1.1 Exergy vs. Energy
Energy Conversion /1

- In a hydraulic power plant, the potential energy difference can be completely converted into work.
- For a thermal plant, Carnot (C1824) discovered that only a portion of heat $Q$ at temperature $T_1$ can be converted into work, with cold sink temperature $T_2$:

$$W = Q \cdot \frac{T_1 - T_2}{T_1} = Q \left(1 - \frac{T_2}{T_1}\right)$$

![Figure 1.1: Comparison of a hydraulic and thermal power plant.](Pic:S05)

Energy Conversion /2

- The preferable way to convert heat $Q$ at $T_1$ into work is to use a natural, unlimited cold sink, such as the natural environment at temperature $T_0$.
- With $T_2 > T_0$ no full use of $Q$ is made; for $T_2 < T_0$ a cooling effort is needed.

$$W_{\text{max}} = Q \cdot \frac{T_1 - T_0}{T_1} = Q \left(1 - \frac{T_0}{T_1}\right)$$

![Figure 1.1: Comparison of a hydraulic and thermal power plant.](Pic:S05)
Exergy /1

EXERGY quantifies how much of a certain amount of energy contained in an energy source can be extracted as useful work.

- The potential of (natural) energy resources for driving a mechanical, thermal, chemical or biological process depends on the deviation from thermodynamic equilibrium with the surrounding environment.
- This allows evaluation of the ability to perform maximum work under certain environmental conditions.
- This involves quality assessments, for example for heat $Q$ its temperature $T$, relating it to temperature $T_0$ of the surrounding environment.

Exergy /2

- Note that work is a path function:
  $$W = f(\text{initial state, path, final state})$$
- For maximising the work output:
  - The process should be reversible
  - The end of the process should be at a dead state which is in equilibrium with the surrounding environment: temperature $T_0$ and pressure $p_0$ as the environment; no kinetic or potential energy relative to the environment; no chemical reactivity with the environment.
    (And no electrical, magnetic etc. effects.)
- This requires a description of the state and, if chemistry is involved, the composition of the local environment for the prevailing chemical species.
Exergy /3

- While the quantities of energy allow for "bookkeeping" with the help of the First Law of Thermodynamics ("energy cannot be produced or destroyed"); the exergy concept follows from the Second Law of Thermodynamics, which involves the quality of energy and its degradation during energy conversion.

- A few useful definitions: Exergy expresses the maximum work output attainable in the natural environment, or the minimum work input necessary to realise the reverse process (Rant, 1956);
  Exergy expresses the amount of mechanical work necessary to produce a material in its specified state from components in the natural environment, in a reversible way, heat being exchanged only with the environment (Rickert, 1974)

- During the 1940s, the term "availability" had been introduced for a similar purpose (Keenan, 1941, K41) – see p. 9

Surroundings - Environment

- Some care should be considered with respect to "the surroundings", which is everything outside the system’s boundaries. Part of the surroundings, referred to as the "immediate surroundings" are affected by the process, the "environment" refers to the region beyond that.

- "Normal conditions" for the reference environment: 
  \[ T^\circ = 298.15 \text{ K}, \ p^\circ = 101.325 \text{ kPa}, \ \text{relative humidity 70\%}, \ \text{atmospheric CO}_2 \text{ concentration 330 - 380 ppm, sea water salinity 3.5 \%}-\text{wt, etc. etc. etc.} \]

- Some data for air: \[ \text{N}_2 = 75.78 \text{ kPa}; \ \text{O}_2 = 20.39 \text{ kPa}, \ \text{Ar} = 906 \text{ Pa}, \ \text{CO}_2 = 33.5 \text{ Pa}, \ \text{H}_2\text{O} = 2200 \text{ Pa}, \ \text{He} = 1.77 \text{ Pa}, \ \text{and Ne, D}_2\text{O, Kr, Xe} < 1 \text{ Pa} \] (SAKS04)

  39.7 Pa would be better – see co2now.org
Notation For Exergy

- In the literature, symbols like Ex, or X for exergy, or ex or x for specific exergy (i.e. exergy per mass, Ex/m = X/m = ex = x) are most common; but

- Also the symbols B and b are used, especially in (and by followers of) the very important work by Szargut et al.

- And, in some (U.S.) literature, availability, B, is defined as
  \[ B_{AV} = H - T^\circ \cdot S, \]
  which can be related to exergy by
  \[ Ex = B_{AV}(T, p) - B_{AV}(T^\circ, p^\circ), \]
  where
  \[ B_{AV}(T^\circ, p^\circ) = (H - T^\circ \cdot S)_{T^\circ, p^\circ} = G_{T^\circ, p^\circ} \]
  which \( \neq 0 \) necessarily (depends on \( U_{T^\circ, p^\circ} \) in \( H_{T^\circ, p^\circ} \))
  \[ Ex(T, p) = (H - T^\circ \cdot S)_{T, p} - (H - T^\circ \cdot S)_{T^\circ, p^\circ} \]

1.2 Reversible Work-Irreversibility
Exergy and Work Potential

Thus: a system will deliver the maximum possible work in a reversible process from a specified initial state to the state of its environment, i.e. the dead state.

- This useful work potential is called **exergy**. It is also the upper limit of work from a device without violating the Laws of Thermodynamics. The part of the energy that cannot be converted into work is called unavailable energy or anergy:
  \[ \text{energy} = \text{exergy} + \text{anergy} \]

- Since exergy depends on the surrounding environment, it is **not a state variable** like U, H, S, V, p, G.

- In some special cases a changing environment can be considered, for example when analysing air flight, or large seasonal or daily changes (day/night).

- Unlike energy, exergy is consumed or destroyed.

Surroundings Work

- During the expansion of a work \( W \) producing closed system, with volume change \( \Delta V = V_{\text{final}} - V_{\text{start}} > 0 \), work \( W_s \) is done on the surroundings at pressure \( p^\circ \):
  \[ W_s = p^\circ \cdot \Delta V \]

- Similarly, \( \Delta V < 0 \) is possible. In many cases this **surroundings work** cannot be recovered, reducing the useful work \( W_u \) of the process:
  \[ W_u = W - W_s = W - p^\circ \cdot \Delta V \]

- This has no significance for 1) cyclic processes and 2) systems with fixed boundaries, but is important for constant pressure processes with large volume changes (for example: combustion furnaces, engines).
Reversible Work

- Reversible work $W_{\text{rev}}$ is the maximum amount of work that can be obtained from a process; it is equal to exergy if the final state is the dead state (which usually is not so!)
- The difference between $W_{\text{rev}}$ and $W_u$ is referred to as the irreversibility:

$$I = W_{\text{rev}} - W_u$$

which is equal to the amount of exergy that is destroyed.
- The irreversibility represents "lost opportunity" to do work.
- If $I = 0$, no entropy is generated.
- For work consuming devices, $W_{\text{rev}} \leq W_u$

Example: Irreversibility 1/1

- A heat engine (HE) receives $Q_{\text{in}} = 500$ kW heat at $T_H = 1200$ K and rejects waste heat at $T_L = 300$ K. The power output of the engine is 180 kW.

Calculate the reversible power $W_{\text{rev}}$ and irreversibility rate $I$, in kW.

- $W_{\text{rev}}$ follows from the Carnot efficiency

$$\eta_{\text{carnot}} = 1 - T_L/T_H = 0.75$$

$$\Rightarrow W_{\text{rev}} = \eta_{\text{carnot}} \cdot Q_{\text{in}} = 375 \text{ kW.}$$

- The actual power output $W_u = 180$ kW, thus $I = W_{\text{rev}} - W_u = 195$ kW

- Note that the 500 kW - 375 kW = 125 kW rejected to the sink was not available for work
Example: Irreversibility 1/2

- The 125 kW rejected to the sink follows from Carnot efficiency; this is the anergy part of the input energy:
  
  \[
  \text{energy} = \text{anergy} + \text{exergy} \\
  500 \text{ kW} = 125 \text{ kW} + 375 \text{ kW}
  \]

- The entropy part of the energy cannot be converted into useful work.

\[
\begin{align*}
\frac{\dot{Q}}{T_{\text{in}}} &= \frac{500 \text{ kW}}{1200 \text{ K}} \\
&= 417 \text{ J/(K \cdot s)}
\end{align*}
\]

\[
\begin{align*}
\frac{\dot{Q}}{T_{\text{out}}} &= \frac{125 \text{ kW}}{300 \text{ K}} \\
&= 417 \text{ J/(K \cdot s)}
\end{align*}
\]

Example: Irreversibility 2/1

- A block of iron (m = 500 kg) is cooled from \(T_H = T_i = 200^\circ \text{C}\) to \(T_L = 27^\circ \text{C}\) by transferring heat to the surrounding air \((T_0 = 27^\circ \text{C})\). Calculate reversible work \(W_{\text{rev}}\) and irreversibility \(I\), in kJ.

- The maximum work equals (assuming a series of reversible heat engines):
  
  \[
  \delta W_{\text{rev}} = \eta_c \cdot \delta Q_m = (1 - \frac{T_L}{T_H}) \cdot \delta Q_m = (1 - \frac{T_0}{T}) \cdot \delta Q_m
  \]
  
  where \(\delta Q_m = -m \cdot c_{\text{avg}} \cdot dT\) which gives

  \[
  W_{\text{rev}} = \int_{T_i}^{T_f} \delta W_{\text{rev}} = m \cdot c_{\text{avg}} \cdot \left( (T_i - T_0) - T_0 \cdot \ln \frac{T_i}{T_0} \right) = 8191 \text{ kJ}
  \]
Example: Irreversibility 2/2

- Here, $c_{avg}$ is an average value for the specific heat of iron, $\sim 450 \text{ J/(kg·K)}$
- In the result, the first part $(m \cdot c_{avg} \cdot \Delta T)$ the heat transferred from the iron block which equals 38925 kJ.
- The 8191 kJ calculated as $W_{rev}$ could have been converted into useful work.
- Since no work was obtained, $W_u = 0$ and the irreversibility therefore equals $I = W_{rev} = 8191 \text{ kJ (21% of } Q_{in})$.
- The remaining $38925 - 8191 = 30734 \text{ kJ (79% of } Q_{in})$ is rejected also to the surroundings.

Irreversibilities and Exergy Loss

- Typical examples of irreversibilities that result in exergy destruction, or exergy losses:
  - Friction, including friction in fluid flows which results in pressure drop
  - Mixing (which increases entropy)
  - Chemical reactions
  - Heat transfer, especially through large temperature differences
  - Unrestrained expansion; throttling
  - Fast compression
  - Electric resistance
  - Adiabatic processes are often more reversible
- Note that fast processes can be more reversible than slow processes; for example discharging a battery
- Slower does not automatically mean more reversible!

Rule of thumb: irreversible processes are processes that look absurd when run backwards
Second-Law Efficiency, $\eta_2$, Revisited

- Second-law efficiency is defined as:

$$\eta_2 = \frac{\text{actual thermal efficiency}}{\text{maximum possible thermal efficiency}} = \frac{\eta}{\eta_{\text{carnot}}}$$

- Equally, it can be defined as (for work producing devices):

$$\eta_2 = \frac{\text{useful work}}{\text{maximum possible useful work}} = \frac{W_u}{W_{\text{rev}}} = 1 - \frac{l}{W_{\text{rev}}}$$

for work done (for work -power- consumed $\eta_2 = W_{\text{rev}} / W_{u, \text{input}}$) with irreversibility, $l$, or, expressed as exergies:

$$\eta_2 = \frac{\text{exergy recovered, i.e. made use of}}{\text{exergy supplied}} = 1 - \frac{\text{exergy destroyed}}{\text{exergy supplied}}$$

Example: Efficiency

- A house, like many in Finland, is electrically heated, using an electric resistance heating element that converts electricity for 100% into heat at room temperature. For indoor $T = 21^\circ C$ and outdoor $T = 10^\circ C$, determine the Second-law efficiency.

- The performance can be described by the so-called coefficient of performance, COP, defined as

$$\text{COP}_{\text{heater}} = \frac{\text{heat output}}{\text{work input}}$$

which here is equal to $\text{COP} = 1$.

- For the most efficient, Carnot, process:

$$\text{COP}_{\text{heater}} = \frac{T_{\text{high}}}{T_{\text{high}} - T_{\text{low}}}$$

with result $\text{COP}_{\text{rev}} = 294/(294-283) = 26.7$.

- Thus, the Second-law efficiency $\eta_2 = \text{COP}/\text{COP}_{\text{rev}} = 0.037 = 3.7\%$
1.3 Physical Exergy

Exergy of ”Non-Heat” Energy

- **Kinetic energy** $E_k = \frac{1}{2}m(v-v_{ref})^2$ can* be completely and reversibly converted into work $\rightarrow \text{Ex}(E_k) = E_k$
- **Potential energy** $E_p = mg(z-z_{ref})$ can* be completely and reversibly converted into work $\rightarrow \text{Ex}(E_p) = E_p$
- **Electric energy** $E_{elec} = i \cdot V \cdot t$ (current $\times$ voltage $\times$ time) can** be completely and reversibly converted into work $\rightarrow \text{Ex}(E_{elec}) = E_{elec}$
- Similar for energy streams $\dot{E}$ (J/s, W) or specific energy (streams) $e = \frac{E}{m} = \frac{\dot{E}}{\dot{m}}$, $\dot{e} = \frac{\dot{E}}{m}$, with mass stream $\dot{m}$ (kg/s) or mass $m$ (kg)

* if frictional losses (giving heat) can be avoided
** if Ohmic losses (giving heat) can be avoided
Exergy of Heat

The exergy of heat follows directly from Carnot’s analysis (C1824): the maximum amount of reversible work that can be obtained from conversion of heat $Q$ at temperature $T$, with temperature $T^\circ$ of the surroundings, equals

$$Ex(Q) = (1 - \frac{T^\circ}{T}) \cdot Q = \text{Carnot factor} \cdot Q$$

with of course $T$'s in K!!

- As noted above: the entropy part of energy (anergy), for heat $Q$ equal to $Q/T$, cannot be converted into work.

Sadi Carnot
1796-1832
see C1824

Exergy of Internal Energy

Internal energy $U$ is composed of sensible heat $(c_vdT)$, latent heat $(\Delta U_{\text{phase transitions}})$, chemical energy and nuclear energy. Chemical (reaction) exergy will be addressed separately (sections 1.8 and 1.9), nuclear (reaction) exergy will not be addressed here.

- Remember that for internal energy, $\Delta U = Q + W$ or $dU = \delta Q + \delta W$, where, as shown above,
  - $Ex(\delta W) = \delta W_u = -(p-p^\circ)dV = -pdV + p^\circ dV = \delta W + p^\circ dV$, with useful work $W_u > 0$, gained by the system (!!) and
  - with $Ex(\delta Q) = (1 - T^\circ/T) \cdot \delta Q$ and $\delta Q = dS/T$ it follows that $Ex(\delta Q) = (1 - T^\circ/T) \cdot TdS = \delta Q - T^\circ dS$
  - $Ex(dU) = Ex(\delta W_u) + Ex(\delta Q) = dU + p^\circ dV - T^\circ dS$

This gives finally:

$$\Rightarrow Ex(U)_{T^\circ,V^\circ,p^\circ} = T^\circ(V^\circ) dU + p^\circ dV - T^\circ dS = (U-U^\circ) + p^\circ (V-V^\circ) - T^\circ (S-S^\circ)$$
Exergy of Enthalpy

- For enthalpy, \( H = U + pV \)
  
  Thus, \( \text{Ex}(H) = \text{Ex}(U) + \text{Ex}(pV) \)

- As shown above, for internal energy:
  
  \[ \text{Ex}(U) = (U-U^\circ) + p^\circ(V-V^\circ) - T^\circ(S-S^\circ) \]

  and since \( \text{Ex}(pV) = (p-p^\circ)V \) (see above: surroundings work \( p^\circ \Delta V \))

  for work done by the system the result is:

  \[ \rightarrow \text{Ex}(H) = U+pV - (U^\circ+p^\circV^\circ) - T^\circ(S-S^\circ) = (H-H^\circ) - T^\circ(S-S^\circ) \]

- Combined with \( E_k + E_p \) for kinetic and potential energy this is also known as "flow exergy",

  with symbol \( \Psi \) typically used for \( \text{Ex}(H) + E_k + E_p \),

- Similarly, symbol \( \Phi \) is often used for \( \text{Ex}(U) + E_k + E_p \)

Exergy of a Flow / Non-flow System

- The exergy of a moving or non-moving (or flow or non-flow) system is a combination of the kinetic, potential and thermo-mechanical exergy

  see Figures below for non-flowing and flowing systems:
Example: Internal Energy Exergy /1

- Calculate the maximum amount of work to be obtained from expanding 200 m³ compressed air at \( p_1 = 10 \) bar, \( T_1 = 300 \) K to ambient conditions \((T^\circ = 300K, p^\circ = 1 \text{ bar})\).

- The maximum work is equal to the exergy of the closed system of compressed gas: \( Ex = Ex(U) = m \cdot ex(u) \), where \( m \) can be found using ideal gas law (temperature and pressure are far from \( T_{crit}, P_{crit} \));
  \[ m = \frac{M_p V_1}{RT_1} \approx 2323 \text{ kg} \]

Example: Internal Energy Exergy /2

- No kinetic energy, no potential energy to be considered.
- \( Ex(U) = (U-U^\circ) + p^\circ(V-V^\circ) - T^\circ(S-S^\circ) \)
- \( T_1 = T^\circ \rightarrow \Delta T = 0 \rightarrow U_1 - U_0 = 0 \)
- Note: \( s_1 = s^\circ + c_p \cdot ln\left(\frac{T_1}{T^\circ}\right) - R \cdot ln\left(\frac{p_1}{p^\circ}\right) \)
  using \( \delta q = du - \delta w \rightarrow Tds = du + pdV = dh - Vdp = c_p dT - (RT/p)dp \)

- \( p^\circ(v_1 - v^\circ) = p^\circ \cdot R\left(\frac{T_1}{p_1} - \frac{T^\circ}{p^\circ}\right) = RT^\circ\left(\frac{p^\circ}{p_1} - 1\right); \quad (T_1 = T^\circ !) \)
- \( T^\circ(s_1 - s^\circ) = T^\circ\left[c_p \cdot ln\left(\frac{T_1}{T^\circ}\right) - R \cdot ln\left(\frac{p_1}{p^\circ}\right)\right] = - R \cdot T^\circ \cdot ln\left(\frac{p_1}{p^\circ}\right) \)

\[ \rightarrow Ex(u_1) = 120.76 \text{ kJ/kg}; \quad Ex(U_1) = m \cdot ex(u_1) = 280.53 \text{ MJ} \]
Open System Exergy, h-s diagram /1

- As for an alternative derivation: Consider an open system that produces work $w$, which is maximal, $w_{\text{max}}$, for a reversible process. Neglect kinetic and potential energy effects.

- For reversible heat exchange $q$, this must occur at a temperature $T^\circ \to q = T^\circ \cdot \Delta s = T^\circ \cdot (s_2 -s_1)$

- Also, the outflow 2 must be at equilibrium with the surroundings: $h_2 = h^\circ$, $T_2 = T^\circ$, $p_2 = p^\circ$, $s_2 = s^\circ$

For those who use $h,s$ diagrams

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Open System Exergy, h-s diagram /2

- The energy balance for this system gives:
  $$w_{\text{max}} = h_1 - h_2 + q = h_1 - h_2 - T^\circ \cdot (s_2 - s_1),$$ and thus for the maximum work, $w_{\text{max}} = ex$, in general:
  $$ex = h - h^\circ - T^\circ \cdot (s - s^\circ)$$

- This can be conveniently plotted in h-s diagrams, with reference line $dh/ds = T^\circ$
1.4 Exergy Destruction; Isolated-Closed-Open Systems

Exergy Destruction /1

- Consider an **isolated system**: no energy or mass transfer across the system boundaries is possible.
- The energy and entropy balance equations give, for time $t_1 \rightarrow t_2$: $\Delta U = U_2 - U_1 = 0$, $S_{\text{gen}} = S_2 - S_1$.
- Combined, and $\times T^\circ \rightarrow T^\circ \cdot S_{\text{gen}} = T^\circ (S_2 - S_1)$.
- For the total exergy of this system:
  
  $Ex_2 - Ex_1 = (U_2 - U_1) + p^\circ \cdot (V_2 - V_1) - T^\circ \cdot (S_2 - S_1)$
  
  $= - T^\circ \cdot (S_2 - S_1) = - T^\circ \cdot S_{\text{gen}}$  \[ \Delta Ex = - T^\circ \cdot S_{\text{gen}} \leq 0 \]

  with exergy destruction $-\Delta Ex = T^\circ \cdot S_{\text{gen}} \geq 0$.

- **For systems in general, this is known as the Gouy-Stodola relation** referring to work reported by Gouy (1889) and by Stodola (1910).
Exergy Destruction /2

- Considering again an open system as in the figure, for a reversible process

\[ w_{rev} = h_1 - h_2 + q^\circ, \]

where \( q^\circ = T^\circ (s_2 - s_1) \),

while for an irreversible process

\[ w_{irrev} = h_1 - h_2 + q \] with \( q < q^\circ \), indicating a net entropy production \( \Delta s = s_2 - s_1 - q^\circ / T^\circ > 0 \)

Thus, \( \Delta ex = w_{rev} - w_{irrev} = T^\circ \cdot \Delta s \) (Gouy – Stodola)

- Similar to the principle of increasing entropy, this is known as the principle of decreasing exergy

- For an entropy production rate the exergy destruction rate is equal to

\[ -\Delta \dot{E}_x = T^\circ \cdot \dot{S}_{gen} \geq 0 \]

Exergy Destruction /3

- For a closed system, which does not involve mass flows a general balance equation reads:

\[ \text{Ex}_{\text{heat}} + \text{Ex}_{\text{work}} - \text{Ex}_{\text{destroyed}} = \Delta \text{Ex}_{\text{system}}, \]

where \( \text{Ex}_{\text{destroyed}} = T^\circ \cdot S_{gen} \geq 0 \)

which gives, for several heat (streams) \( Q_i \):

\[ \sum_i \left( 1 - \frac{T^0}{T_i} \right) \cdot Q_i + (W - \rho_0 (V_2 - V_1)) - T_0 \cdot S_{gen} = \text{Ex}_2 - \text{Ex}_1 \]

or as rate:

\[ \sum_i \left( 1 - \frac{T^0}{T_i} \right) \cdot \dot{Q}_i + (W - \rho_0 \frac{dV}{dt}) - T_0 \cdot \dot{S}_{gen} = \frac{d\text{Ex}}{dt} \]

or with non-constant \( T_i \) for \( Q_i \):

\[ \sum_i \left( 1 - \frac{T^0}{T_i} \right) \cdot \delta Q_i + (W - \rho_0 (V_2 - V_1)) - T_0 \cdot \dot{S}_{gen} = \text{Ex}_2 - \text{Ex}_1 \]
Exergy Destruction /4

- For an open system, which does involve mass flows a general balance equation reads:

\[ \text{Ex}_{\text{heat}} + \text{Ex}_{\text{work}} + \text{Ex}_{\text{in}} - \text{Ex}_{\text{out}} - \text{Ex}_{\text{destroyed}} = \Delta \text{Ex}_{\text{system}}, \]

where \( \text{Ex}_{\text{destroyed}} = T^\circ \cdot S_{\text{gen}} \geq 0 \)

which gives, for several heat (streams) \( Q_i \) and incoming and outgoing enthalpy streams with exergy \( \psi_j \) and \( \psi_k \):

\[ \sum_i \left( 1 - \frac{T^0}{T_i} \right) \cdot Q_i + (W - p_0 (V_2 - V_1)) + \sum_j m_j \cdot \psi_j - \sum_k m_k \cdot \psi_k - T_0 \cdot S_{\text{gen}} = \text{Ex}_2 - \text{Ex}_1 \]

or as rate:

\[ \sum_i \left( 1 - \frac{T^0}{T_i} \right) \cdot \dot{Q}_i + (\dot{W} - p_0 \frac{dV}{dt}) + \sum_j \dot{m}_j \cdot \psi_j - \sum_k \dot{m}_k \cdot \psi_k - T_0 \cdot \dot{S}_{\text{gen}} = \frac{d\text{Ex}}{dt} \]

or with non–constant \( T_i \) for \( Q_i \):

\[ \sum_i \int \left( 1 - \frac{T^0}{T_i} \right) \cdot \partial Q_i + (W - p_0 (V_2 - V_1)) + \sum_j m_j \cdot \psi_j - \sum_k m_k \cdot \psi_k - T_0 \cdot S_{\text{gen}} = \text{Ex}_2 - \text{Ex}_1 \]

Example: Exergy Analysis-Open System /1

- A 200 m³ storage tank for air, at \( p_1 = 100 \text{ kPa}, T_1 = 300\text{ K} \) is to be used for air storage at \( p_2 = 1 \text{ MPa}, T_2 = 300\text{ K} \). Air is supplied by a compressor that takes in air at \( p^\circ = 100 \text{ kPa}, T^\circ = 300 \text{ K} \). Calculate the minimum work requirement for this process.

- Ideal gas behaviour can be assumed; no kinetic or potential energy effects.

- Note that for the incoming air, \( \psi_1 = \psi^\circ = \Phi^\circ = 0 \)

- Final mass follows from ideal gas law \( \rightarrow m_2 \approx 2323\text{kg} \). 
Example: Exergy Analysis-Open System /2

- For the final state, $Ex(U_2) = m_2 \cdot \Phi_2$ is to be calculated, where $u_2 - u^\circ = 0$ since $\Delta T = 0$

- $p^\circ(v_2-v_0) = RT^\circ(p^\circ/p_2 - 1)$ and
- $T^\circ(s_2-s_1) = -RT^\circ(ln(p^\circ/p_2))$

Thus, $\Phi_2 = ex(u) = (u_2-u^\circ) + p^\circ(v_2-v^\circ) - T^\circ(s_2-s^\circ)$

$= 0 + RT^\circ(p^\circ/p_2 - 1) + RT^\circ(ln(p^\circ/p_2))$

$= 120.76 \text{ kJ/kg}$

$\Rightarrow W_{\text{rev}} = m_2 \cdot \Phi_2 = 280.53 \text{ MJ}$

see also slides 27 – 28...

1.5 Physical Exergy: Applications
heat exchangers, tube flow, combustion, endoreversibility
Heat Transfer and Exergy Losses

- During the transfer of heat $Q$ from medium 1 to medium 2, with temperatures $T_1 > T_2$, the entropy of the heat $Q$ increases from $Q_{1}$ to $Q_{2}$.

- The entropy increase $\Delta S = S_{\text{gen}}$ is equal to

$$S_{\text{gen}} = \frac{Q}{T_1} - \frac{Q}{T_2} = Q \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

- And the exergy losses are equal to $-\Delta Ex = T^\circ \cdot S_{\text{gen}}$

Heat Transfer Efficiency (PTG course)

- A simple steady-state heat transfer process; heat is transported from medium 1 to medium 2 by conduction through a material that separates them.

- Temperature $T_1 > T_2$

- Thermodynamic analysis
  - Energy balance $\dot{Q}_1 = \dot{Q}_2$
  - Entropy balance
    $$\frac{\dot{Q}_1}{T_1} + \dot{S}_{\text{gen}} = \frac{\dot{Q}_2}{T_2} \Rightarrow \dot{S}_{\text{gen}} = \dot{Q}_1 \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \dot{Q}_1 \frac{T_1 - T_2}{T_1 T_2} > 0$$

- This shows that $\dot{S}_{\text{gen}}$ is large for large temperature differences ($T_1 - T_2$) and low temperatures $T_1$ and $T_2$
Quality Diagram: $1/T$ versus $Q$

- Heat exchange: hot side $T_1 \rightarrow T_2$, cold side $T_3 \rightarrow T_4$
- Exergy loss = $T_0 \times$ the surface between lines in the quality diagram

Heat Exchanger Exergy Losses

- A heat exchanger involves two media at temperatures $T_{\text{Cin}}$ and $T_{\text{Cout}}$ on the cold side, $T_{\text{Hin}}$ and $T_{\text{Hout}}$ on the hot side. (Note: $T_{\text{Cin}} = T_{\text{Cout}}$ or $T_{\text{Hin}} = T_{\text{Hout}}$ is possible!)
- For a heat exchanger transferring a heat stream $Q$, to a cold mass stream $\dot{m}_C$ from hot mass stream $\dot{m}_H$:

$$\Delta \dot{E}_C = \int_{T_{\text{Cin}}}^{T_{\text{Cout}}} (1 - \frac{T_0}{T}) \delta Q = \left[ \frac{T_{\text{Cout}}}{T_{\text{Cin}}} - T_0 \ln \frac{T_{\text{Cout}}}{T_0} \right] > 0$$

$$\Delta \dot{E}_H = \int_{T_{\text{Hin}}}^{T_{\text{Hout}}} (1 - \frac{T_0}{T}) \delta Q = \left[ \frac{T_{\text{Hout}}}{T_{\text{Hin}}} - T_0 \ln \frac{T_{\text{Hout}}}{T_0} \right] < 0$$

and the exergy losses are then equal to

$$- \Delta \dot{E} = - (\Delta \dot{E}_C + \Delta \dot{E}_H) = T_0 \cdot \left( \dot{m}_H c_{pH} \ln \frac{T_{\text{Hout}}}{T_{\text{Hin}}} + \dot{m}_C c_{pC} \ln \frac{T_{\text{Cout}}}{T_{\text{Cin}}} \right)$$

with specific heats $c_{pH}, c_{pC}$ for the hot and cold streams.
Heat Exchanger Exergy Losses /2

- Also, $\Delta Ex = T^0 \cdot [\dot{m}_H \cdot (s_{H_{out}} - s_{H_{in}}) + \dot{m}_C \cdot (s_{C_{out}} - s_{C_{in}})]$
- The efficiency of a heat exchanger, $\eta_{HX}$, can then be defined as

$$\eta_{HX} = \frac{Q}{Q + T_0 \cdot \Delta S} = \frac{Q}{Q - \Delta Ex} \times 100\%$$

- In cases where electric power $P_{elec}$ is (for example) used on the hot side:

$$-\Delta Ex = P_{elec} + \dot{m}_C \cdot c_p \cdot \left(T_0 \cdot \ln \frac{T_{out}}{T_{in}} - (T_{out} - T_{in})\right)$$

Heat Exchanger Exergy Losses /3

- Heat exchanger exergy analysis shows that the temperature difference between the flows (or with the flow, for only on medium flow) should be as small as possible (but too small $\Delta T$ requires much surface $A$!).
- This shows that counter-current heat exchangers perform much better than co-current heat exchangers.
- Ideally, the flows aquire each others temperature: the exergy losses will then be zero. For this, the heat capacities $\dot{m} \cdot c_p$ for the streams should be equal:

$$\dot{m}_C \cdot c_{pC} = \dot{m}_H \cdot c_{pH}$$

- This is anyhow a requirement for a high "effectiveness" of the heat exchanger, which depends on the ratio

$$\frac{(\dot{m}_C \cdot c_{pC})}{(\dot{m}_H \cdot c_{pH})}$$

(see course PTG 424101 # 4.3)
Example: Heat Exchanger

Consider heat flow $Q$ through a $5\text{m} \times 6\text{m}$ wall with thickness $d_{\text{wall}} = 0.3\text{ m}$ and heat conductivity $\lambda = 0.69\text{ W/(m·K)}$, from an indoor temperature of $27^\circ\text{C}$ to an outside temperature of $0^\circ\text{C}$. The inside and outside wall temperatures are $20^\circ\text{C}$ and $5^\circ\text{C}$, respectively.

Calculate the heat flow $Q$ and the exergy destruction rate $-\Delta \text{Ex}$ in W.

- $Q = -\lambda (\Delta T_{\text{wall}}/d_{\text{wall}}) = 1035\text{ W}$
- $-\Delta \text{Ex} = \text{Ex}(Q_{\text{inside}}) - \text{Ex}(Q_{\text{outside}})$
  $= Q \cdot [(1-T^\circ/T_{\text{wall,in}}) - (1-T^\circ/T_{\text{wall,out}})] = 52.0\text{ W}$ in the wall,
  and $= Q \cdot [(1-T^\circ/T_{\text{inside}}) - (1-T^\circ/T_{\text{outside}})] = 93.2\text{ W}$ in total

A Process Example

Bilge water (waste oil/water mixtures) processing for recycled fuel oil (in Turku)

Significant savings could be obtained by

- Replacing the heating centre and, more importantly, the electric heating (!) by heat from the local district heat network
- Making use of hot raw material deliveries

Source: ZHPSS07
Heat Exchange and Driving Force

- **Heat transfer theory** states that heat transfer is driven by a temperature difference \( \Delta T = T_H - T_L \):
  \[ Q \sim A \cdot (T_H - T_L) \]
  for heat flow \( Q \) through a surface \( A \) from higher temperature \( T_H \) to lower temperature \( T_L \).

- Exergy analysis shows that
  
  \[-\Delta \dot{E}_{\text{loss}} = Q \cdot T_0 \cdot \left( \frac{1}{T_L} - \frac{1}{T_H} \right)\]
  which suggests a thermodynamic driving force equal to \( \Delta (1/T) \) instead, and

- the exergy losses are the product of three factors, being
  1) surroundings temperature \( T_0 \),
  2) the heat flow \( Q \), and
  3) the driving force \( \Delta (1/T) \).

As irreversible, or **non-equilibrium thermodynamics** shows: \( \dot{s}_{\text{gen}} = \sum J_i \cdot X_i \) for flows \( J_i \) and driving forces \( X_i \)

---

Exergy Losses and Tube Flow /1

- For fluid flow \( \dot{V} \) (m³/s) through a tube, viscous friction results in pressure drop \( \Delta p \) (Pa), which must be compensated for by pumping power \( \dot{W} = \Delta p \cdot \dot{V} \). This energy is converted to heat at fluid flow temperature \( T \) (so not all is lost!)

- Thus the exergy losses can be calculated as:

  \[ \Delta \dot{E}_x = \Delta p \cdot \dot{V} - \Delta p \cdot \dot{V} \cdot (1 - T^\circ/T) = \Delta p \cdot \dot{V} \cdot T^\circ/T \]

- Mechanical dissipation \( \times \) loss factor \( T^\circ/T \); or \( \Delta \dot{E}_x = (\Delta p/\rho) \cdot T^\circ/T \)

- Note that \( \Delta \dot{E}_x > \Delta p \cdot \dot{V} \) if \( T < T^\circ \). (No cooling for free!)

---

Note: \( 4f = \zeta = \text{Blasius, Darcy friction factor} \)
\[ f = \text{Fanning friction factor} \]

For pressure drop \( \Delta p \):
\[ (p_1 - p_2) = -\Delta p = \tau_w \cdot L \cdot (4/D_h) \]
\[ = 4f \cdot \tau_w \cdot \rho \cdot <v>^2 \cdot L/D_h \]

with hydraulic diameter \( D_h = 4 \cdot A/S \)

\( A = "\text{wet" area, } S = "\text{wet" perimeter} \)
Exergy Losses and Tube Flow /2

- The pressure drop can be related to the fluid flow with cross sectional averaged velocity \( \langle v \rangle = \frac{V}{A} \), with friction factor \( f \), where \( 4f = \frac{64}{Re} \) for \textit{laminar} circular tube flow, or for \textit{turbulent} flow in smooth tubes with hydraulic diameter \( D_h \):
  \[
  4f = 0.316 \cdot Re^{-0.25} \quad (2500 < Re < 10^5) \quad \text{(Blasius)}.
  \]

- This gives dissipation losses for \textit{turbulent flow} along \textit{round} tube length \( x \):
  \[
  \frac{\delta \dot{W}}{dx} = \frac{\delta W}{\dot{m}}/dx = (-\frac{dp}{dx})/\rho = c_p \cdot dT/dx,
  \]
  which is equal to
  \[
  \frac{\delta \dot{W}}{dx} = \frac{1.79 \cdot \eta^{0.25} \cdot \dot{m}^{1.75}}{\pi^{1.75} \cdot \rho^2 \cdot D^{4.75}},
  \]
  for fluid density \( \rho \), dynamic viscosity \( \eta \), mass flow \( \dot{m} \).

---

Exergy Losses and Tube Flow /3

- For a \textit{round tube} with diameter \( D \), with insulation material, giving overall heat transfer coefficient \( U \) (W/m²·K), carrying \textit{turbulent} flow at temperature \( T \) (for example a heat exchanger tube) the heat exchange per meter with the environment is:
  \[
  \frac{\delta q}{dx} = \frac{\delta Q}{\dot{m} \cdot dx} = \frac{U(T - T^0) \pi D}{\dot{m}}
  \]
  which gives for the total exergy losses per length section \( dx \):
  \[
  \frac{d\dot{ex}}{dx} = \frac{1.79 \eta^{0.25} \cdot \dot{m}^{1.75} \cdot T^0}{\pi^{1.75} \cdot \rho^2 \cdot D^{4.75}} \cdot \frac{U(T - T^0)^2 \pi D}{\dot{m} T}
  \]
  which shows that losses due to pressure drop decrease with diameter, while those for heat losses increase with diameter!
Exergy Losses and Tube Flow

For a given **optimal value** for the diameter, \( D_{optimal} \), the exergy losses are minimal:

\[
D^{5,75}_{optimal} = 0.365 \frac{\eta^{0.25} \cdot \dot{m}^{2.75} \cdot T^0}{U \cdot \rho^2 \cdot (T - T^0)^2}
\]

---

Energy Conversion Stages in “conventional” Electricity Production, i.e. condensing power plant

- Energy in chemical bonds of fuel
  \( \downarrow \) Furnace
- Thermal energy of hot flue gas
  \( \downarrow \) Heat transfer to steam cycle
- Thermal energy of water / steam
  \( \downarrow \) Steam cycle generator
- Electrical energy

- Sources of exergy loss:
- Friction in flow lines, pressurising and depressurising
- Heat transfer at low temperatures and/or across large temperature differences
- Conversion of chemical (potential) energy into thermal energy (heat)
Exergy Loss in Expansion Turbine

- \( p_1, T_1, S_1 \rightarrow p_2, T_2, S_2 \) is non-isotropic due to friction
- Frictional heat \( Q = \text{surface } 1-2'-S_2'-S_1-1 \) in \( T,S \) diagram
- Frictional heat to fluid = surface 1-2'-4-3-1 = \((1-T_0/T_{av})Q\)
- Exergy loss \( \Delta Ex = \text{surface } 3-4-S_2-S_1-3 = (T_0/T_{av})Q \)
- Loss factor \( T_0/T_{av} \) i.e. less serious at increasing average temperature \( T_{av} \)

Transformation of Work into Heat

Exergy Losses in Combustion

- Combustion = Oxidation, i.e. transfer of electrons from fuel to oxygen \( \rightarrow \) Two “extreme” options:
  1. “Conventional electric power generation”
     - Mix fuel and oxygen at (adiabatic) temperature \( T \), and produce heat \( Q \) at temperature \( T \).
     - Fuel exergy \( Ex \) → exergy of hot gas + exergy loss
     - Exergy of hot gas = \((1-T_0/T)Q\)
  2. “Electric power generation” using fuel cells
     - Separate the release of electrons from the fuel from the take-up of electrons by oxygen, connect this, allow for the positive ions from the fuel to combine with the negative oxygen ions.
     - Fuel exergy \( Ex \) → Electrical energy \( W_e \) + exergy losses
     - Exergy loss due to heat production \( Q_p : Ex = W_e + (1-T_0/T)Q_p \)
**Exergy Losses in Combustion /2**

**Quality Diagram for Furnace**

- **Fuel:** area = exergy / T₀
- **Product gases:** calculate exergy from T_{furnace} to T₀

\[ Q \]

\[ 1/T_{furnace} \]

\[ 1/T_{stack} \]

\[ 1/T₀ \]

\[ \downarrow 1/T \]

Fuel

Flue gases

Ex flue gases

Ex fuel

**Exergy Losses in Combustion /3**

**Quality Diagram for Total System**

- Exergy input (fuel) = Exergy loss in combustion + Stack losses + Heat transfer loss to steam cycle + Exergy taken up by steam cycle

\[ Q \]

\[ 1/T_{furnace} \]

\[ 1/T_{stack} \]

\[ 1/T₀ \]

\[ \downarrow 1/T \]

Fuel

Combustion losses

Exergy to steam cycle

Stack losses

Ex flue gases

Ex fuel
### Energy and Exergy Analysis PFBC

#### Energy and exergy balances for the PFBC plant

<table>
<thead>
<tr>
<th></th>
<th>Energy rate (MW)</th>
<th>Exergy rate (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inputs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>1712</td>
<td>1783</td>
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<tr>
<td><strong>Outputs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net electricity</td>
<td>683</td>
<td>683</td>
</tr>
<tr>
<td><strong>Losses</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>External</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stack gas</td>
<td>103</td>
<td>77</td>
</tr>
<tr>
<td>Solid wastes, ash, fines</td>
<td>33</td>
<td>19</td>
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<tr>
<td>Condenser waste heat</td>
<td>731</td>
<td>25</td>
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<tr>
<td>Other waste heat</td>
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<td>0</td>
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<tr>
<td>Total external loss</td>
<td>1027</td>
<td>121</td>
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<tr>
<td>Internal</td>
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<td></td>
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<tr>
<td>PFBC subsystem</td>
<td>796</td>
<td></td>
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<tr>
<td>Gas turbine cycle</td>
<td>—</td>
<td>73</td>
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<tr>
<td>Steam turbine cycle</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Gas turbine heat recovery</td>
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<td>21</td>
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<tr>
<td>Total internal loss</td>
<td>0</td>
<td>978</td>
</tr>
</tbody>
</table>

#### Efficiencies for selected sections of the PFBC plant

<table>
<thead>
<tr>
<th>Plant section</th>
<th>Product outputs</th>
<th>Inputs</th>
<th>Energy (%)</th>
<th>Exergy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall plant</td>
<td>Net electricity</td>
<td>Coal</td>
<td>40.0</td>
<td>38.4</td>
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<tr>
<td>PFBC subsystem</td>
<td>Combustion gas</td>
<td>Coal</td>
<td>94.4</td>
<td>58.7</td>
</tr>
<tr>
<td></td>
<td>Net steam/water</td>
<td>Compressed air</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas turbine cycle (with</td>
<td>Selection net electricity</td>
<td>Combustion gas</td>
<td>92.6</td>
<td>88.6</td>
</tr>
<tr>
<td>turbine exhaust product)</td>
<td></td>
<td>Compressed air</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas turbine cycle (</td>
<td>Turbine exhaust gas</td>
<td>44.5</td>
<td>53.2</td>
</tr>
<tr>
<td></td>
<td>without turbine</td>
<td>Compressed air</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>exhaust product)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam turbine cycle</td>
<td>Section net electricity</td>
<td>Net steam/water</td>
<td>49.9</td>
<td>76.1</td>
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<td>Turbine exhaust gas</td>
<td>70.8</td>
<td>55.8</td>
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<tr>
<td>Gas turbine heat recovery</td>
<td>Net heated coal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Net steam/water</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Pics: ACA95**
Endoreversibility /1

The maximum work output from a Carnot engine operating on heat input $Q_{in}$, between $T=TH$ and $T=T^o$ is equal to $W_{max} = Q_{in}(1-TH/TL)$, with isothermal transfer of heat $Q_{in}T^o/TH$ to the environment at $T=T^o$.

However, isothermal heat transfer cannot exist; a driving force $\Delta T$ or, more correctly, $\Delta(1/T)$ is needed, which then gives losses

$$Q_{in}T^o\Delta(1/T)$$

Endoreversible Carnot engine operating between $T_{HC}$ and $T_{LC}$

Endoreversible Carnot engine operating between $T_{HC}$ and $T_{LC}$

See also Curzon & Ahlhorn Am. J. Phys. 43 (1975) 22

Pics: SAKS04

Endoreversibility /2

If these are the only losses, the process is referred to as endoreversible.

If $Q_{in} \to 0$, $W \to 0$, the endoreversible process $\to$ reversible with $T_{HC} \approx TH$, $T_{LC} \approx T^o$, $W = 0$

If $Q_{in} \to Q_{in,max}$, temperatures $T_{HC} \approx T_{LC}$ and $W \to 0$.

Maximum power $W_{max}$ is achieved for

$$\frac{T_{optimum}^{LC}}{T_{optimum}^{HC}} = \sqrt{\frac{T^o}{TH}}$$

at efficiency

$$\eta = 1 - \frac{T_{optimum}^{LC}}{T_{optimum}^{HC}} = 1 - \sqrt{\frac{T^o}{TH}}$$
1.6 Mixing Exergy

Exergy of Mixing

- Assuming two gases, each at temperature and pressure $T_0$ and $p_0$, separated by a barrier;
- Removing the barrier results in (diffusive) mixing, giving a homogeneous mixture in which the chemical potential (i.e. Gibbs energy) of each of the components decreases.
- The exergy change is given by

$$
\Delta E_{x, \text{mix}} = \Delta H_{\text{mix}} - T_0 \cdot \Delta S_{\text{mix}} = \Delta G_{\text{mix}} (p_0, T_0)
$$

- For ideal mixing (no changes in $p$, $T$, total $V$, and activity coefficients $\gamma_i = 1$), which means also $\Delta H_{\text{mix}} = 0$:

$$
\Delta S_{\text{mix}} = -R \sum_i x_i \cdot \ln x_i \rightarrow \Delta E_{x, \text{mix}} = RT_0 \sum_i x_i \cdot \ln x_i
$$

- This is important for separation processes (e.g. distillation!)

See SAKS04 §7.2, §6.3
Exergy of Mixing /2

- Consider adiabatic mixing of cold and hot water, at $T^\circ=25^\circ C$, $p=p^\circ=1$ atm.

- $\dot{E}_x = \dot{m}_i \cdot ((h_i-h^\circ) - T^\circ(s_i-s^\circ))$, with enthalpy $h^\circ$, entropy $s^\circ$ for liquid water at $T^\circ$, $p^\circ$.

- $p=$constant; $s_i-s^\circ=c_p \cdot \ln(T_i/T^\circ)$

- Water/steam table data give the results as in the so-called Grassmann exergy flow diagram.

- $\dot{E}_{x\text{lost}} = T^\circ \cdot (\dot{m}_3 s_3 - \dot{m}_2 s_2 - \dot{m}_1 s_1)$

- $\eta = \dot{E}_{x\text{out}} / \dot{E}_{xin} = 0.216$

- $\dot{E}_{x\text{lost}} = 78.4 \%$

- Pics: SAKS04

Exergy of Mixing /3

Source: S05

- More general, for mixing of two molar streams $n_1$, $n_2$ with molar fractions $x_i$ in the original streams and molar fractions $x_j$ in the final stream:

$$\Delta E_{x\text{mix}} = R T_i \left( (n_i + n_2) \sum_{j} x_j \cdot \ln x_j - n_1 \sum_{i} x_{i1} \cdot \ln x_{i1} - n_2 \sum_{i} x_{i2} \cdot \ln x_{i2} \right)$$
Exergy of Mixing /4

- For example: oxygen-rich (x=30%-vol O₂) gas for a blast furnace is produced by mixing technical oxygen (x=95%-vol O₂) and atmospheric air (x=21%-vol O₂).

- The consumption of technical oxygen per mole of product gas, \( \frac{n_{to}}{n_{pg}} \), follows from:

\[
0.3 = 0.95 \cdot \frac{n_{to}}{n_{pg}} + 0.21 \cdot (1 - \frac{n_{to}}{n_{pg}}) \rightarrow \frac{n_{to}}{n_{pg}} = 0.122 \text{ mol/mol (}= \text{m}^3/\text{m}^3)\]

→ for the exergy loss per mole of product gas

\[
\Delta e_{mix} = 8.314 \cdot 298 \cdot \left(0.3 \cdot \ln 0.3 + 0.7 \ln 0.7 - 0.122 \cdot (0.95 \cdot \ln 0.95 + 0.05 \cdot \ln 0.05) - 0.878 \cdot (0.21 \cdot \ln 0.21 + 0.79 \cdot \ln 0.79)\right) = 326.4 \text{ J/mol}
\]

1.7 Heat Radiation Exergy

See S05 §1.4.6; §2.7 and P10
Thermal Radiation /1

- The radiation $Q_R$ (W) from a surface with emissivity $\varepsilon$ (-) surface $A$ (m$^2$) and temperature $T$(K) equals

$$Q_R = \varepsilon \cdot \sigma \cdot A \cdot T^4$$

with Stefan-Boltzmann coefficient $\sigma = 5.67 \times 10^{-8}$ W/m$^2$K$^4$

- For a blackbody surface
  - $\varepsilon = 1$ in the Stefan-Boltzmann Law
  - all incident radiation is absorbed
  - radiation is maximum for its temperature at each wavelength, $\lambda$ (m)
  - the intensity of the emitted radiation is independent of direction: it is a diffuse emitter

\[\text{Pictures: T06}\]

Thermal Radiation /2

- For a blackbody, the entropy flux associated with thermal radiation is not, as might be expected, $\dot{S}_{R,BB} = Q_R/T = \sigma \cdot A \cdot T^3$, but

$$\dot{S}_{R,BB} = \left(\frac{4}{3}\right) \cdot \sigma \cdot A \cdot T^3 = \left(\frac{4}{3}\right) \cdot Q_R/T$$

- For emitting and absorbing blackbody surfaces with equal surface $A_e = A_a$ that can "see" each other completely (i.e. view factors $F_{a\rightarrow e} = F_{e\rightarrow a} = 1$) the entropy generation during heat radiation equals

$$\dot{S}_{gen,BB} = \sigma \left[ \frac{4}{3} (T_a^3 - T_e^3) + \frac{T_e^4 - T_a^4}{T_a} \right]$$

$$= \sigma \left[ \frac{1}{3} T_a^3 + T_e^3 \cdot \frac{T_e}{T_a} - \frac{4}{3} \right]$$

See also Petela, R., J. of Heat & Mass. Transf. Ser. C, 86 (1964) 187-192; and S05 section 2.7

\[\text{Pic: WRS02}\]
Thermal Radiation /3

For gray surfaces, emissivity $\varepsilon = \varepsilon(\lambda, T, \theta)$, absorptivity $\alpha = \alpha(\lambda, T, \theta)$, reflectivity $\rho = \rho(\lambda, T, \theta)$, transmissivity $\tau = \tau(\lambda, T, \theta)$, are all $0 < .. < 1$.

- Energy balance $\alpha + \rho + \tau = 1$, and Kirchhoff’s law (from Second law) gives $\varepsilon = \alpha$ for gray bodies and not-too-large temperature differences.
- The exergy of (blackbody) radiation, $e_{\text{BB}}$, with respect to its energy content, $e_{\text{BB}}$:

$$\frac{e_{\text{BB}}}{e_{\text{BB}}} = 1 - \frac{4T^0}{3T} + \frac{1}{3} \left( \frac{T^0}{T} \right)^4$$

which does not depend on $\varepsilon^o = \varepsilon_{\text{environment}}$, and can be used for gray bodies if $\varepsilon \neq \varepsilon(\lambda)$

Thermal Radiation /4

- Recently (see e.g. W07) it was shown that for the entropy of gray radiation

$$\dot{S}_{R,\text{GB}} = \frac{4}{3} \frac{Q_{R,\text{BR}}}{T} \frac{45}{4\pi^2} I(\varepsilon) = S_{R,\text{BR}} \frac{45}{4\pi^2} I(\varepsilon) = \frac{4}{3} \sigma \varepsilon T^4 \left( 1 - \frac{45}{4\pi^2} (2.336 - 0.260 \varepsilon) \ln(\varepsilon) \right);$$

or in general $\dot{S}_{R,\text{GB}} = n(\varepsilon) \cdot \varepsilon \cdot \frac{Q_{R,\text{BB}}}{T}$, where $n(\varepsilon) = \frac{4}{3} \left( 1 - \frac{45}{4\pi^2} (2.336 - 0.260 \varepsilon) \ln(\varepsilon) \right)$

Net radiation from a black-body (BB) with incident blackbody radiation (BR)  
Net radiation from a BB with incident BR, with gray-body radiation (GR)  
Net radiation for incident GR on a blackbody

1.8 Chemical Exergy

Exergy of Chemical Substances /1

- Chemical exergy gives the exergy of a substance with respect to a reference environment. Note, again, that the environment is not a dead state at thermodynamic equilibrium, due to a constant influx of solar energy.

- For each chemical element a reference species that contains, it is chosen, which gives the lowest exergy level in nature (yet indeed appearing!), i.e. the most common component of the environment (which can be the air, seawater, the earth’s crust).

"Normal conditions" for the reference environment (see also slide 8): $T^\circ = 298.15 \text{ K}$, $p^\circ = 101.325 \text{ kPa}$, relative humidity 70%, atmospheric CO$_2$ concentration 330 - 380 ppm, sea water salinity 3.5 %-wt, etc. Some data for air: N$_2 = 75.78 \text{ kPa}$, O$_2 = 20.39 \text{ kPa}$, Ar = 906 Pa, CO$_2 = 33.5 \text{ Pa}$, H$_2$O = 2.2 kPa, He = 1.77 Pa, Ne, D$_2$O, Kr, Xe < 1 Pa (SAKS04)
Exergy of Chemical Substances /2

- Examples for reference species are atmospheric O\textsubscript{2} and CO\textsubscript{2} for oxygen and carbon, CaCO\textsubscript{3} for calcium, Fe\textsubscript{2}O\textsubscript{3} for iron, etc. at 298.15 K, 101.325 kPa

- The **standard chemical exergy** \( e^{°}_{\text{chem}} = b^{°}_{\text{chem}} \) of a compound or element follows from an exergy balance of a reversible standard reference reaction, where:

\[
b^{°}_{\text{chem}} = \Delta_r G^{°} + \sum_{\text{product}} b^{°}_{\text{chem,product}} - \sum_{\text{react tan t}} b^{°}_{\text{chem,react tan t}}
\]

Exergy of Chemical Substances /3

- **For example**, for Ca+½O\textsubscript{2}+CO\textsubscript{2} \( \rightarrow \) CaCO\textsubscript{3}, with \( -\Delta_r G^{°} = 738.6 \text{ kJ/mol} \); for the elements (see *Tables on following pages*), the normal standard values for the chemical exergy for the references species are 16.3 kJ/mol for CaCO\textsubscript{3}, 19.87 kJ/mol for CO\textsubscript{2} and 3.97 kJ/mol for O\textsubscript{2}.

- This gives for calcium, Ca:

\[
e^{°}_{\text{chem}} = b^{°}_{\text{chem}} = -738.6 + 16.3 - 19.87 - 1\times 3.97 = 729.1 \text{ kJ/mol}
\]
Exergy of Chemical Substances /4

- For chemical compounds, the standard chemical exergy can be more easily calculated from the reversible standard formation reaction, with \( \Delta G = \Delta_f G^° \)

\[
\begin{align*}
\text{b}^°_{\text{chem}} &= \text{ex}^°_{\text{chem}} = \Delta_f G^° + \sum_{\text{elements}} n_{\text{element}} \times \text{ex}^°_{\text{chem, element}}
\end{align*}
\]

where \( n_{\text{element}} \) is the number of moles of the element per mole of compound, and \( \text{ex}^°_{\text{chem, element}} = \text{b}^°_{\text{ch}} \) from tables.

Exergy of Chemical Substances /5

- For the constituents of air (N₂, O₂, Ar, CO₂, ...), at \( T^° = 298.15 \text{ K} \) and the average pressure \( p^°_{\text{avg}} = 99.31 \text{ kPa} \) the exergy value = 0.

- Note that ideal gas law usually applies.

Thus, for a pure component at \( T^°, p^° \), since \( \Delta \text{Ex}_{\text{separate}} = \Delta H_{\text{separate}} - T^° \cdot \Delta S_{\text{separate}} = -T^° \cdot \Delta S_{\text{separate}} = T^° \cdot \Delta S_{\text{mix}} \), and \( \Delta S_{1,2} = -R \ln(p_2/p_1) \) gives

\[
\begin{align*}
\text{E}^°_{\text{chem, i}} &= RT^° \ln(p^°/p_i) \text{ for these.}
\end{align*}
\]
Standard Chemical Exergy of the Elements 1/5

<table>
<thead>
<tr>
<th>Chemical symbol</th>
<th>Concentration in Earth's crust $n_{\text{atm}}$ kmol/kg</th>
<th>Chemical formula</th>
<th>state</th>
<th>$c$, $\gamma$</th>
<th>$\rho$, $m$, $x$</th>
<th>Standard chem. exergy $h_A$ kJ</th>
<th>Free exergy of formation $\Delta G$ kJ/mol</th>
<th>State</th>
<th>Standard chem. exergy $h_A$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Ag</td>
<td>3.7 × 10^{-10}</td>
<td>AgCl</td>
<td>aq</td>
<td>$\gamma = 0.6$ m=2.7×10^{-9}</td>
<td>15.3</td>
<td>-215.5</td>
<td>s</td>
<td>70.2</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>3.05 × 10^{-2}</td>
<td>Al_2O_3</td>
<td>s</td>
<td>$\gamma = 0.01$ m=2.1×10^{-3}</td>
<td>2441.0</td>
<td>s</td>
<td>795.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>2.4 × 10^{-8}</td>
<td>Ar</td>
<td>g</td>
<td>$p=0.309$</td>
<td>11.69</td>
<td>11.69</td>
<td>g</td>
<td>494.6</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>2.1 × 10^{-10}</td>
<td>H_2SO_4</td>
<td>aq</td>
<td>$\gamma = 0.6$ m=2.1×10^{-4}</td>
<td>50.5</td>
<td>0</td>
<td>s</td>
<td>50.5</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>3.5 × 10^{-9}</td>
<td>Bi(OH)_3</td>
<td>aq</td>
<td>$\gamma = 0.1$ m=3.4×10^{-4}</td>
<td>968.8</td>
<td>s</td>
<td>628.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>3.1 × 10^{-10}</td>
<td>Bi_2O_3</td>
<td>s</td>
<td>$\gamma = 0.01$ m=4.2×10^{-6}</td>
<td>30.7</td>
<td>0</td>
<td>11.7</td>
<td>755.1</td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>3.1 × 10^{-7}</td>
<td>BeO</td>
<td>s</td>
<td>$\gamma = 0.01$ m=2.1×10^{-7}</td>
<td>38.1</td>
<td>0</td>
<td>234.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>8.13 × 10^{-10}</td>
<td>Bi_2O_3</td>
<td>aq</td>
<td>$\gamma = 0.6$ m=4.1×10^{-10}</td>
<td>-146.4</td>
<td>s</td>
<td>274.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>3.1 × 10^{-10}</td>
<td>KBr</td>
<td>aq</td>
<td>$\gamma = 0.01$ m=8.7×10^{-10}</td>
<td>-104.0</td>
<td>s</td>
<td>101.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1.7 × 10^{-10}</td>
<td>CO_2</td>
<td>g</td>
<td>$p=0.0335$</td>
<td>19.87</td>
<td>394.36</td>
<td>s</td>
<td>410.26</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>1.03 × 10^{-3}</td>
<td>CaCO_3</td>
<td>calcite</td>
<td>$\gamma = 0.6$ m=1.4×10^{-5}</td>
<td>16.3</td>
<td>-1129.0</td>
<td>s</td>
<td>729.1</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>1.88 × 10^{-4}</td>
<td>CdCl_2</td>
<td>aq</td>
<td>$\gamma = 1.0$ m=6.9×10^{-10}</td>
<td>-359.4</td>
<td>s</td>
<td>293.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>4.3 × 10^{-6}</td>
<td>CeO_2</td>
<td>s</td>
<td>$\gamma = 0.02$ m=8.8×10^{-4}</td>
<td>33.8</td>
<td>0</td>
<td>105.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>3.7 × 10^{-7}</td>
<td>Cl_2</td>
<td>aq</td>
<td>$\gamma = 0.01$ m=5.6×10^{-7}</td>
<td>-131.26</td>
<td>s</td>
<td>123.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>3.5 × 10^{-10}</td>
<td>CoFe_2O_4</td>
<td>s</td>
<td>$\gamma = 0.002$ m=9.5×10^{-11}</td>
<td>40.1</td>
<td>0</td>
<td>1032.6</td>
<td>s, III</td>
<td>312.0</td>
</tr>
<tr>
<td>Cr</td>
<td>1.5 × 10^{-7}</td>
<td>Cr_2O_3</td>
<td>s</td>
<td>$\gamma = 0.01$ m=1.7×10^{-6}</td>
<td>34.3</td>
<td>-1882.3</td>
<td>s</td>
<td>584.7</td>
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</tr>
<tr>
<td>Cs</td>
<td>2.2 × 10^{-7}</td>
<td>Cs_2O</td>
<td>aq</td>
<td>$\gamma = 0.01$ m=2.3×10^{-6}</td>
<td>-282.2</td>
<td>s</td>
<td>404.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>8.7 × 10^{-7}</td>
<td>Cu_2O</td>
<td>aq</td>
<td>$\gamma = 0.2$ m=7.3×10^{-5}</td>
<td>-65.5</td>
<td>s</td>
<td>132.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1.4 × 10^{-8}</td>
<td>D_2</td>
<td>g</td>
<td>$p=3.45×10^{-4}$</td>
<td>31.2</td>
<td>-224.55</td>
<td>s, D$_g$</td>
<td>263.8</td>
<td></td>
</tr>
</tbody>
</table>

$\gamma$ = activity coefficient in seawater, m = molarity in seawater, p = %-vol, x = molar fraction

Standard Chemical Exergy of the Elements 2/5

<table>
<thead>
<tr>
<th>Chemical symbol</th>
<th>Concentration in Earth's crust $n_{\text{atm}}$ kmol/kg</th>
<th>Chemical formula</th>
<th>state</th>
<th>$c$, $\gamma$</th>
<th>$\rho$, $m$, $x$</th>
<th>Standard chem. exergy $h_A$ kJ</th>
<th>Free exergy of formation $\Delta G$ kJ/mol</th>
<th>State</th>
<th>Standard chem. exergy $h_A$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>22</td>
<td>23</td>
<td>24</td>
<td>25</td>
<td>26</td>
<td>27</td>
<td>28</td>
<td>29</td>
<td>30</td>
</tr>
<tr>
<td>Dy</td>
<td>1.8 × 10^{-8}</td>
<td>Dy(OH)_3</td>
<td>s</td>
<td>$\gamma = 0.02$ m=4.9×10^{-4}</td>
<td>41.7</td>
<td>-292.93</td>
<td>s, a</td>
<td>975.9</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>1.7 × 10^{-8}</td>
<td>Er(OH)_3</td>
<td>s</td>
<td>$\gamma = 0.002$ m=4.6×10^{-4}</td>
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<td>-1290.1</td>
<td>s</td>
<td>972.8</td>
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<tr>
<td>Eu</td>
<td>7.9 × 10^{-9}</td>
<td>Eu(OH)_3</td>
<td>s</td>
<td>$\gamma = 0.02$ m=2.1×10^{-4}</td>
<td>43.8</td>
<td>-1230.1</td>
<td>s</td>
<td>1003.8</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>3.3 × 10^{-5}</td>
<td>Fe(OH)_3</td>
<td>s</td>
<td>$\gamma = 0.01$ m=1.8×10^{-4}</td>
<td>26.6</td>
<td>-1280.5</td>
<td>s, III</td>
<td>504.9</td>
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</tr>
<tr>
<td>Fe</td>
<td>1.0 × 10^{-5}</td>
<td>Fe_2O_3</td>
<td>s</td>
<td>$\gamma = 0.01$ m=1×10^{-5}</td>
<td>12.14</td>
<td>-742.1</td>
<td>s, a</td>
<td>374.3</td>
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</tr>
<tr>
<td>Ga</td>
<td>2.2 × 10^{-7}</td>
<td>Ga_2O_3</td>
<td>s</td>
<td>$\gamma = 0.002$ m=3×10^{-7}</td>
<td>37.2</td>
<td>-996.5</td>
<td>s</td>
<td>514.9</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>3.4 × 10^{-8}</td>
<td>Ga(OH)_3</td>
<td>s</td>
<td>$\gamma = 0.002$ m=9.2×10^{-8}</td>
<td>40.2</td>
<td>-1288.9</td>
<td>s, a</td>
<td>969.0</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>1.4 × 10^{-8}</td>
<td>GeO_2</td>
<td>s</td>
<td>$\gamma = 0.005$ m=9.5×10^{-8}</td>
<td>40.1</td>
<td>-521.5</td>
<td>s</td>
<td>555.6</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>1.4 × 10^{-9}</td>
<td>H_2O</td>
<td>s</td>
<td>$p=0.22$</td>
<td>49.49</td>
<td>-228.59</td>
<td>s, a</td>
<td>236.09</td>
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</tr>
<tr>
<td>He</td>
<td>1.4 × 10^{-9}</td>
<td>He</td>
<td>g</td>
<td>$p=0.85×10^{-4}$</td>
<td>30.37</td>
<td>0</td>
<td>g</td>
<td>39.37</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>1.7 × 10^{-8}</td>
<td>HfO_2</td>
<td>s</td>
<td>$\gamma = 0.05$ m=1×10^{-5}</td>
<td>12.18</td>
<td>0</td>
<td>115.9</td>
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</tr>
<tr>
<td>Hg</td>
<td>4.0 × 10^{-10}</td>
<td>HgCl_2</td>
<td>s</td>
<td>$\gamma = 0.01$ m=3×10^{-10}</td>
<td>43.9</td>
<td>-1294.8</td>
<td>s, a</td>
<td>978.6</td>
<td></td>
</tr>
<tr>
<td>Ho</td>
<td>7.2 × 10^{-9}</td>
<td>Ho(OH)_3</td>
<td>s</td>
<td>$\gamma = 0.02$ m=1×10^{-9}</td>
<td>43.9</td>
<td>-1294.8</td>
<td>s, a</td>
<td>978.6</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>3.9 × 10^{-9}</td>
<td>I_2</td>
<td>aq</td>
<td>$\gamma = 0.6$ m=5×10^{-7}</td>
<td>48.7</td>
<td>-830.9</td>
<td>s</td>
<td>438.6</td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>8.7 × 10^{-10}</td>
<td>In_2O_3</td>
<td>s</td>
<td>$\gamma = 0.005$ m=2×10^{-9}</td>
<td>75.1</td>
<td>-185.6</td>
<td>s</td>
<td>256.7</td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>1.04 × 10^{-11}</td>
<td>IrO_2</td>
<td>s</td>
<td>$\gamma = 0.005$ m=3×10^{-12}</td>
<td>75.1</td>
<td>-185.6</td>
<td>s</td>
<td>256.7</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>5.4 × 10^{-8}</td>
<td>K</td>
<td>aq</td>
<td>$\gamma = 0.64$ m=1×10^{-7}</td>
<td>282.4</td>
<td>0</td>
<td>366.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kr</td>
<td>2.2 × 10^{-7}</td>
<td>Kr</td>
<td>g</td>
<td>$p=9.7×10^{-10}$</td>
<td>34.39</td>
<td>0</td>
<td>34.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>2.2 × 10^{-7}</td>
<td>La(OH)_3</td>
<td>s</td>
<td>$\gamma = 0.02$ m=6×10^{-7}</td>
<td>35.5</td>
<td>-1319.2</td>
<td>s, a</td>
<td>994.6</td>
<td></td>
</tr>
</tbody>
</table>
Standard Chemical Exergy of the Elements 3/5

Table 2.2: Standard chemical exergies of the elements (continued)

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>Reference species</th>
<th>Standard chem. exergy $b_a$ kJ/mmol</th>
<th>Free exergy of formation $\Delta_f G$ kJ/mol</th>
<th>Chemical element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source: S05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

11 jan 15

Standard Chemical Exergy of the Elements 4/5

Table 2.2: Standard chemical exergies of the elements (continued)

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>Reference species</th>
<th>Standard chem. exergy $b_a$ kJ/mmol</th>
<th>Free exergy of formation $\Delta_f G$ kJ/mol</th>
<th>Chemical element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source: S05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Standard Chemical Exergy of the Elements 5/5

Remember the meaning of chemical exergy: it gives the maximum amount of work that can be made available from a mole of the species in a given environmental surroundings.

Standard exergies for solids based on reference species dissolved in seawater

Source: S05
Chemical Exergies of Fuels

Ratio of the standard chemical exergy to the lower and higher heating value for several hydrocarbon fuels \((H_L = LHV; H_H = HHV)\)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>(b_{ch}/H_L)</th>
<th>(b_{ch}/H_H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard coal</td>
<td>1.09</td>
<td>1.03</td>
</tr>
<tr>
<td>Lignite</td>
<td>1.17</td>
<td>1.04</td>
</tr>
<tr>
<td>Coke</td>
<td>1.06</td>
<td>1.04</td>
</tr>
<tr>
<td>Wood</td>
<td>1.15</td>
<td>1.05</td>
</tr>
<tr>
<td>Liquid HC-fuels</td>
<td>1.07</td>
<td>0.99</td>
</tr>
<tr>
<td>Natural gas (high CH₄)</td>
<td>1.04</td>
<td>0.94</td>
</tr>
<tr>
<td>Coke-oven gas</td>
<td>1.00</td>
<td>0.85</td>
</tr>
<tr>
<td>Blast-furnace gas</td>
<td>0.98</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Source: S05

Example: Standard Chemical Exergy

- Calculate the standard chemical exergy of larnite, \(Ca_2SiO_4\), for which the energy of formation is \(-\Delta_f G^\circ = 2191.6\) kJ/mol.

\[
b_{\text{chem}} = -2191.6 + 2 \times b_{\text{chem,elCa}} + 2 \times b_{\text{chem,elO}_2} + b_{\text{chem,elSi}}
\]

\[
= -2191.6 + 2 \times 729.1 + 2 \times 3.97 + 854.9 = 129.4 \text{ kJ/mol}
\]

- Tableised data in S05 give \(b_{\text{chem}} = 95.7\) kJ/mol .......

(mixing exergy cannot explain this)
Example: Mineral Carbonation /1

1. \( x\text{MgO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O} (s) + (x-z)\text{H}_2\text{O} \leftrightarrow \ldots \rightarrow x\text{Mg(OH)}_2 (s) + y\text{SiO}_2 (s) \)
2. \( \text{Mg(OH)}_2 (s) + \text{CO}_2 \leftrightarrow \text{MgCO}_3 (s) + \text{H}_2\text{O} \)

- Chemical exergies of the chemical species are calculated using \( e_{\text{chem}}(T, p) = e^o_{\text{chem}} + \Delta e_{\text{chem}} (T^o, p^o \rightarrow T, p) \) where \( \Delta e_{\text{chem}}(T^o, p^o \rightarrow T, p) = \Delta h(T^o, p^o \rightarrow T, p) - T^o \Delta s(T^o, p^o \rightarrow T, p) \)

For liquids and solids: \( \Delta e_{\text{chem}}(T^o, p^o \rightarrow T, p) = \Delta e_{\text{chem}}(T^o \rightarrow T) - T^o \Delta s(T^o \rightarrow T) \) and \( e_{\text{chem}}(T, p) = e_{\text{chem}}(T) \)

- Standard exergies of formation are calculated using:

\[
e^o_{\text{chem}} = \Delta_f G^o + \sum_{\text{elements}} n_{\text{element}} \times e^o_{\text{chem, element}}
\]

where \( n_{\text{element}} \) is the number of moles of the element in a mole of a certain compound, and \( e^o_{\text{chem, element}} \) from Tables

Example: Mineral Carbonation /2

- The exergy of \( \text{CO}_2 \) as a function of temperature and pressure can be calculated, with \( h = h(T) \) and \( s = s(T) \) (for ideal gas) as

\[
e_{\text{Chem,CO}_2}(p, T) = e^o_{\text{Chem,CO}_2} + (h(T) - h^o) - T^o \cdot (s(T) - s^o) + RT^o \cdot \ln(p/p^o)
\]

using a reference concentration of 0.0375 %-vol of \( \text{CO}_2 \) in the dry atmosphere \( (p^o = 0.000375 \cdot p^o)^* \).

- \( R = 8.314 \text{ J/(mol·K)}, T^o = 298.15 \text{ K}, p^o = 101.325 \text{ kPa}. \)

- For all compounds “reaction exergies” can be calculated as exergy differences between reactant and product exergies

- With entropy difference \( \Delta S(T) \) for the carbonation reaction at temperature \( T \), the irreversibility or exergy loss is defined as

\[
\Delta E_{\text{Ex,loss}}(T) = -\Delta E_x(T) = T^o \cdot \Delta S(T)
\]

* In 2014, atmospheric \( \text{CO}_2 \) concentration has risen to 0.0397 %-vol
Example: Mineral Carbonation /3

<table>
<thead>
<tr>
<th>Element</th>
<th>Standard chemical exergy (kJ/mol) (Kotas 1995)</th>
<th>Standard chemical exergy (kJ/mol) (Szargut et al. 1988)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>626.71</td>
<td>633.8</td>
</tr>
<tr>
<td>O₂</td>
<td>3.97</td>
<td>3.97</td>
</tr>
<tr>
<td>Si</td>
<td>803.01</td>
<td>854.60</td>
</tr>
<tr>
<td>H₂</td>
<td>238.49</td>
<td>236.09</td>
</tr>
<tr>
<td>C</td>
<td>410.82</td>
<td>410.26</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calculated results using data from SMS88 and K95</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>59.78</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>35.55</td>
</tr>
<tr>
<td>Mg₃SiO₄</td>
<td>6.49</td>
</tr>
<tr>
<td>Mg₂SiO₄(OH)₄</td>
<td>-56.97</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>31.30</td>
</tr>
<tr>
<td>SiO₂</td>
<td>-49.46</td>
</tr>
</tbody>
</table>

Calculated results using data from SMS88 and K95 taken from ZK04

Table II: Standard Gibbs Energy of Formation of Relevant Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Standard Gibbs energy of formation (ΔG°) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>-568.94</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>-833.62</td>
</tr>
<tr>
<td>Mg₃SiO₄</td>
<td>-2057.88</td>
</tr>
<tr>
<td>Mg₂SiO₄(OH)₄</td>
<td>-4037.96</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>-1113.28</td>
</tr>
<tr>
<td>SiO₂</td>
<td>-856.44</td>
</tr>
</tbody>
</table>

Table III: Standard Reference Exergies of Some Relevant Compounds as Given by Kotas (1995) and Szargut et al. (1988)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Standard chemical exergy (kJ/mol) (Kotas 1995)</th>
<th>Standard chemical exergy (kJ/mol) (Szargut et al. 1988)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>59.17</td>
<td>66.8</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>33.83</td>
<td>40.9</td>
</tr>
<tr>
<td>Mg₃SiO₄</td>
<td>140.77</td>
<td>74.9</td>
</tr>
<tr>
<td>Mg₂SiO₄(OH)₄</td>
<td>no data</td>
<td>61.3 (crosite)</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>13.7</td>
<td>37.9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.86</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Example: Mineral Carbonation /4

Irreversibility of the reaction of CO₂ with several MgO-containing species, per mol CO₂ (1 bar)

Chemical exergies of MgO, Mg(OH)₂, Mg₃SiO₄, Mg₂SiO₄(OH)₄ and MgCO₃, per mol Mg.

taken from ZK04
1.9 Simplified Exergy Analysis With Chemical Reactions

Simplified Process Analysis /1

Exergy optimisation of processes with many heat streams (in / out), giving an overall excess output:

\[ \sum_j \text{Ex}(Q_{out,j}) - \sum_i \text{Ex}(Q_{in,i}) = \max, \ \text{with} \ \text{Ex}(Q) = (1 - \frac{T_0}{T})Q \]

- From this it can be assessed if \( \sum Q_{out,j} - \sum Q_{in,j} > 0 \) indeed gives an exergy output (or if <0 : minimal losses...)
- For processes with chemical conversions (if exotherm, \( \Delta H < 0 \) \( \rightarrow Q_{out} > 0 \), if endotherm \( \Delta H > 0 \) \( \rightarrow Q_{in} > 0 \)), these typically will give the largest exergy losses due to entropy changes \( \Delta S \) \( \rightarrow \Delta \text{Ex}_{\text{loss}} = T^0 \cdot \Delta S, \ or = T^0 \cdot \sum \Delta S_i \)
- The optimisation becomes, for a process with \( k \) chemical conversion steps:
  and calculate the values for \( \Delta S_k \) and from that \( \Delta \text{Ex}_{\text{loss}} \),

\[ \sum_k \left( 1 - \frac{T^*}{T_k} \right) (-\Delta H_k) = \max \]
Simplified Process Analysis /2

- This is very effective for finding the optimum temperature combinations for a process with several reactions/reactors at different temperatures.
- **Example**: the ÅA route for serpentinite carbonation

1. **Magnesium extraction** solid/solid ~ 400-450°C
   - \( \text{Mg}_2\text{Si}_2\text{O}_5\text{(OH)}_4 + 3(\text{NH}_4)\text{SO}_4 + \text{heat} \leftrightarrow 3\text{MgSO}_4 + 2\text{SiO}_2 + 5\text{H}_2\text{O}(g) + 6\text{NH}_3(g) \)

2. **Mg(OH)\text{2} production** aqueous solution
   - \( \text{MgSO}_4 + 2\text{NH}_4\text{OH(aq)} \leftrightarrow (\text{NH}_4)_2\text{SO}_4(aq) + \text{Mg(OH)}_2 \)

3. **Mg(OH)\text{2} carbonation** gas/solid, 20-30 bar, ~500°C
   - \( \text{Mg(OH)}_2(s) + \text{CO}_2(g) \leftrightarrow \text{MgCO}_3(s) + \text{H}_2\text{O}(g) + \text{heat} \)

---

Simplified Process Analysis /3

- **Example**: the ÅA route for serpentinite carbonation

**Grassman diagram**

**Exergy consumption**

- 5.54 GJ (~1.5 MWh)/ton CO\text{2}
Simplified Process Analysis /4

- Another approach: various temperatures and electrolysis.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>T (°C)</th>
<th>ΔH (kJ/mol)</th>
<th>ΔG (kJ/mol)</th>
<th>ΔEx (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1: $2\text{Mg}_2\text{Si}_2\text{O}_5\text{(OH)}_4 \rightarrow 3\text{Mg}_2\text{Si}_2\text{O}_5 + 4\text{H}_2\text{O}$</td>
<td>650</td>
<td>279.411</td>
<td>-248.034</td>
<td>267.3</td>
</tr>
<tr>
<td>R2: $2\text{NaCl(aq)} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH(aq)} + \text{Cl}_2(g) + \text{H}_2(g)$</td>
<td>85</td>
<td>426.608</td>
<td>412.834</td>
<td>423.2</td>
</tr>
<tr>
<td>R3: $\text{Cl}_2(g) + \text{H}_2(g) \rightarrow 2\text{HCl(aq)}$</td>
<td>25</td>
<td>-351.935</td>
<td>-254.468</td>
<td>-263.4</td>
</tr>
<tr>
<td>R4: $4\text{HCl(aq)} + \text{Mg}_2\text{Si}_2\text{O}_5 \rightarrow 2\text{MgCl}_2\text{(aq)} + 2\text{SiO}_2 + 2\text{H}_2\text{O}$ or $6\text{HCl(aq)} + \text{Mg}_2\text{Si}_2\text{O}_5\text{(OH)}_4 \rightarrow 3\text{MgCl}_2\text{(aq)} + 2\text{SiO}_2 + 5\text{H}_2\text{O}$</td>
<td>70</td>
<td>-236.137</td>
<td>-195.95</td>
<td>-15.0</td>
</tr>
<tr>
<td>R5: $\text{CO}_2(g) + \text{NaOH(aq)} \rightarrow \text{NaHCO}_3\text{(aq)}$</td>
<td>25</td>
<td>-68.865</td>
<td>-36.586</td>
<td>0.4</td>
</tr>
<tr>
<td>R6: $5\text{MgCl}_2\text{(aq)} + 10\text{NaHCO}_3\text{(aq)} \rightarrow \text{Mg}_5\text{(OH)}_2\text{(CO}_3\text{)}_4\cdot 4\text{H}_2\text{O} + 10\text{NaCl(aq)} + 6\text{CO}_2(g)$</td>
<td>55</td>
<td>488.753</td>
<td>-104.527</td>
<td>-6.7</td>
</tr>
</tbody>
</table>
Process Integration, Pinch /1

- Process integration deals primarily with process energy and efficient design of heat exchanger networks (HENs)
- Important for the system is the so-called pinch point; heat should not be "transferred across the pinch"
- Combining the hot streams and cold streams of a system into two composite curves (temperature versus enthalpy) shows the minimum temperature: the pinch
- The pinch divides the system in two "regions"

Example process with two hot streams to be cooled and two cold streams to be heated up.

\[ CP = \text{stream heat capacity} = \dot{m} \cdot c_p \ (W/°C) \]

with \( c_p \) averaged between \( T_{in} \) and \( T_{out} \)

Picture: CR93

---

Process Integration, Pinch /2

\[ \Delta T_{\text{min}} = 10 \text{ K} \]

↑ Hot stream temperatures versus enthalpy

For the example on previous slide

↑ Grid for the four-stream network

Proposed heat exchanger network for \( \Delta T_{\text{min}} = 10 \text{ K} \)

Pictures: CR93
Exergy Analysis vs. Pinch Analysis

- It has been argued by Linnhoff (1987) that pinch analysis is superior to exergy analysis.
- A study (1991) on the process integration of a new nitric acid plant, however, showed that exergy analysis allowed for energy savings 3× higher than what pinch analysis suggested.
- Note, however, that pinch analysis is limited to heat exchanger network (HEN) optimisation, and then with certain restrictions, such as
  - so-called threshold problems (no pinch!)
  - integrating with heat pumps (where heat is transported to higher temperatures)

Source: S08

1.11 Final Remarks
Common-sense 2nd Law Guidelines

1. Do not use excessively large or excessively small thermodynamic driving forces in process operations.
2. Minimize the mixing of streams with differences in temperature, pressure or chemical composition.
3. Do not discard heat at high temperatures to the ambient, or to cooling water.
4. Do not heat refrigerated streams with hot streams or with cooling water.
5. When choosing streams for heat exchange, try to match streams where the final temperature of one is close to the initial temperature of the other.
6. When exchanging heat between two streams, the exchange is more efficient if the flow heat capacities of the streams are similar. If there is a big difference between the two, consider splitting the stream with the larger flow heat capacity.
7. Minimize the use of intermediate heat transfer fluids when exchanging heat between two streams.
8. Heat (or refrigeration) is more valuable, the further its temperature is from the ambient.
9. The economic optimal ΔT at a heat exchanger decreases as the temperature decreases, and vice versa,
10. Minimize the throttling of steam, or other gases.
11. The larger the mass flow, the larger the opportunity to save (or to waste) energy.
12. Use simplified exergy (or availability) consumption calculations as a guide to process modifications.
13. Some second law inefficiencies cannot be avoided; others can. Concentrate on those which can.

Taken from: Sama, 2008 (S08)

Closing Remarks

- The First and Second laws of thermodynamics as formulated by Baehr (B88):
  - 1. The sum of anergy and exergy is always constant
  - 2. Anergy can never be converted into exergy

- “Accepting exergy losses should always have some economic justification. If such a justification does not exist, it indicates that the exergy loss results only from an error in the art of engineering” (S05)
Sources


K41: Keenan, J.H. Thermodynamics, MIT press (1941) Chapter 17


P03: Petela, R. "Exergy of undiluted thermal radiation” Solar energy 74 (2003) 469-488


VL77: Van Lier, J.J.C. Thermodynamic processes in the power plant and possibilities to improve these processes, (in Dutch) course compendium Delft Univ. of Technol., Delft (1977)


Sources (cont’d)