Introduction to "Exergy"

2.83/2.813

T. G. Gutowski

2008

Readings and Handouts

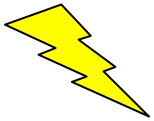
1. Ch.2 “Thermodynamics Revisited” Jakob de Swaan Arons
2. Ch.10 “Exergy” Norio Sato
3. Appendix, tables of standard chemical exergy, Szargut
4. Derivation of Mixing Entropy

Why available work?

1. rigorous framework
2. based on 2nd law (lost Vs transformed)
3. can account for materials energy potential (credit)
4. allows combined accounting of fuel and non-fuel materials
5. other advantages when dealing with waste heat (quality of waste heat)

Outline

- Thermodynamics Review
- Exergy & Exergy Accounting
- Physical Exergy
  - hot & cold water mixing
- Chemical Exergy
  - chemical reactions; burning carbon, and oxidizing aluminum
  - iron ore processing
- 5 Homeworks



Energy from 1st Law

- U = internal energy of molecules and atoms

- E = U + K.E. + P.E. = $U + \frac{1}{2}mv^2 + mgz$
- "isolated" systems $\Delta E=0$, or $\Delta U=0$ (v=const, z=const)
- "closed" system $\Delta U = Q_{in} - W_{out}$
- "open system" can exchange energy and mass

The 1st Law

$$\Delta U = Q_{in} - W_{out}$$

$$dU = \delta Q_{in} - \delta W_{out}$$

$$\oint dQ - \oint dW = 0$$

Availability

"The First Law states that in every cyclic process either work is converted into heat or heat is converted into work. In this sense it makes no distinction between work and heat except to indicate a means of measuring each in terms of equivalent units. Once this technique of measurement is established, work and heat become entirely equivalent for all applications of the First Law."

Keenan, 1941

Availability

- “The Second Law, on the other hand, marks the distinction between these two quantities by stating that heat from a single source whose temperature is uniform cannot be completely converted into work in any cyclic process, whereas work from a single source can always be completely converted into heat.”

Keenan, 1941

Availability

“The efforts of the engineer are very largely directed toward the control of processes so as to produce the maximum amount of work, or so as to consume the minimum amount of it. The success of these efforts can be measured by comparing the amount of work produced in a given process with the maximum possible amount of work that could be produced in the course of a *change of state* identical with that which occurs in the process.”

Keenan, 1941

State Variables

$$\oint dU = 0$$

$$\int_1^2 d\phi = \phi_2 - \phi_1$$

$$\oint \frac{dQ}{T} = 0$$

$$\oint d(U + PV) = 0$$

State Variables

- T = temperature
- P = pressure

intensive variables

- V = volume
- U = internal energy
- H = enthalpy (H = U + PV)
- S = entropy

extensive
and
intensive
variables

Enthalpy $H=U+PV$

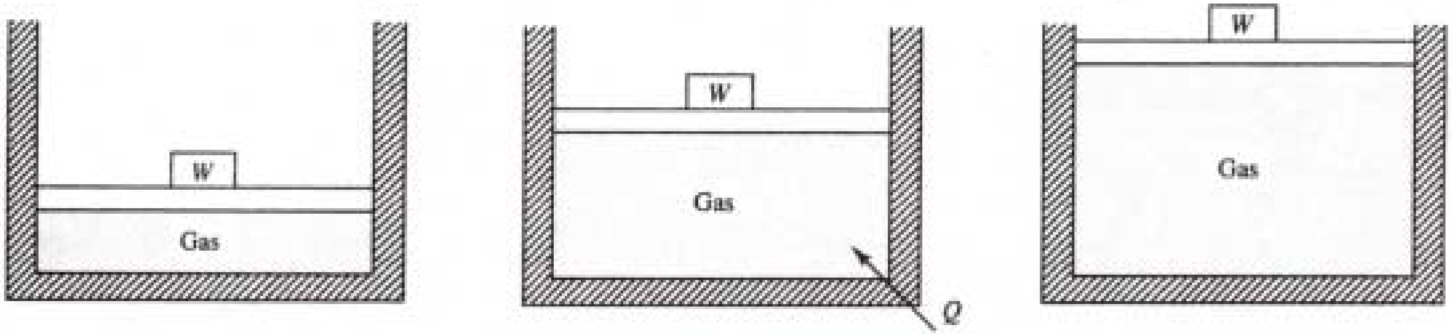


Fig. 4-4 Constant-Pressure Heat Addition

Here the Work done is $W = P(V_2 - V_1)$

The First Law can be written as $Q = (U+PV)_2 - (U + PV)_1$

The quantity in parenthesis is Enthalpy $H = U + PV$

The First Law can be written as $Q_{in} = \Delta H$

Constant Pressure Equilibrium Process

Open flow system

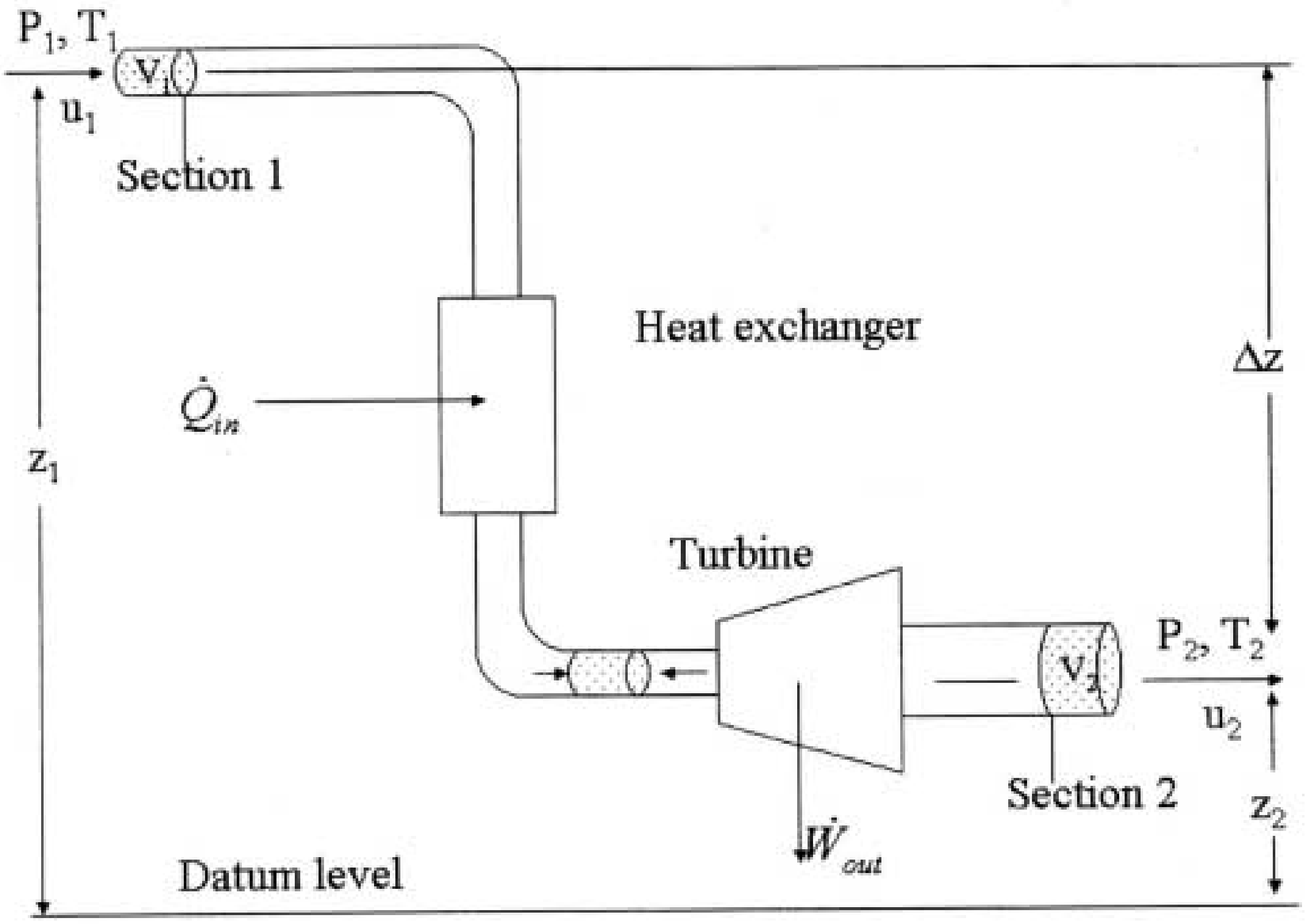


Figure 1 Changes in steady-state flow.

Energy Balance for an Open System

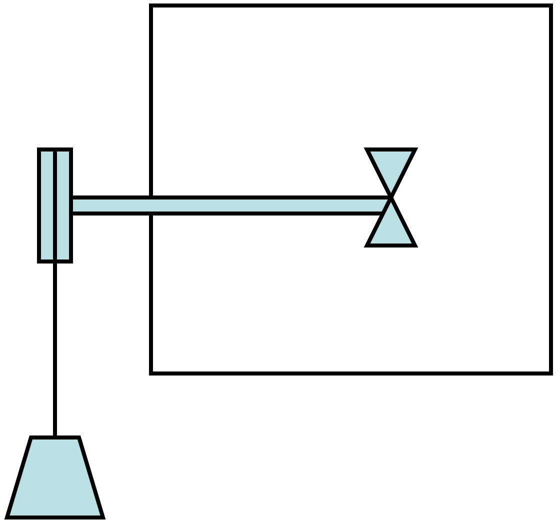
$$\cancel{\left(\frac{dU}{dt}\right)_{cv}} = \sum_{in} \dot{m}_i \left(h_i + \cancel{\frac{u_i^2}{2}} + \cancel{gz_i} \right)$$

$$-\sum_{out} \dot{m}_j \left(h_j + \cancel{\frac{u_i^2}{2}} + \cancel{gz_j} \right)$$

$$+\sum \dot{Q}_{in} - \sum \dot{Q}_{out} + \sum \dot{W}_{sh,in} - \sum \dot{W}_{sh,out}$$

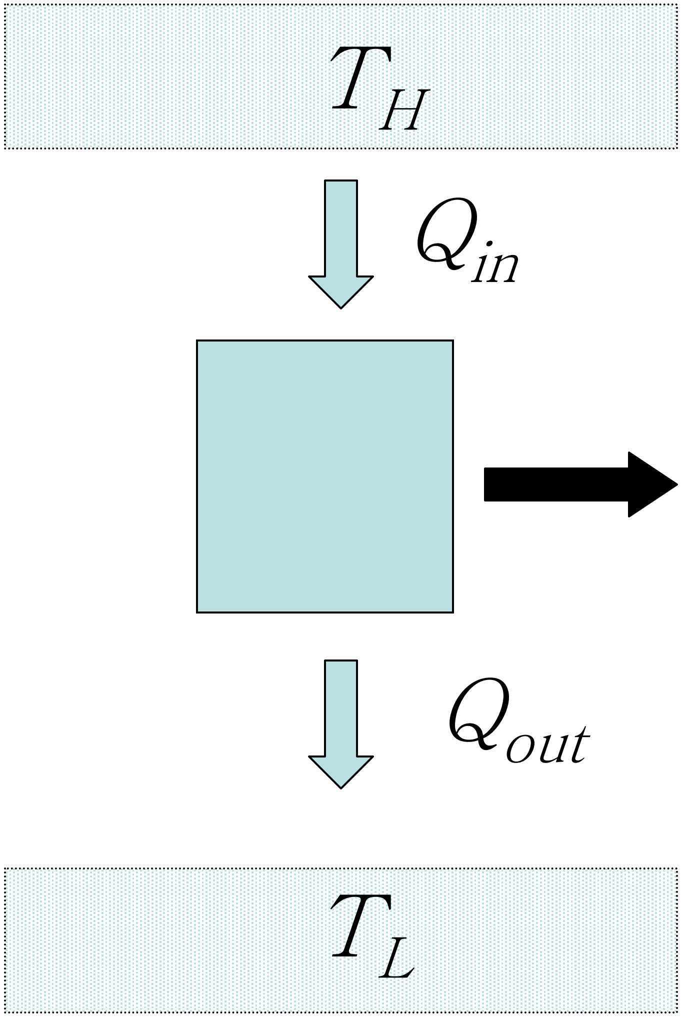
Eq 1

The Second Law



- ΔW and ΔQ are not equivalent
- something gets lost

Heat Engine



$$W_{out} = Q_{in} - Q_{out}$$

$$\eta = \frac{W_{out}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}}$$

The Second Law

$$\eta = \frac{W_{out}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}}$$

$$\frac{Q_{in}}{T_H} = \frac{Q_{out}}{T_L}$$

$$\oint \frac{dQ}{T} = \frac{Q_{in}}{T_H} - \frac{Q_{out}}{T_L} = 0$$

$$\eta = \frac{T_H - T_L}{T_H}$$

Entropy: State Variable

$$dS = \frac{dQ}{T}$$

$$\oint dS = 0$$

Reversible process

$$\oint dS \geq 0$$

Real process

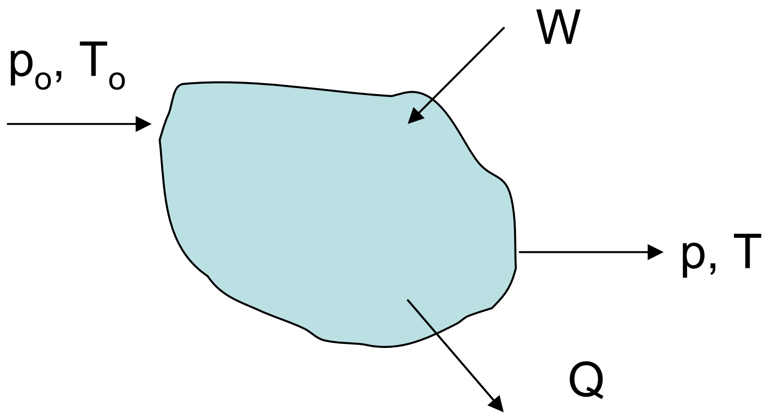
Entropy Balance for an Open System

$$\cancel{\left(\frac{dS}{dt}\right)}_{cv} = \sum_{in} \dot{m}_i S_i - \sum_{out} \dot{m}_j S_j$$

$$+ \sum_{in} \frac{Q_k}{T_k} - \sum_{out} \frac{Q_l}{T_l} + \dot{S}_{generated}$$

Eq 2

Consider the Work



…to bring the system from the reference environment at standard conditions, *T_o, p_o to the state at T, p*

From EQ 1 & 2

$$\dot{m}\left(\Delta H + \frac{\Delta u^2}{2} + g\Delta z\right) - \dot{Q}_{out} + \dot{W}_{in} = 0$$

$$\dot{m}\Delta S - \frac{\dot{Q}_{out}}{T_o} + \dot{S}_{generated} = 0$$

$$\boxed{\dot{\mathrm{W}} = \dot{m}\left(\Delta H + \frac{\Delta u^2}{2} + g\Delta z\right) - \dot{m}T_o\Delta S + T_o\dot{S}_{generated}}$$

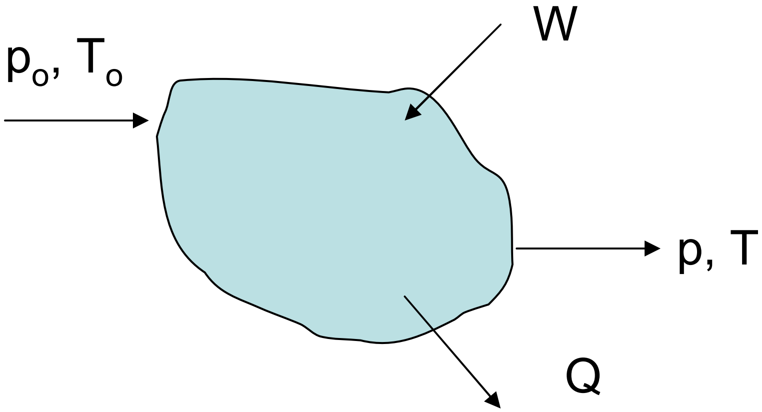
Work to bring system from P_o, T_o to P, T

Minimum Work

$$W_{\min} = \frac{\dot{W}_{rev}}{\dot{m}} = \Delta H - T_o \Delta S$$

$$= (H_{p,T} - H_{p_o,T_o}) - T_o (S_{p,T} - S_{p_o,T_o})$$

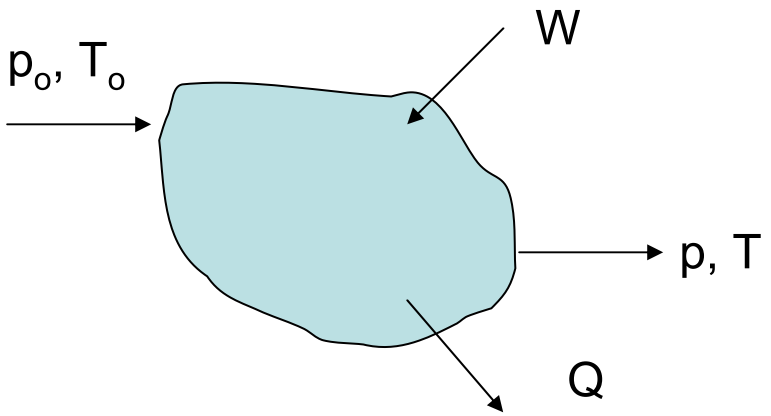
Minimum work to bring system from p_o, T_o to p, T



where (for u=0, z=0):

Exergy is…

$$b \equiv \frac{\dot{W}_{\min}}{\dot{m}} = w_{\min}$$

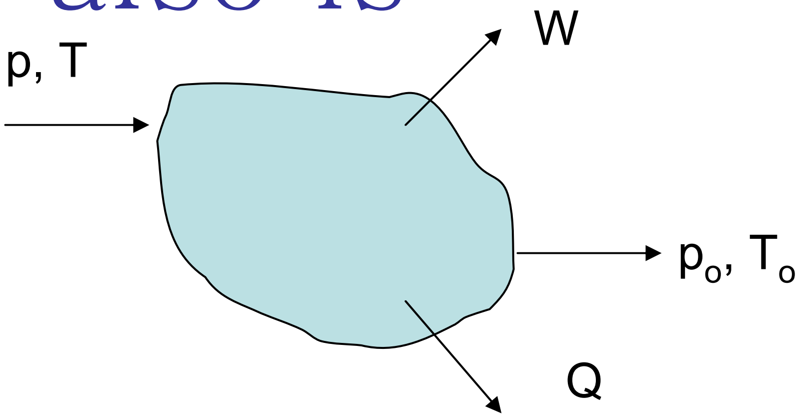


$$B = (H - T_o S) - (H - T_o S)_o$$

This is the minimum amount of work to bring the system from the reference environment at standard conditions, *T_o, p_o to the state at T, p*

Standard ref. values $T_0 = 298.2^\circ K, P_o = 101.3 kPa$

Exergy also is …



$$b \equiv \frac{\dot{W}_{\max}}{\dot{m}} = w_{\max}$$

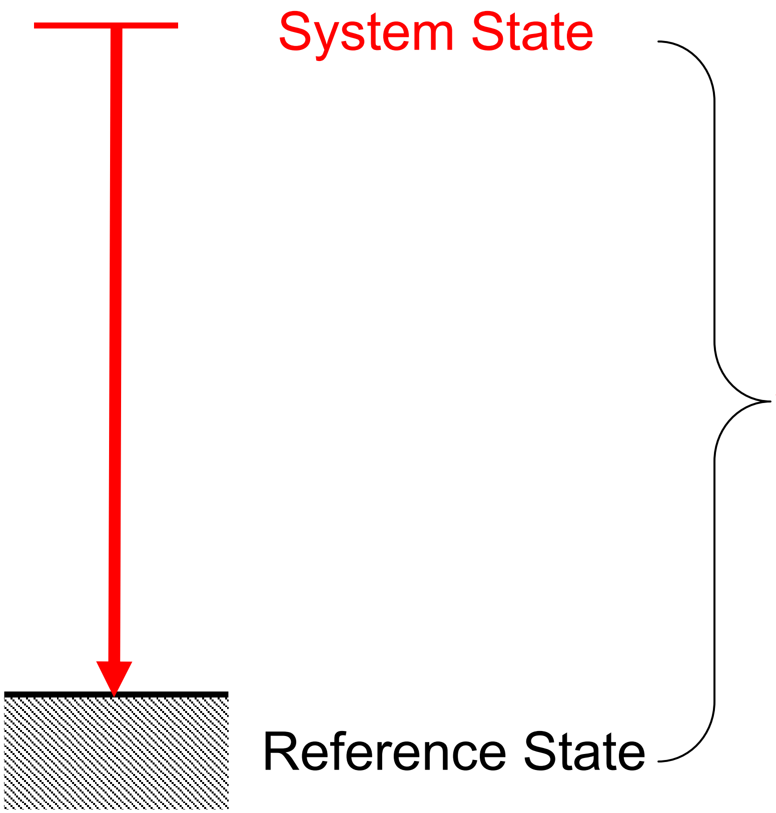
$$B = (H - T_o S) - (H - T_o S)_o$$

… the maximum amount of work that can be obtained from a system in reference to the environment at standard conditions, T_o, P_o

Standard ref. values $T_0 = 298.2^\circ K, P_o = 101.3 kPa$

See if you can derive this as a homework problem

Exergy

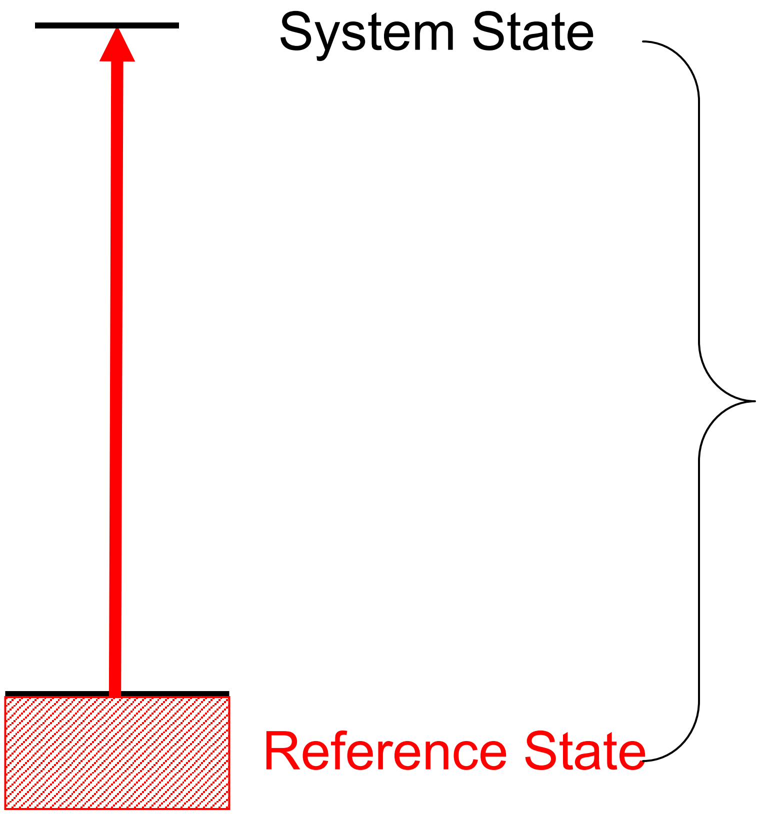


System State

Maximum work obtainable between System and Reference States.

Reference State

Exergy

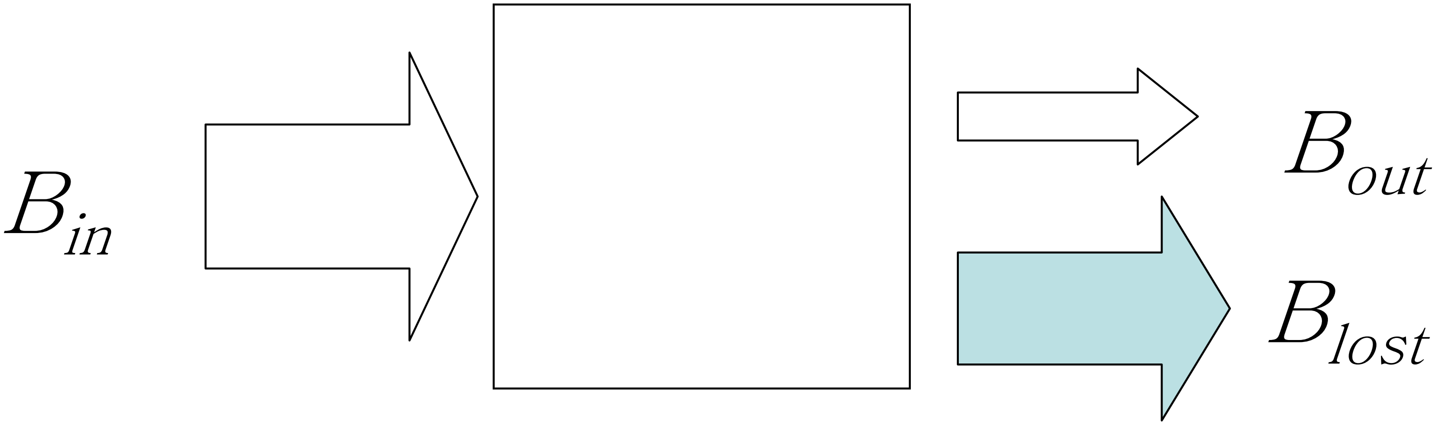


Maximum work obtainable between System and Reference States; or minimum work needed to raise System from the reference state to the System State

Definition of Exergy “B”

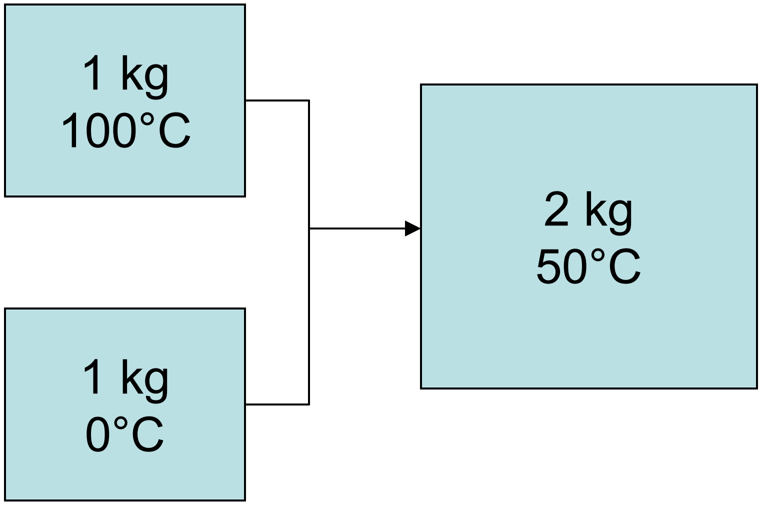
“Exergy is the amount of work obtainable when some matter is brought to a state of thermodynamic equilibrium with the common components of the natural surroundings by means of reversible processes, involving interaction only with the above mentioned components of nature” [Szargut et al 1988].

Exergy Accounting



$$B_{in} - B_{out} = B_{lost}$$

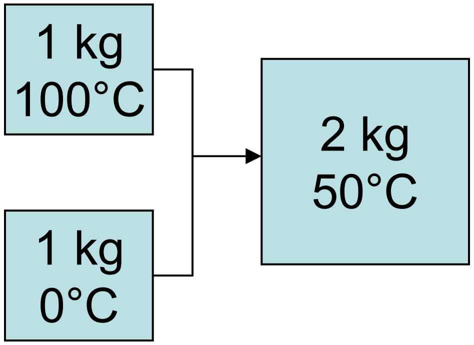
Example: mixing hot and cold water



1st Law: $H_1 + H_2 = H_3$

recall; $\Delta H = \int m\, C_p\, \Delta T$

Example: mixing hot and cold water



1 kg
100°C

1 kg
0°C

2 kg
50°C

To calculate the 2nd law property;

$\Delta B = \Delta H - T_o \Delta S$

$T_{ref} = 25°C$

Pressure = constant

We need to know the temperature dependence of enthalpy and entropy

temperature and pressure dependence of H and S

$$dH = c_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p \right] dP$$

$$dS = \frac{c_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_p dP$$

for constant pressure

$$dH = c_p dT + \cancel{\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]} dP$$

$$dS = \frac{c_p}{T} dT - \cancel{\left(\frac{\partial V}{\partial T}\right)_p} dP$$

calculating ΔH-T_0ΔS

$$H_1 - T_o S_1 = C_p(75) - 298.2C_p \ln\frac{373.2}{298.2} = 8.1C_p$$

$$H_2 - T_o S_2 = C_p(-25) - 298.2C_p \ln\frac{273.2}{298.2} = 1.1C_p$$

$$H_3 - T_o S_3 = 2C_p(25) - 2x298.2C_p \ln\frac{323.2}{298.2} = 2C_p$$

$B_{in} – B_{out} = B_{lost}$

$$B_{lost} = \left(H_2 - T_o S_2\right) + \left(H_1 - T_o S_1\right) - \left(H_3 - T_o S_3\right)$$

$$B_{lost} = \left(8.1 + 1.1 - 2\right) C_p = 7.2 C_p$$

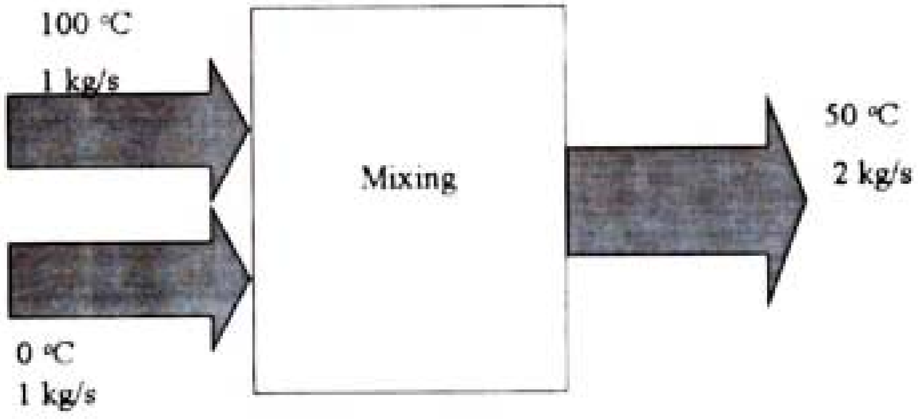


Figure 2 Flow diagram for the mixing of a hot and a cold stream.

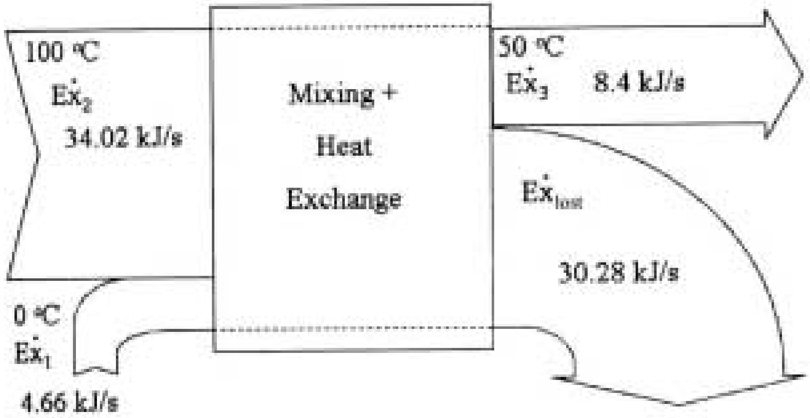


Figure 3 Exergy flow diagram or Grassmann diagram for the example of Fig. 2.

Ref Sussmann ‘80 and de Swaan Arons ‘04

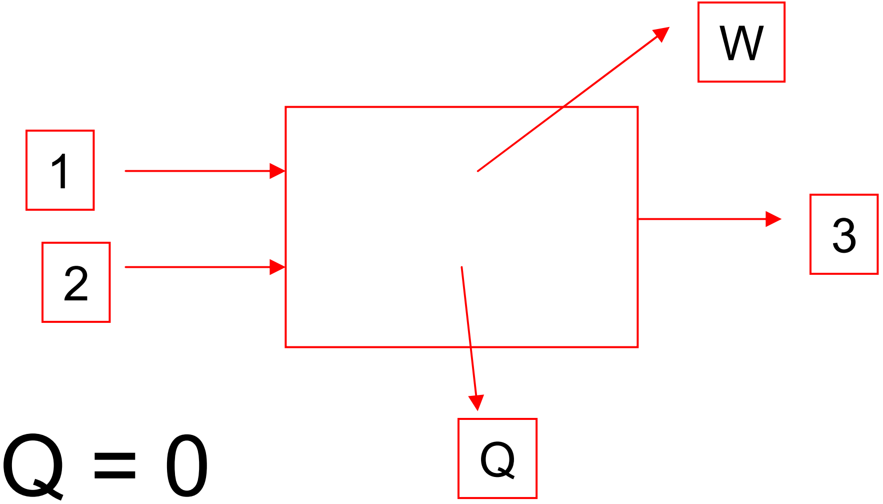
Physical and Chemical Exergy

- $B = B^{ph} + B^{ch}$
- $B^{ph}(T=T_o, p=p_o) = 0$
  - – this is the "restricted dead state"

- $B^{ch}(\mu=\mu_o) = 0$
- when $B = B^{ph} + B^{ch} = 0$
  - – this is the "dead state"

Chemical Reaction

$$n_1 R_1 + n_2 R_2 \rightarrow n_3 \Pi_3$$



- $H_1 + H_2 - H_3 - W - Q = 0$
- $S_1 + S_2 - S_3 - Q/T + S_{gen} = 0$

$\mu = h - T\,s, \quad \Delta G°_f = n_3\mu_3 - n_1\mu_1 - n_2\,\mu_2$

$$W = -\,\Delta G°_f - TS_{gen}$$

$W_{ideal} = -\,\Delta G°_f = B_1 + B_2 - B_3$

Chemical Reactions

stoichiometric mass balance

$$v_a R_a + v_b R_b + ... \rightarrow v_j \Pi_j + v_k \Pi_k + ...$$

exergy "balance"

$$v_a b_{R_a} + v_b b_{R_b} + ... - v_j b_{\Pi_j} - v_k b_{\Pi_k} = B_{lost}$$

where exergy b is given in kJ/mole

Example: Burning Carbon

$$C \quad + \quad O_2 \rightarrow CO_2$$

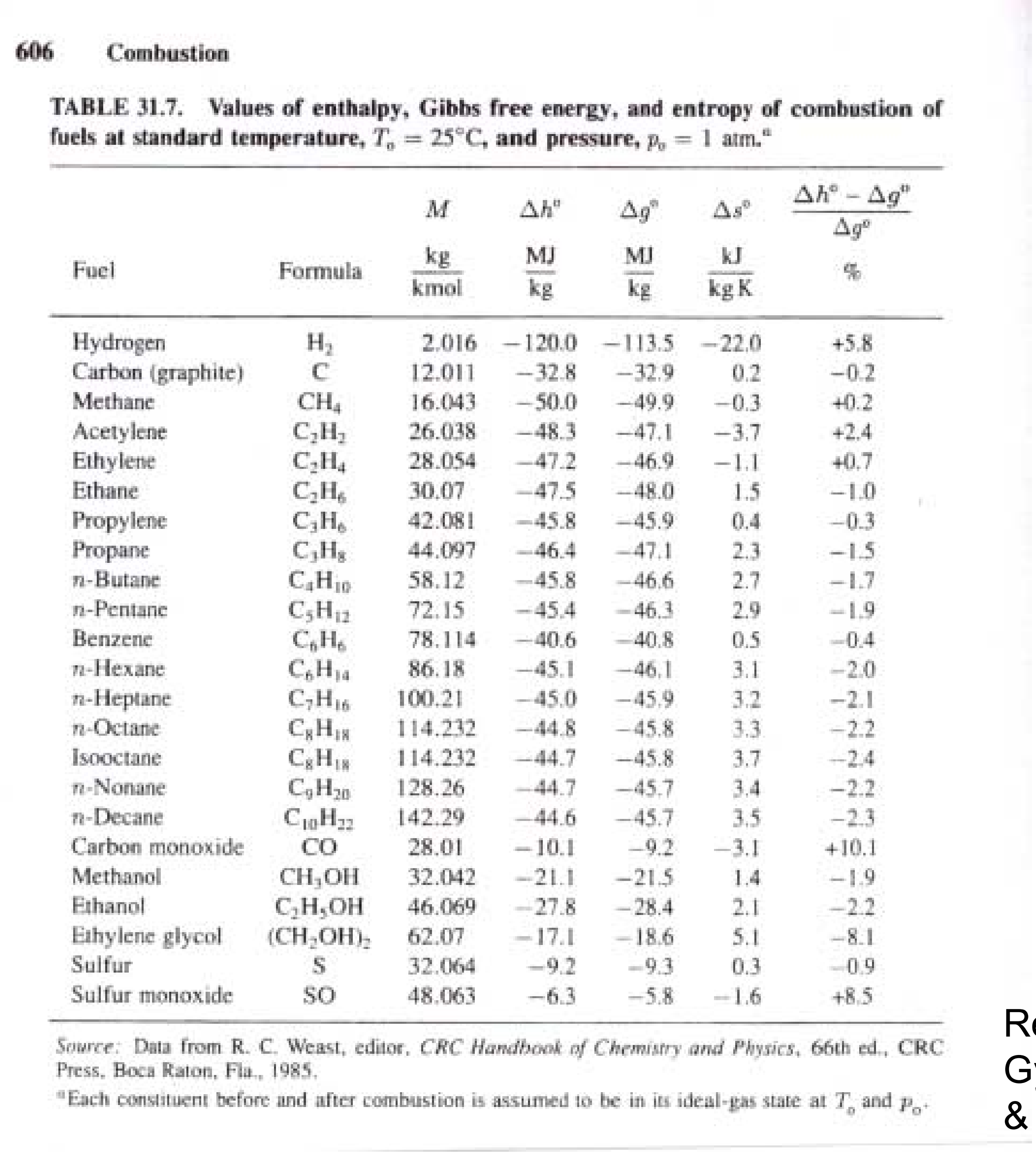
$$B_C \quad + \quad B_{O2} \quad - \quad B_{CO_2} \quad = \quad \Delta B$$

$$410.3\ \frac{kJ}{mole} + 3.97\ \frac{kJ}{mole} - 19.9\ \frac{kJ}{mole} = 394.4 kJ$$

The maximum work you can get out of one mole of carbon is

$$\frac{394.4\ kJ}{\text{mole of carbon}} = 32.9\ \frac{MJ}{kg}$$

Note that $\Delta g° \approx \Delta h°$
(lower heating value) for fuels



606 Combustion

TABLE 31.7. Values of enthalpy, Gibbs free energy, and entropy of combustion of fuels at standard temperature, $T_o = 25°C$, and pressure, $p_o = 1$ atm.[a]

Fuel	Formula	M $\frac{\text{kg}}{\text{kmol}}$	$\Delta h°$ $\frac{\text{MJ}}{\text{kg}}$	$\Delta g°$ $\frac{\text{MJ}}{\text{kg}}$	$\Delta s°$ $\frac{\text{kJ}}{\text{kg K}}$	$\frac{\Delta h° - \Delta g°}{\Delta g°}$ %
Hydrogen	H_2	2.016	−120.0	−113.5	−22.0	+5.8
Carbon (graphite)	C	12.011	−32.8	−32.9	0.2	−0.2
Methane	CH_4	16.043	−50.0	−49.9	−0.3	+0.2
Acetylene	C_2H_2	26.038	−48.3	−47.1	−3.7	+2.4
Ethylene	C_2H_4	28.054	−47.2	−46.9	−1.1	+0.7
Ethane	C_2H_6	30.07	−47.5	−48.0	1.5	−1.0
Propylene	C_3H_6	42.081	−45.8	−45.9	0.4	−0.3
Propane	C_3H_8	44.097	−46.4	−47.1	2.3	−1.5
n-Butane	C_4H_{10}	58.12	−45.8	−46.6	2.7	−1.7
n-Pentane	C_5H_{12}	72.15	−45.4	−46.3	2.9	−1.9
Benzene	C_6H_6	78.114	−40.6	−40.8	0.5	−0.4
n-Hexane	C_6H_{14}	86.18	−45.1	−46.1	3.1	−2.0
n-Heptane	C_7H_{16}	100.21	−45.0	−45.9	3.2	−2.1
n-Octane	C_8H_{18}	114.232	−44.8	−45.8	3.3	−2.2
Isooctane	C_8H_{18}	114.232	−44.7	−45.8	3.7	−2.4
n-Nonane	C_9H_{20}	128.26	−44.7	−45.7	3.4	−2.2
n-Decane	$C_{10}H_{22}$	142.29	−44.6	−45.7	3.5	−2.3
Carbon monoxide	CO	28.01	−10.1	−9.2	−3.1	+10.1
Methanol	CH_3OH	32.042	−21.1	−21.5	1.4	−1.9
Ethanol	C_2H_5OH	46.069	−27.8	−28.4	2.1	−2.2
Ethylene glycol	$(CH_2OH)_2$	62.07	−17.1	−18.6	5.1	−8.1
Sulfur	S	32.064	−9.2	−9.3	0.3	−0.9
Sulfur monoxide	SO	48.063	−6.3	−5.8	−1.6	+8.5

Source: Data from R. C. Weast, editor, *CRC Handbook of Chemistry and Physics*, 66th ed., CRC Press, Boca Raton, Fla., 1985.

[a] Each constituent before and after combustion is assumed to be in its ideal-gas state at T_o and p_o.

Ref
Gyftopolous
& Beretta

Example: Oxidation of Aluminum

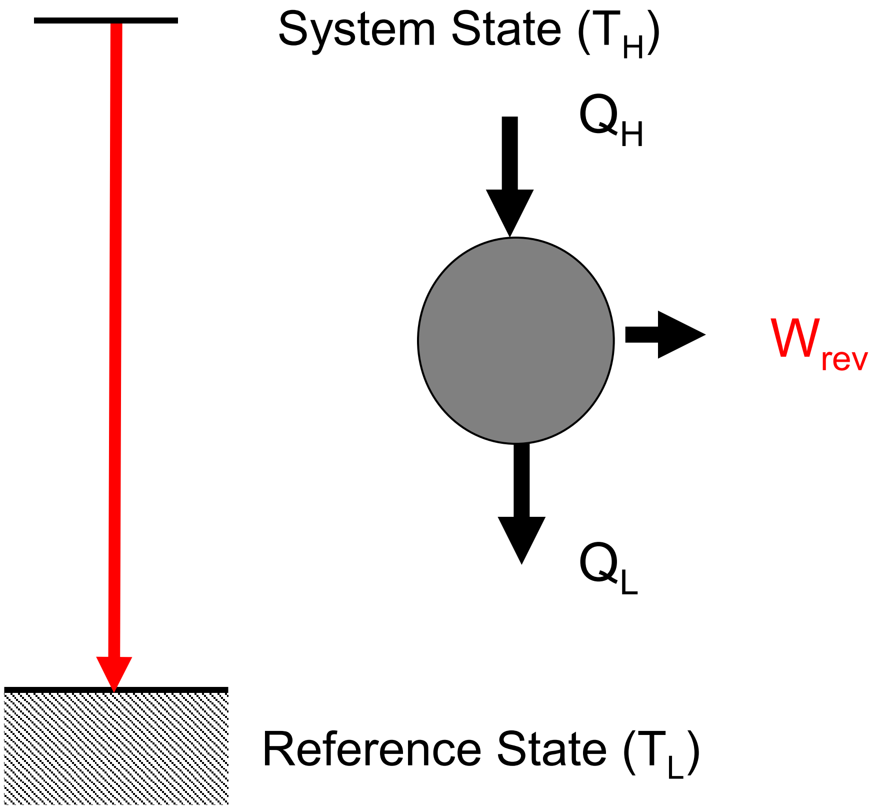
$$2Al \quad + \quad \frac{3}{2}O_2 \quad \rightarrow \quad Al_2O_3$$

$$2\times 888.4\frac{kJ}{mole}+\frac{3}{2}\times 3.97\frac{kJ}{mole}-200.4\frac{kJ}{mole}=B_{lost}$$

$$B_{lost}=(1776.8+6.0-200.4)=1582.4\frac{kJ}{mole(Al_2O_3)}$$

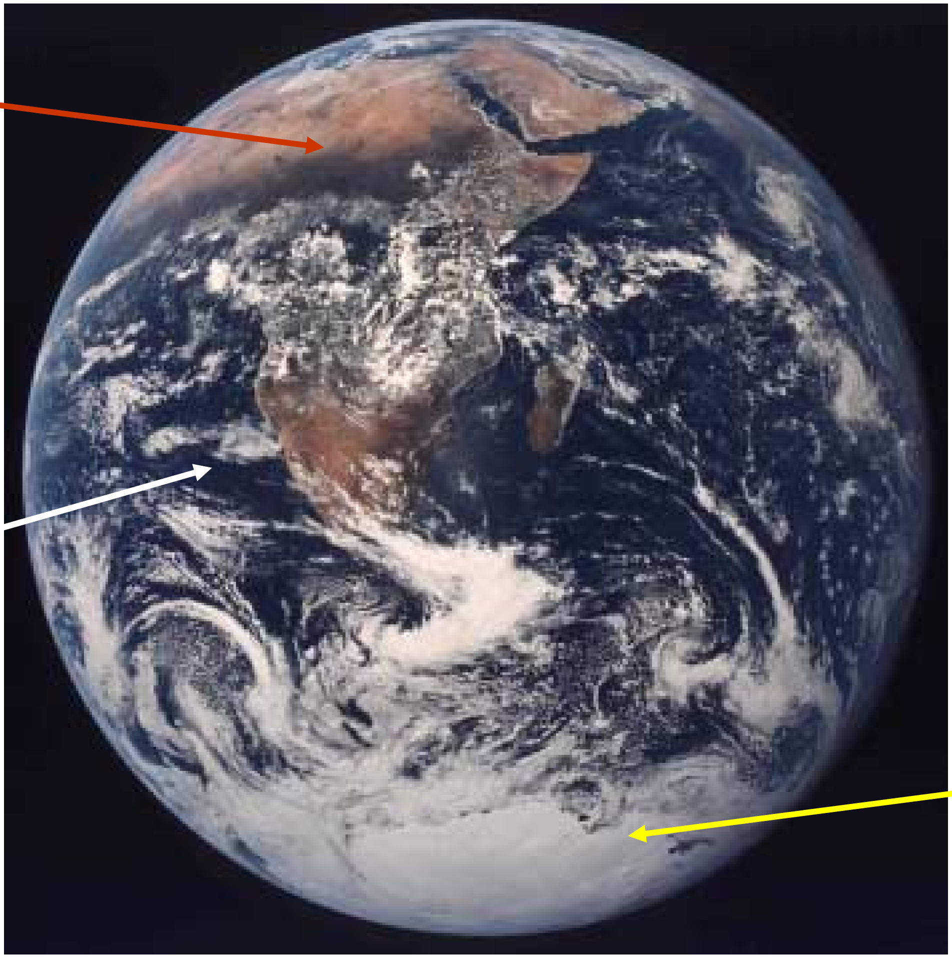
See Appendix of Szargut for exegy values

Materials can do work?



Insert reversible heat engine between high and low temperatures

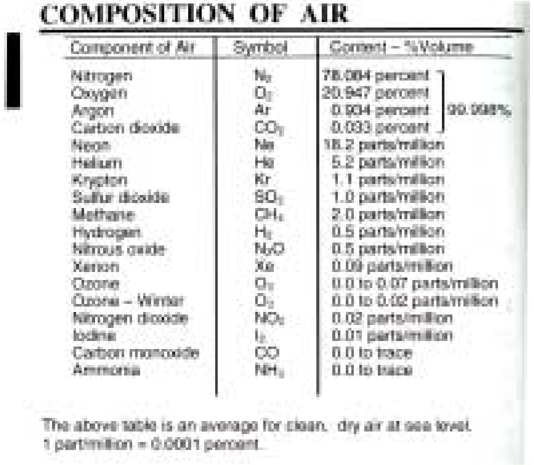
Chemical Properties referenced to the “environment”



Crust

Oceans

Atmosphere



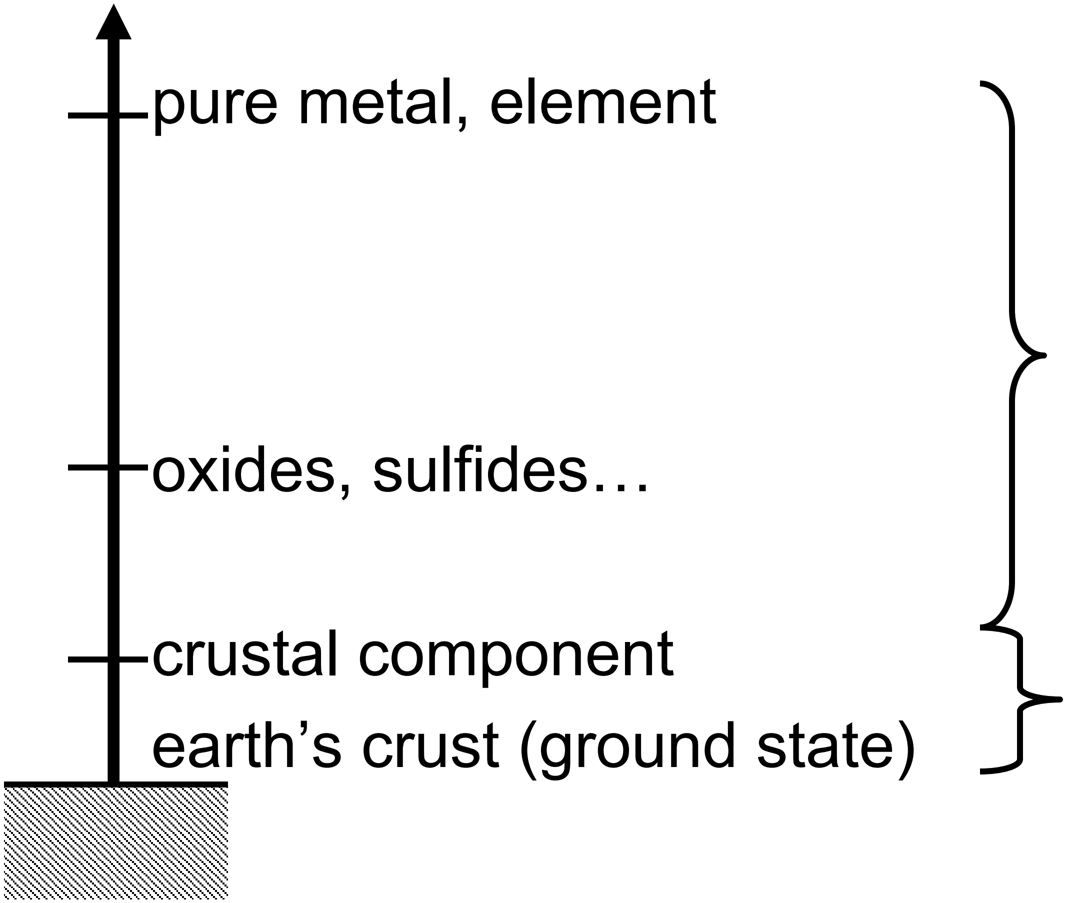
COMPOSITION OF AIR

Component of Air	Symbol	Content – %Volume	
Nitrogen	N_2	78.084 percent	99.998%
Oxygen	O_2	20.947 percent	
Argon	Ar	0.934 percent	
Carbon dioxide	CO_2	0.033 percent	
Neon	Ne	18.2 parts/million	
Helium	He	5.2 parts/million	
Krypton	Kr	1.1 parts/million	
Sulfur dioxide	SO_2	1.0 parts/million	
Methane	CH_4	2.0 parts/million	
Hydrogen	H_2	0.5 parts/million	
Nitrous oxide	N_2O	0.5 parts/million	
Xenon	Xe	0.09 parts/million	
Ozone	O_3	0.0 to 0.07 parts/million	
Ozone – Winter	O_3	0.0 to 0.02 parts/million	
Nitrogen dioxide	NO_2	0.02 parts/million	
Iodine	I_2	0.01 parts/million	
Carbon monoxide	CO	0.0 to trace	
Ammonia	NH_3	0.0 to trace	

The above table is an average for clean, dry air at sea level.
1 part/million = 0.0001 percent.

T_0 = 298.2 K, P_0 = 101.3 kPA

Exergy Reference System



pure metal, element

oxides, sulfides…

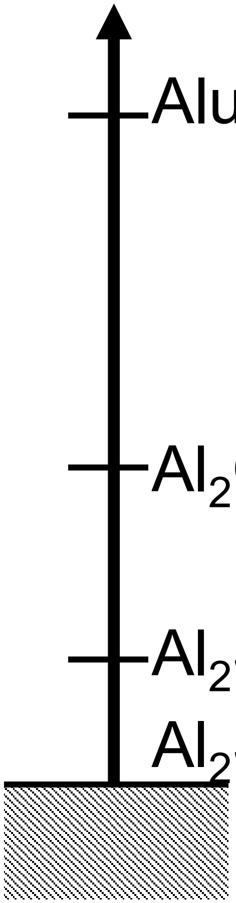
crustal component

earth’s crust (ground state)

chemical reactions

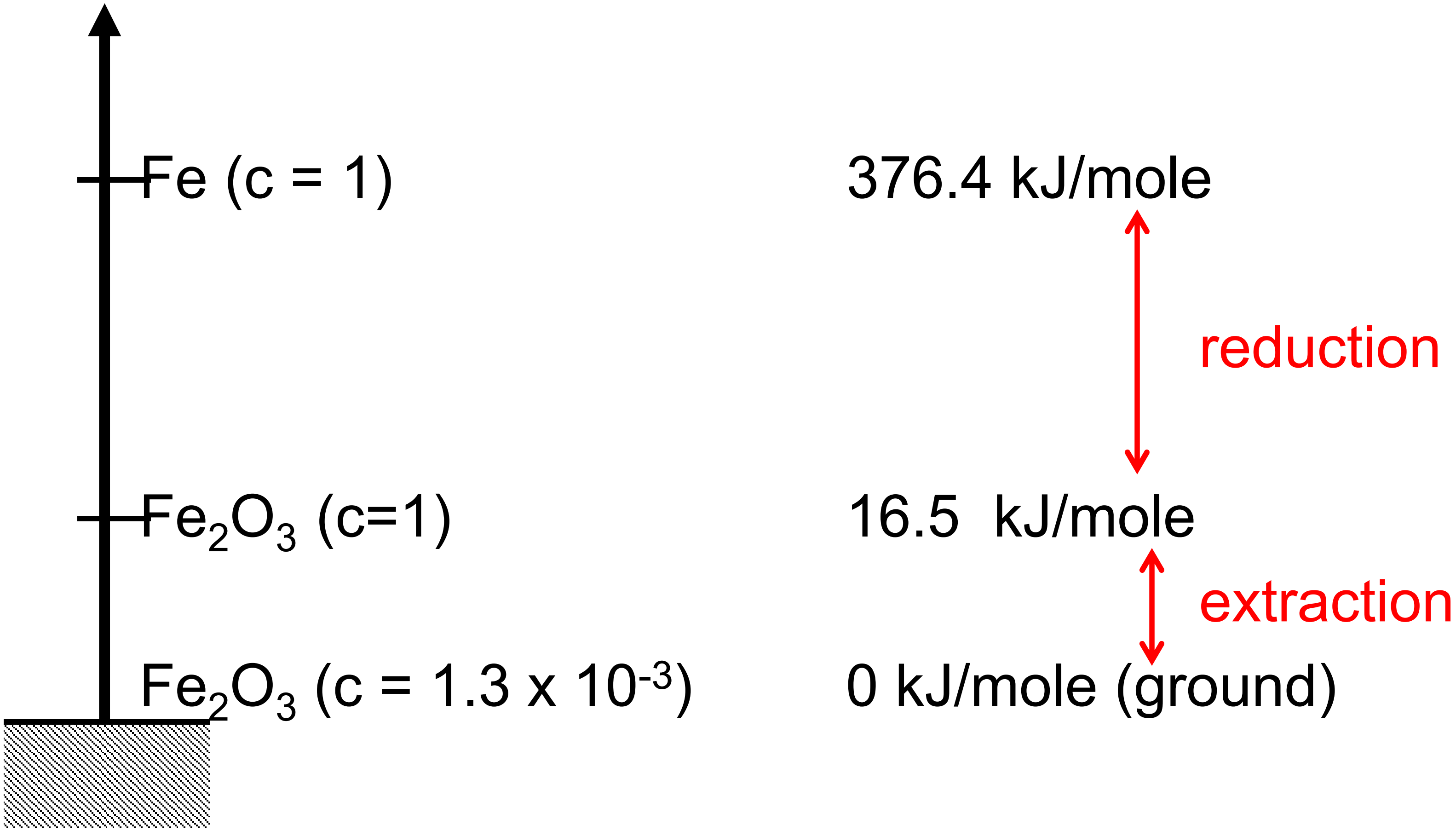
extraction

Exergy Reference System



Aluminum (c=1)	888.4 kJ/mole
Al_2O_3 (c=1)	200.4 kJ/mole
Al_2SiO_5 (c=1)	15.4kJ/mole
Al_2SiO_5 ($c = 2 \times 10^{-3}$)	0 kJ/mole (ground)

Example; making pure iron from the crust



Fe (c = 1) 376.4 kJ/mole

reduction

Fe_2O_3 (c=1) 16.5 kJ/mole

extraction

Fe_2O_3 (c = 1.3×10^{-3}) 0 kJ/mole (ground)

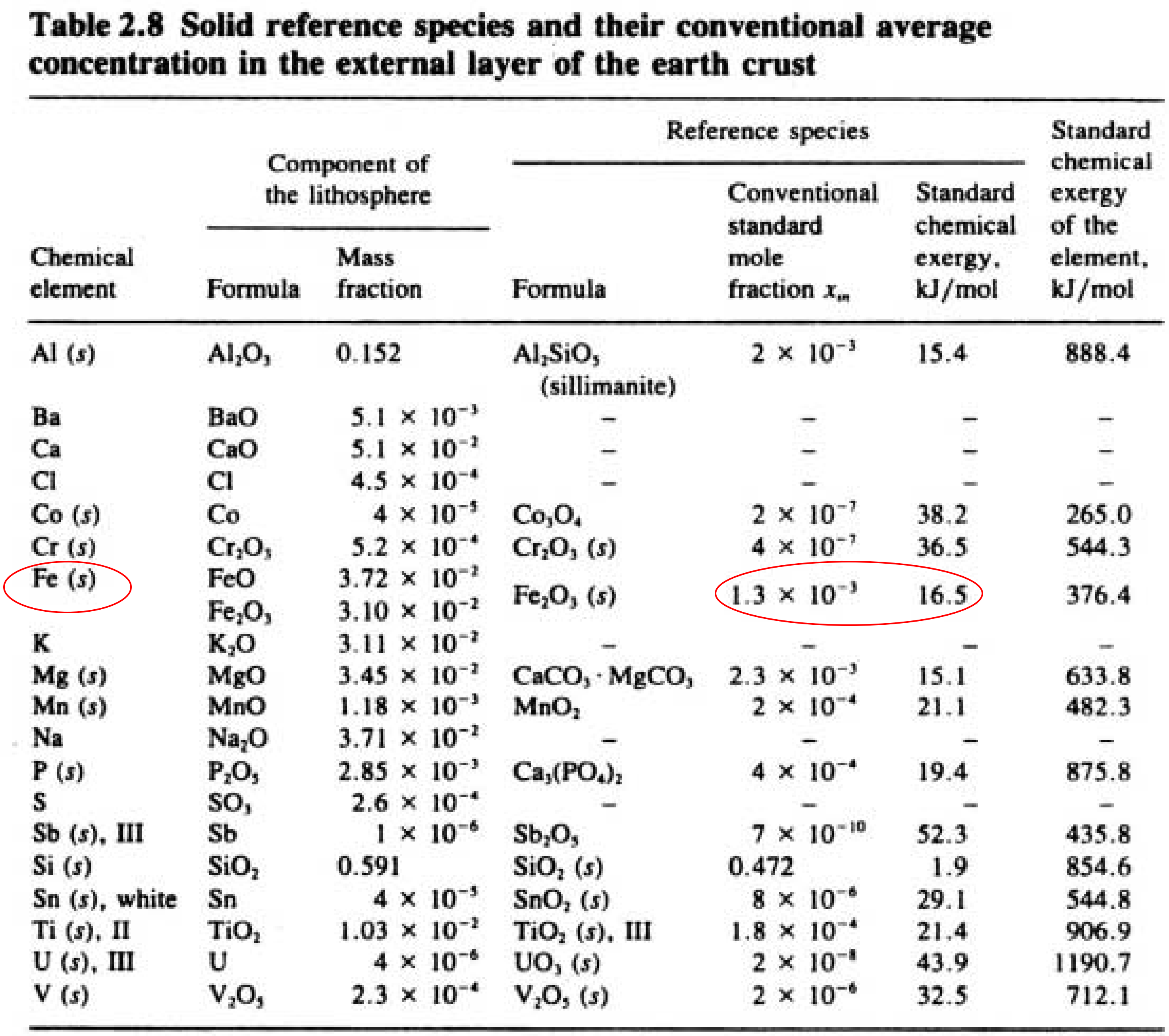


Table 2.8 Solid reference species and their conventional average concentration in the external layer of the earth crust

	Component of the lithosphere		Reference species			Standard chemical exergy of the element, kJ/mol
Chemical element	Formula	Mass fraction	Formula	Conventional standard mole fraction x_{in}	Standard chemical exergy, kJ/mol	
Al (*s*)	Al_2O_3	0.152	Al_2SiO_5 (sillimanite)	2×10^{-3}	15.4	888.4
Ba	BaO	5.1×10^{-3}	–	–	–	–
Ca	CaO	5.1×10^{-2}	–	–	–	–
Cl	Cl	4.5×10^{-4}	–	–	–	–
Co (*s*)	Co	4×10^{-5}	Co_3O_4	2×10^{-7}	38.2	265.0
Cr (*s*)	Cr_2O_3	5.2×10^{-4}	Cr_2O_3 (*s*)	4×10^{-7}	36.5	544.3
Fe (*s*)	FeO	3.72×10^{-2}	Fe_2O_3 (*s*)	1.3×10^{-3}	16.5	376.4
	Fe_2O_3	3.10×10^{-2}				
K	K_2O	3.11×10^{-2}	–	–	–	–
Mg (*s*)	MgO	3.45×10^{-2}	$CaCO_3 \cdot MgCO_3$	2.3×10^{-3}	15.1	633.8
Mn (*s*)	MnO	1.18×10^{-3}	MnO_2	2×10^{-4}	21.1	482.3
Na	Na_2O	3.71×10^{-2}	–	–	–	–
P (*s*)	P_2O_5	2.85×10^{-3}	$Ca_3(PO_4)_2$	4×10^{-4}	19.4	875.8
S	SO_3	2.6×10^{-4}	–	–	–	–
Sb (*s*), III	Sb	1×10^{-6}	Sb_2O_5	7×10^{-10}	52.3	435.8
Si (*s*)	SiO_2	0.591	SiO_2 (*s*)	0.472	1.9	854.6
Sn (*s*), white	Sn	4×10^{-5}	SnO_2 (*s*)	8×10^{-6}	29.1	544.8
Ti (*s*), II	TiO_2	1.03×10^{-2}	TiO_2 (*s*), III	1.8×10^{-4}	21.4	906.9
U (*s*), III	U	4×10^{-6}	UO_3 (*s*)	2×10^{-8}	43.9	1190.7
V (*s*)	V_2O_5	2.3×10^{-4}	V_2O_5 (*s*)	2×10^{-6}	32.5	712.1

Extraction from the crust

$$\text{Extracting } \mathrm{Fe_2O_3} \text{ from } \mathrm{c} = 1.3\mathrm{x}10^{-3} \text{(crust) to } \mathrm{c} = 1$$

$$B = T_o R \ln \frac{1}{1.3x10^{-3}}$$

$$B = 298.2^o K \times 8.314 \frac{J}{mole^o K} \times \ln \frac{1}{1.3 \times 10^{-3}} = 16.5 \frac{kJ}{mole}$$

Note: R = k N_{avo} (Boltzmann’s constant X Avogadro’s number)

Reduction of Fe_2O_3 (Hematite)

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$$

$$2 \times 16.5 + 3 \times 410.3 - 4 \times 376.4 - 3 \times 19.9 =$$

$$B_{lost} = - 301.4 \text{ kJ}$$

this is an endothermic reaction

i.e. minimum energy required to reduce 2 mole of hematite

Iron Ore Reduction

Recall $C + O_2 \rightarrow CO_2$ produces 394.8 kJ/mole C

We need $\frac{301.4}{394.8} = 0.76$ moles of carbon

$2Fe2O_3 + 3.76C + 0.76O_2 \rightarrow 4Fe + 3.76\ CO_2$

Iron Ore Reduction

but the efficiency of the use of carbon
is only 30.3%

therefore the actual reaction is

$$2Fe_2O_3 + 12.42C + 9.42O_2 \rightarrow 4Fe + 12.42CO_2$$

33kJ + 5095.9 + 37.7 - 1505.6 - 247.2kJ =

3,413.8 kJ for 4 mole of Fe

this is $\boxed{15.2\ \text{MJ/kg (Fe)}}$

Iron Ore Reduction

$$\text{Fuel (C) Intensity} = \frac{12.42 \times 394.8}{4 \times 55.85 g} = \frac{4.903 MJ}{.2234 kg} = \boxed{22 \frac{MJ}{kg}}$$

$$CO_2 \text{ Intensity} = \frac{12.42 \times 44}{4 \times 55.85} = \boxed{2.5 \frac{kg\ CO_2}{kg\ Fe}}$$

$$\text{Exergy value of pure Fe is 376.4 kJ/mole} = \boxed{\text{6.7 MJ/kg}}$$

Summary for Iron Ore

$$\text{fuel used} = 22\ \text{MJ/kg} \approx 15.2(B_{lost}) + 6.7(B_{Fe})$$

“Credit” for producing pure iron from the crust

Lost exergy from making iron from Fe_2O_3

Homework Problem

- Calculate the minimum work to reduce iron using hydrogen
- $Fe_2O_3 + H_2 = 2\ Fe_3O_4 + H_2O$ (1)
  $Fe_3O_4 + H_2 = 3\ FeO + H_2O$
  $FeO + H_2 = Fe + H_2O$
- Now assume the H_2 comes from electrolysis and add this in
- $2\ H_20 = 2\ H_2 + O_2$

Energy data from Smil

Table 6 Ranges of Energy Densities of Common Fuels and Foodstuffs

Energy density	(MJ/kg)
Hydrogen	114.0
Gasolines	46.0–47.0
Crude oils	42.0–44.0
Pure plant oils	38.0–37.0
Natural gases	33.0–37.0
Butter	29.0–30.0
Ethanol	29.6
Best bituminous coals	27.0–29.0
Pure protein	23.0
Common steam coals	22.0–24.0
Good lignites	18.0–20.0
Pure carbohydrates	17.0
Cereal grains	15.2–15.4
Air-dried wood	14.0–15.0
Cereal straws	12.0–15.0
Lean meats	5.0–10.0
Fish	2.9–9.3
Potatoes	3.2–4.8
Fruits	1.5–4.0
Human feces	1.8–3.0
Vegetables	0.6–1.8
Urine	0.1–0.2

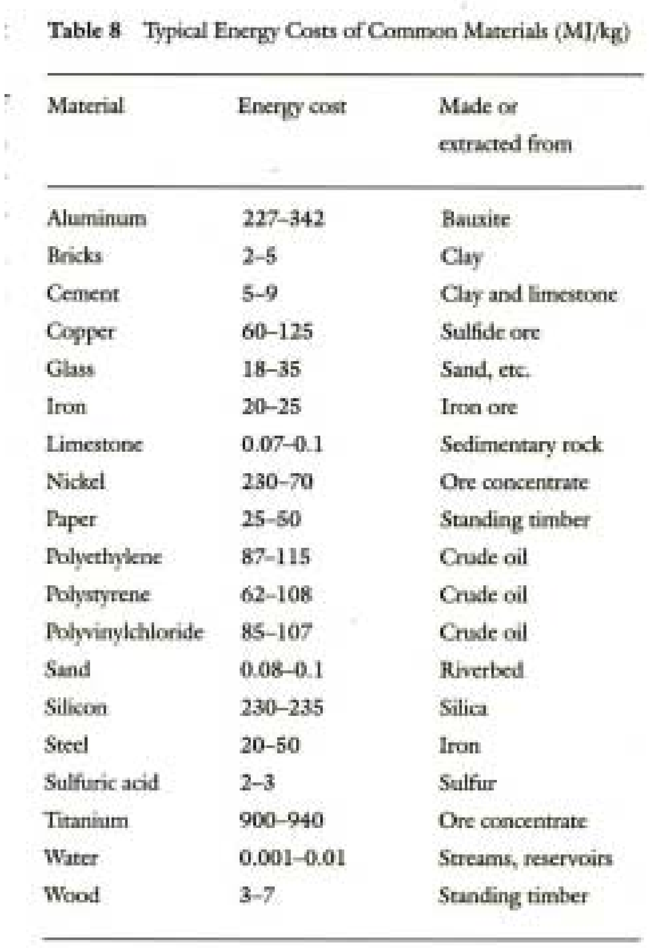


Table 8 Typical Energy Costs of Common Materials (MJ/kg)

Material	Energy cost	Made or extracted from
Aluminum	227–342	Bauxite
Bricks	2–5	Clay
Cement	5–9	Clay and limestone
Copper	60–125	Sulfide ore
Glass	18–35	Sand, etc.
Iron	20–25	Iron ore
Limestone	0.07–0.1	Sedimentary rock
Nickel	230–70	Ore concentrate
Paper	25–50	Standing timber
Polyethylene	87–115	Crude oil
Polystyrene	62–108	Crude oil
Polyvinylchloride	85–107	Crude oil
Sand	0.08–0.1	Riverbed
Silicon	230–235	Silica
Steel	20–50	Iron
Sulfuric acid	2–3	Sulfur
Titanium	900–940	Ore concentrate
Water	0.001–0.01	Streams, reservoirs
Wood	3–7	Standing timber

Summary

- Exergy = Available work referred to the “dead state”
- Both fuel and non-fuel materials have exergy equivalents
- Exergy is not conserved

$$B_{in} - B_{out} = \Delta B_{lost}$$

Exergy Homeworks

3. What is the minimum work required for photosynthesis?
4. What is the maximum work one could obtain from auto-respiration?
5. What is the maximum work one could obtain from burning the following fuels with oxygen: octane? methane? methanol? hydrogen? How much CO_2 is generated for each?

Applications

- Exergy Analysis of Extraction, Smelting
- Exergy Analysis of Industry (Ayres et al)
- Exergy Analysis of Natural Systems (Bakshi)
- Exergy of Mfg Processes
- Exergy Analysis of Recycling Flows