Introduction to the "Exergy" Concept

2.83/2.813

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Readings for Sustainability discussion on Wed Feb 26

Topic	**Author**	**Pages of text**	**Source**
Ecology	Rockstrom	~3	(Nature)
Economics	Dasgupta	~6	(Roy. Soc. B)
Triple bottom line	Slaper	~7 (space&half)	(on line)
Easter Island	Diamond	~3	(Discover Magazine)
Chaco Canyon	Browswimmer	~4	(Ecocide)
Tragedy of the Commons	Hardin	~6	(Science)
Total Reading		**~29 pages**	

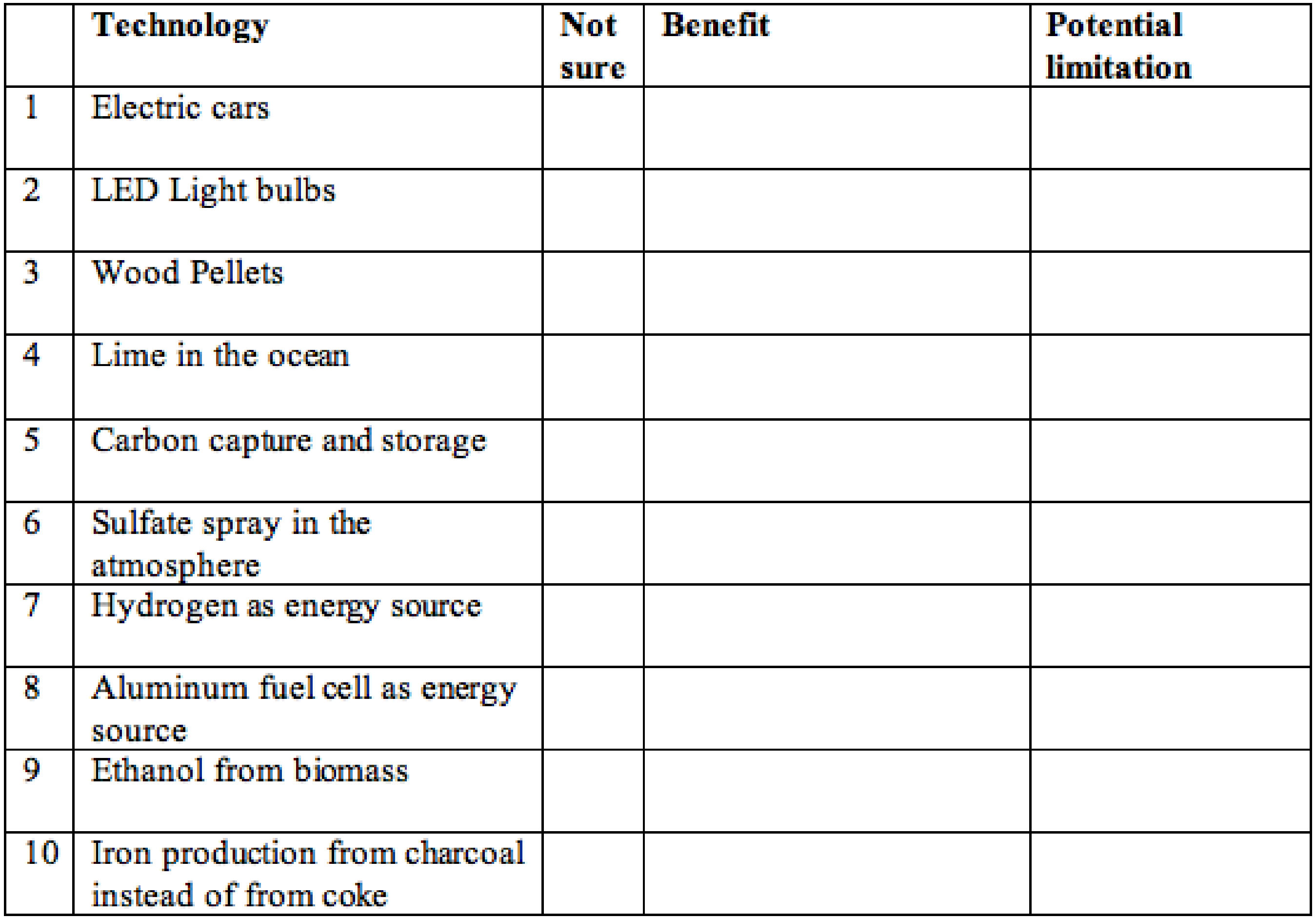
Readings

1. Ch.2 Thermodynamics Revisited (p 7-13), and
2. Ch 6 Exergy, a Convenient Concept (p 59-62), Jakob de Swaan Arons, 2004
3. Ch 6 Thermodynamic Analysis of Resources Used in Mfg Processes, Gutowski & Sekulic, in Thermodynamics and the Destruction of Resources "TDR" (Bakshi, Gutowski & Sekulic) 2011
4. Appendix, Tables of Standard Chemical Exergy, Szargut, Morris & Steward, 1988

Why Exergy?

- Rigorous
- Explicitly shows loses (unlike energy)
- Can aggregate materials and energy resources
- Provides theoretical comparison
- Can analyze “new ideas”

Example Problems



	Technology	Not sure	Benefit	Potential limitation
1	Electric cars			
2	LED Light bulbs			
3	Wood Pellets			
4	Lime in the ocean			
5	Carbon capture and storage			
6	Sulfate spray in the atmosphere			
7	Hydrogen as energy source			
8	Aluminum fuel cell as energy source			
9	Ethanol from biomass			
10	Iron production from charcoal instead of from coke			

Exergy Accounting

- Exergy Units: Joules J, rate in Watts, W
- Exergy symbols: *B, Ex, X, and b,* e_x, *x*
- Similar quantities: “Availability” by Keenan, 1941 and “Available Energy”, Ω^R, *by Gyftopoulos and Beretta, 1991*

Notation

- $Ex = B$ = exergy
- $\phi = H - T_o S$ = availability function
- $B = \phi - \phi_o$ = exergy
- $G = H - TS$ = Gibbs free energy

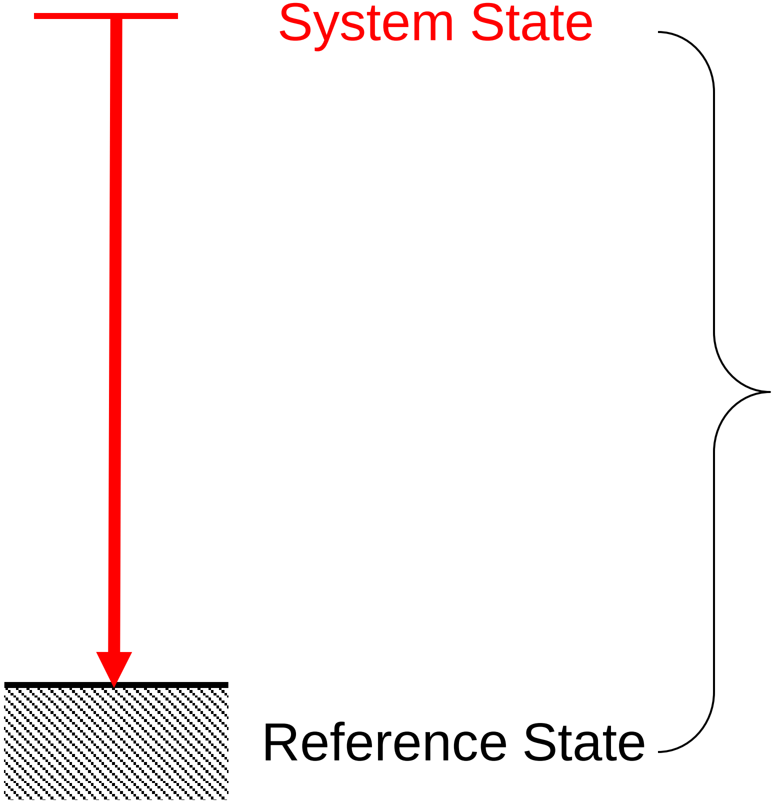
$$\mu_i = \left[\frac{\partial G}{\partial n_i}\right]_{p,T,n_j} \quad = \text{chemical potential}$$

The subscript "o" indicates the reference state

Definition #1 of Exergy

"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…" [Szargut et al 1988].

Exergy



System State

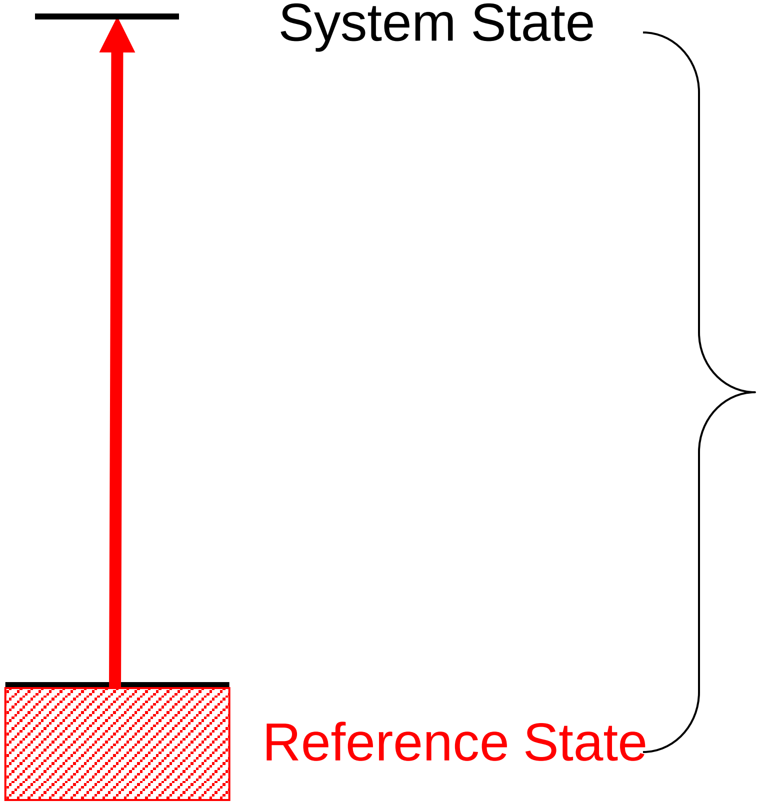
Reference State

Maximum work obtainable between System and Reference States.

Definition #2 Exergy

Exergy is the work required to raise some matter from a state of thermodynamic equilibrium with the common components of the natural surroundings to a higher state by means of reversible processes.

Exergy

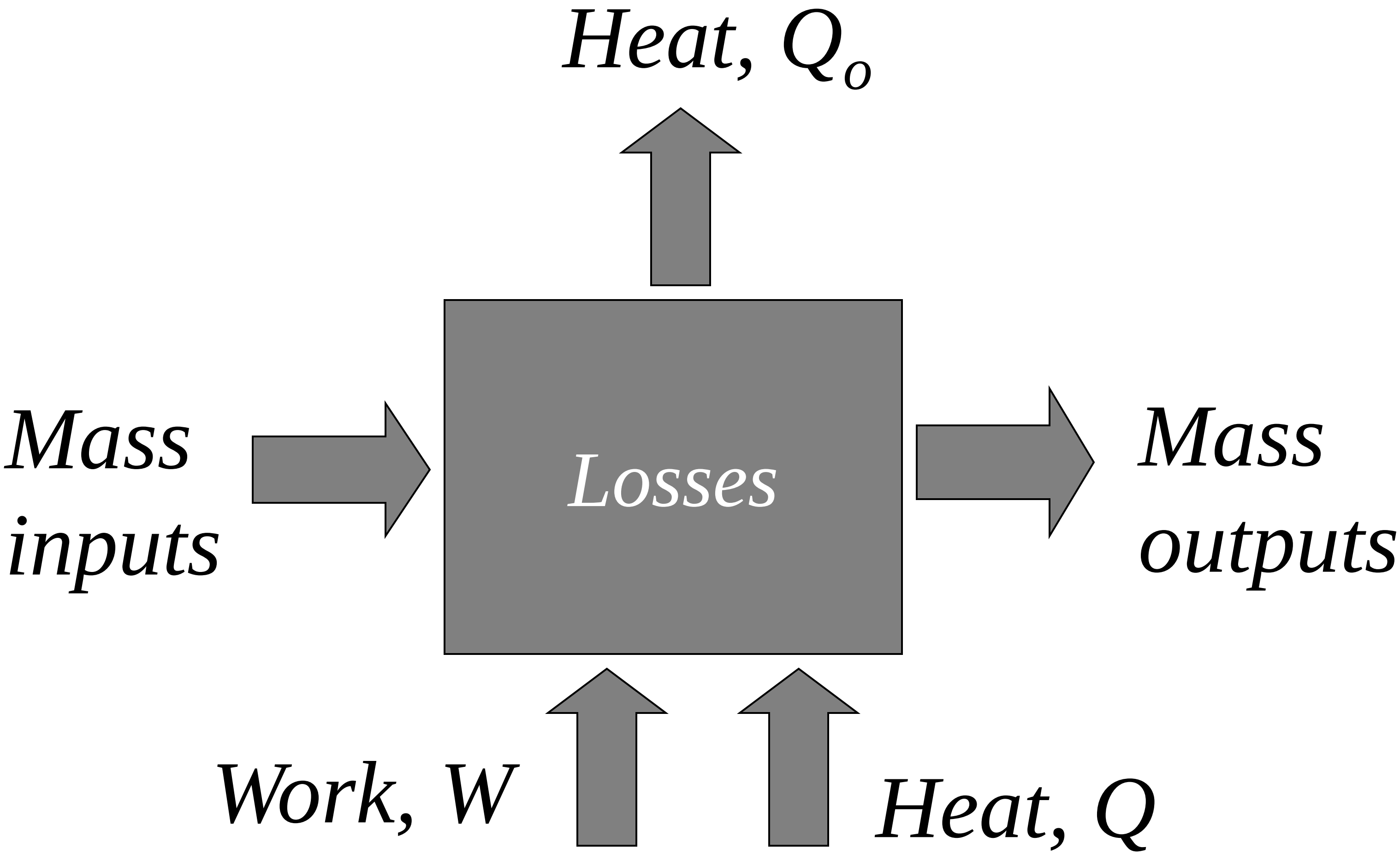


System State

Reference State

The minimum work needed
to raise System from the reference
state to the System State

Open System - steady state



Heat, Q_o

Mass inputs

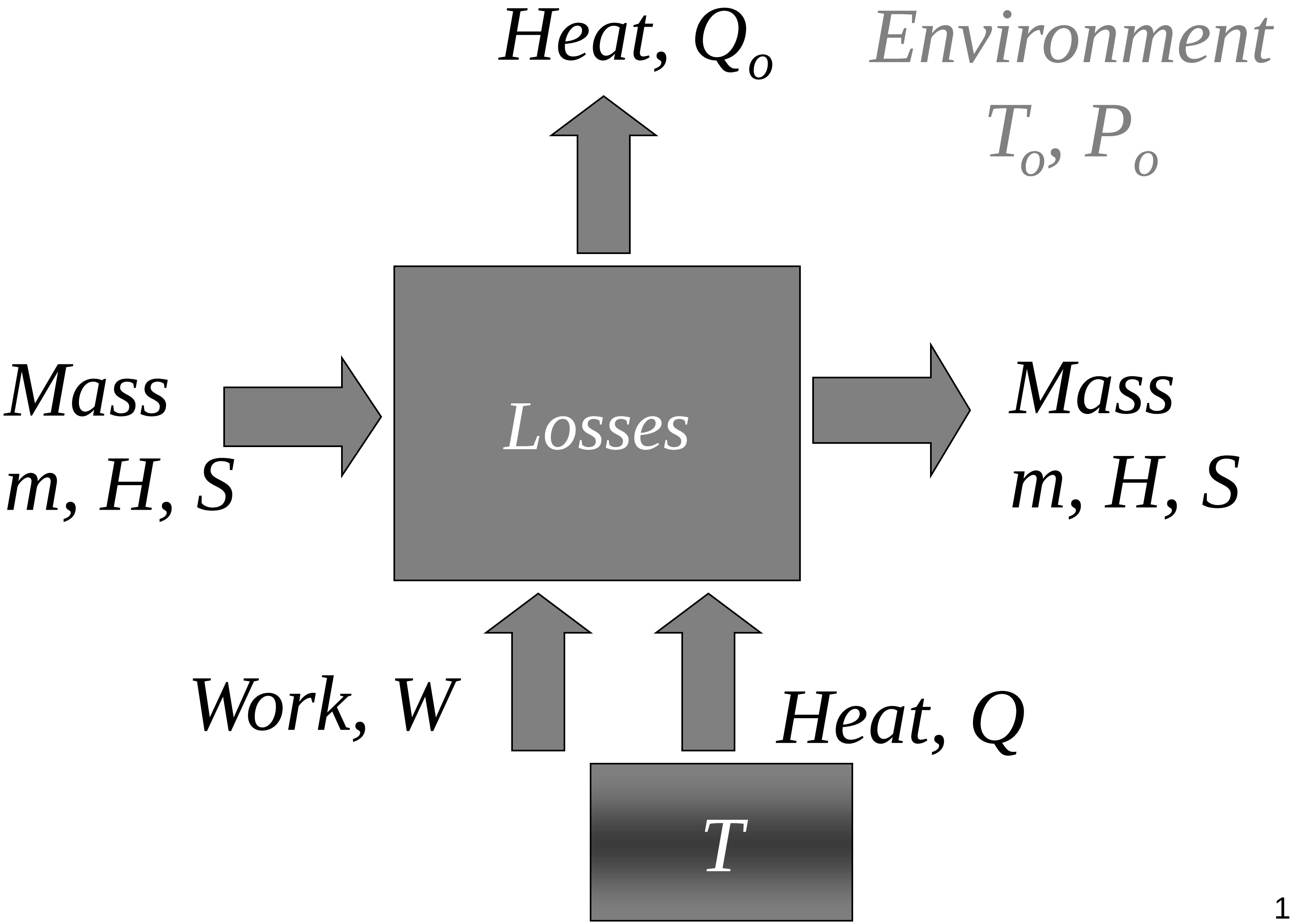
Losses

Mass outputs

Work, W

Heat, Q

Open System - steady state



Heat, Q_o

Environment

T_o, P_o

Mass

m, H, S

Losses

Mass

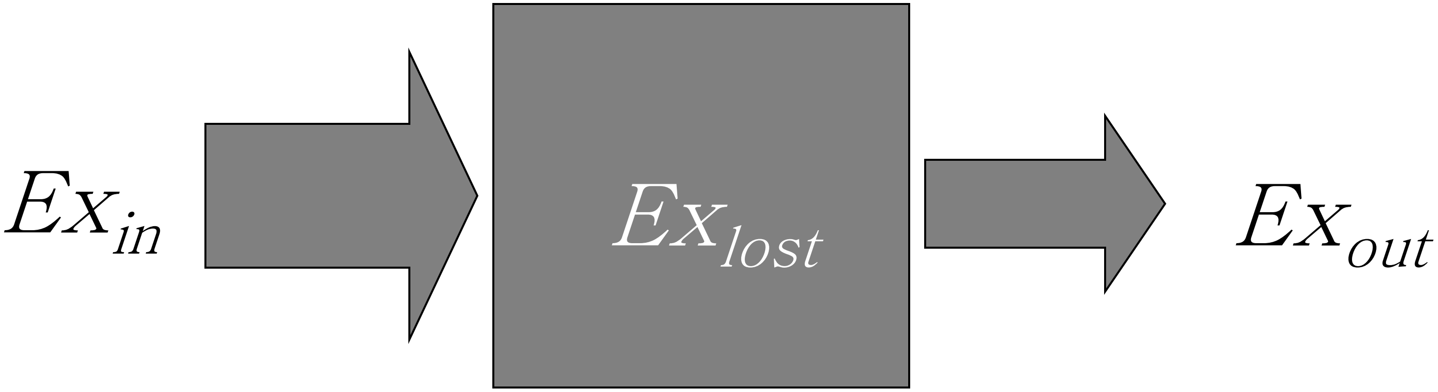
m, H, S

Work, W

Heat, Q

T

Aggregated Exergy Accounting; open system, steady state



$$Ex_{in} = Ex_{out} + Ex_{lost}$$

Interactions and Energy Carriers

- Energy
- Work, W
- Heat, Q
- Mass Flow, dm/dt

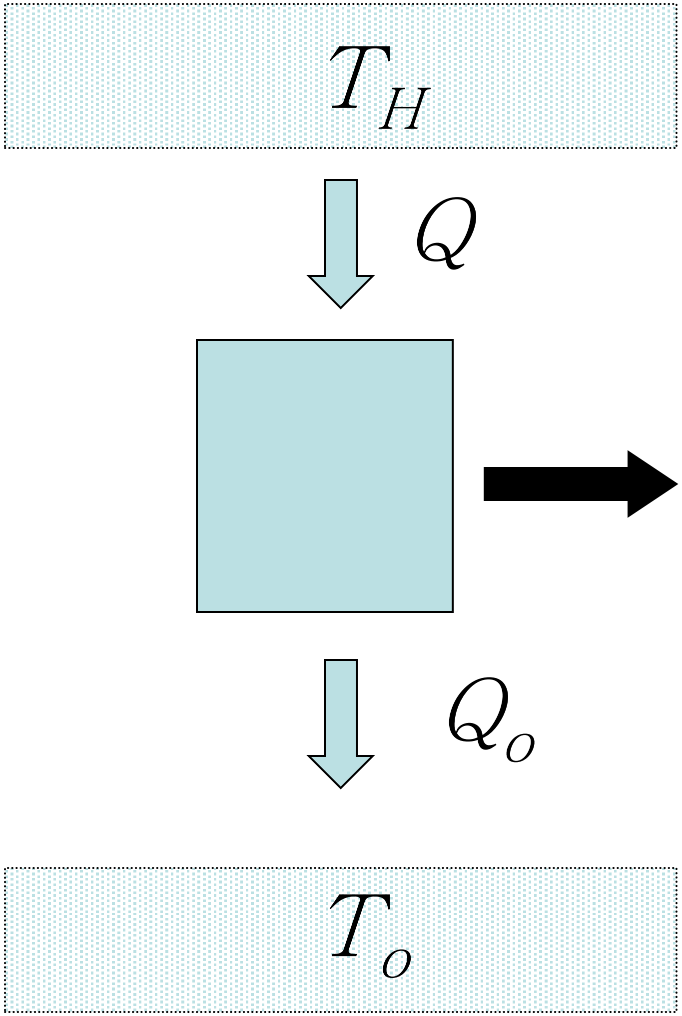
U, mV^2, mgz, pv

- Exergy
- $Ex\ (work) = W$
- $Ex(heat) = Q(1-To/T)$
- $Ex(mass\ flow) =$

$mV^2, mgz,$ *and*

$f(m, H, S)$

Heat Interaction Q



$$W_{out} = Q - Q_o$$

$$\eta = \frac{W_{out}}{Q} = 1 - \frac{Q_o}{Q}$$

Carnot’s “Reversible” Heat Engine

$$\eta_{reversible} = f(T_H, T_L) \qquad \frac{Q_{out}}{Q_{in}} = \frac{T_L}{T_H}$$

$$\boxed{\eta = 1 - \frac{T_L}{T_H}}$$

Maximum Work Output

$$W_{out}^{\max} = Q_{in}(1 - \frac{T_L}{T_H})$$

- *Q_{in} is at T_H, let T_L be T_{ref} or T_o*
- *This gives the "available energy" of a heat interaction at T_H in reference T_o.*
- Work and Heat are no longer equivalent!

Exergy "Ex" of Heat Interaction

$$E_X^Q = Q(1 - \frac{T_o}{T})$$

- Exergy, *"Ex"* is the available energy w.r.t. a reference environment, T_0, and P_0…
- *Ex(work) = W;* *Ex (heat) = Q(1-*T_0*/T)*

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

Review of basic concepts

- Enthapy
- Entropy
- Heat interaction
- Work interaction

Enthalpy, H

- State property of a material
- $H = U + PV$
- $h = u + Pv$
- Condensed phase: $\Delta h = c_{ave}\,\Delta T + v\,\Delta P$
- Gas phase: $\Delta h = c_p\,\Delta T$
- Phase change $\Delta h = h_{fg}$, vaporization

See Ch 6 for a discussion of condensed and gas phases

Enthalpy $H=U+PV$

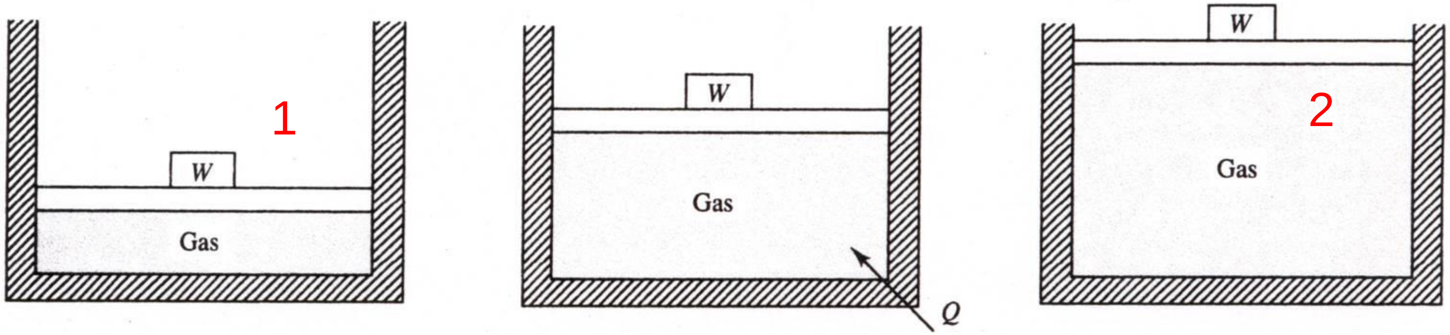


Fig. 4-4 Constant-Pressure Heat Addition

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

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

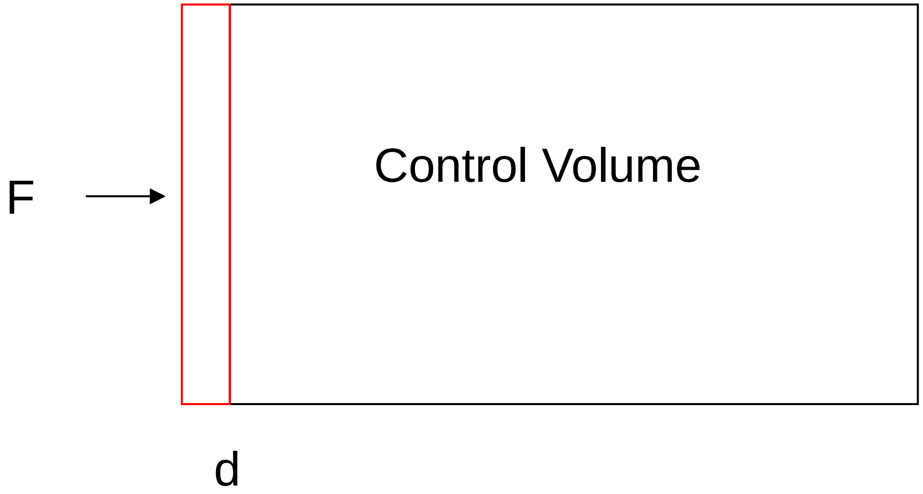
The quantity in parenthesis is Enthalpy $H = U + PV$

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

Constant Pressure Equilibrium Process

For Flow System Energy

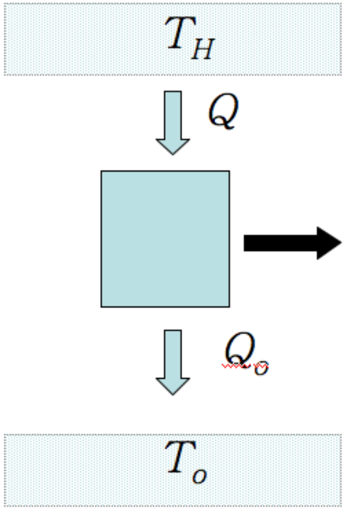
$$\boxed{U + Pv} + \frac{1}{2}mV^2 + mgz = \boxed{H} + \frac{1}{2}mV^2 + mgz$$



$$W_{boundary} = Fd = Pv$$

Entropy-system property

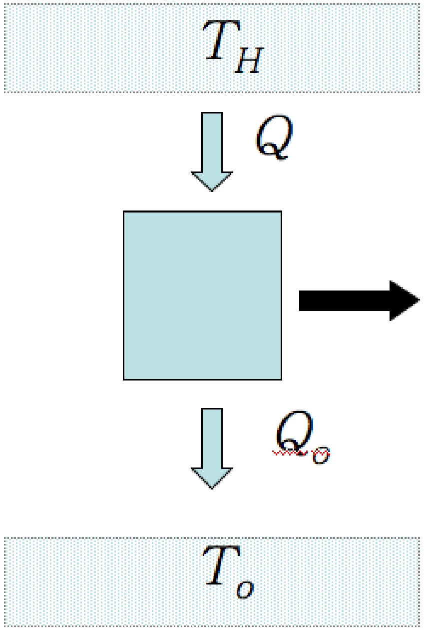
Recall from Carnot reversible cycle



$$W_{out}^{\max} = Q_{in}(1 - \frac{T_L}{T_H})$$

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

Reversible Carnot Cycle



$$\frac{Q_{in}}{T_H} = \frac{Q_{out}}{T_L} \Rightarrow \oint \frac{Q}{T} = 0$$

$$S = \frac{Q}{T}$$

Entropy Balance: $$\boxed{S_{in} - S_{out} + S_{irr} = \Delta S}$$

Entropy-system property

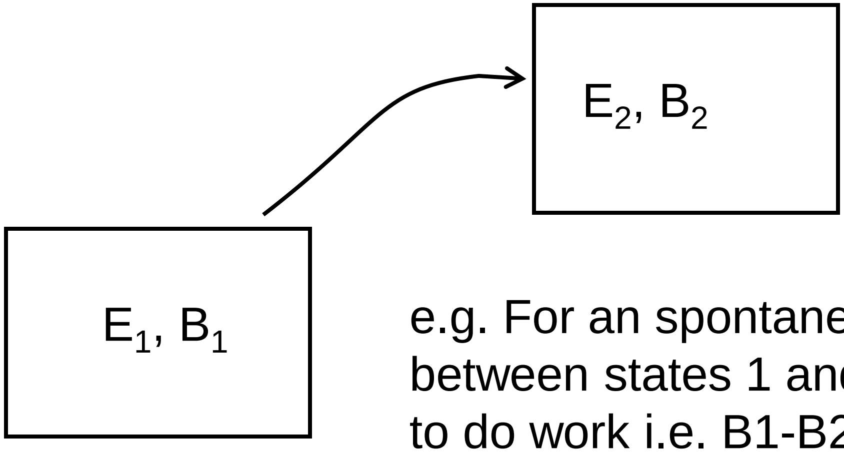
$$E_X^Q = Q(1 - \frac{T_o}{T}) = Q - T_o S$$

$$S = \frac{1}{T_o}(Q - Ex)$$

i.e. entropy written this way
shows it is a measure of something
that is not available.

See Gyftopoulous & Beretta, 2005

Energy, E and Exergy, $B = Ex$



e.g. For an spontaneous irreversible process between states 1 and 2 there is a loss of ability to do work i.e. B1-B2>0, while energy is conserved, E1-E2 = 0.
For the reversible process B1-B2 = E1-E2 = 0

$B_1 - B_2 = E_1 - E_2$ reversible process

$B_1 - B_2 > E_1 - E_2$ irreversible process

Gyftopoulos and Beretta, 2005 p 216, or TDR p22

Define Entropy

$$S_1 = S_o + \frac{1}{C_R}\left[\left(E_1 - E_o\right) - (B_1 - B_o)\right]$$

- They show $C_R = T_R = T_0$
- Entropy is a Property
- Entropy is a measure of something lost

Gyftopoulos and Beretta, 2005 p217, or TDR p23

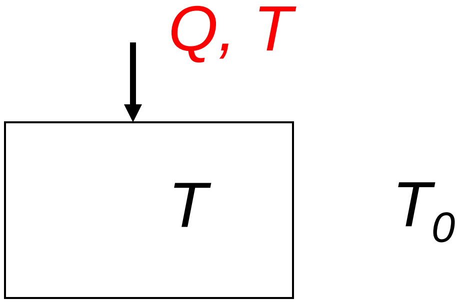
Entropy Difference

$$S_2 - S_1 = \frac{1}{C_R}\left[\left(E_2 - E_1\right) - (B_2 - B_1)\right]$$

- $\Delta S = 0$, reversible process
- $\Delta S > 0$, irreversible process

Gyftopoulos and Beretta, 2005 p218, or TDR p23

Example, Heat Interaction



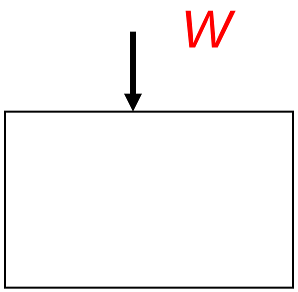
$$E_2 = E_1 + Q$$

$$B_2 = B_1 + Q(1 - T_0/T)$$

$$\Delta S = (1/T_0)(Q - Q + Q(T_0/T)) = Q/T$$

$$\boxed{\Delta S = Q/T}$$

Example, Work Interaction



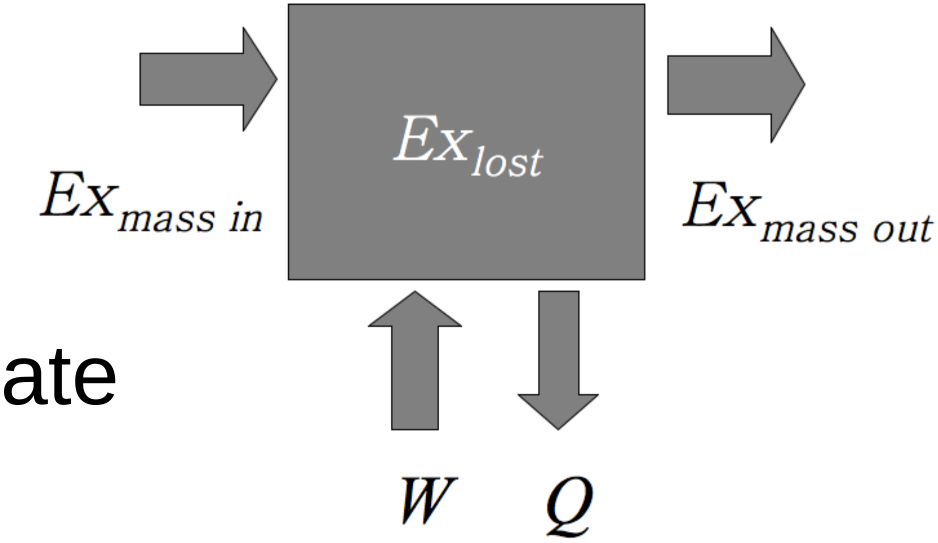
$$E_2 = E_1 + W$$

$$B_2 = B_1 + W$$

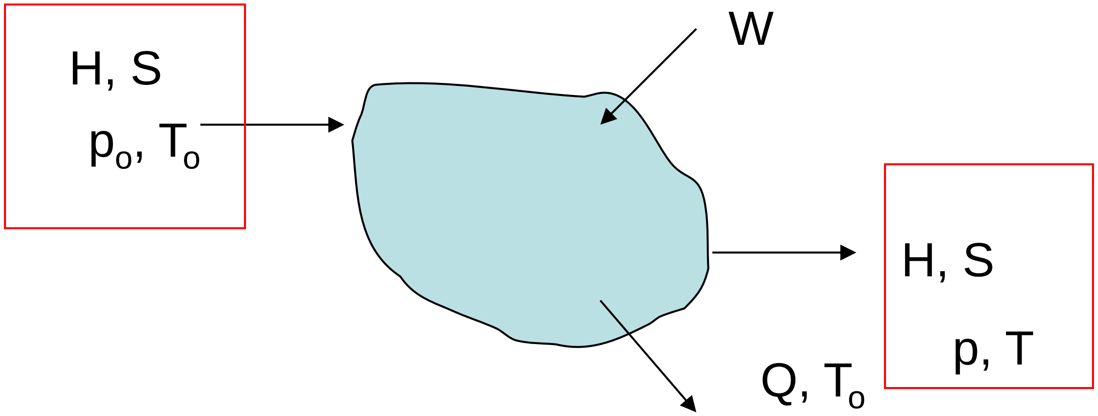
$$\boxed{\Delta S = (W - W) = 0}$$

Putting this all together…

- Define system boundaries, inputs, outputs
- Balance mass
- Balance energy
- Balance entropy
- Simplify to steady state



Open System with H, S



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

See Ch 6 de Swaan Arons

From EQ 1 & 2(Ch 6), de Swaan Arons

$$\dot{H}_{in} - \dot{H}_{out} - \dot{Q}_{out} + \dot{W}_{in} = 0$$

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

$$\boxed{\dot{\mathrm{W}} = \Delta\dot{H} - T_o\Delta\dot{S} + T_o\dot{S}_{generated}}$$

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

Minimum Work = Exergy

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

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

$$\boxed{B = (H - T_o S) - (H - T_o S)_o}$$

$$W_{\min} = \frac{\dot{W}_{rev}}{\dot{m}} = B_{out} - B_{in}$$

Lost Work & Lost Exergy

Recall:

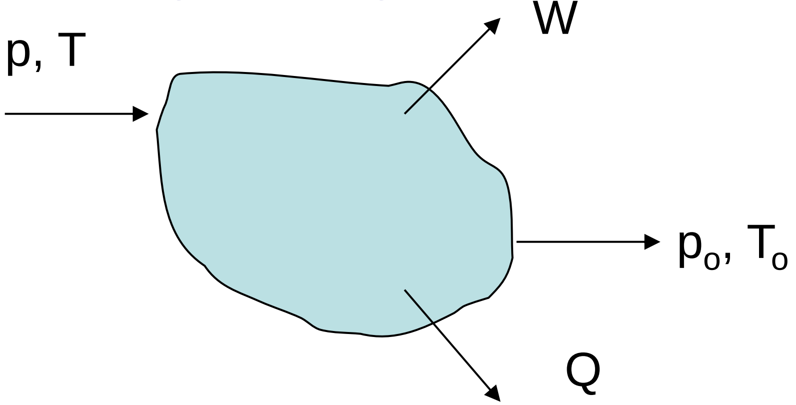
$$\dot{\mathrm{W}} = \dot{B}_{out} - \dot{B}_{in} + T_o \dot{S}_{generated}$$

Let: $\dot{\mathrm{W}} = \dot{\mathrm{W}}_{\min} + \mathrm{W}_{lost}$ then

$$\dot{\mathrm{W}}_{lost} = \dot{\mathrm{B}}_{lost} = T_o \dot{S}_{generated}$$

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

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

Open flow system

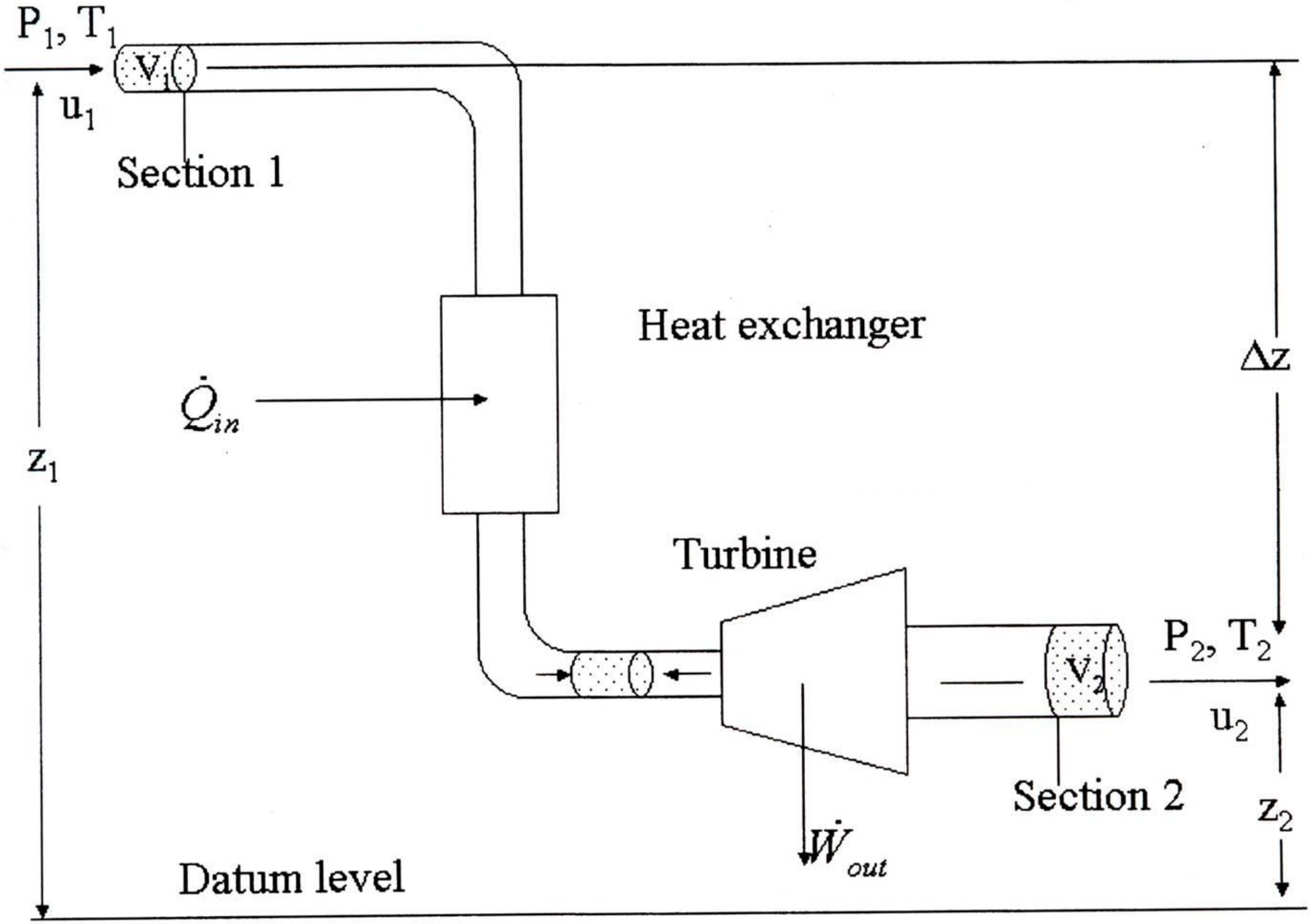


Figure 1 Changes in steady-state flow.

De Swaan Arons

First Law for a Flow System

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

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

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

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

EQ 1

one stream steady state

Second Law for a Flow System

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

$$+ \sum_{in} \int \frac{\delta \dot{Q}_k}{T} - \sum_{out} \int \frac{\delta \dot{Q}_1}{T} + \dot{S}_{generated}$$

$$\boxed{\dot{m}\Delta S + \frac{\dot{Q}_{surr}}{T} + \dot{S}_{generated} = 0}$$

EQ 2

one stream steady state

From EQ 1 & 2

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

$$\dot{m}\Delta S + \frac{\dot{Q}}{T_{0}} + \dot{S}_{generated} = 0$$

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

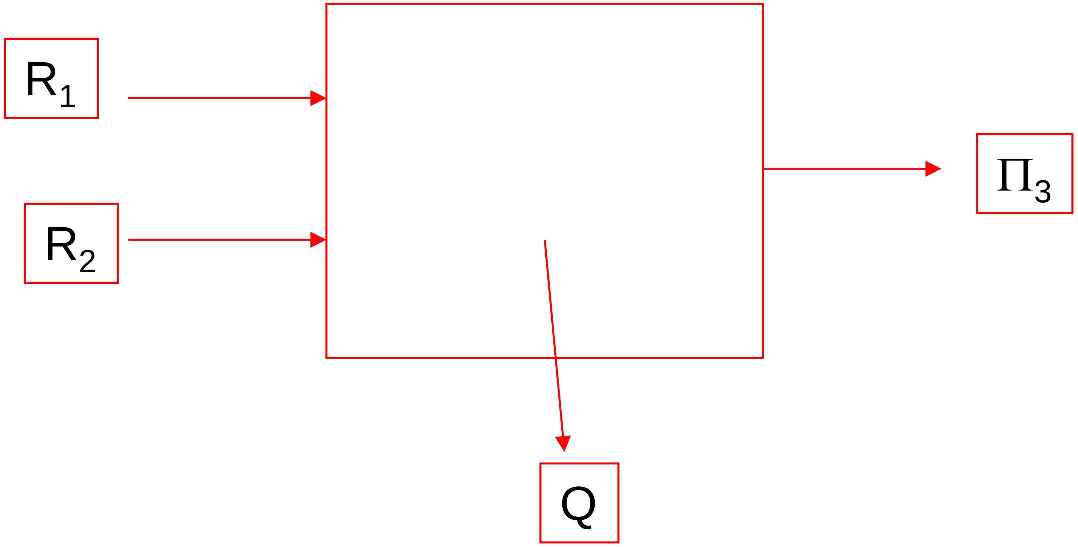
Physical and Chemical Exergy

- $B = B^{ph} + B^{ch}$
- $B^{\mathbf{ph}}(T=T_o, p=p_o, \mu = \mu^* \neq \mu_{\square}) = 0$
  - *this is the “restricted dead state”*

- $B^{ch}(\mu^* = \mu_{\square}) = 0$
- *when* $B = B^{ph} + B^{ch} = 0$
  - *this is the “dead state”*

Chemical Reaction, at T_o, p_o

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



R_1

R_2

Π_3

Q

Chemical Reactions

stoichiometric mass balance

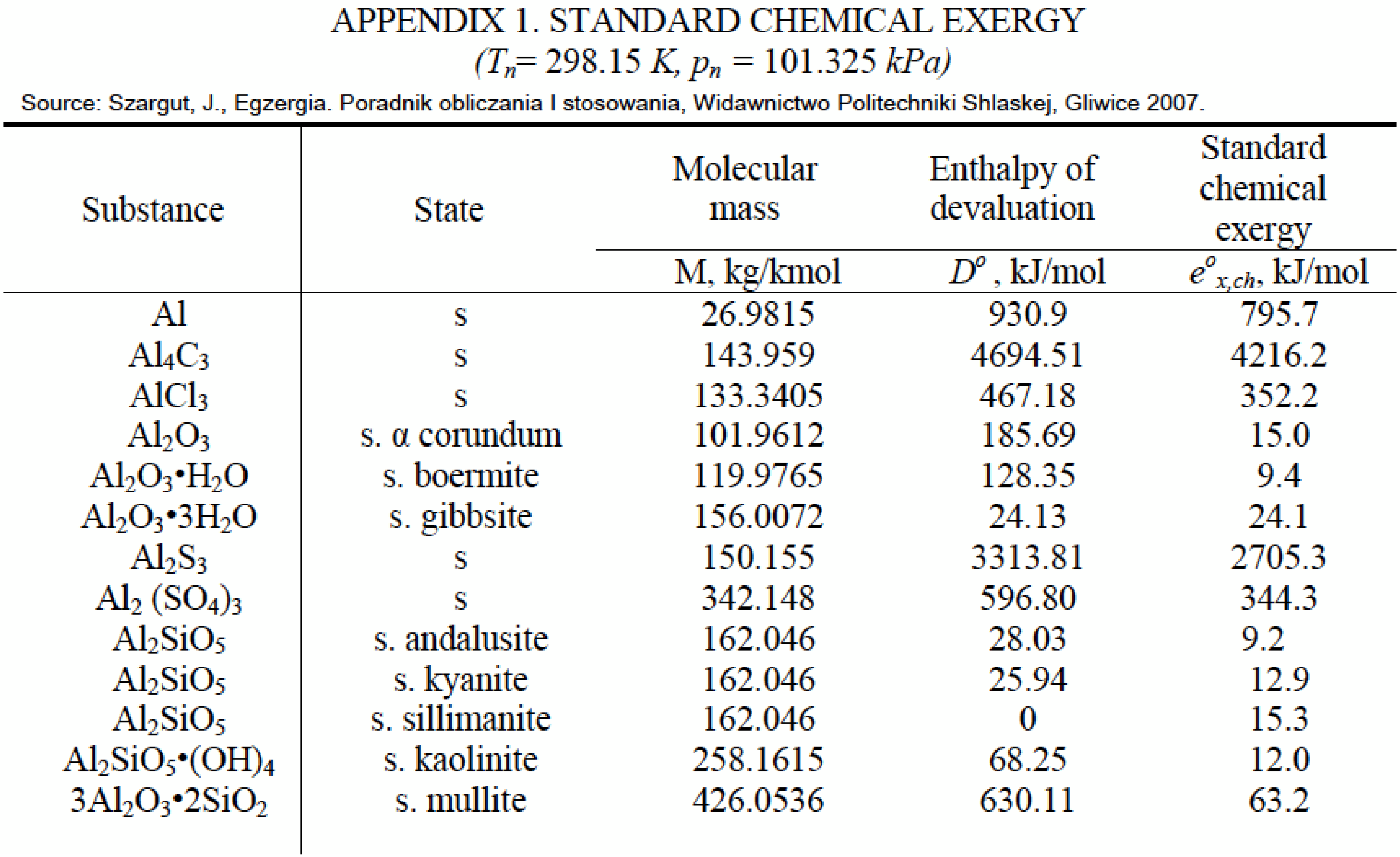
$$v_a R_a + v_b R_b + ... \rightarrow v_j \Pi_j + v_k \Pi_k + ...$$

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

Thank you Jan Szargut



APPENDIX 1. STANDARD CHEMICAL EXERGY

(T_n= 298.15 K, p_n = 101.325 kPa)

Source: Szargut, J., Egzergia. Poradnik obliczania I stosowania, Widawnictwo Politechniki Shlaskej, Gliwice 2007.

Substance	State	Molecular mass	Enthalpy of devaluation	Standard chemical exergy
		M, kg/kmol	D^o , kJ/mol	$e^o_{x,ch}$, kJ/mol
Al	s	26.9815	930.9	795.7
Al_4C_3	s	143.959	4694.51	4216.2
$AlCl_3$	s	133.3405	467.18	352.2
Al_2O_3	s. α corundum	101.9612	185.69	15.0
$Al_2O_3 \cdot H_2O$	s. boermite	119.9765	128.35	9.4
$Al_2O_3 \cdot 3H_2O$	s. gibbsite	156.0072	24.13	24.1
Al_2S_3	s	150.155	3313.81	2705.3
$Al_2 (SO_4)_3$	s	342.148	596.80	344.3
Al_2SiO_5	s. andalusite	162.046	28.03	9.2
Al_2SiO_5	s. kyanite	162.046	25.94	12.9
Al_2SiO_5	s. sillimanite	162.046	0	15.3
$Al_2SiO_5 \cdot (OH)_4$	s. kaolinite	258.1615	68.25	12.0
$3Al_2O_3 \cdot 2SiO_2$	s. mullite	426.0536	630.11	63.2

Also see: http://www.exergoecology.com/excalc

Example: Burning Carbon

$$C + O_2 \rightarrow CO_2$$

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

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

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

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

These exergy values come from Szargut's Appendix Tables

Compare this with reality

- The composition of coal…
- The source of oxygen
- The output gases and particulates
- Gibbs Free Energy of formation for CO2
- Published values for the heating values for coal

Burning Octane

$$2C_8H_{18(l)} + 25\ O_{2(g)} \rightarrow 16\ CO_{2(g)} + 18H_2O_{(g)}$$

$$2(5413.1) + 25(3.97) - 16(19.87) - 18(9.5) = \Delta B$$

$$\Delta B = 10{,}436.53\ \text{kJ/2 mols of octane}$$

$$\frac{10{,}436.53}{(2[(8 \times 12) + 18] = 228\text{g})} = \boxed{45.8\ \frac{\text{MJ}}{\text{kg}}}$$

Ashby gives the “energy intensity” of gasoline as 45MJ/kg p45

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

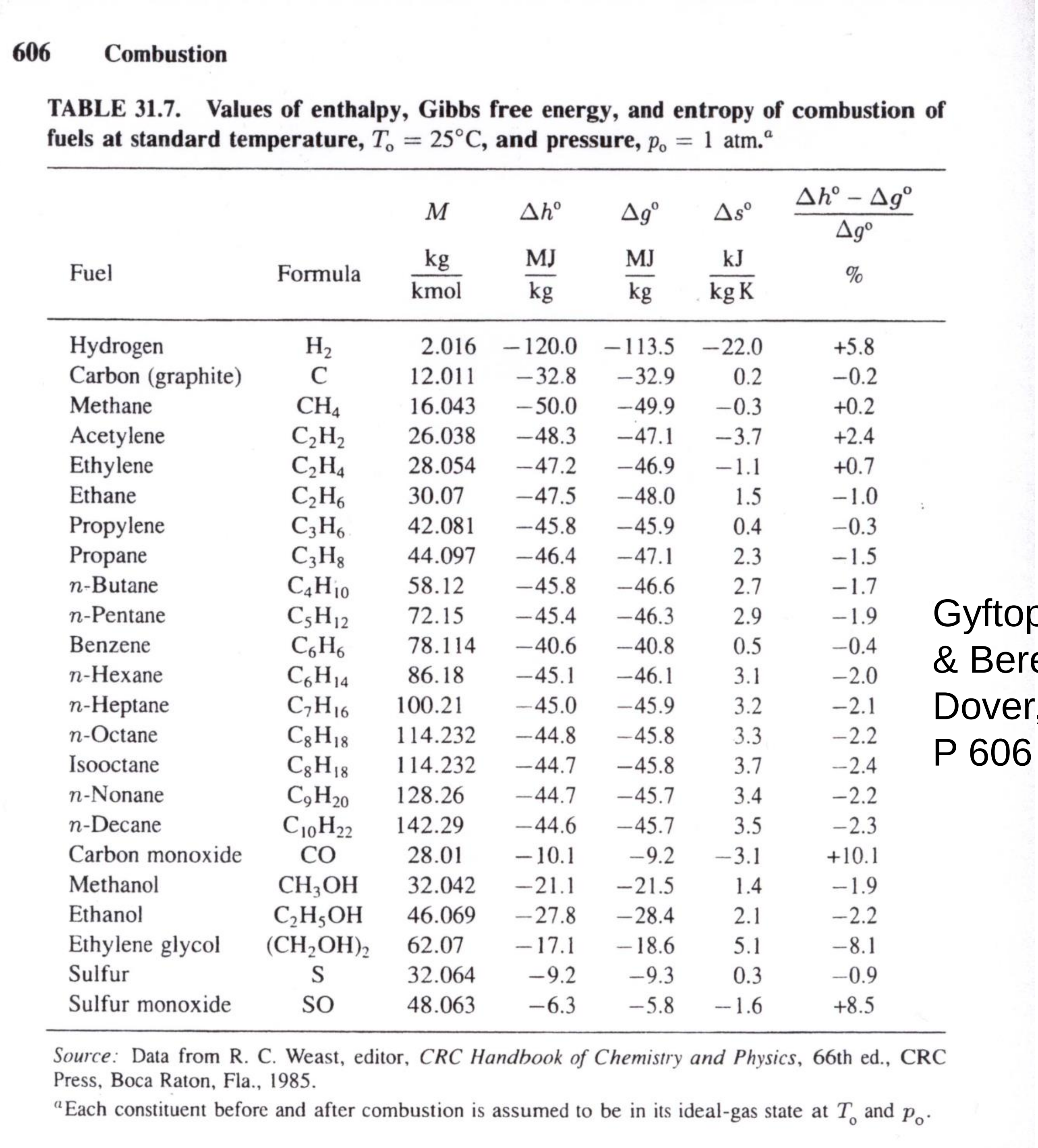


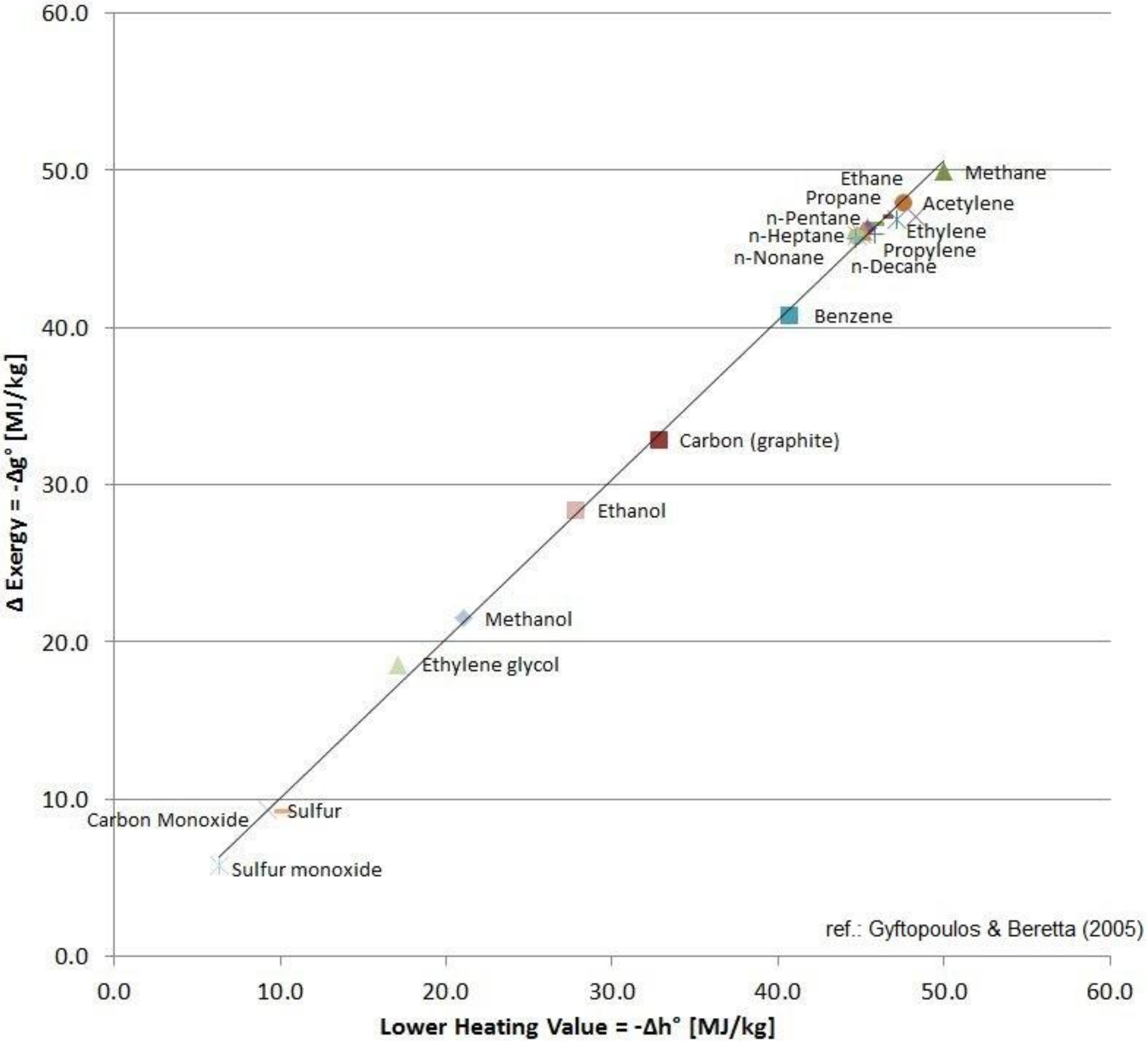
TABLE 31.7. Values of enthalpy, Gibbs free energy, and entropy of combustion of fuels at standard temperature, $T_o = 25°C$, and pressure, $p_o = 1$ atm.[a]

Fuel	Formula	M $\frac{\text{kg}}{\text{kmol}}$	Δh^o $\frac{\text{MJ}}{\text{kg}}$	Δg^o $\frac{\text{MJ}}{\text{kg}}$	Δs^o $\frac{\text{kJ}}{\text{kg K}}$	$\frac{\Delta h^o - \Delta g^o}{\Delta g^o}$ %
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.

Gyftopoulos
& Beretta
Dover, 2005
P 606



ref.: Gyftopoulos & Beretta (2005)

Example: Oxidation of Aluminum

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

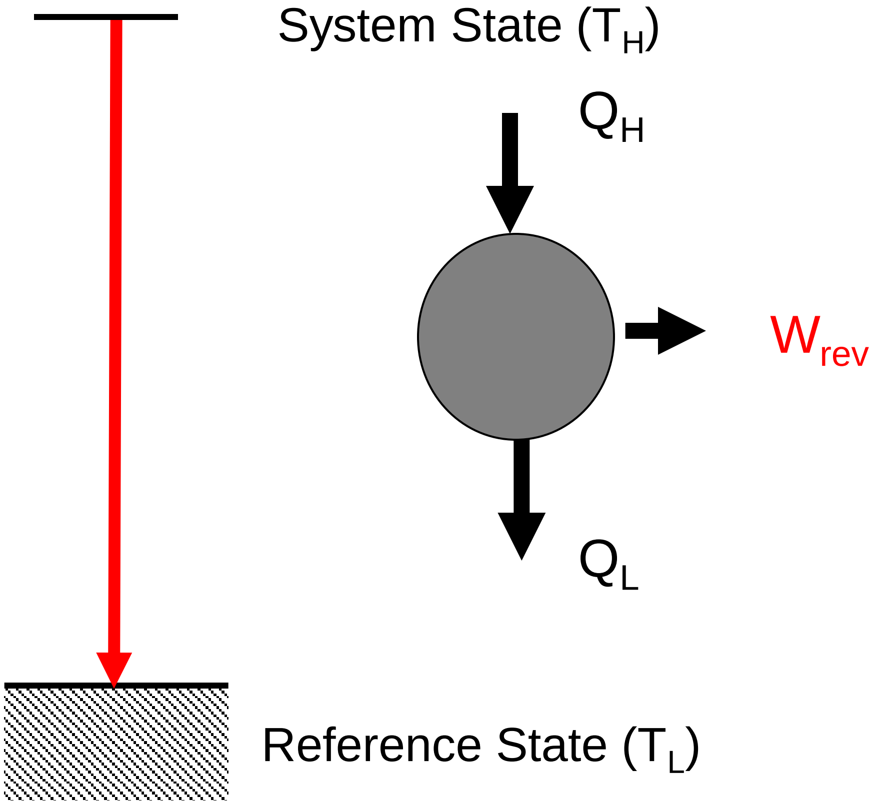
$$2 \times 888.4\frac{kJ}{mol} \quad + \quad \frac{3}{2} \times 3.97\frac{kJ}{mol} \quad - \quad 200.4\frac{kJ}{mol} \quad = \quad B_{lost}$$

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

The “fuel” value of aluminum would be 1582.4/(2X26.98) = 29.3 MJ/kg

See Appendix of Szargut for exegy values

Materials can do work?



System State (T_H)

Q_H

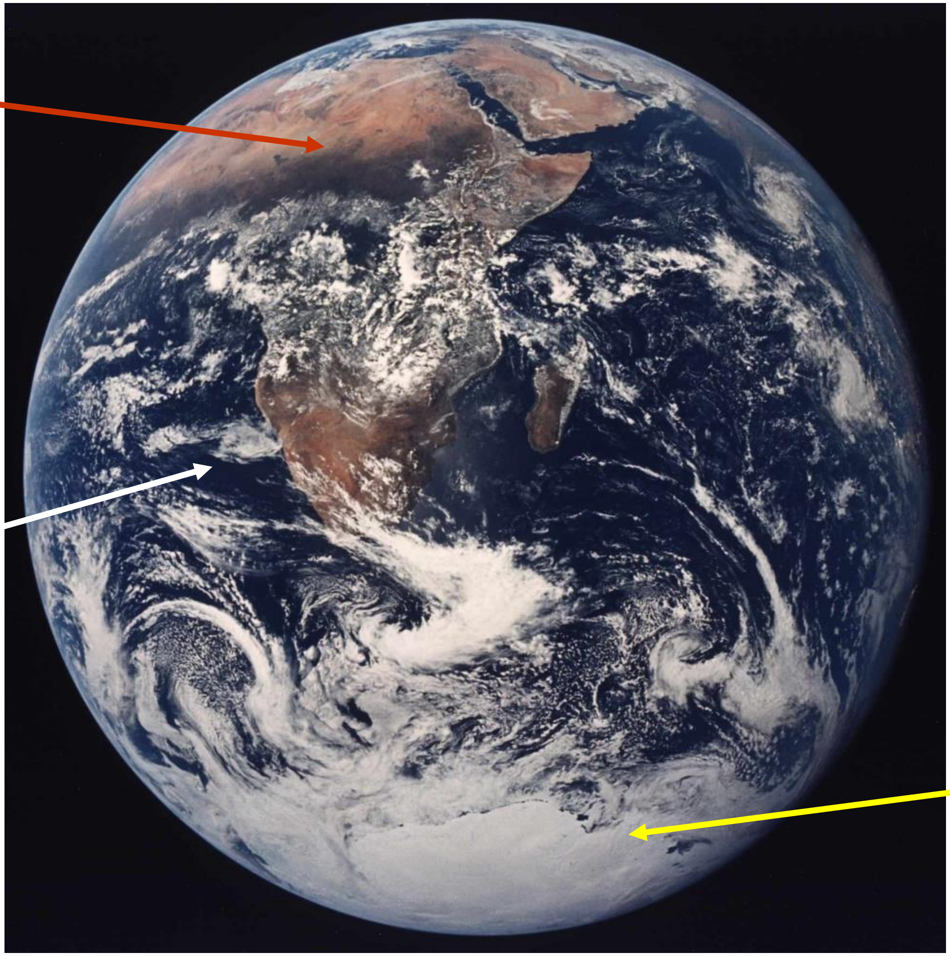
W_{rev}

Q_L

Reference State (T_L)

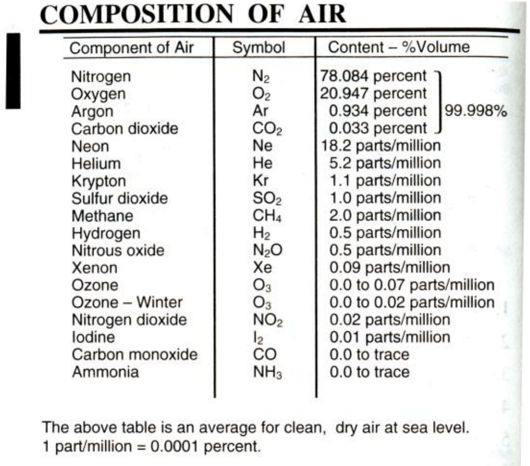
Insert reversible heat engine between high and low temperatures

Chemical Properties referenced to the “environment”



Crust

Oceans



COMPOSITION OF AIR

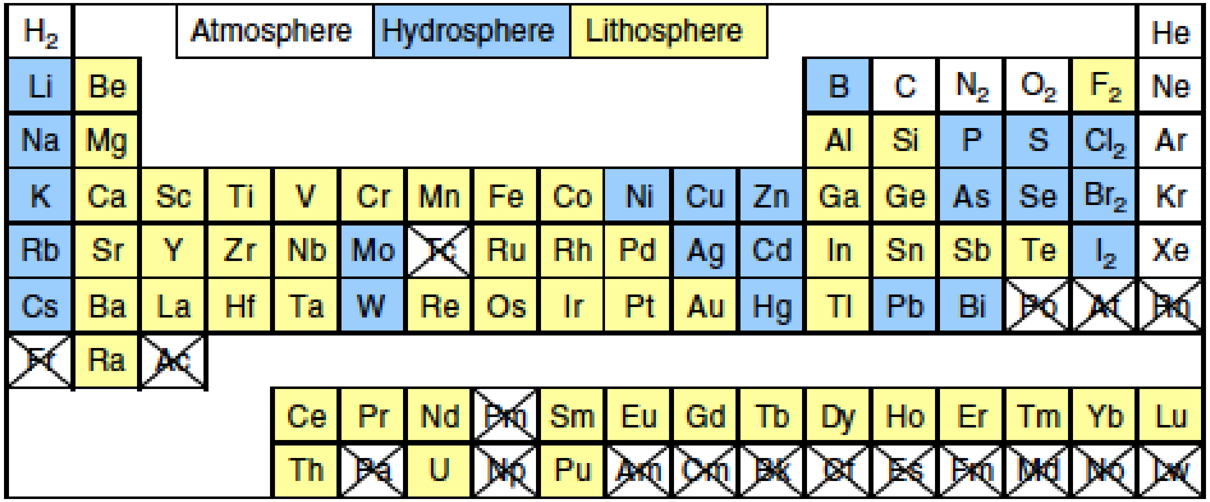
Component of Air	Symbol	Content – %Volume	
Nitrogen	N_2	78.084 percent	99.998%
Oxygen	O_2	20.947 percent	
Argon	Ar	0.934 percent	
Carbon dioxide	CO_2	0.033 percent	
Neon	Ne	18.2 parts/million	
Helium	He	5.2 parts/million	
Krypton	Kr	1.1 parts/million	
Sulfur dioxide	SO_2	1.0 parts/million	
Methane	CH_4	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.

Atmosphere

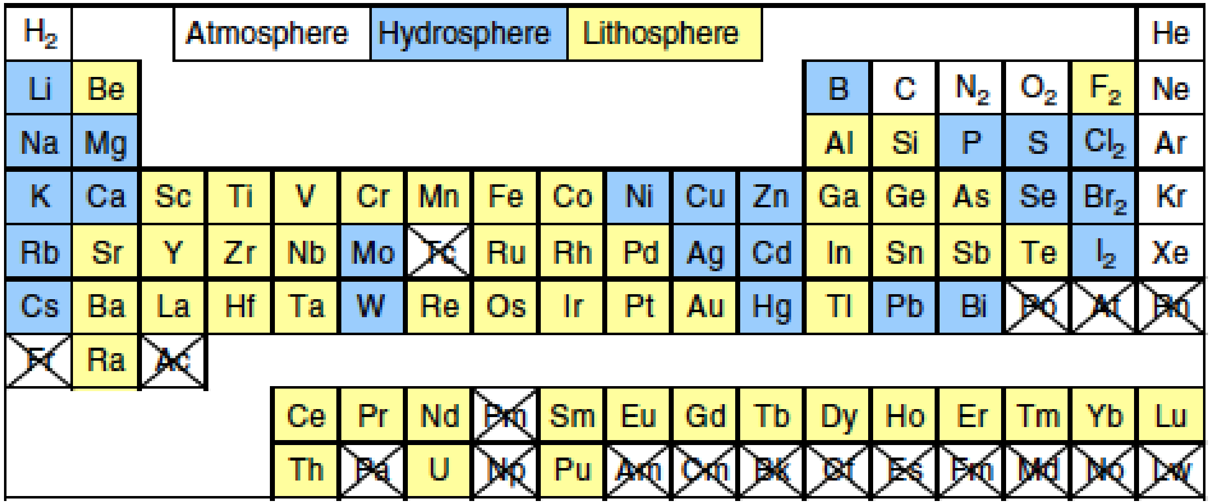
$T_0 = 298.2$ K, $P_0 = 101.3$ kPA

R. Rivero, M. Garfias / Energy 31 (2006) 3310–3326



H_2 ⬜			Atmosphere ⬜	Hydrosphere 🟦	Lithosphere 🟨												He ⬜
Li 🟦	Be 🟨											B 🟦	C ⬜	N_2 ⬜	O_2 ⬜	F_2 🟨	Ne ⬜
Na 🟦	Mg 🟨											Al 🟨	Si 🟨	P 🟦	S 🟦	Cl_2 🟦	Ar ⬜
K 🟦	Ca 🟨	Sc 🟨	Ti 🟨	V 🟨	Cr 🟨	Mn 🟨	Fe 🟨	Co 🟨	Ni 🟦	Cu 🟦	Zn 🟦	Ga 🟨	Ge 🟨	As 🟦	Se 🟦	Br_2 🟦	Kr ⬜
Rb 🟦	Sr 🟨	Y 🟨	Zr 🟨	Nb 🟨	Mo 🟦	Tc ☒	Ru 🟨	Rh 🟨	Pd 🟨	Ag 🟦	Cd 🟦	In 🟨	Sn 🟨	Sb 🟨	Te 🟨	I_2 🟦	Xe ⬜
Cs 🟦	Ba 🟨	La 🟨	Hf 🟨	Ta 🟨	W 🟦	Re 🟨	Os 🟨	Ir 🟨	Pt 🟨	Au 🟨	Hg 🟦	Tl 🟨	Pb 🟦	Bi 🟦	Po ☒	At ☒	Rn ☒
Fr ☒	Ra 🟨	Ac ☒															
				Ce 🟨	Pr 🟨	Nd 🟨	Pm ☒	Sm 🟨	Eu 🟨	Gd 🟨	Tb 🟨	Dy 🟨	Ho 🟨	Er 🟨	Tm 🟨	Yb 🟨	Lu 🟨
				Th 🟨	Pa ☒	U 🟨	Np ☒	Pu 🟨	Am ☒	Cm ☒	Bk ☒	Cf ☒	Es ☒	Fm ☒	Md ☒	No ☒	Lw ☒

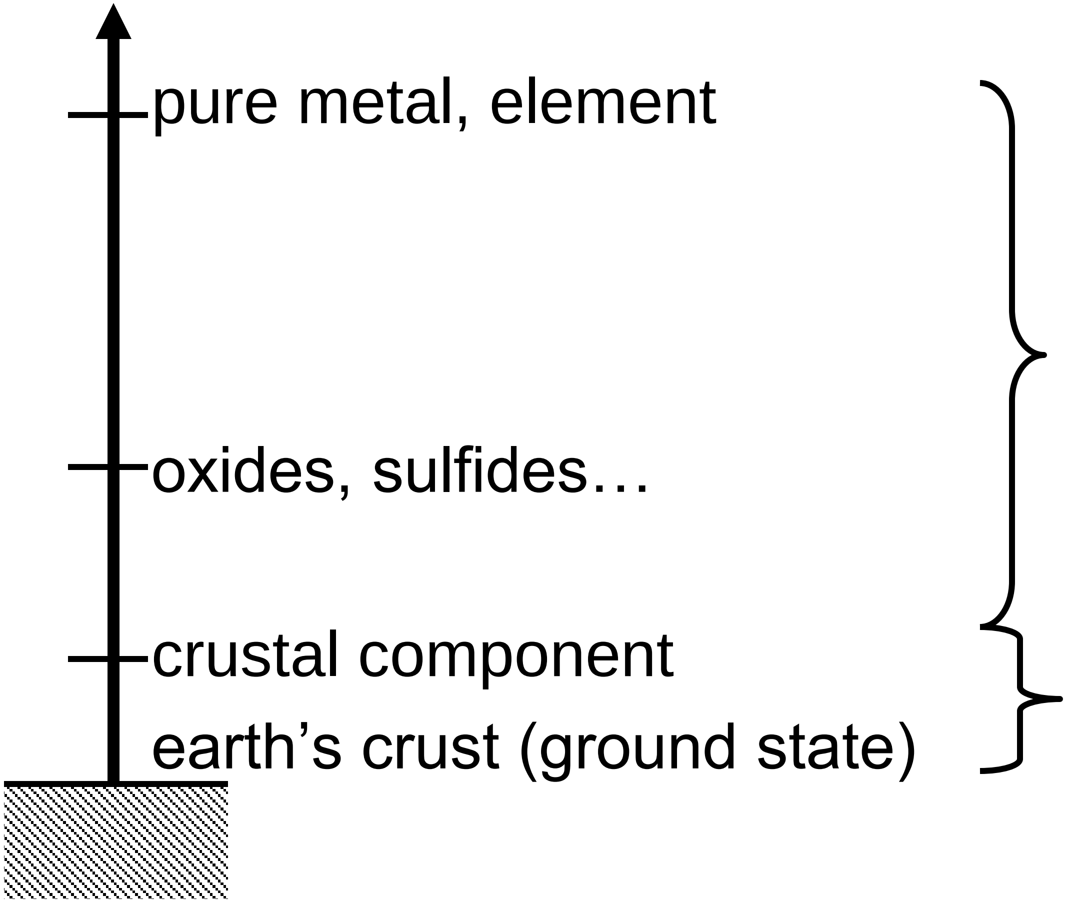
Fig. 3. Reference species media for elements according to Szargut [3].



H_2 ⬜			Atmosphere ⬜	Hydrosphere 🟦	Lithosphere 🟨												He ⬜
Li 🟦	Be 🟨											B 🟦	C ⬜	N_2 ⬜	O_2 ⬜	F_2 🟨	Ne ⬜
Na 🟦	Mg 🟦											Al 🟨	Si 🟨	P 🟦	S 🟦	Cl_2 🟦	Ar ⬜
K 🟦	Ca 🟦	Sc 🟨	Ti 🟨	V 🟨	Cr 🟨	Mn 🟨	Fe 🟨	Co 🟨	Ni 🟦	Cu 🟦	Zn 🟦	Ga 🟨	Ge 🟨	As 🟨	Se 🟦	Br_2 🟦	Kr ⬜
Rb 🟦	Sr 🟨	Y 🟨	Zr 🟨	Nb 🟨	Mo 🟦	Tc ☒	Ru 🟨	Rh 🟨	Pd 🟨	Ag 🟦	Cd 🟦	In 🟨	Sn 🟨	Sb 🟨	Te 🟨	I_2 🟦	Xe ⬜
Cs 🟦	Ba 🟨	La 🟨	Hf 🟨	Ta 🟨	W 🟦	Re 🟨	Os 🟨	Ir 🟨	Pt 🟨	Au 🟨	Hg 🟦	Tl 🟨	Pb 🟦	Bi 🟦	Po ☒	At ☒	Rn ☒
Fr ☒	Ra 🟨	Ac ☒															
				Ce 🟨	Pr 🟨	Nd 🟨	Pm ☒	Sm 🟨	Eu 🟨	Gd 🟨	Tb 🟨	Dy 🟨	Ho 🟨	Er 🟨	Tm 🟨	Yb 🟨	Lu 🟨
				Th 🟨	Pa ☒	U 🟨	Np ☒	Pu 🟨	Am ☒	Cm ☒	Bk ☒	Cf ☒	Es ☒	Fm ☒	Md ☒	No ☒	Lw ☒

Fig. 4. Reference species media for elements according to Valero et al. [10].

Exergy Reference System



pure metal, element

oxides, sulfides…

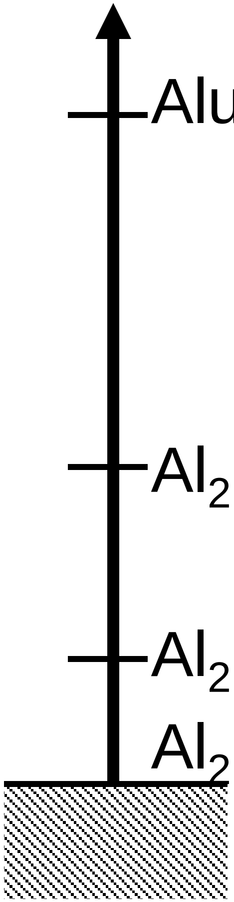
crustal component

earth’s crust (ground state)

chemical reactions

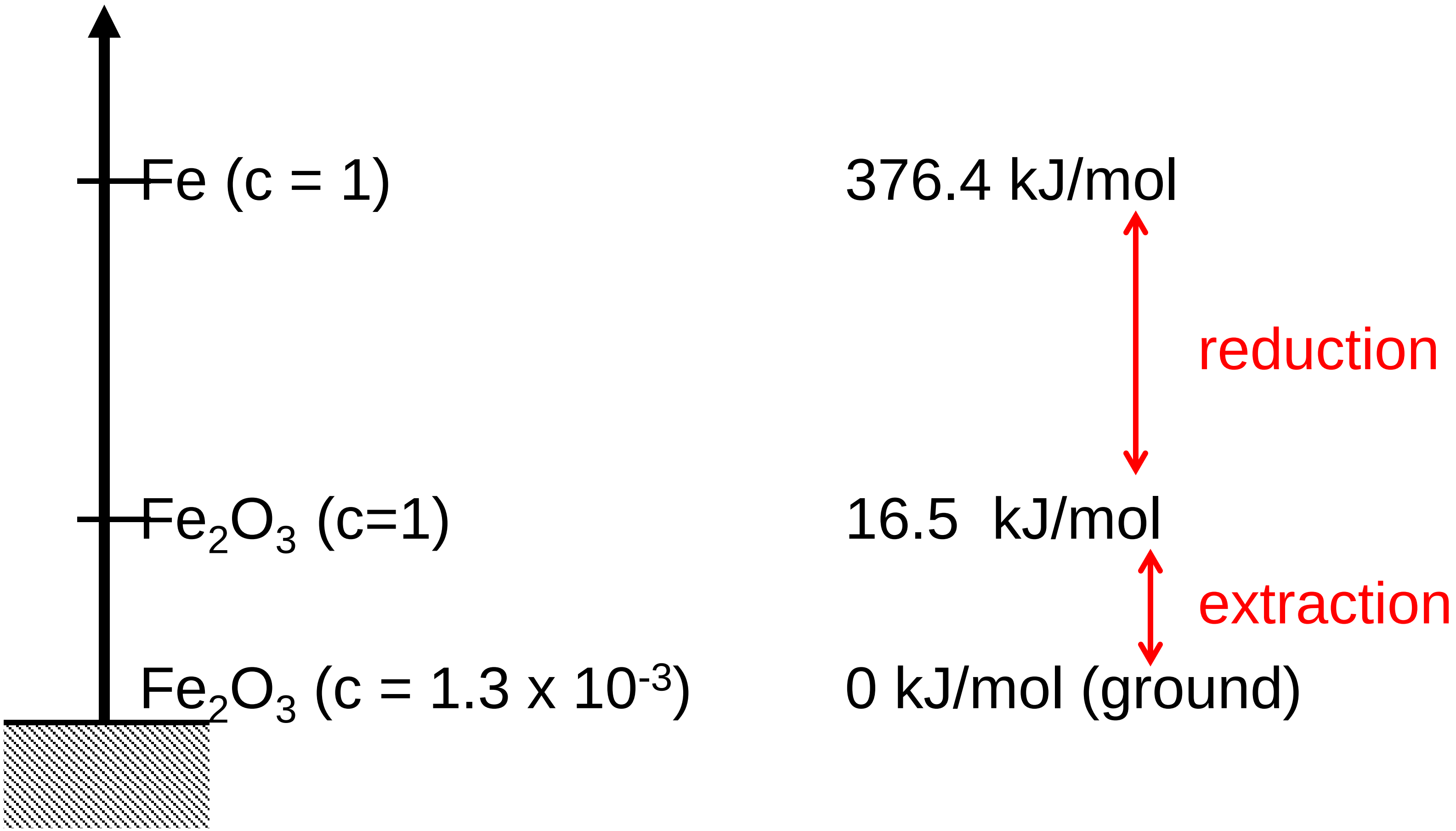
extraction

Exergy Reference System



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

Example; making pure iron from the crust



Fe (c = 1) 376.4 kJ/mol

reduction

Fe_2O_3 (c=1) 16.5 kJ/mol

extraction

Fe_2O_3 ($c = 1.3 \times 10^{-3}$) 0 kJ/mol (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

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

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

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

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

Reduction of Fe_2O_3 with carbon

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

2 x 16.5 + 3 x 410.3 – 4 x 376.4 – 3 x 19.9 =

B_{lost} = - 301.4 kJ

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

Stoichiometrically balanced but not spontaneous

We need more carbon

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

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

$2Fe_2O_3 + 3.76C + 0.76O_2 \rightarrow 4Fe + 3.76\ CO_2$

Ref Baumgärtner & de Swaan Arons JIE 2003

And more carbon…

but the efficiency <u>of the use of carbon</u> 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 mol of Fe

this is 15.2 MJ/kg (Fe)

Iron Ore Reduction

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

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

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

Summary for Iron Ore

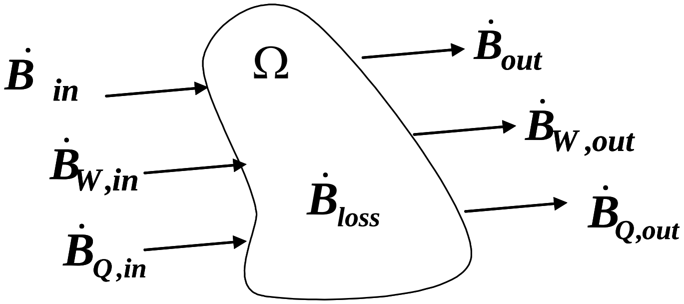
$$\text{fuel used} = 22\ \text{MJ/kg} \approx 15.2(B_{\text{lost}}) + 6.7(B_{\text{Fe}})$$

“Credit” for producing pure iron from the crust

Lost exergy from making iron from Fe_2O_3

See Smil Table A.12, iron from ore 20 - 25 MJ/kg

Exergy Balance for open system



$$\dot{B}_{in} + \dot{B}_{W,in} + \dot{B}_{Q,in} = \dot{B}_{out} + \dot{B}_{W,out} + \dot{B}_{Q,out} + \dot{B}_{loss}$$

These terms include materials flows (with chemical and physical exergy), work and heat interactions and internal irreversibilities, where:

$$\dot{B}_{in/out} = \dot{B}^{ph}_{in/out} + \dot{B}^{ch}_{in/out}$$

$$\dot{B}_{W,in/out} = \dot{W}_{in/out}$$

$$\dot{B}_{Q,in/out} = \left(1 - T_o / T\right)\dot{Q}_{in/out}$$