Introduction to the "Exergy" Concept"

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Readings

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

Exergy Accounting

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

Definition 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, involving interaction only with the above mentioned components of nature" [Szargut et al 1988].

Exergy



Exergy



Aggregate Exergy Accounting



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

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Thermodynamics Overview

- Systems
- Heat Interactions
- Exergy of heat interaction
- Entropy and Enthapy
- Physical and Chemical Exergy

Open System

Work interaction



Heat interaction

Closed System



Isolated System



The 1st Law

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

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

Heat Interaction Q.



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Carnot's "Reversible" Heat Engine

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

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

Maximum Work Output

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

- 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, T₀, and P₀...
- 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."

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."

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. 20 Keenan, 1941

Energy, E and Exergy, B = Ex





Properties for two different states of the system shown by the boxes. This change may come about due to spontaneous changes or due to heat or work interaction, or mass transfer.

 $B_1 - B_2 = E_1 - E_2 \quad \cancel{reversible process}$ $B_1 - B_2 \ge E_1 - E_2 \quad \cancel{reversible process}$

Ref: Gyftopoulos and Beretta

Define Entropy

$$S_{1} = S_{o} + \frac{1}{C_{R}} \left[\left(E_{1} - E_{o} \right) - \left(B_{1} - B_{o} \right) \right]$$

- They show $C_R = T_R = T_{OP}$
- Entropy is a Property
- Entropy is a measure of something lost

Ref: Gyftopoulos and Beretta

Entropy Difference

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

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

Ref: Gyftopoulos and Beretta

Example, Heat Interaction $P_{Q, T}$ T T_{0}

$$E_2 - E_1 + Q \mathcal{P}$$

$$B_2 = B_1 + Q(1 - T_0/T) \mathcal{P}$$

$$\Delta S = (1/T_0)(Q - Q + Q(T_0/T)) = Q/T \mathcal{P}$$

$$\mathcal{P}$$

Example, Work Interaction



$$E_2 = E_1 + W \not$$

$$B_2 = B_1 + W \not$$

$$\Delta S = (W - W) = O \not$$

Homeworks 1 & 2>



 Calculate the entropy change for a reversible heat engine, and
 Calculate the entropy loss for a reversible heat engine.

Use the results given in this Presentation.

Answers for 1 & 2

Consider the process in two stages; 1) you transfer heat in, and 2) You transfer heat and work out. Use the result from Carnot to Show that the change in entropy is zero. This leads to the result that The exergy lost is also zero.

$$\Delta S = S_2 - S_1 = \frac{1}{T_o} \left[\left(E_2 - E_1 \right) - \left(B_2 - B_1 \right) \right] = \frac{Q_L}{T_L} - \frac{Q_H}{T_H}$$
$$B_{lost} = Q_H - Q_L + T_o \Delta S - W$$

Properties or State Variables



State Variables $\oint dU = 0 \qquad \int_{1}^{2} d\phi = \phi_{2} - \phi_{1}$ dO

 $\oint \frac{dQ}{T} = 0 \qquad \oint d(U + PV) = 0$

Enthalpy H=U+PV♪





Here the Work done is

$$W = P(V_2 - V_1)$$

 $Q_{in} = \Delta H$

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

Constant Pressure Equilibrium Process



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)

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

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

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

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

Minimum Work = Exergy)

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

= $(H_{p,T} - H_{p_o,T_o}) - T_o(S_{p,T} - S_{p_o,T_o})$
 $B = (H - T_o S) - (H - T_o S)_o$
 $W_{\min} = \frac{\dot{W}_{rev}}{\dot{m}} = B_{out} - B_{in}$

Lost Work & Lost Exergy

Recall:

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

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

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



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

... the <u>maximum</u> amount of work that can be \triangleright obtained from a system in reference to the \triangleright environment at standard conditions, T_o , P_o ,

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

Open flow system



Figure 1 Changes in steady-state flow.

First Law for a Flow System?

$$\left(\frac{dU}{dt}\right)_{cv} = \sum_{in} \dot{m}_i \left(h_i + \frac{u_i^2}{2} + gz_i\right)$$
$$-\sum_{out} \dot{m}_j \left(h_j + \frac{u_i^2}{2} + gz_j\right)$$
$$+\sum \dot{Q}_{in} - \sum \dot{Q}_{out} + \sum \dot{W}_{sh,in} - \sum \dot{W}_{sh,out}$$
$$\dot{m} \left(\Delta H + \frac{\Delta u^2}{2} + g\Delta z\right) + \dot{Q}_{in} - \dot{W}_{out} = 0$$
EQ 1

one stream steady state

Second Law for a Flow System



From EQ 1 & 2

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

$$\dot{m}\Delta S + \frac{\dot{Q}}{T_0} + \dot{S}_{generated} = 0$$

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

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Physical and Chemical Exergy

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

•
$$B^{ch}(\mu * = \mu_o) = 0$$

• when $B = B^{ph} + B^{ch} = 0$

- this is the "dead state"

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°, kJ/mol	$e^{o}_{x,ch}$, kJ/mol
Al	S	26.9815	930.9	795.7
Al ₄ C 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 ₂ O ₃ •H ₂ O	s. boermite	119.9765	128.35	9.4
$Al_2O_3 \bullet 3H_2O$	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 ₂ SiO ₅	s. andalusite	162.046	28.03	9.2
Al ₂ SiO ₅	s. kyanite	162.046	25.94	12.9
Al_2SiO_5	s. sillimanite	162.046	0	15.3
Al ₂ SiO ₅ •(OH) ₄	s. kaolinite	258.1615	68.25	12.0
$3Al_2O_3 \cdot 2SiO_2$	s. mullite	426.0536	630.11	63.2

Chemical Reaction, at T_o , p_o $n_1R_1 + n_2R_2 \rightarrow n_3\Pi_{3}$,



Chemical Reactions

stoichiometric mass balance $V_a R_a + V_b R_b + \dots \rightarrow V_j \Pi_j + V_k \Pi_k + \dots$

exergy "balance"

$$V_a b_{R_a} + V_b b_{R_b} + \dots - V_j b_{\Pi_j} - V_k b_{\Pi_k} = B_{lost}$$

where exergy b is given in kJ/mole



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

<u> 394.4 kJ </u>	=	32.9	MJ
mol of carbon			kg

These exergy values come from Szargut's Appendix Tables

Burning Octane

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

 $2(5413.1) + 25(3.97) - 16(19.87) - 18(9.5) = \Delta B$ $\Delta B = 10,436.53 \text{ kJ/2 mols of octane}$

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

Note: $\Delta B = -\Delta G^{o}_{f} = \Delta H - T_{o}\Delta S \approx LHV$

606 Combustion

		М	Δh^{o}	Δg^{o}	Δs^{o}	$rac{\Delta h^{ m o}-\Delta g^{ m o}}{\Delta a^{ m o}}$
Fuel	Formula	kg kmol	$\frac{MJ}{kg}$	$\frac{MJ}{kg}$	kJ kgK	%
Hydrogen	H ₂	2.016	-120.0	-113.5	-22.0	+5.8
Carbon (graphite)	С	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
<i>n</i> -Butane	C_4H_{10}	58.12	-45.8	-46.6	2.7	-1.7
<i>n</i> -Pentane	$C_{5}H_{12}$	72.15	-45.4	-46.3	2.9	-1.9
Benzene	C_6H_6	78.114	-40.6	-40.8	0.5	-0.4
<i>n</i> -Hexane	$C_{6}H_{14}$	86.18	-45.1	-46.1	3.1	-2.0
<i>n</i> -Heptane	$C_7 H_{16}$	100.21	-45.0	-45.9	3.2	-2.1
n-Octane	C ₈ H 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
<i>n</i> -Nonane	$C_{9}H_{20}$	128.26	-44.7	-45.7	3.4	-2.2
<i>n</i> -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 ₃ OH	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

TABLE 31.7. Values of enthalpy, Gibbs free energy, and entropy of combustion of fuels at standard temperature, $T_o = 25^{\circ}$ C, and pressure, $p_o = 1$ atm.^a

Ref Gyftopolous & Beretta

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

^aEach constituent before and after combustion is assumed to be in its ideal-gas state at T_0 and p_0 .

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Example: Oxidation of Aluminum

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

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

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

See Appendix of Szargut for exegy values₄₉

Materials can do work? >



Chemical Properties referenced to the "environment"

Crust

Oceans



COMPOSITION OF AIR

Component of Air	Symbol	Content – %Volume
Nitrogen	N ₂	78.084 percent
Oxygen	O2	20.947 percent
Argon	Ar	0.934 percent 99.998%
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	CH₄	2.0 parts/million
Hydrogen	H ₂	0.5 parts/million
Nitrous oxide	N ₂ O	0.5 parts/million
Xenon	Xe	0.09 parts/million
Ozone	O3	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
lodine	l 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

$T_0 = 298.2 \text{ K}, P_0 = 101.3 \text{ kPA}$

Exergy Reference System



Exergy Reference System



Example; making pure iron from the crust



	Component of		Reference species			Standard
the		ithosphere		Conventional standard	Standard chemical	exergy of the
Chemical element	Formula	Mass fraction	Formula	mole fraction x _{in}	exergy, kJ/mol	element, kJ/mol
Al (s)	Al ₂ O ₃	0.152	Al ₂ SiO 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)	Со	4×10^{-5}	Co ₃ O ₄	2×10^{-7}	38.2	265.0
Cr (s)	Cr ₂ O ₃	5.2×10^{-4}	$Cr_2O_3(s)$	4×10^{-7}	36.5	544.3
Fe (s)	FeO Fe ₂ O ₃	3.72×10^{-2} 3.10×10^{-2}	$Fe_2O_3(s)$	1.3×10^{-3}	16.5	376.4
K	K ₂ O	3.11×10^{-2}	-	-	-	_
Mg (s)	MgO	3.45×10^{-2}	CaCO ₃ · 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 ₂ O	3.71×10^{-2}		-	-	
P (s)	P ₂ O 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 ₂ O 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 ₂ O ₅	2.3×10^{-4}	$V_2O_5(s)$	2×10^{-6}	32.5	712.1

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

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Extraction from the crust

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

$$B = T_o R \ln \frac{1}{1.3x 10^{-3}}$$

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

Note: $R = k N_{avo}$ (Boltzmann's constant X Avogadro's number) 56 Reduction of Fe_2O_3 (Hematite))

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

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

B_{lost} = - 301.4 kJ 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/mol C

We need
$$\frac{301.4}{394.8} = 0.76$$

mols of carbon

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

Iron Ore Reduction

but the efficiency <u>of the use of carbon</u> is only 30.3% therefore the actual reaction is

Iron Ore Reduction



Summary for Iron Ore

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

Exergy Balance, Open System



Includes: materials flows, heat and work interactions