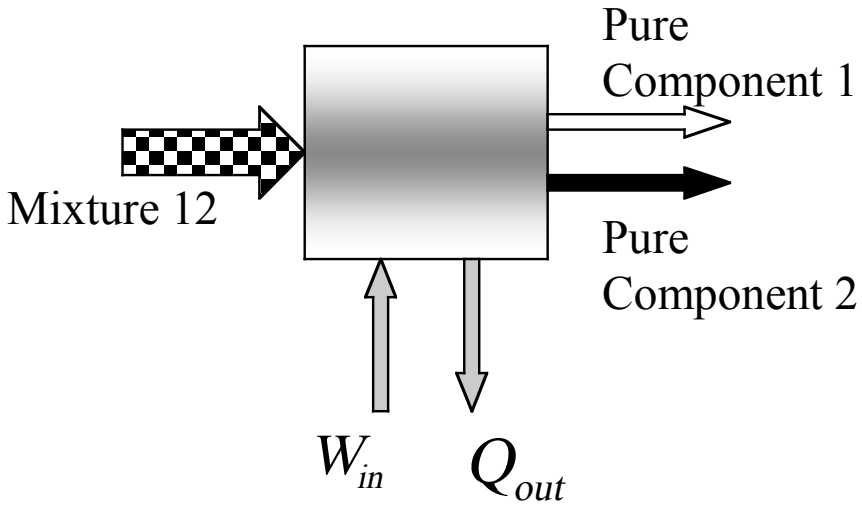
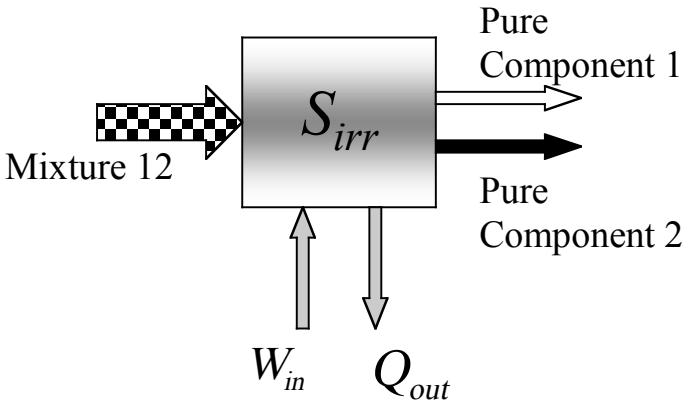
Thermodynamics of separation



What is the minimum work to separate a mixture into it's pure components? Ex. Mining, Desalination, Material Purification, Recycling.

Balance Eq'ns for Mass, Energy & Entropy



$$\frac{dN_{i,sys}}{dt} = N_{i,in} - N_{i,out}$$

$$\frac{dE}{dt} = -Q_{out} + W_{in} + H_{12} - H_1 - H_2$$

$$\frac{dS}{dt} = -\frac{Q_{out}}{T_0} + S_{12} - S_1 - S_2 + S_{irr}$$

$$W_{in} = ((H_1 + H_2) - H_{12}) - T_o((S_1 + S_2) - S_{12}) + T_o S_{irr}$$

$$W_{in} = -N_{12}(h_{mix} - T_0 s_{mix}) + T_0 S_{irr}$$

Minimum Work of Separation

$$W_{in} = ! \; N_{12}(\;\; h_{mix} \; ! \; T_0 \;\; s_{mix}) + T_0 S_{irr}$$

$$W_{in} = ! \; N_{12} \;\; g^{o}_{mix} + T_0 S_{irr}$$

$$w_{\min} = \frac{W_{\min}}{N_{12}} = ! \;\; g^{\#}_{mix}$$

*Gibbs Free Energy of Mixing**

$$\Delta g^{o}_{mix} = \Delta h^{o}_{mix} - T_0 \, \Delta s^{o}_{mix}.$$

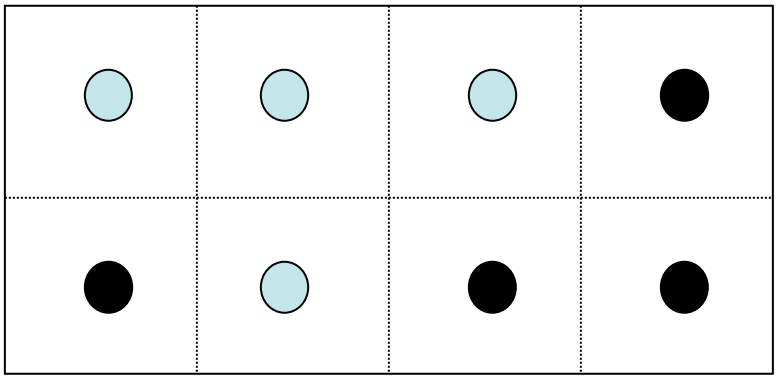
$$\Delta g^{o}_{mix} \approx -T_0 \, \Delta s_{mix} = -T_0 \, (s_{12} - x_1 s_1 - x_2 s_2)$$

For non-interacting molecules entropy can dominate often resulting in a negative Gibbs Free Energy and hence spontaneous mixing. I.e. $\Delta g^{o}_{mix} < 0$

* at standard conditions

Boltzmann's entropy equation

$$S = k \ln \Omega$$

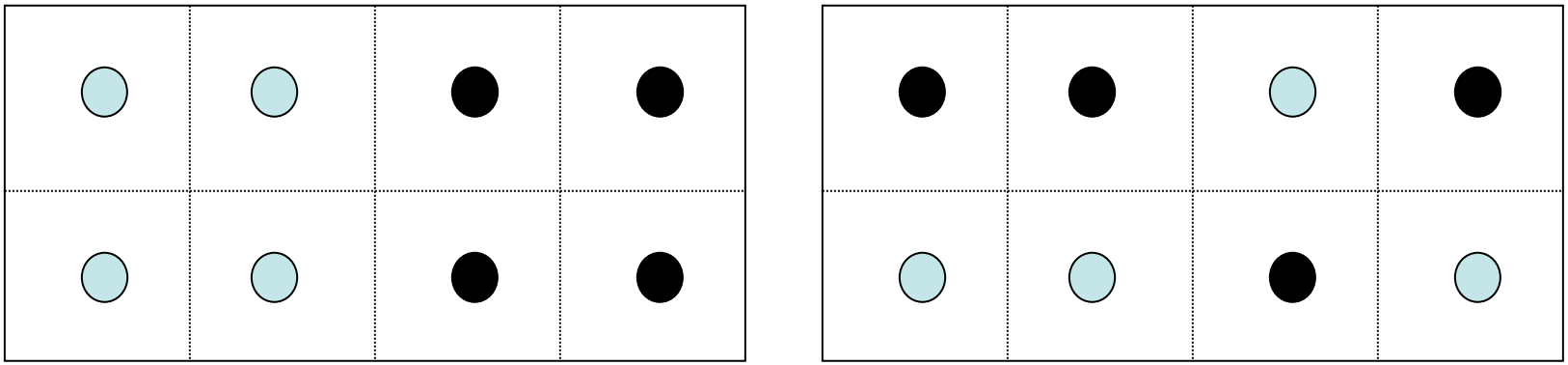


How many ways can "r" atoms be positioned in a lattice with "n" locations?

$$! = \frac{n!}{r!(n \quad r)!}$$

Ex. 4 atoms in 8 locations

$$! \;_{12} = \frac{n!}{r!(n \quad r)!} = \frac{8!}{4!4!} = \frac{70}{1}$$



$$w_{min} = T_0 \Delta s_{mix} = k\, T_0 (ln\ \Omega_{12})$$

Using Stirling's Approximation

$$ln\ N! = N\ ln\ N - N$$

$$w_{\min} = -T_0 R(x \ln x + (1 - x)\ln(1 - x))$$

Where x is mol fraction r/n, and $R = k\ N_{avo}$

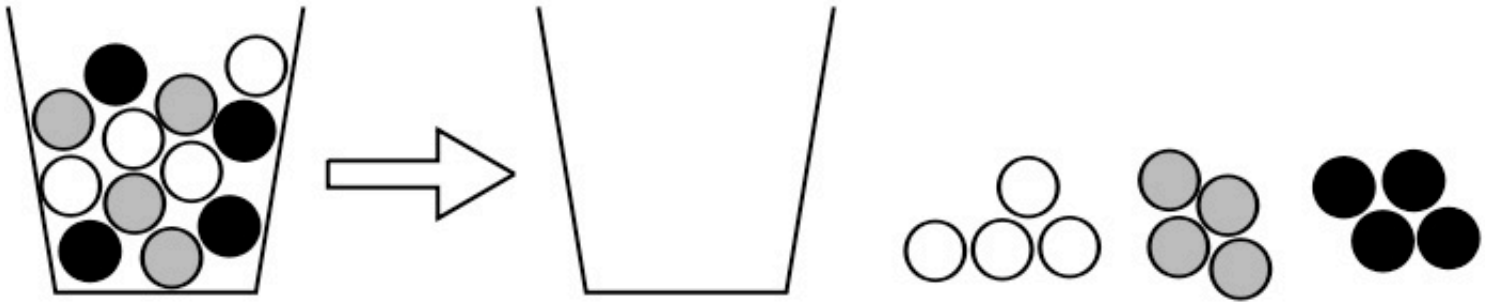
Multi-component System

$$! = \frac{n!}{n_1!n_2!.....n_j!}$$

$$w_{\min} = ! T_0 R \sum_{i=1}^{j} x_i \ln x_i$$

"Separation"

$$w_{\min} = ! T_0 R \sum_{i=1}^{n} x_i \ln x_i$$

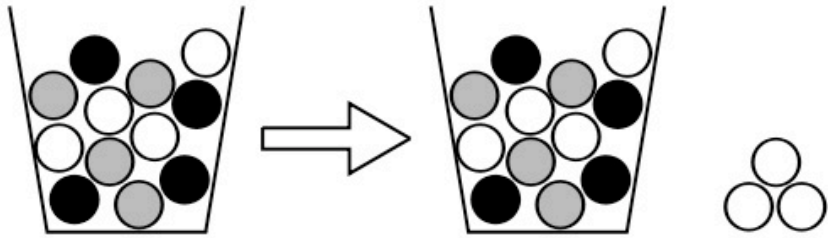


"Extraction"

$$W_{min}^{(N_i)} = ! \; T_0 R(N_1 \; ln \; x + N_2 \; ln(1 ! \; x))$$

$$W_{\min}^{(N_1 ! \, 1)} = ! \; T_0 R((N_1 \; ! \; 1) \ln x + N_2 \ln(1 ! \; x))$$

$$w_{\min,\,1} = T_0 R(\ln \frac{1}{x_1})$$



Separation Examples

- From the atmosphere
- From the Ocean
- Solutions
  - Polymer
  - Water based
  - Liquid metals (activity coef)

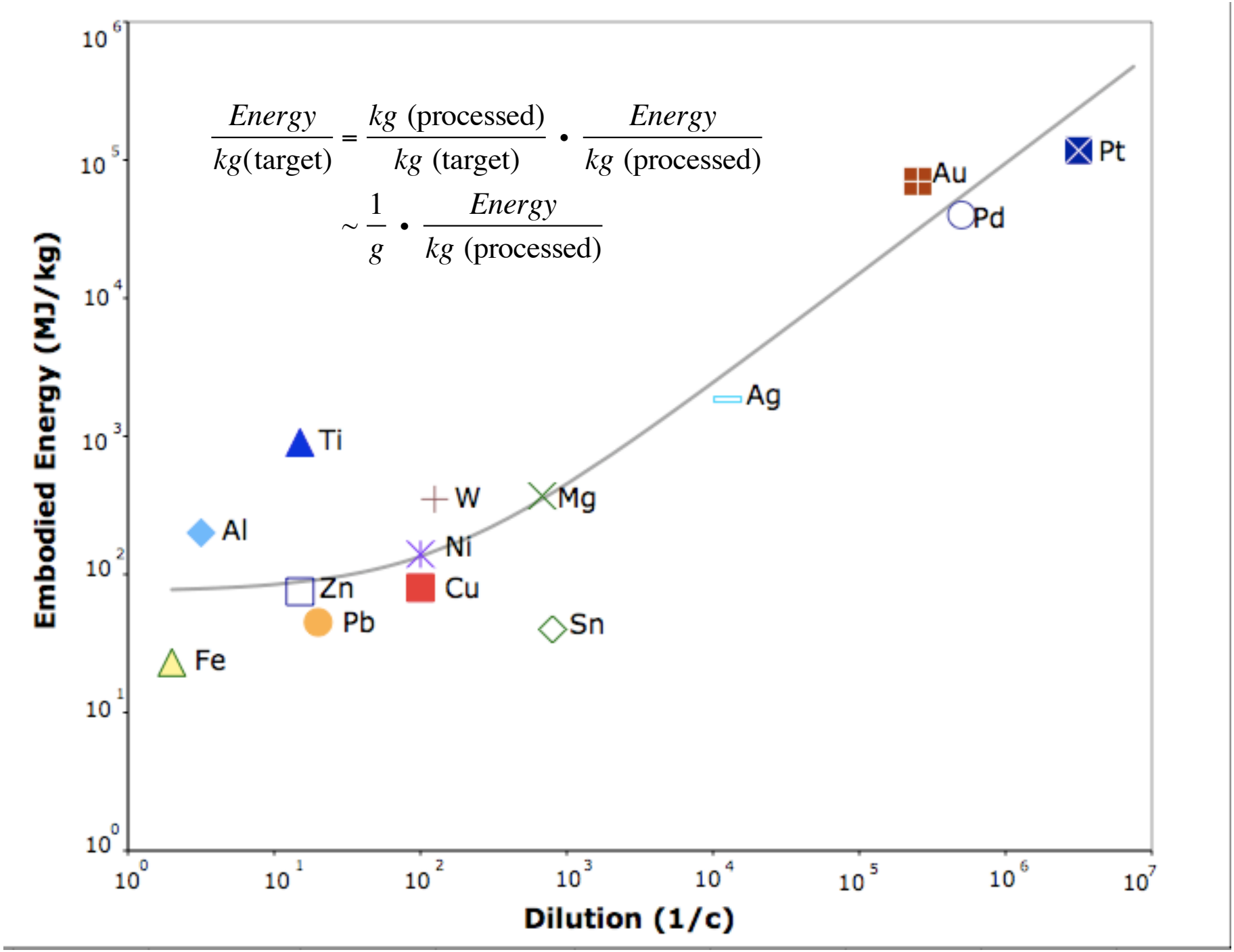
The minimum work to separate O_2 from the atmosphere

Table from the EngineeringToolBox.com

Gas	Ratio compared to Dry Air *(%)*		Molecular Mass *- M - (kg/kmol)*	Chemical Symbol	Boiling Point	
	By volume	By weight			*(K)*	*(^oC)*
Oxygen	20.95	23.20	32.00	O_2	90.2	-182.95
Nitrogen	78.09	75.47	28.02	N_2	77.4	-195.79
Carbon Dioxide	0.03	0.046	44.01	CO_2	194.7	-78.5
Hydrogen	0.00005	~ 0	2.02	H_2	20.3	-252.87
Argon	0.933	1.28	39.94	Ar	84.2	-186
Neon	0.0018	0.0012	20.18	Ne	27.2	-246
Helium	0.0005	0.00007	4.00	He	4.2	-269
Krypton	0.0001	0.0003	83.8	Kr	119.8	-153.4
Xenon	$9\ 10^{-6}$	0.00004	131.29	Xe	165.1	-108.1

$$e^{o}_{x,O_2} = T_0 R(\ln\frac{1}{x_{O_2}}) \; ! \quad 298(K) \,\#\, 8.314(J/molK)\ln(0.212) = 3.84(kJ/mol)$$

In wet air you get 3.97 kJ/mol : compare with Szargut


$\frac{Energy}{kg(\text{target})} = \frac{kg\ (\text{processed})}{kg\ (\text{target})} \bullet \frac{Energy}{kg\ (\text{processed})}$
$\sim \frac{1}{g} \bullet \frac{Energy}{kg\ (\text{processed})}$
Embodied Energy (MJ/kg)
Dilution (1/c)
Fe
Al
Ti
Zn
Pb
W
Ni
Cu
Mg
Sn
Ag
Au
Pd
Pt

energy requirements for mining and milling, possible future trends

underground ~ 1000/g (MJ/t metal)

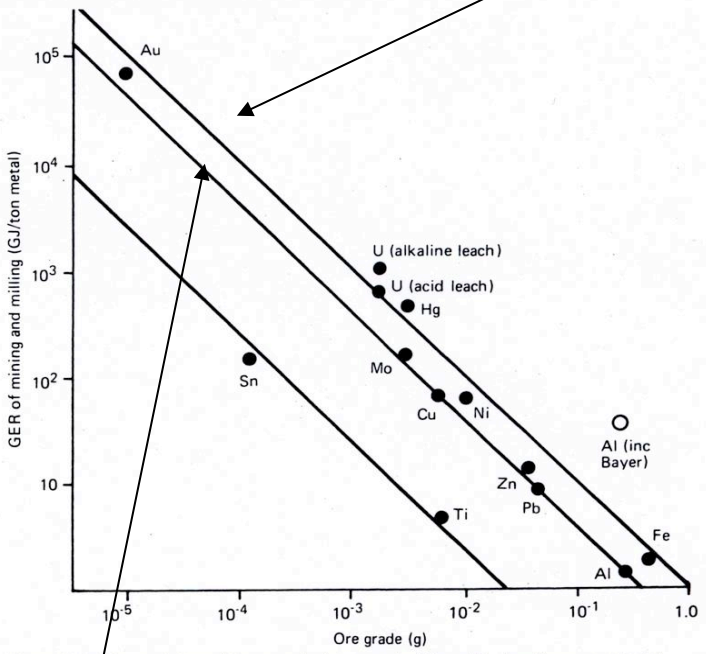


Figure 7.9 The variation of the ger of mining and milling (F_{mm}) with ore grade (g)

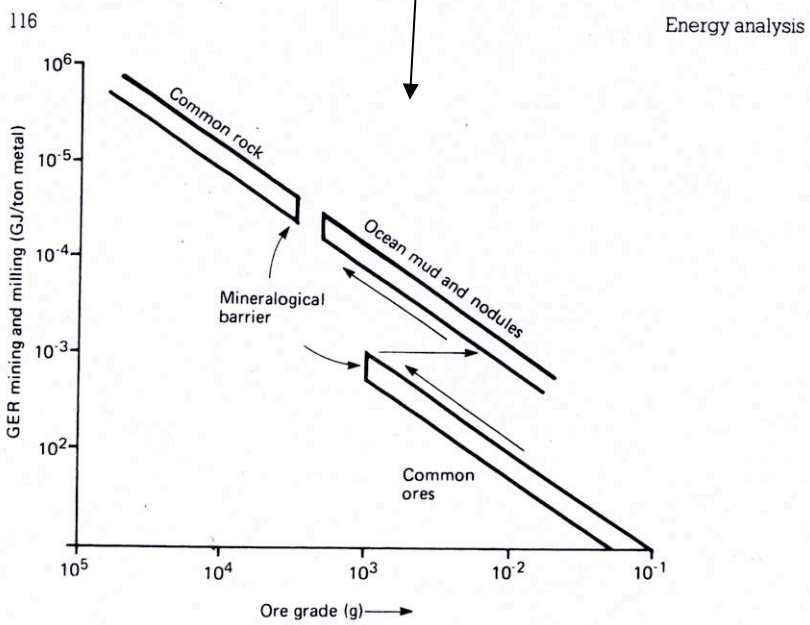
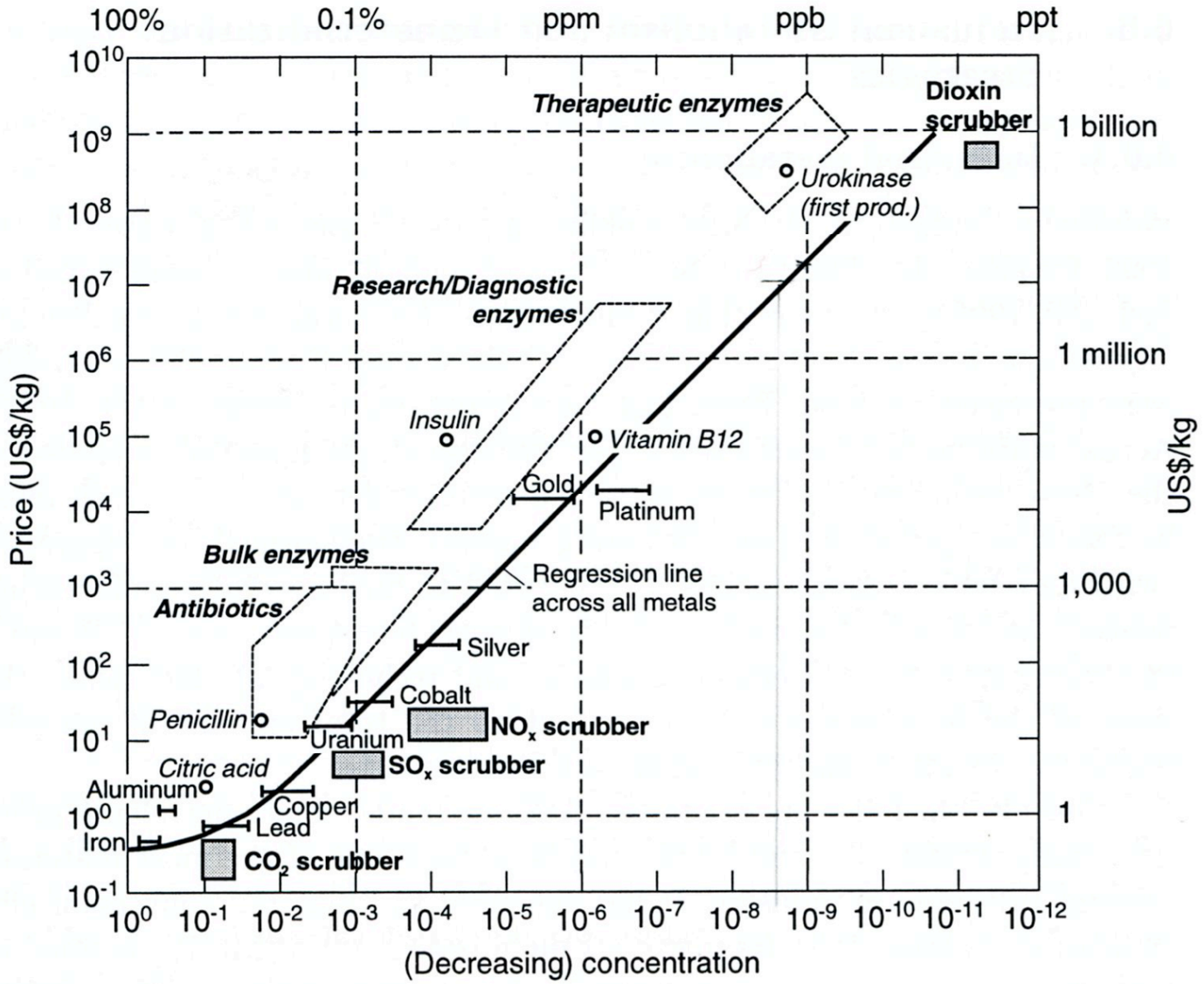


Figure 7.11 A possible sequence of sources of copper and their energy requirements (*Source*: Skinner[30])

open pit ~ 400/g (MJ/t metal)

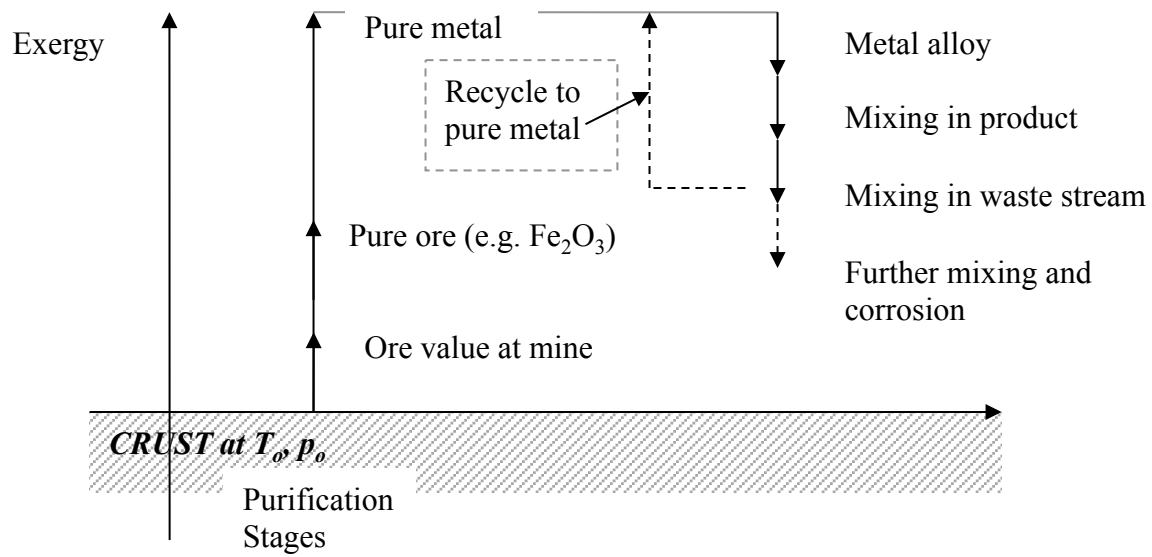
Chapman and Roberts p 113 & 116



Sherwood plot showing the relationship between the concentration of a target material in a feed stream and the market value of (or cost to remove) the target material [Grübler 1998].

Exergy of a Mixture

$$e^{o}_{\mathbf{x},\,\text{mixture}} = \sum_i x_i e^{o}_{x,\,i} + \mathrm{RT}_0 \sum_i x_i \ln x_i$$



Theoretical Exergy Values for a metal extracted from the earth's crust shown at various stages of a product life cycle (not to scale)