MSE-422 – Advanced Metallurgy

Exercise 6: Thermodynamic Modeling & Metals Processing

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Thermodynamic Modeling

1. Thermodynamic Modeling

A binary alloy system is modeled using a regular solution approach. The Gibbs free energy of mixing is:

$$\Delta G_{mix} = RT\,(x_A \ln x_A + x_B \ln x_B) + \Omega x_A x_B$$

1. Derive the condition for spinodal decomposition by finding the second derivative of ΔG_{mix} with respect to x_A. Express the spinodal curve as a relationship between Ω and T.

The spinodal decomposition condition is reached when the system becomes unstable to small compositional fluctuations. This corresponds to:

$$\frac{\partial^2(\Delta G_{mix})}{\partial x_A^2} = 0$$

Start by calculating the first derivative:

$$\frac{\partial(\Delta G_{mix})}{\partial x_A} = RT\,(\ln x_A + 1 - \ln x_B - 1) + \Omega\,(x_B - x_A)$$

Simplify:

$$\frac{\partial(\Delta G_{mix})}{\partial x_A} = RT \ln \frac{x_A}{x_B} + \Omega(x_B - x_A)$$

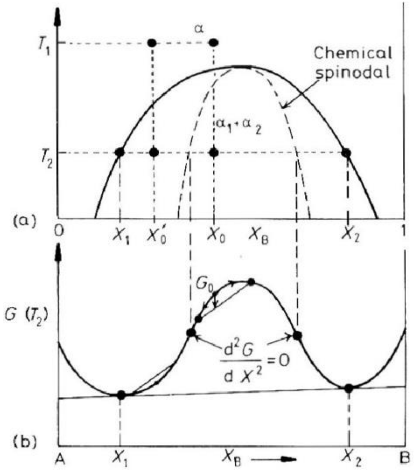
1. Thermodynamic Modeling

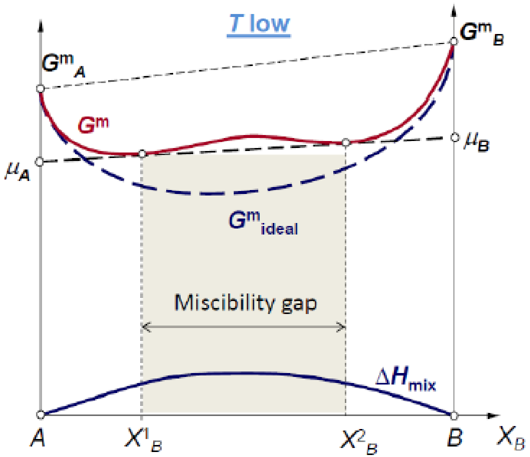
Now calculate the second derivative:

$$\frac{\partial^2(\Delta G_{mix})}{\partial x_A^2} = \frac{RT}{x_A} + \frac{RT}{x_B} - 2\Omega$$

At the spinodal:

$$\frac{RT}{x_A} + \frac{RT}{x_B} = 2\Omega$$





1. Thermodynamic Modeling

2. For $\Omega = 20,000$ J/mol, and $R = 8.314$ J/mol·K, calculate the critical temperature T_c, where spinodal decomposition occurs assuming $x_A = x_B = 0.5$:

$$T_c = \frac{\Omega}{2R}$$

At T_c, the alloy is fully miscible, and $x_A = x_B = 0.5$. Substitute into the spinodal condition:

$$\frac{RT}{0.5} + \frac{RT}{0.5} = 2\Omega \implies 4RT = 2\Omega$$

Solve for Tc:

$$T_c = \frac{\Omega}{2R}$$

Given $\Omega = 20,000$ J/mol, and $R = 8.314$ J/mol·K

$$T_c = \frac{20,000}{2 \times 8.314} \approx 1202\,\mathrm{K}$$

1. Thermodynamic Modeling

3. At $T = T_c$, calculate the Gibbs free energy of mixing, ΔG_{mix}, for $x_A = 0.5$ and $x_B = 0.5$. Compare the ideal solution contribution to the regular solution term.

Substitute $x_A = x_B = 0.5$, $T = 1202$ K, and $\Omega = 20,000$ J/mol into:

$$\Delta G_{mix} = RT\left(x_A \ln x_A + x_B \ln x_B\right) + \Omega x_A x_B$$

For the ideal mixing term:

$$\Delta G_{mix,ideal} = RT\left(0.5 \ln 0.5 + 0.5 \ln 0.5\right)$$

Since $\ln 0.5 = -0.693$:

$$\Delta G_{mix,ideal} = 1202 \cdot 8.314 \cdot (2 \cdot 0.5 \cdot -0.693) \approx -6923.2\,\mathrm{J/mol}$$

For the regular solution term:

$$\Delta G_{mix,regular} = \Omega x_A x_B = 20,000 \cdot 0.25 = 5000\,\mathrm{J/mol}$$

Total:

$$\Delta G_{mix} = \Delta G_{mix,ideal} + \Delta G_{mix,regular} = -6923.2 + 5000 = -1923.2\,\mathrm{J/mol}$$

2. Sub-Regular Solution: Practical Example with Cu-Ni Alloy

The Gibbs free energy of mixing for a binary Cu-Ni system is modeled using the sub-regular solution model:

$$\Delta G_{mix} = RT\left(x_{Cu}\ln x_{Cu} + x_{Ni}\ln x_{Ni}\right) + x_{Cu}x_{Ni}\left(L_0 + L_1(x_{Cu} - x_{Ni})\right)$$

where:

- $R = 8.314$ J/mol·K,
- $T = 1000$ K,
- $L_0 = -5000$ J/mol,
- $L_1 = 2000$ J/mol,
- $x_{Ni} = 1 - x_{Cu}$.

1. For compositions xCu = 0.2, 0.5, 0.8, compute the Gibbs free energy of mixing.

Compare the contributions of the ideal solution term ($RT\left(x_{Cu}\ln x_{Cu} + x_{Ni}\ln x_{Ni}\right)$) and the interaction parameter term ($x_{Cu}x_{Ni}\left(L_0 + L_1(x_{Cu} - x_{Ni})\right)$) to ΔG_{mix}.

2. Sub-Regular Solution: Practical Example with Cu-Ni Alloy

Ideal Solution Term:

$$\Delta G_{mix,ideal} = RT\left(x_{Cu}\ln x_{Cu} + x_{Ni}\ln x_{Ni}\right)$$

For $x_{Cu} = 0.2$, $x_{Ni} = 0.8$, and ln 0.2 = −1.609, ln 0.8 = −0.223:

$$\Delta G_{mix,ideal} = 8314 \cdot (0.2 \cdot -1.609 + 0.8 \cdot -0.223) \approx -2676.3\,\mathrm{J/mol}$$

Regular Solution Term:

$$\Delta G_{mix,regular} = x_{Cu}x_{Ni}\left(L_0 + L_1(x_{Cu} - x_{Ni})\right)$$

Substituting $x_{Cu} = 0.2$, $x_{Ni} = 0.8$, $L0 = -5000$, $L1 = 2000$:

$$\Delta G_{mix,regular} = 0.2 \cdot 0.8 \cdot (-5000 + 2000 \cdot (0.2 - 0.8)) = -992\,\mathrm{J/mol}$$

Total:

$$\Delta G_{mix} = \Delta G_{mix,ideal} + \Delta G_{mix,regular} = -2676.3 - 992 = -3668.3\,\mathrm{J/mol}$$

Repeat for $x_{Cu} = 0.5$ and $x_{Cu} = 0.8$.

2. Sub-Regular Solution: Practical Example with Cu-Ni Alloy

2. Phase Stability Analysis: A phase is stable if small fluctuations in composition do not cause a decrease in the total Gibbs free energy. Mathematically, stability requires:

$$\frac{\partial^2(\Delta G_{mix})}{\partial x_{Cu}^2} > 0$$

If $\frac{\partial^2(\Delta G_{mix})}{\partial x_{Cu}^2} < 0$, the system is unstable, and phase separation occurs.

Based on the provided values of $L_0 = -5000$ J/mol and $L_1 = 2000$ J/mol, identify regions of phase stability and instability for the given compositions ($x_{Cu} = 0.2, 0.5, 0.8$).

Compute the second derivative:

$$\frac{\partial^2(\Delta G_{mix})}{\partial x_{Cu}^2} = \frac{RT}{x_{Cu}} + \frac{RT}{x_{Ni}} + 2\left(L_0 + 2L_1(x_{Cu} - x_{Ni})\right)$$

For $x_{Cu} = 0.2$, $x_{Ni} = 0.8$:

$$\frac{\partial^2(\Delta G_{mix})}{\partial x_{Cu}^2} = \frac{8314}{0.2} + \frac{8314}{0.8} + 2 \cdot (-5000 + 2 \cdot 2000 \cdot (0.2 - 0.8)) = 37162\,\mathrm{J/mol}$$

Repeat for $x_{Cu} = 0.5$ and $x_{Cu} = 0.8$.

2. Sub-Regular Solution: Practical Example with Cu-Ni Alloy

3. Discuss how the signs and magnitudes of L_0 and L_1 affect the phase diagram and the miscibility gap.

L_0 represents the symmetric interaction between components. A negative L_0 decreases the free energy and promotes mixing, while a positive L_0 increases the free energy and encourages phase separation.
L_1 introduces asymmetry into the free energy curve: - A positive L_1 destabilizes the composition where $x_{Cu} \neq x_{Ni}$, potentially favoring one component. - A negative L_1 stabilizes asymmetric compositions, suppressing phase separation and broadening the miscibility range.
The interplay between L_0 and L_1 determines the shape of the miscibility gap and the tendency for phase separation. By varying their values, one can predict or design specific behaviors in alloy systems.

Metals Processing

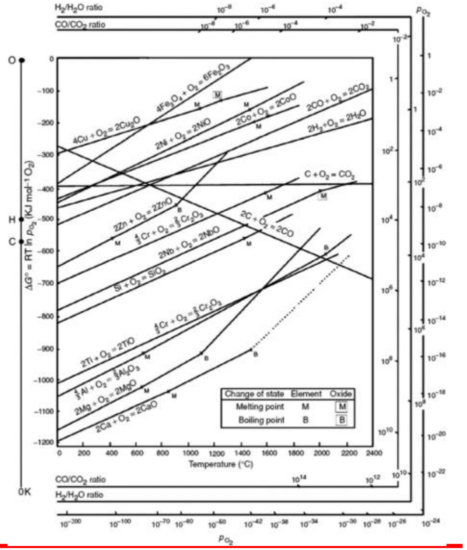
3. Ti Making Process

Considering the low productivity and high cost of the Kroll process for Ti production, many researchers around the world are attempting to develop a new Ti melting process in which metallic Ti of the requested specification can be produced with a high productivity and low cost. One representative processes under development is the preform reduction process (PRP). High-purity metallic Ti powder (up to 99% pure) are produced by reduction with metal vapor.

1. Based on the Ellingham diagram define possible metals, which can be use for reduction of TiO_2.

2. Select the most appropriate reductant and explain why.

3. Define the overall reaction of the reduction process.



3. Ti Making Process

1. Based on the Ellingham diagram define possible metals, which can be use for reduction of TiO_2.

- ➢ The Ellingham diagram shows the temperature dependence of the stability of compounds, specifically the ease of reduction of metal oxides.
- → Prediction of conditions for ore reduction to its metal.
- → Guide for purification of metals, especially the removal of trace elements

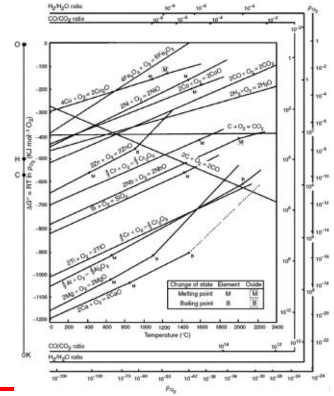


Figure 1: Ellingham diagram

3. Ti Making Process

1. Based on the Ellingham diagram define possible metals, which can be use for reduction of TiO_2.

- If the curves for two metals at a given temperature are compared, the metal with the lower Gibbs free energy of oxidation on the diagram will reduce the oxide with the higher Gibbs free energy of formation.
- The greater the gap between any two lines, the greater the effectiveness of the reducing agent corresponding to the lower line.
- The intersection of two lines implies an oxidation-reduction equilibrium. Reduction using a given reductant is possible at temperatures above the intersection point.

3. Ti Making Process

2. Select the most appropriate reductant and explain why.

- Al, Mg and Ca are possible options.
- Ca is the most efficient metal for reduction.
- Reduction reaction:

$$TiO_2(s) + 2Ca\,(g) = Ti(s) + 2CaO(s)$$

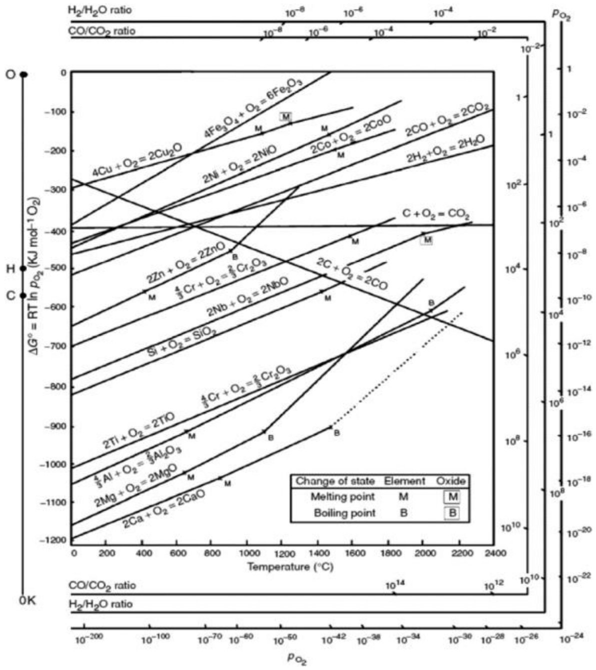
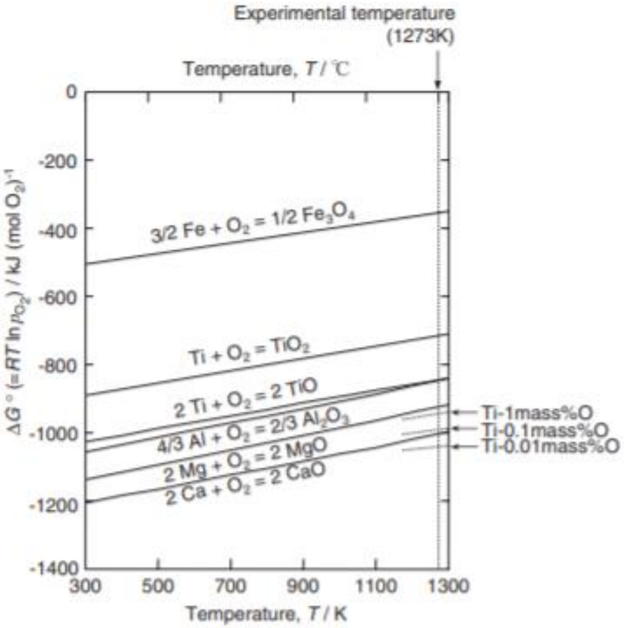


Figure 1: Ellingham diagram

3. Ti Making Process

3. Define the overall reaction of the reduction process.

- Ca is the most efficient metal for reduction.
- Reduction reaction:



- $Ti + O_2 = TiO_2$
- $2Ca + O_2 = 2CaO$

Overall reaction:

- $TiO_2(s) + 2Ca\ (g) = Ti(s) + 2CaO(s)$

4. Iron making: The Blast Furnace

In a blast furnace, iron ore is reduced according to the following reaction:

$$Fe_2O_3 + 6CO = 2Fe + 3CO_2 + 3CO$$

Coke of composition 94% C is used to produce CO by combustion with air at the bottom of the furnace. Of the coke charged, 90.5% burns to CO only.

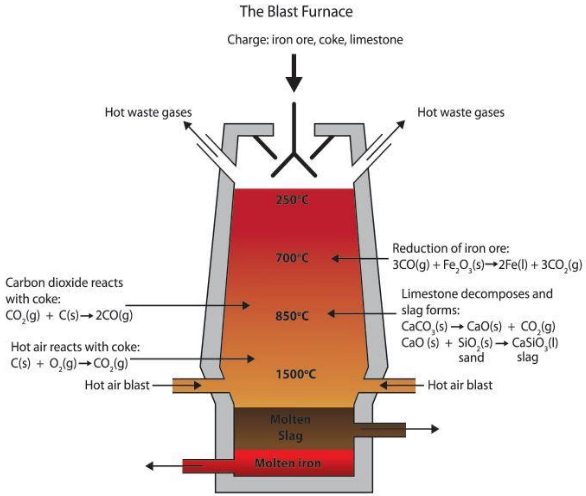
1. Define the input and the output of the process.

2. Define the function of coke, which is charged in the furnace.

3. Define the combustion reaction to produce CO.

4. Calculate the volume of CO to produce 1000 Kg iron.

5. Calculate the weight of coke required to produce 1000 Kg iron.



4. Iron making: The Blast Furnace

In a blast furnace, iron ore is reduced according to the following reaction:

$$Fe_2O_3 + 6CO = 2Fe + 3CO_2 + 3CO$$

1. Define the input and the output of the process.

➢ **Input:**

- Iron ore (Ematite: Fe_2O_3)
- Coke
  - → Heat production
  - → Reduction of iron ore
- Air
  - → Combustion of coke
- Flux (lime CaO or limestone $CaCO_3$)
  - → Elimination of silica impurities

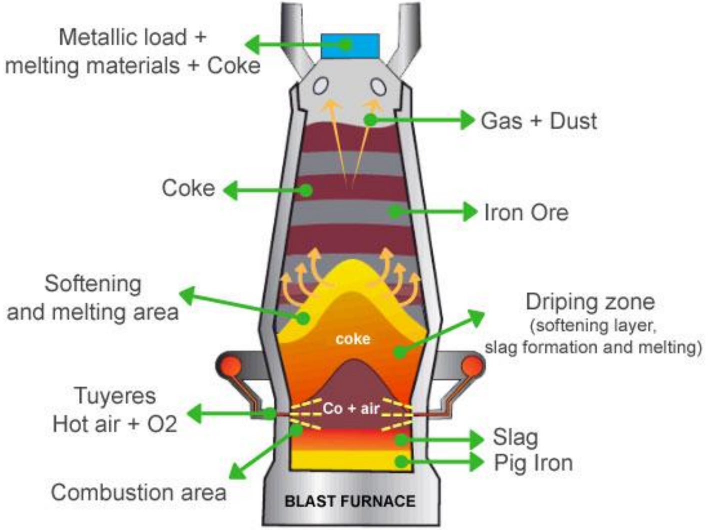


Figure 2: Blast furnace

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In a blast furnace, iron ore is reduced according to the following reaction:

$$Fe_2O_3 + 6CO = 2Fe + 3CO_2 + 3CO$$

1. Define the input and the output of the process.

➢ **Output:**

- Pig iron (molten)
- Slag (molten)
- Gas (CO_2+N_2)

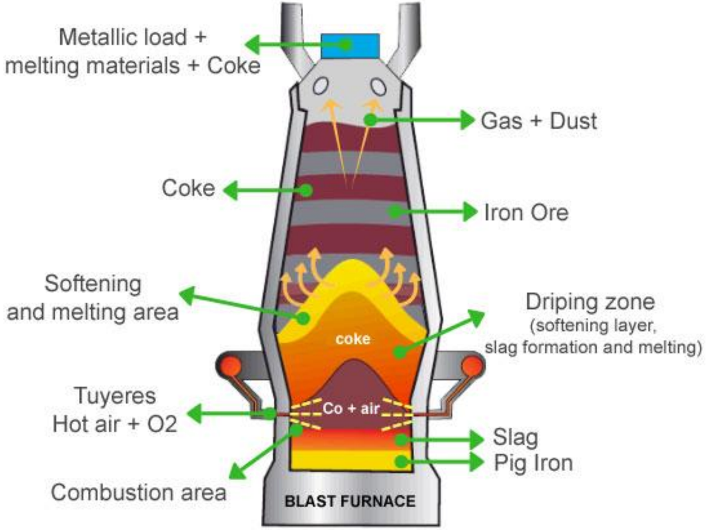


Figure 2: Blast furnace

4. Iron making: The Blast Furnace

In a blast furnace, iron ore is reduced according to the following reaction:

$$\mathrm{Fe_2O_3} + 6\mathrm{CO} = 2\mathrm{Fe} + 3\mathrm{CO_2} + 3\mathrm{CO}$$

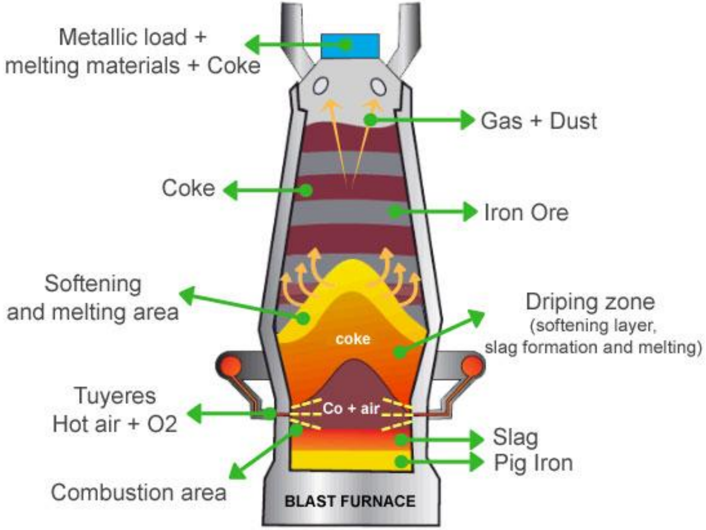
2. Define the function of coke, which is charged in the furnace.

- Coke

→ Source of energy (heat)

Combustion air enriched blown and react with coke

(temperature up to 2200~C → melting of iron and slag)



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$$Fe_2O_3 + 6CO = 2Fe + 3CO_2 + 3CO$$

2. Define the function of coke, which is charged in the furnace.

- Coke

→ Reductant for iron ore (iron oxides)

1. Reduction of CO_2

$CO_2(g) + C(s) \rightarrow 2CO(g)$

2. Reduction of iron oxide

$2Fe_2O_3(s) + 3C(s) \rightarrow 4Fe(l) + 3CO_2(g)$

$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$

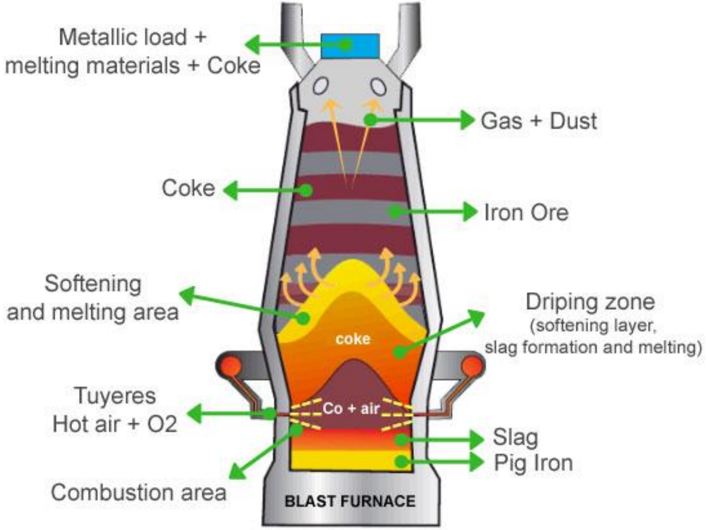

Figure 2: Blast furnace

4. Iron making: The Blast Furnace

In a blast furnace, iron ore is reduced according to the following reaction:

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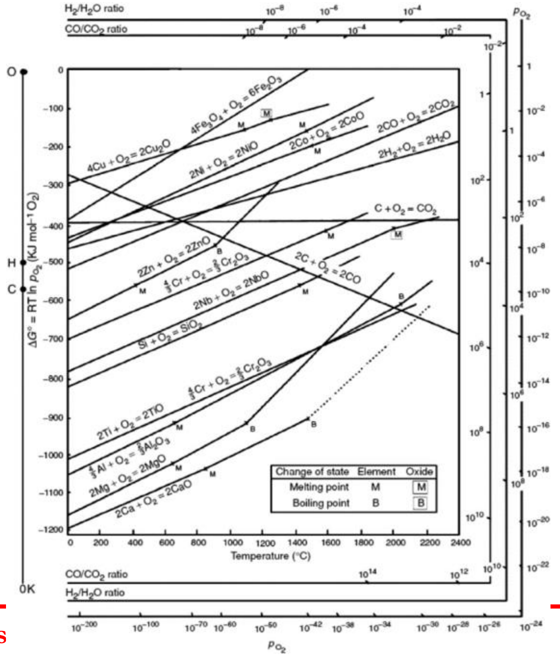
3. Define the combustion reaction to produce CO.

Combustion reaction: $2C + O_2 = 2CO$



4. Iron making: The Blast Furnace

In a blast furnace, iron ore is reduced according to the following reaction:

$$Fe_2O_3 + 6CO = 2Fe + 3CO_2 + 3CO$$

Coke of composition 94% C is used to produce CO by combustion with air at the bottom of the furnace. Of the coke charged, 90.5% burns to CO only.

4. Calculate the volume of CO to produce 1000 Kg iron.

Coke burns to produce CO (reduction agent)

- Moles of Fe: $\frac{m_{Fe}}{[Fe]} = \frac{1000}{0.055845} = 17907$ mol
- Moles of CO: 53720 mol
- Volume of CO: 1200000 L = 1200 m^3

→ For ideal gas at T and P standard (STP) the volume of a mole is 22,414 **L/mol**

4. Iron making: The Blast Furnace

In a blast furnace, iron ore is reduced according to the following reaction:

$$Fe_2O_3 + 6CO = 2Fe + 3CO_2 + 3CO$$

Coke of composition 94% C is used to produce CO by combustion with air at the bottom of the furnace. Of the coke charged, 90.5% burns to CO only.

5. Calculate the weight of coke required to produce 1000 Kg iron.

- Coke reaction: $C(s) + O(g) = CO$
- Mol of C = Mol of CO = $53720\ mol$
- Mass of C which burns to CO (90.5%) = Mol of CO * [CO]=53720 * 12 = 644640 g
- Mass of C (total) = $\frac{644640}{0.905} = 712\text{ kg}$

5. Oxygen converter process

For a BOF heat, the following data are given:

Table 1: composition of the pig iron to be converted

Hot metal	1% Si	0.15% P	0.25% Mn	3.5% C	
Slag	54% CaO	18% FeO	2.5% MgO	2.5% MnO	$CaO/SiO_2 = 3.2$

The weight of the scrap is 10% of the hot metal, the steel at the tap contains 0.2%C.

1. Name the reaction equations and oxidation products of the process.
2. Explain why lime is normally added during the converter process.
3. Calculate per ton of steel the weight of hot metal charge (Assume scrap as pure Fe).
4. Calculate per ton of steel the weight of slag produced.
5. Calculate per ton of steel the quantity of lime required.

5. Oxygen converter process

BOF process

1. **Name the reaction equations and oxidation products of the process.**
2. **Lime is normally added during the converter process. Explain why.**

- Basic oxygen steelmaking (BOS) is a method of primary steelmaking in which carbon-rich molten pig iron (from the blast furnace) is made into steel by reducing carbon content and impurities.

  → Oxygen reacts with C in steel to increase the temperature, reduce amount of C in steel, melt the slag, remove impurities.

5. Oxygen converter process

BOF process

1. **Name the reaction equations and oxidation products of the process.**
2. **Lime is normally added during the converter process. Explain why.**

- $\{O_2\} \rightarrow 2[O]$
- $[Si] + 2[O] \rightarrow SiO_2$
- $[Fe] + [O] \rightarrow FeO$
- $[Mn] + [O] \rightarrow (MnO)$
- $2[P] + 5[O] \rightarrow (P_2O_5)$
- $2(FeO) + [O] \rightarrow (Fe_2O_3)$
- $3(CaO) + (P_2O_5) \rightarrow (CaO)_3(P_2O_5)$ → Burnt lime or dolomite form slag to absorb impurities
- $[C] + [O] \rightarrow \{CO\}$
- $\{CO\} + [O] \rightarrow \{CO2\}$

5. Oxygen converter process

For a BOF heat

- Mass balance: $\mathrm{mass}_{\mathrm{IN}} = \mathrm{mass}_{\mathrm{OUT}}$
- $\mathrm{mass}_{\mathrm{Fe-HM}} = \mathrm{m}_{\mathrm{H}M} * \mathrm{w}_{\mathrm{Fe-HM}}$

5. Oxygen converter process

For a BOF heat, the following data are given:

Hot metal	1% Si	0.15% P	0.25% Mn	3.5% C	
Slag	54% CaO	18% FeO	2.5% MgO	2.5% MnO	$CaO/SiO_2 = 3.2$

The weight of the scrap is 10% of the hot metal, the steel at the tap contains 0.2%C.
3. Calculate per ton of steel the weight of hot metal charged.

- Si in hot metal = Si in slag as SiO_2
- $1000 * 0.01 = m_{slag}\left(0.169 * \frac{[Si]}{[SiO_2]}\right) \rightarrow m_{slag} = 127\ \text{Kg}$

→ assuming as first approximation 1t of hot metal
→ $[Si] = 28.09$ g/mol
→ $[SiO_2] = 60.08$ g/mol

5. Oxygen converter process

For a BOF heat, the following data are given:

Hot metal	1% Si	0.15% P	0.25% Mn	3.5% C	Fe: 100-4.9
Slag	54% CaO	18% FeO	2.5% MgO	2.5% MnO	CaO/SiO_2 = 3.2

The weight of the scrap is 10% of the hot metal, the steel at the tap contains 0.2%C.

3. Calculate per ton of steel the weight of hot metal charged.

- Fe in hot metal + Fe in scrap = Fe in steel + Fe in slag
- $m_{HT} * W_{Fe-HT} + m_{scrap} * W_{Fe-scrap} = m_{steel} * W_{Fe-steel} + m_{slag} * W_{Fe-slag}$
- $m_{HT} * 0.951 + (m_{HT} 0.1)*1 = 1*(1-0.002) + 0.127*0.14$
- m_{HT} = 966 Kg

$(W_{Fe-slag} = W_{FeO} * \frac{[Fe]}{[FeO]})$

5. Oxygen converter process

For a BOF heat, the following data are given:

Hot metal	1% Si	0.15% P	0.25% Mn	3.5% C	Fe: 100-4.9
Slag	54% CaO	18% FeO	2.5% MgO	2.5% MnO	$CaO/SiO_2 = 3.2$

The weight of the scrap is 10% of the hot metal, the steel at the tap contains 0.2%C.

4. Calculate per ton of steel the weight of slag produced.

5. Calculate per ton of steel the quantity of lime required.

- Si in hot metal = Si in slag as SiO_2
- $966 * 0.01 = m_{slag}(0.169 * \frac{[Si]}{[SiO_2]})$ → $m_{slag} = 122.49$ Kg
- CaO to be added = CaO in slag = 122.49*0.54= 66.14 Kg

6. Environmental aspect of steel production

In the last years, wind power has been considered as regenerative CO2 emission-free energy source.

- Wind power plants

- Direct emissions: 0

- Indirect emission from the manufacturing and installation (use of steel):

  Amount of CO2 / ton of steel produced: 1500 Kg/ton

  Amount of steel / wind capacity: 400 ton/1MW

- Coal power plants

- Direct Emission: 0.8 kg CO2/1 kWh of electricity generated

a) Calculate the minimum operating time that the installed wind power capacity has to run in order to offset the CO2 emitted during steel production compared to conventional electricity production via hard coal power plants.

6. Environmental aspect of steel production

In the last years, wind power has been considered as regenerative CO2 emission-free energy source.

a) Considering a wind power plant of 1 MW, how much energy can we produce with a coal power plant emitting the same amount of CO_2?

400 t * 1500 Kg/t = 600000 Kg of $\mathrm{CO_2}$

600000 Kg of $\mathrm{CO_2}$/Kg of $\mathrm{CO_2}$ for every KWh

$\frac{600000}{0.8}$=750000 KWh=750 MWh

6. Environmental aspect of steel production

In the last years, wind power has been considered as regenerative CO2 emission-free energy source.

b) Calculate the minimum operating time that the installed wind power capacity has to run in order to offset the CO2 emitted during steel production compared to conventional electricity production via hard coal power plants.

Assume a 1 MW capacity plant → 400 t steel required

400 t * 1500 Kg/t = 600000 Kg of CO_2

600000 Kg of CO_2/Kg of CO_2 for every KWh

$\frac{600000}{0.8}$=750000 KWh=750 MWh

Need for 750 h of wind power activity for the wind plant to be «beneficial»