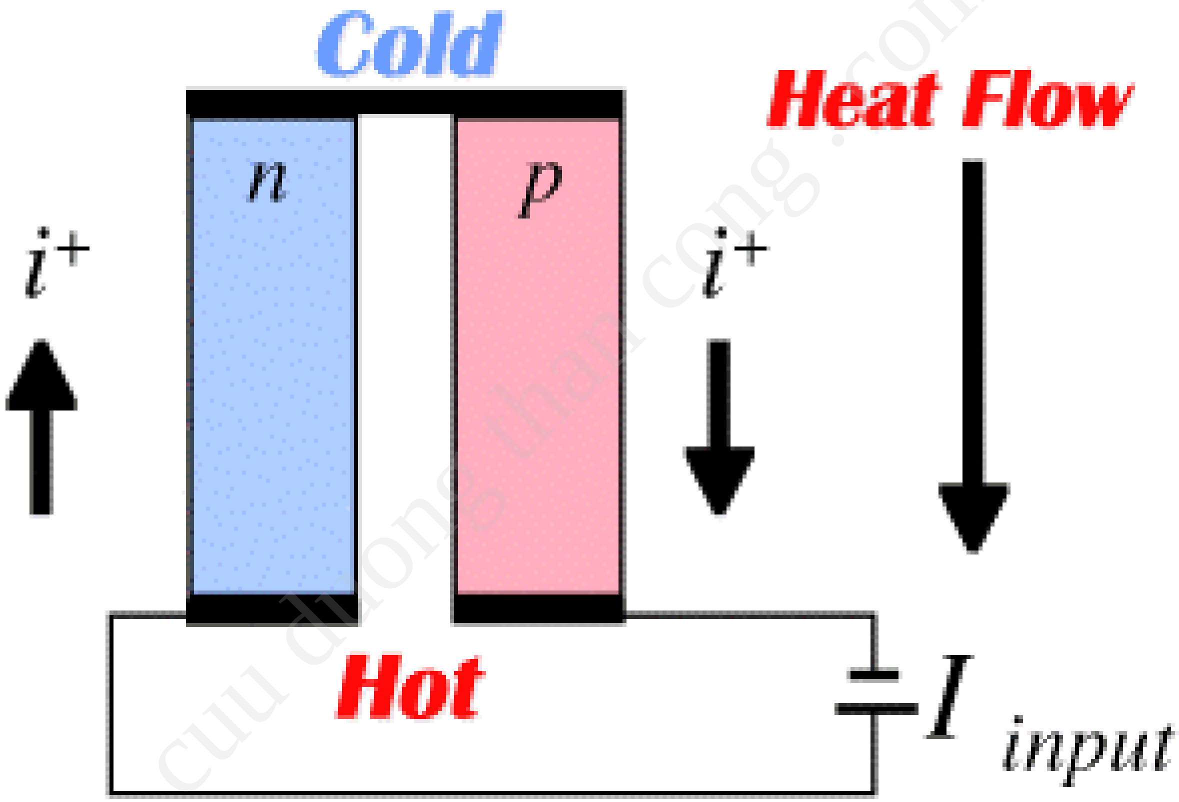
$$zT = \frac{\alpha^2 T}{\rho\kappa} \qquad \eta_{max} = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1+zT}-1}{\sqrt{1+zT}+1}$$

zT = Thermoelectric Figure of Merit

$\frac{\Delta T}{T_h}$ = Carnot efficiency

Peltier Cooling

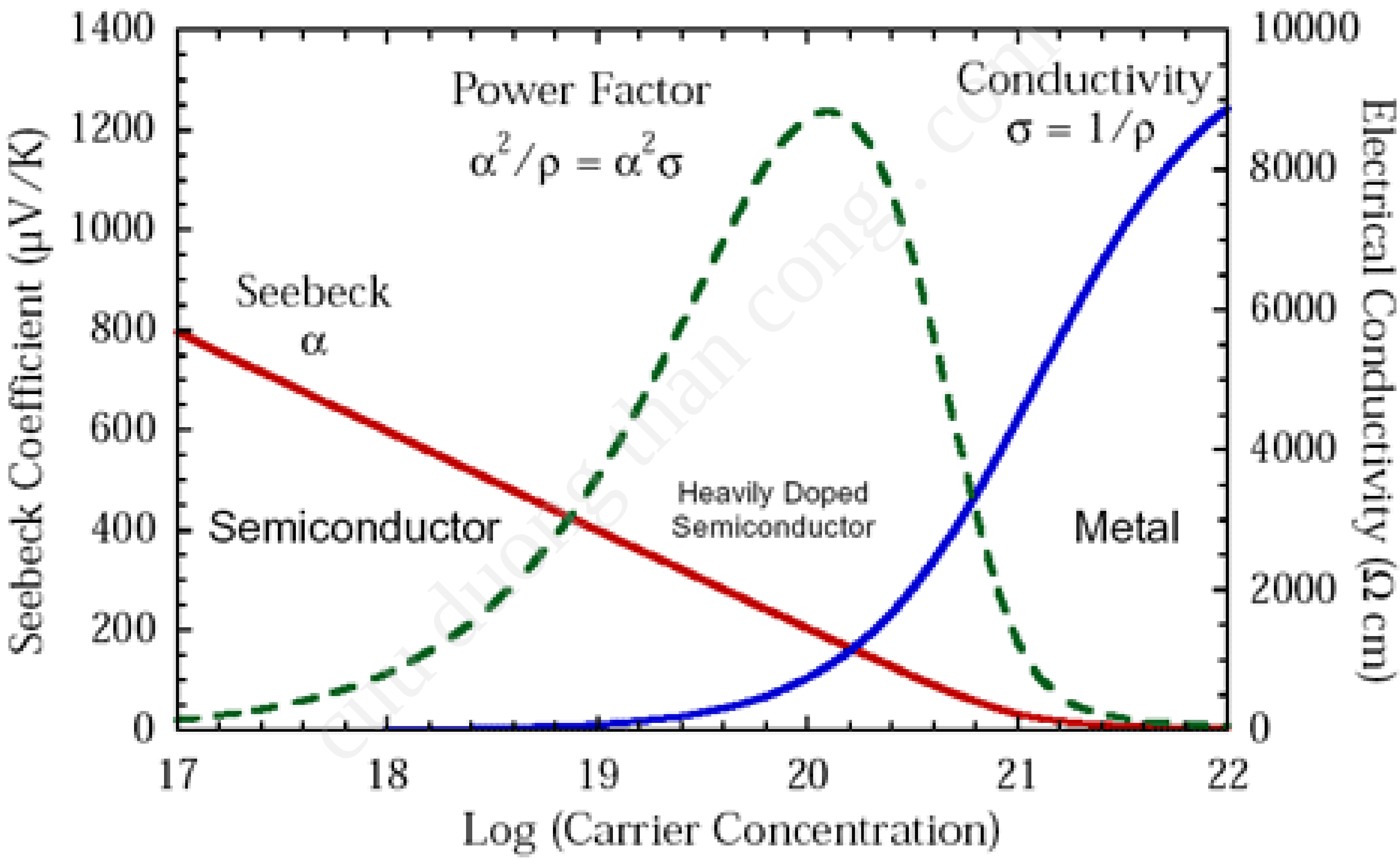
If instead of having the heat flow drive the charge flow, we use an external electric potential to drive the heat carrying charges, then we can force heat to flow from one end to the other. The coefficient of performance and the maximum temperature drop that can be achieved is again related to the efficiency of the thermoelectric materials through the thermoelectric figure of merit zT.


Cold
Heat Flow
n
p
i^+
i^+
Hot
I_{input}

Thermoelectric Materials Development A material with a large thermoelectric power factor and therefore zT, needs to have a large Seebeck coefficient (found in low carrier concentration semiconductors or insulators) and a large electrical conductivity (found in high carrier concentration metals).

The thermoelectric power factor maximizes somewhere between a metal and semiconductors. Good thermoelectric materials are typically heavily doped semiconductors with carrier concentration of 10^{19} to 10^{21} carriers/cm^3.

To ensure that the net Seebeck effect is large, there should only be a single type of carrier. Mixed n-type and p-type conduction will lead to opposing Seebeck effect and low thermopower (defined here as absolute value of Seebeck coefficient).



Power Factor
$\alpha^2/\rho = \alpha^2\sigma$
Conductivity
$\sigma = 1/\rho$
Seebeck
α
Semiconductor
Heavily Doped
Semiconductor
Metal
Seebeck Coefficient (μV/K)
Electrical Conductivity (Ω cm)
Log (Carrier Concentration)
1400
1200
1000
800
600
400
200
0
10000
8000
6000
4000
2000
0
17
18
19
20
21
22

By having a band gap large enough, n-type and p-type carriers can be separated, and doping will produce only a single carrier type.

Thus good thermoelectric materials have band gaps large enough to have only a single carrier type but small enough to sufficiently high doping and high mobility (which leads to high electrical conductivity).

A good thermoelectric material also needs to have low thermal conductivity.

Thermal conductivity in such materials comes from two sources of heat transport.

Phonons travelling through the crystal lattice transport heat and lead to lattice thermal conductivity.

The electrons (or holes) also transport heat and lead the electronic thermal conductivity. The electronic term is related to the electrical conductivity

$$\kappa_E = L\sigma T$$

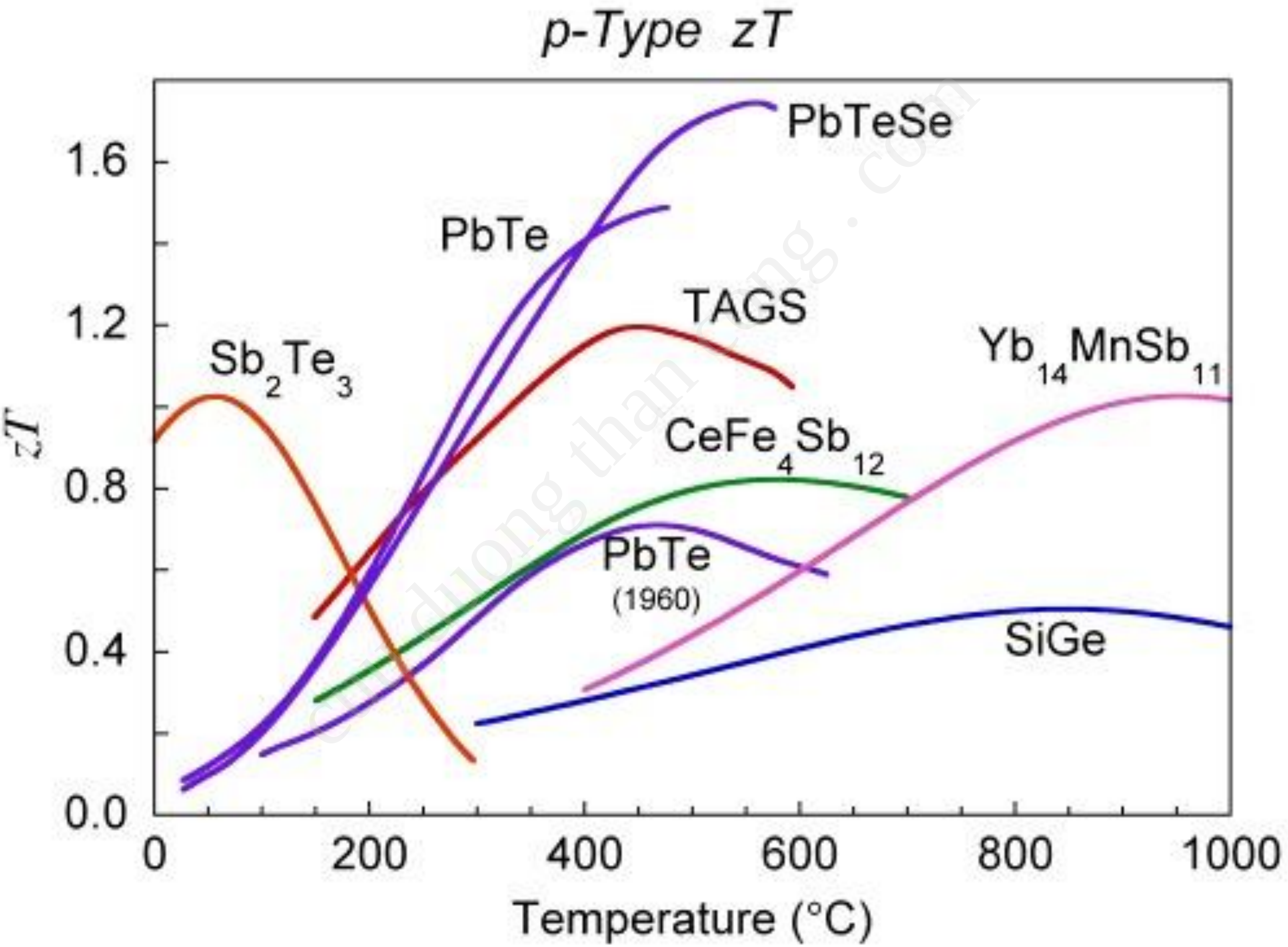
through the Wiedeman-Franz law, where L is the Lorenz factor L. A good estimate for L (at any temperature) based only on the measured thermopower (absolute value of the Seebeck coefficient) is:

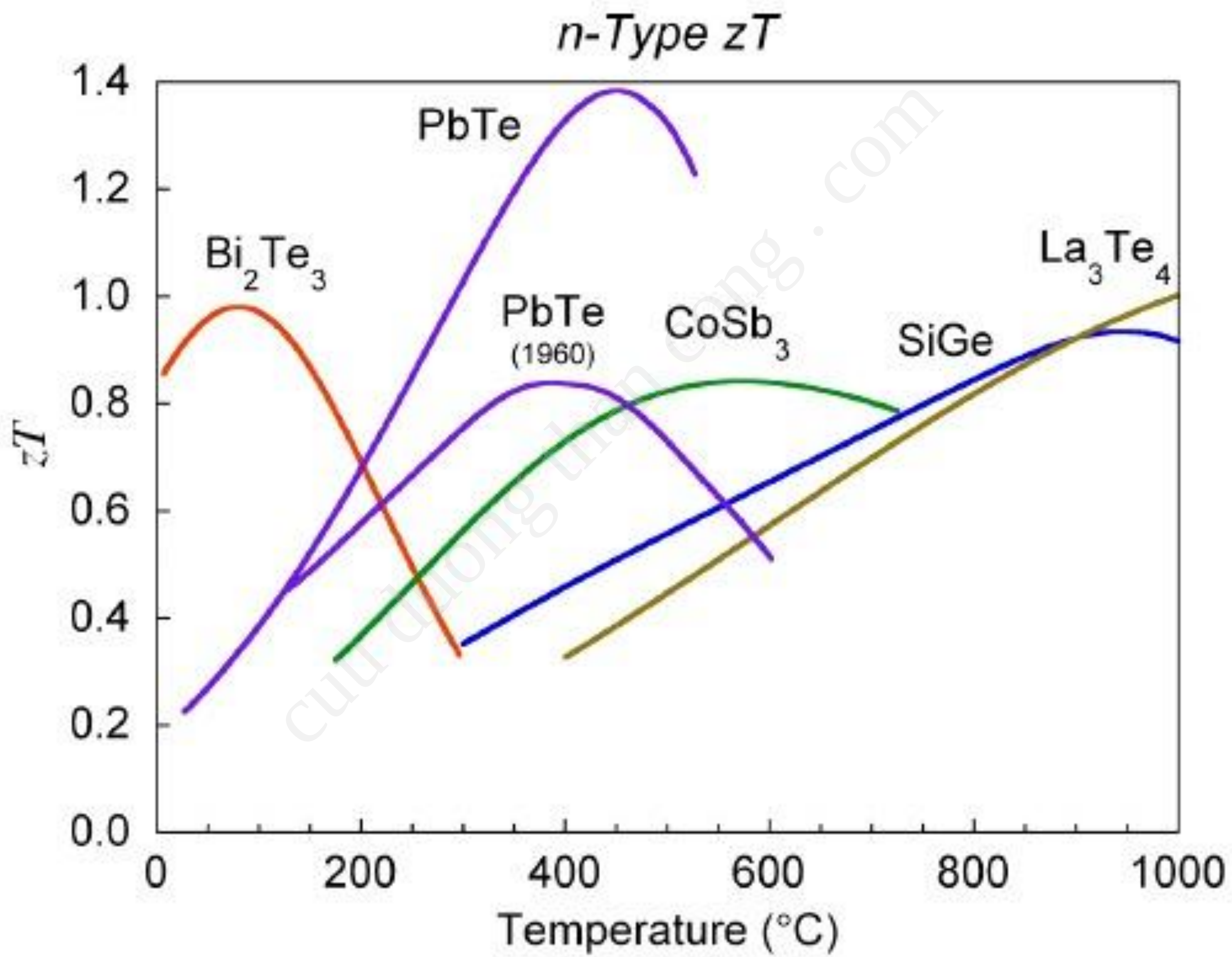
$$L = 1.5 + Exp\left[-\frac{|S|}{116}\right]$$

where L is measured in 10^{-8} WΩ K^{-2} and S in μV/K.

Thus the greatest opportunity to enhance zT is to minimize the lattice thermal conductivity. This can be done by increasing the phonon scattering by introducing heavy atoms, disorder, large unit cells, clusters and rattling atoms.

a variety of high zT materials have been developed. Many materials have an upper temperature limit of operation, above which the material is unstable. Thus no single material is best for all temperature ranges, so different materials should be selected for different applications based on the temperature of operation. This leads to the use of a segmented thermoelectric generator.


p-Type zT
PbTeSe
PbTe
TAGS
Yb14MnSb11
Sb2Te3
CeFe4Sb12
PbTe
(1960)
SiGe
zT
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
Temperature (°C)


n-Type zT
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
zT
PbTe
Bi_2Te_3
PbTe
(1960)
$CoSb_3$
SiGe
La_3Te_4
0
200
400
600
800
1000
Temperature (°C)