

Evaluation PHY555 Energy & Environment

Friday 16st December 2022

Part III, 10 points, recommended time 2h

Is carbon-free steel production possible?

An important source of energy consumption and CO_2 emission by mankind is the production of pure metals like iron for our war-machines, lawn-mowers, bicycles, and maidens. This problem examines why this is so, and critically examines potential alternatives.

The problem is organized as followed:

- Part 0 is a reminder and reference guide of the thermodynamics of chemical reactions for stressed students. If you are familiar with the topic, you might directly jump to Part 1.
- Part 1 concerns generalities about iron oxides
- Part 2 examines classical (i.e. carbon based) steel production
- Part 3 examines the possibility of hydrogen-base (possibly carbon-free) production of steel.
- Part 4 concentrates on the production of green hydrogen from wind energy.

Note 1: All parts of the problem are **independent**. (assuming important results from previous sections)

Note 2: The physical constants needed in the problem are grouped in tables at the end of the subject (Part 5, page 23)

Note 3: Use green paper sheets for your answers.

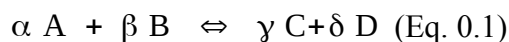
Note 4: Questions are classified by difficulty. Questions denoted as (*) are considered easy, questions denoted as (**) medium, and questions denoted as (***) are more difficult to answer.

Part 0 Thermo-chemistry reminder

This part is a reminder and reference guide of the thermodynamics of chemical reactions for stressed students. If you are familiar with the topic, you might directly jump to Part 1.

1. Chemical Reactions and advancement parameters

We note that standard chemical reactions take the form:

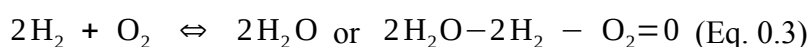


where A, B, C, D are chemical bodies and $\alpha, \beta, \gamma, \delta$ are the “Stoichiometric coefficients”.

It can also be noted:

$$\sum v_i A_i = 0 \quad (\text{Eq. 0.2})$$

where the Stoichiometric coefficients v_i are taken as positive for the products and negative for the reactants. For instance the reaction for the formation of water:



The “**advancement parameter**” or “**extent of reaction**”, denoted ξ , characterizes the evolution of the reaction. For an advancement or extent ξ , $\xi \times \gamma$ (resp. $\xi \times \delta$) moles of C (resp. D) are formed and $\xi \times \alpha$ (resp. $\xi \times \beta$) moles of A (resp. B) are consumed.

2. Standard reaction thermodynamic quantities

- The “**reaction quantity**” $\Delta_r Q$ is the amount of variation of the quantity Q for a unit advancement $\xi=1$. For instance, $\Delta_r H$ is the change of enthalpy for the production of γ (resp. δ) moles of C (resp. D). One therefore has, for an infinitesimal advancement:

$$dQ = \Delta_r Q \times d\xi \quad (\text{Eq. 0.4})$$

- The “**standard reaction quantity**” $\Delta_r Q^\circ$ is the “**reaction quantity**” $\Delta_r Q$ for “standard thermodynamic conditions” ($T^\circ = 298 \text{ K}$, $P^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$).

A reaction is called “**exothermic**” if its reaction enthalpy is **negative** (enthalpy of the bodies decreases, thus enthalpy is released to the surrounding medium as heat). It is “**endothermic**” if its reaction enthalpy is **positive**.

3. Standard and non-standard quantities

The evolution of reaction quantity with temperature (and eventually pressure) can be determined in a similar way to the underlying thermodynamic potential, e.g. the Kirchhoff relations:

$$\left. \frac{\partial H}{\partial T} \right|_P = C_p \Rightarrow \left. \frac{\partial \Delta_r H}{\partial T} \right|_P = \Delta_r C_p \Rightarrow \Delta_r H(T, P^\circ) = \Delta_r H^\circ(T^\circ, P^\circ) + \int \Delta_r C_p(T) dT \quad (\text{Eq. 0.5})$$

In the current problem, we will in most cases assume that the standard reaction enthalpy and the standard reaction entropy are independent of temperature, i.e. $\Delta_r H(T) = \Delta_r H^\circ$ and $\Delta_r S(T) = \Delta_r S^\circ$. This is the so-called “Ellingham approximation”, which is equivalent to ignoring the heat capacity ($C_p \approx 0$).

4. Standard formation enthalpy

The “**standard formation enthalpy**” ΔH_f° is the “**standard reaction enthalpy**” corresponding to the reaction of formation of the considered body from its elementary constituents. By convention, the standard formation enthalpy is set to zero for pure bodies *in their most stable form*. For instance, the standard formation enthalpy of molecular hydrogen (H_2) is zero, that of atomic hydrogen (H) is not. The formation enthalpy of the chemical bodies used in the problem are given in the third

column of table 1. The standard reaction enthalpy of a given chemical reaction can be computed from the difference between the standard formation enthalpies of the reaction products and those of the reactants, multiplied by the corresponding stoichiometric coefficients (HESS law). For instance, for the reaction of formation of water:

$$2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} \quad \Delta_r H^\circ = \underbrace{2\Delta H_f^\circ(\text{H}_2\text{O})}_{=-241,8} - \underbrace{2\Delta H_f^\circ(\text{H}_2)}_{=0} - \underbrace{\Delta H_f^\circ(\text{O}_2)}_{=0} = -483,6 \text{ kJ/mol}$$

This reaction is strongly exothermic.

5. Standard entropy

As for the standard formation enthalpy, one defines a “**standard entropy**” S° for each chemical body. Here we have an absolute scale, the entropy of a pure body being zero at absolute zero temperature. The standard entropies of chemical bodies used in the problem are given in the fourth column of table 1. As for the standard reaction enthalpies, the standard reaction entropies can be computed from the difference between the standard entropies of the reaction products and those of the reactants, multiplied by the corresponding stoichiometric coefficients.

6. Standard reaction Gibbs energy

The “**standard reaction Gibbs free energy**”, also called “**standard reaction free enthalpy**” is computed from the difference between the standard reaction enthalpies and the standard reaction entropies multiplied by the temperature:

$$\Delta_r G^\circ = \Delta_r H^\circ - T \times \Delta_r S^\circ \quad (\text{Eq. 0.6})$$

For reactions occurring at constant temperature and pressure, $\Delta_r G^\circ$ is the thermodynamic potential that allows one to determine the spontaneous evolution of the reaction, as G will always evolve towards a minimum. **Negative** values of $\Delta_r G^\circ$ will correspond to reactions evolving towards the **right (increase of ξ)** while **positive** values of $\Delta_r G^\circ$ will correspond to reactions evolving towards the **left (decrease of ξ)**.

For instance, for the reaction of the formation of water:

$$\begin{aligned} \Delta_r H^\circ &= \underbrace{2\Delta H_f^\circ(\text{H}_2\text{O})}_{=-241,8} - \underbrace{2\Delta H_f^\circ(\text{H}_2)}_{=0} - \underbrace{\Delta H_f^\circ(\text{O}_2)}_{=0} = -483,6 \text{ kJ/mol} \\ \Delta_r S^\circ &= \underbrace{2S^\circ(\text{H}_2\text{O})}_{=188,8} - \underbrace{2S^\circ(\text{H}_2)}_{=130,7} - \underbrace{S^\circ(\text{O}_2)}_{=205,2} = -90 \text{ J/K/mol} \quad (\text{Eq. 0.7}) \\ \Delta_r G^\circ &= \Delta_r H^\circ - T \times \Delta_r S^\circ = (-483,6 + 0,090 \times T) \text{ kJ/mol} \end{aligned}$$

At low temperature, the reaction of the formation of water is spontaneous (negative reaction Gibbs energy). There exists a “dissociation” temperature $T = 483,6 / 0,090 = 5373 \text{ K}$ above which the reaction will go in the opposition direction: water will spontaneously dissociate into hydrogen and oxygen. This is called “thermolysis”. Here we assumed $\Delta_r H$ and $\Delta_r S$ are constant with temperature, thus $\Delta_r H = \Delta_r H^\circ$.

7. Chemical potential and activities

The Gibbs free energy can be written as function of the chemical potentials $\mu_i(T, P)$:

$$dG = V dP - S dT + \sum \mu_i dn_i = V dP - S dT + \left(\sum \mu_i \nu_i \right) d\xi \quad (\text{Eq. 0.8})$$

The chemical potentials can be written as function of their standard values μ_i^0 and the **activity** a_i :

$$\mu_i(T, P) = \mu_i^0 + RT \ln a_i$$

For a pure body, the activity takes on a value of one. For a perfect mixture of gases, the activity corresponds to the partial pressure $P_i = x_i \times P_0$:

$$\mu_i(T, P) = \mu_i^\circ + RT \ln \left(\frac{P_i}{P_0} \right) \quad (\text{Eq. 0.9})$$

At constant temperature and pressure:

$$\Delta_r G = \sum \mu_i \nu_i = \Delta_r G^\circ + RT \sum \nu_i \ln a_i = \Delta_r G^\circ + RT \ln \left(\prod a_i^{\nu_i} \right) \quad (\text{Eq. 0.10})$$

8. **Equilibrium and reaction rate constant**

The quantity $K = \prod a_i^{\nu_i}$ is called the “**reaction rate constant**”. It is related to the reaction (Gibbs) free energy by

$$\Delta_r G = \Delta_r G^\circ + RT \ln K \quad \Rightarrow \quad K = \exp \left(\frac{\Delta_r G - \Delta_r G^\circ}{RT} \right) \quad (\text{Eq. 0.11})$$

At equilibrium, the Gibbs free energy reaches a minimum, thus:

$$0 = dG = \Delta_r G \times d\xi \quad \Rightarrow \quad \Delta_r G = 0$$

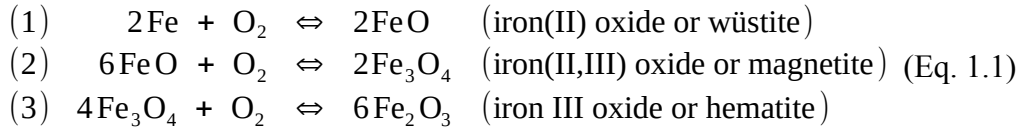
We then obtain:

$$0 = \Delta_r G = \Delta_r G^\circ + RT \ln K \quad \Rightarrow \quad K = \exp \left(-\frac{\Delta_r G^\circ}{RT} \right) \quad (\text{Eq. 0.12})$$

Part 1 Carbon oxides and Ellingham Diagrams

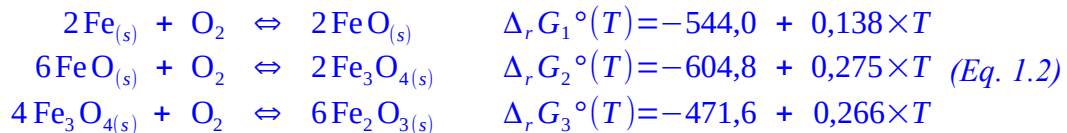
1. Introduction - Iron Ore in Nature

1. Iron can be oxidized to different levels through the chemical reactions:



For the three different oxidation equations, give the expression of the reaction (Gibbs) free energy as a function of temperature using the Ellingham approximation (i.e. assuming reaction enthalpy and entropy are temperature independent, and using values from table 1. The answer should be given in the form $\Delta_r G^\circ(T) = A + B \times T$, when A and B are numerical values to be determined and T is the temperature in Kelvin.

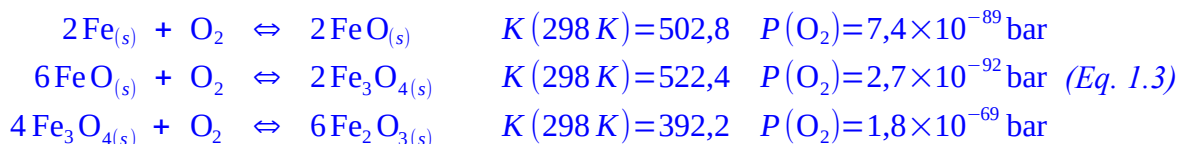
Using table 1, we obtain the following reaction (Gibbs) free energies (in kJ/mol):



2. Using values from table 1, explain why iron is found mostly in oxidised form in the Earth's crust?

Those reactions have large negative free Gibbs energies, meaning that they are spontaneous, and that the equilibrium is completely shifted towards the right. More precisely for oxidation reaction in presence of only atmospheric oxygen as gas on the left side we have:

$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = -K = RT \ln P(\text{O}_2)$ where $P(\text{O}_2)$ is the partial pressure of oxygen (see below, question 6). For the three reactions above we obtain at standard temperature the equilibrium partial pressures of oxygen:



Thus, when in contact with oxygen, iron becomes fully oxidized.

3. Is the combustion of iron endo- or exothermic? How much energy is absorbed/released by the combustion of 1 kg of steel filaments at room temperature (the combustion of iron ends with the formation of magnetite)?

The enthalpies are negative, thus the combustion is exothermic. The balance reaction is $(3(1)+(2))/2$:



This is for one mole of O_2 . Dividing the molar mass of iron $M = 55.845 \text{ g/mol}$ and by the stoichiometric coefficient $3/2$, one obtains a calorific power of $6,7 \text{ MJ/kg}$

4. How does this compare to 1 kg of oil?

Oil has a higher calorific value of ~ 40 MJ/kg, a factor of 6 higher. Iron is not a very good fuel.

2. Temperature based reduction of iron oxides – Ellingham diagrams

5. An Ellingham diagram is a diagram showing the value of $\Delta_r G^\circ$ as function of temperature for various oxidation equations. By convention, all reaction equations are written for one mole of dioxygen on the left. Draw the oxidation curves for the various iron oxides as an Ellingham diagram. Use the sheet provided for the subject (Annex to part 3).

See Fig. 1.

6. Show that, at equilibrium the partial pressure of oxygen $P(\text{O}_2)$ is related to the standard reaction Gibbs free energy by the relation:

$$\Delta_r G^\circ = RT \ln P(\text{O}_2) \quad (\text{Eq. 1.5})$$

On your Ellingham diagram, draw the lines corresponding to partial oxygen pressures of 0.2, 0.01 and 10^{-4} bar

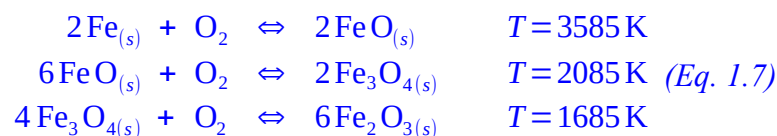
Using Eq. 0.12 one has $\Delta_r G^\circ = -RT \ln K = RT \ln P(\text{O}_2)$ where $P(\text{O}_2)$ is the partial pressure of oxygen. The vertical axis also gives the partial oxygen pressure at equilibrium times the temperature. See Fig. 1 for the drawing.

7. At what temperature can the various iron oxides be reduced in standard atmosphere?

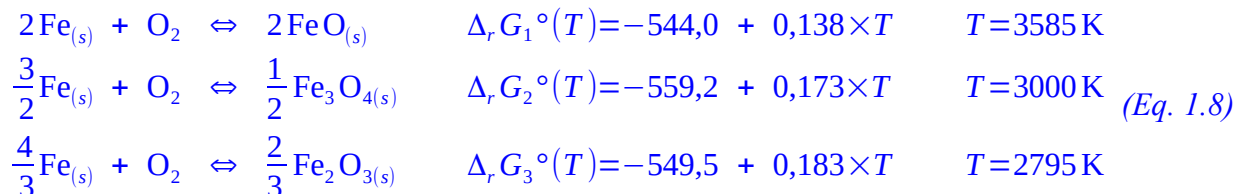
We use Eq. 1.5: $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = -K = RT \ln P(\text{O}_2)$ where $P(\text{O}_2) = 0.2$ bar is the partial pressure of oxygen in standard atmosphere. Thus we obtain the equilibrium temperature:

$$T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ + R \ln P(\text{O}_2)} \quad (\text{Eq. 1.6})$$

One obtains



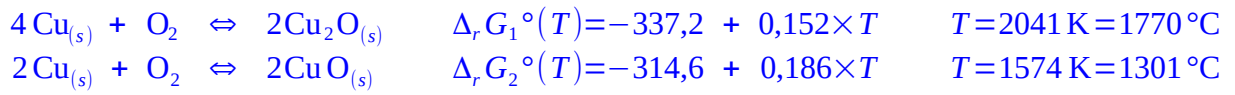
For the reaction starting from iron, we have:



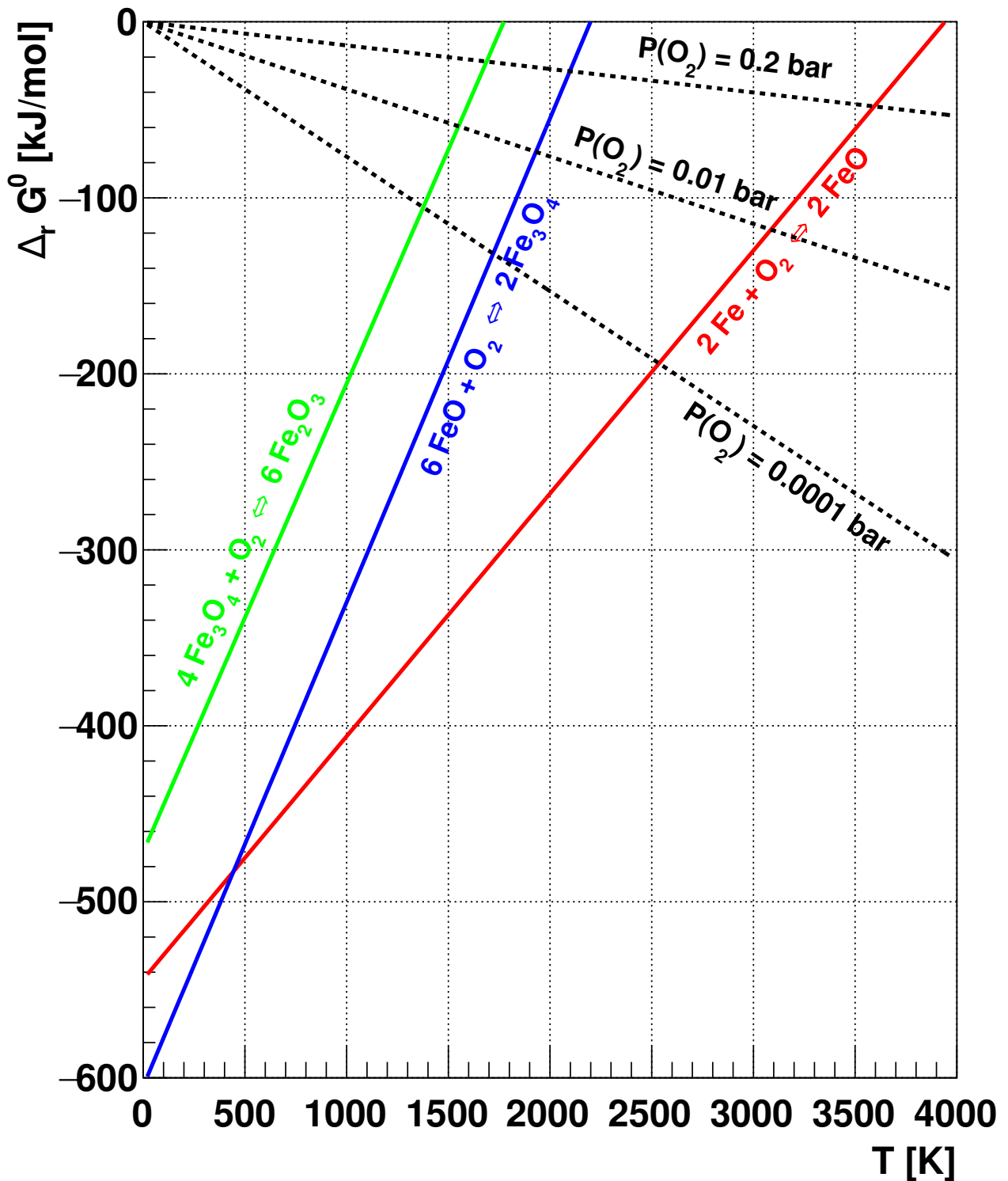
So high temperature of the order of ~ 3000 K are needed for direct reduction by heat, which is almost inaccessible.

8. (**) Why did the copper age precede the iron age?

For copper oxides we have similarly:



Ellingham Diagram of Iron



(Eq. 1.9)

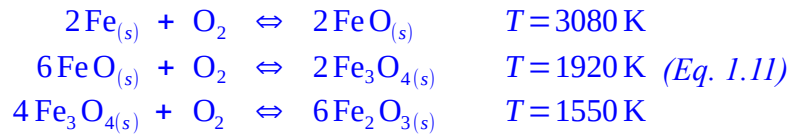
The requested temperature are much lower, and accessible with not too complicated designs

9. Historically, the first metallurgical methods consisted only of heating. This was only useful for relatively weakly reducing metals, because the temperature at which reduction occurs increases with the reducing character. The second strategy consisted of lowering the oxygen pressure in the furnace using a restricting air entry (limiting the oxygen supply). How does this help reducing metal oxides?

From Eq. 1.6 we have

$$T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ + R \ln P(\text{O}_2)} \quad (\text{Eq. 1.10})$$

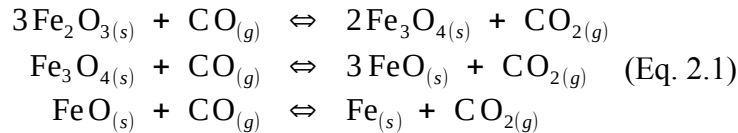
where all values $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\ln P(\text{O}_2)$ are negative. Decreasing the oxygen pressure increases the absolute value at the denominator and thus limits the reduction temperature. For instance, for $P(\text{O}_2) = 0.01$ bar, one obtains:



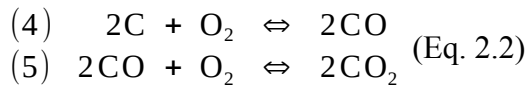
Part 2 Classical Steel production

1. Carbon-based reduction of iron oxides

Current steel-making processes are based on the reduction of iron oxides in the presence of carbon monoxide:

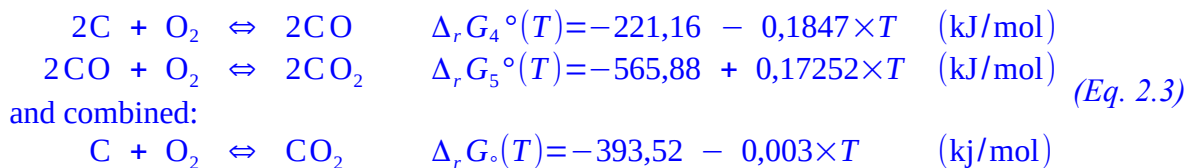


10. The carbon equilibrium is given by the chemical reaction: $\text{C} + \text{CO}_2 \Leftrightarrow 2\text{CO}$. This can be written as two different oxidation reactions:



For the two different oxidation equations, give the expression of the reaction free Gibbs energy as function of temperature, using values from table 1. The answer should be given in the form $\Delta_r G^\circ(T) = A + B \times T$, when A and B are numerical values to be determined and T is the temperature in Kelvin.

We obtain:



11. Add these carbon oxidation curves to the Ellingham diagram. Can the various slopes be explained intuitively? What can be noticed regarding CO?

$\text{C} + \text{O}_2 \Leftrightarrow \text{CO}_2$ corresponds to an horizontal line because it involves the production of one mole of gas and the consumption of one mole of gas, so the change of entropy is zero.

$2\text{C} + \text{O}_2 \Leftrightarrow 2\text{CO}$ has a negative slope because one net mole of gas is produced, leading to an increase of entropy.

Carbon monoxide is one of the rare element which has a negative slope in the Ellingham diagram. For that reason it is called a "universal reducer": the highest the temperature, the higher its reducing power is.

Use of Carbon allows to reduce the temperature a lot, since the iron curves cross the carbon lines around temperatures of the order of 1000 K or below. See Fig. 2 for the drawing of the Ellingham diagram of iron in the presence of Carbon.

12. We consider a carbon equilibrium $\text{CO}_2 + \text{C} \Leftrightarrow 2\text{CO}$ at a total pressure of 1 atmosphere. Compute the ratio of partial pressures $p(\text{CO}_2)/p(\text{CO})$ in the gas in equilibrium with carbon (in the absence of oxygen) at temperatures of 200°C and 1600°C. Show that below a critical temperature, the system is a mixture of CO_2 and C, while above this temperature, the system is almost pure CO. We remind that the standard reaction Gibbs energy can be expressed as:

$$\Delta_r G^\circ = -RT \ln \left(\frac{P^2(\text{CO})}{P(\text{CO}_2)} \right) \text{ and } P_{\text{tot}} = P(\text{CO}) + P(\text{CO}_2) \text{ (Eq. 2.4)}$$

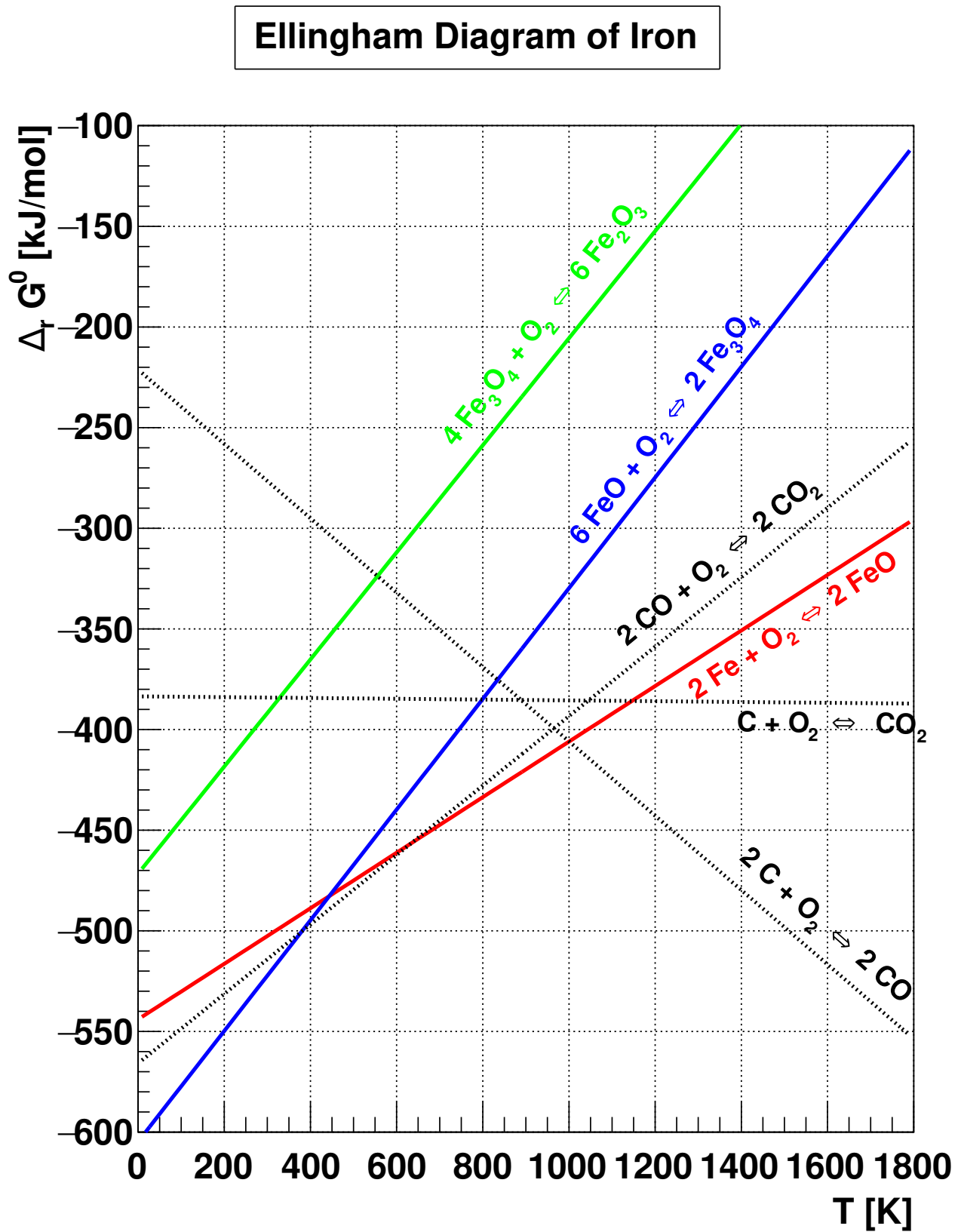


Figure 2: Ellingham Diagram of Iron in the presence of Carbon

The equilibrium $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$ corresponds to $((2)-(5))/2$ for which we have $\Delta_r G^\circ = 172.5 - 0.175 \times T$ (kJ/mol). Thus

$$\frac{P^2(\text{CO})}{P(\text{CO}_2)} = \exp\left(\frac{-(172.5 - 0.175 \times T) \times 10^3}{8.314 \times T}\right) \equiv r \quad (\text{Eq. 2.5})$$

Using $P_{\text{tot}} = P(\text{CO}) + P(\text{CO}_2) = 1 \text{ bar}$ one obtains

$$1 + P^2(\text{CO}_2) - (2+r)P(\text{CO}_2) = 0 \Rightarrow P(\text{CO}_2) = \frac{r+2 - \sqrt{(2+r)^2 - 4}}{2} \quad (\text{Eq. 2.6})$$

At a temperature of 200°C one obtains $p(\text{CO}_2)/p(\text{CO}) \approx 8.4 \times 10^4$. Conversely, at high temperatures CO is more stable than CO_2 and thus the gas in equilibrium with carbon is predominantly CO. At a temperature of 1600°C the ratio $p(\text{CO}_2)/p(\text{CO})$ in the gas has the value 4.2×10^{-5} .

13. At what temperature is equilibrium reached?

The equilibrium temperature, at which $r=1$, corresponds to

$$\frac{(172.5 - 0.175 \times T) \times 10^3}{8.41 \times T} = 0 \Leftrightarrow T \approx 980 \text{ K} \approx 707^\circ\text{C} \quad (\text{Eq. 2.7})$$

14. Why is carbon-based reduction more efficient than direct thermal reduction?

Above $T \sim 1000 \text{ K}$, CO is more stable than CO_2 and CO can efficiently reduce iron oxides. Actually, according to the Ellingham diagram, CO could reduce Fe_3O_4 above $\sim 555 \text{ K}$ and FeO above $\sim 835 \text{ K}$, but at these temperatures, CO is less stable than CO_2 and is present at low concentrations.

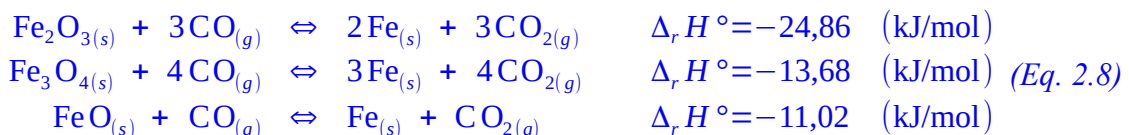
15. According to the Ellingham Diagram, what is the approximate minimum temperature required to perform the reduction of iron oxides in the presence of Carbon?

To the first approximation (i.e. ignoring the carbon equilibrium), we need to look where the Carbon line ($\text{C} + \text{O}_2 \Rightarrow \text{CO}_2$) is below the iron oxide line. This corresponds to temperatures of respectively $\sim 1000 \text{ K}$, $\sim 800 \text{ K}$ and $\sim 600 \text{ K}$ for the various oxides. To be more precise, one would need to write the constant of reaction, and to include, as function of temperature, the partial pressures of CO and CO_2 as obtained in question 12.

2. Thermal balance

16. Is the reduction of iron oxides endo- or exothermic?

The reduction equation have standard reaction enthalpies:



They are all endothermic. Heat is needed both to raise the temperature of the ore and to perform the reduction. Heat is brought by the partial combustion of carbon.

17. We consider "natural ore" containing high quantities of hematite Fe_3O_4 (about 60% iron by mass), which can be fed directly into iron-making blast furnaces, at a temperature of 1000°C . Estimate the heat quantities needed to:

- Raise the ore temperature to 1000°C
- Perform the reduction

Express these quantities in terms of kJ/kg of iron produced.

Only hematite was asked for in the subject to limit the amount of calculations, but the correction contains the answers for the 3 different oxides for reference.

Using the molar masses from table 1 we obtain the following iron concentration by mass and heat quantities to raise the ore temperature to 1000°C (for ore containing 60% by mass)

Ore	Iron Fraction by mass (pure ore)	Temp. Heat (J/mol_{ore})	Temp. Heat/Iron (60% ore) (kJ/kg_{Fe})
$\text{FeO}_{(s)}$	77,7 %	44 655,0	1 035,9
$\text{Fe}_2\text{O}_{3(s)}$	69,9 %	101 302,5	1 057,3
$\text{Fe}_3\text{O}_{4(s)}$	72,4 %	139 815,0	1 006,4

The corresponding reduction heat quantities are (warning, we have here to take into account that the ore contains 60% of iron by mass, so the reduction heat is lowered compared to pure ore):

Ore	Reduc. Heat (pure ore) (J/mol_{ore})	Reduc. Heat (60% ore) (J/mol_{ore})	Reduc. Heat/Iron (60% ore) (kJ/kg_{Fe})
$\text{FeO}_{(s)}$	11 020,0	8 506,4	197,3
$\text{Fe}_2\text{O}_{3(s)}$	24 860,0	21 326,3	222,6
$\text{Fe}_3\text{O}_{4(s)}$	13 680,0	11 343,5	81,7

In total we have:

Ore	Total Heat (60% ore) (J/mol_{ore})	Total Heat/Iron (60% ore) (kJ/kg_{Fe})
$\text{FeO}_{(s)}$	53 161,4	1 233,2
$\text{Fe}_2\text{O}_{3(s)}$	122 628,8	1 279,9
$\text{Fe}_3\text{O}_{4(s)}$	151 158,5	1 088,1

18. A fraction of this heat is brought by the partial combustion of coke ($2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$). Heat produced in this reaction is also wasted in warming the exhaust gas to the furnace temperature.

Exhaust gas consist of the reaction product plus the nitrogen (N_2) from air (~80%) which is unused in the reaction. Estimate the “usable heat”, that is the remaining available heat after warming of the exhaust gas.

For the reaction above, the exhaust consist of 2 moles of CO and 4 moles of N_2 remaining from the incoming air.

$$Q_{\text{usable}} = Q - C_p(\text{exhaust}) \times \Delta T = \Delta_r H - (2C_p(\text{CO}) + 4C_p(\text{N}_2)) \times \Delta T \quad (\text{Eq. 2.9})$$

We obtain $Q_{\text{usable}} = 33,2 \text{ kJ/mol}(\text{O}_2) = 16,6 \text{ kJ/mol}(\text{CO})$ (Eq. 2.10)

19. Assuming that one produces exactly the right number of CO molecules, estimate the missing heat.

We compute the requested heat minus the available heat produced by the partial combustion of CO. Here again, we have to take into account the ore concentration to estimate the number of needed moles of CO.

Ore	$n(\text{CO})$ (60% ore)	Total Heat (60% ore) (J/mol_{ore})	From CO (J/mol_{ore})	Remaining (J/mol_{ore})
$FeO_{(s)}$	0,77	53 161,4	12 819,4	40 342,0
$Fe_2O_{3(s)}$	2,57	122 628,8	42 740,6	79 888,3
$Fe_3O_{4(s)}$	3,32	151 158,5	55 084,1	96 074,4

20. The rest of the heat is brought by total combustion of coke ($C + O_2 \rightarrow CO_2$). Computing again the available heat in the combustion, compute the number of additional moles of carbon needed.

For the reaction above, the exhaust consist of 1 moles of CO_2 and 4 moles of N_2 remaining from the incoming air.

$$\begin{aligned} Q_{\text{usable}} &= Q - C_p(\text{exhaust}) \times \Delta T = \Delta_r H - (C_p(\text{CO}) + 4C_p(\text{N}_2)) \times \Delta T \\ &= 226,3 \text{ kJ/mol}(\text{CO}_2) \end{aligned} \quad (\text{Eq. 2.11})$$

We obtain the additional number of needed complete combustion:

Ore	$n(\text{CO})$ (60% ore)	Remaining Needed Heat (J/mol_{ore})	$n(\text{CO}_2)$ (60% ore)	Total (60% ore)
$FeO_{(s)}$	0,77	40 342,0	0,18	0,95
$Fe_2O_{3(s)}$	2,57	79 888,3	0,35	2,93
$Fe_3O_{4(s)}$	3,32	96 074,4	0,42	3,74

21. Estimate the total heat used in the processes. The literature indicates an energy intensity of ~20 GJ/ton_{iron} for the whole steel manufacturing process, with ~10 GJ/ton for the blast furnace itself.

We can easily estimate the total involves heat by the amount of carbon atom used:

<i>Ore</i>	<i>n(C)/mol ore (60% ore)</i>	<i>Total Heat/mol (J/mol_{ore})</i>	<i>Total Heat (60% ore) (kJ/kg_{Fe})</i>
<i>FeO_(s)</i>	<i>0,95</i>	<i>373 909,4</i>	<i>8 674,0</i>
<i>Fe₂O_{3(s)}</i>	<i>2,93</i>	<i>1 151 666,7</i>	<i>12 019,8</i>
<i>Fe₃O_{4(s)}</i>	<i>3,74</i>	<i>1 472 297,5</i>	<i>10 598,1</i>

We obtain total heat of the order of 8–12MJ/ton , compatible with values from the literature.

3. Carbon balance & conclusions

22. Estimate the amount of emitted CO₂ per ton of iron produced. If you did not manage to obtain a result in question 21, you may start from the energy intensity given in the literature.

The calculation is straightforward from the above result. 1 mole of consumed coke corresponds to 1 mole of emitted CO₂ , thus to 44 g.

<i>Ore</i>	<i>n(C)/mol(ore) (60% ore)</i>	<i>kg(CO₂)/kg(iron) (60% ore)</i>
<i>FeO_(s)</i>	<i>0,95</i>	<i>0,75</i>
<i>Fe₂O_{3(s)}</i>	<i>2,93</i>	<i>1,15</i>
<i>Fe₃O_{4(s)}</i>	<i>3,74</i>	<i>0,98</i>

23. In 2021, the IEA estimated the carbon intensity of steel production to be of the order of 1.4 tons emitted CO₂ per ton of produced steel. How does this value compare with our calculations?

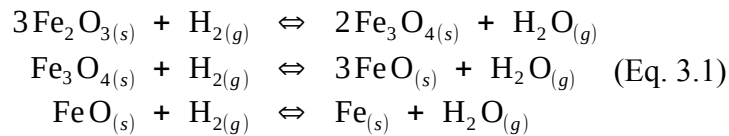
The orders of magnitude are completely correct! Beside the furnace itself, several processes add to the balance above.

24. A large fraction of the heat is lost in the temperature of the exhaust gas. Is it possible to recover a fraction of it? If yes, how?

- The exhaust gas can be used to preheat the incoming air via a heat exchanger.*
- The exhaust gas can be used in a steam turbine to produce electricity, with a yield of the order of ~40%. It cannot be used in a gas turbine because the gas is exhausted at the atmospheric pressure.*

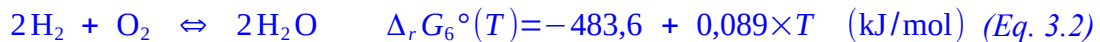
Part 3 Hydrogen based reduction of iron oxides

In order to reduce the carbon foot-print of steel production, we now consider steel-making processes based on the reduction of iron oxides in the presence of dihydrogen:



25. Add the hydrogen equilibrium $2\text{H}_2 + \text{O}_2 \Rightarrow 2\text{H}_2\text{O}$ to the Ellingham diagram.

The hydrogen equilibrium reads:



See Fig. 3 for the corresponding Ellingham diagram.

26. Explain qualitatively why hydrogen can be used to reduce oxides. How different is this process compared to the one using CO?

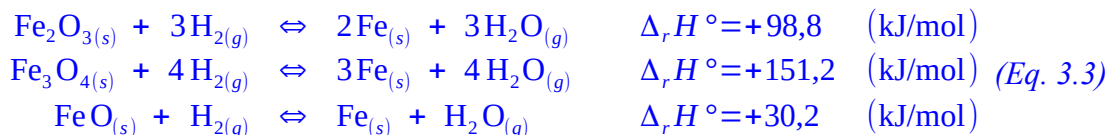
Above some temperature, Hydrogen line is below the oxides lines. Hydrogen is thus more reductive than the iron oxides and can reduce them. One important aspect though is that the slope for hydrogen is positive, meaning that it does not become a better reductant with an increased temperature, in contrast to carbon.

27. At what temperature can hydrogen reduce iron oxides?

Hydrogen can efficiently reduce iron oxides above temperatures of the order of 1000 K, when the hydrogen line is below the various oxides lines.

28. Write the chemical reaction equations for the reduction of the various iron oxides in the presence of hydrogen. Are these reactions endo- or exothermic?

The reduction equations have standard reaction enthalpies:



In contrast to carbon-based reduction, they are all exothermic.

29. As in the case of the carbon-based iron reduction, iron ore still needs to be brought up to the furnace temperature. The same applies to the hydrogen. In contrast to carbon-based reduction, no air needs to be heated, so the amount of heat wasted is much less. For every mole of Carbon oxide, estimate the heat needed to bring the reactant to the furnace temperature.

We need to bring the heat quantity

$$Q_{\text{heat}} = (C_p(\text{oxide}) + n_{\text{H}_2} C_p(\text{H}_2)) \times \Delta T$$

We obtain the following quantities: per mole of ore:

Ellingham Diagram of Iron

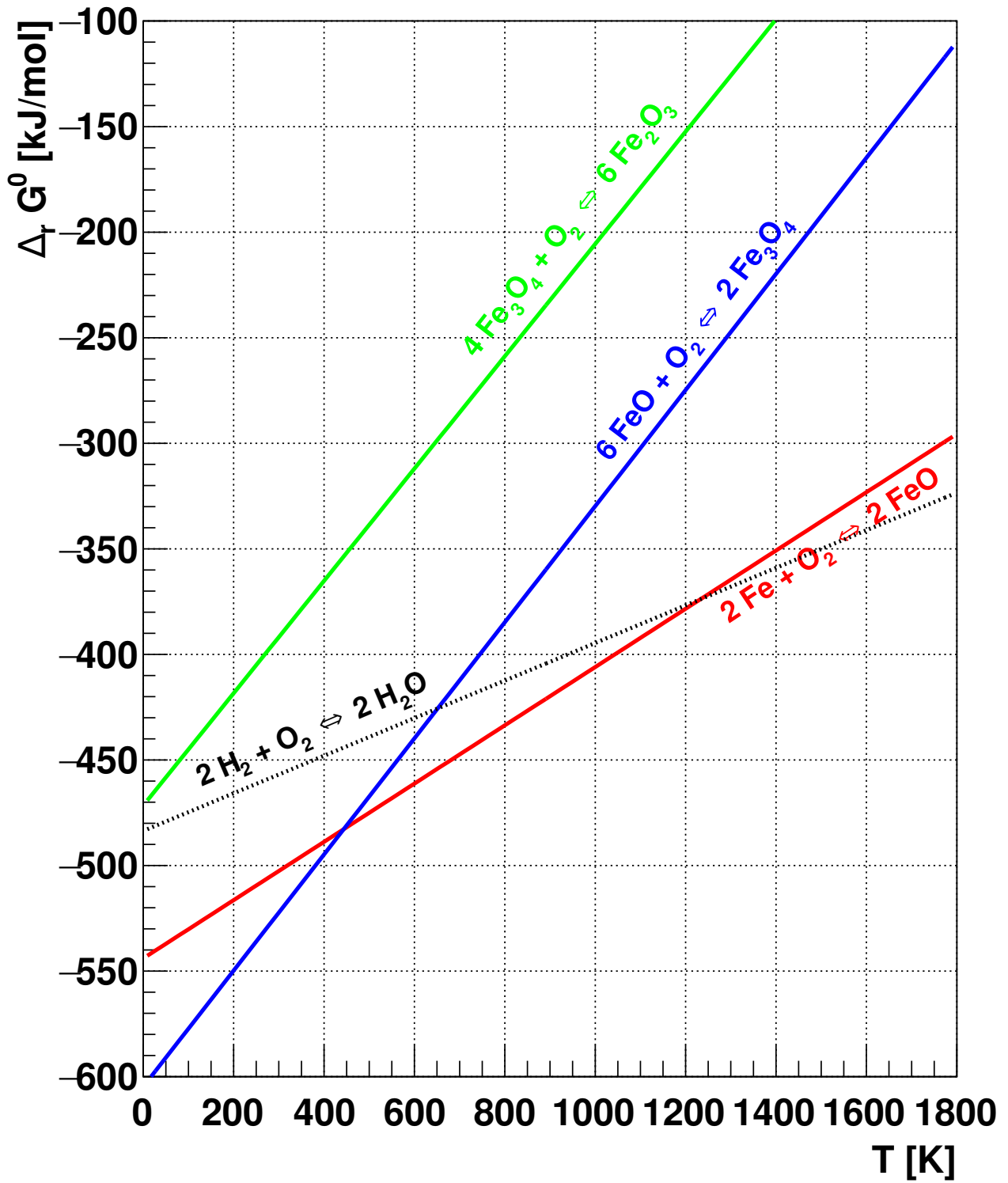


Figure 3: Ellingham Diagram of Iron in the presence of Hydrogen

<i>Ore</i>	<i>n(H₂) (60% ore)</i>	<i>Ore Heat (60% ore) (J/mol_{ore})</i>	<i>H₂ Heat (60% ore) (J/mol_{ore})</i>	<i>Total Heat (60% ore) (J/mol_{ore})</i>
<i>FeO_(s)</i>	<i>0,77</i>	<i>44 655,0</i>	<i>21 675,1</i>	<i>66 330,1</i>
<i>Fe₂O_{3(s)}</i>	<i>2,57</i>	<i>101 302,5</i>	<i>72 265,8</i>	<i>173 568,3</i>
<i>Fe₃O_{4(s)}</i>	<i>3,32</i>	<i>139 815,0</i>	<i>93 136,4</i>	<i>232 951,4</i>

Except for the first one, the heat needs are not covered by the reduction reaction. External heating is still needed.

30. In the case that external heating is needed, propose some solutions and discuss their possible advantages and/or drawbacks.

Heat can be brought by several mechanisms

- Direction combustion of hydrogen in the furnace. This implies injection of air or pure oxygen. In the case we inject air, we will also inject nitrogen which will part of the exhaust gases, thus resulting in wasted heat. Injection of pure oxygen limits the wasted heat, but implies air separation which is also costly. In both case, adjunction of oxygen in significant quantities will make the atmosphere of the furnace more oxidating, and will reduce the efficiency of the reduction process.*
- Direct injection of heat without injection of gases: this would be the preferred option to avoid wasted heat. Electric oven can be used for this purpose.*

31. What fraction of hydrogen is currently produced from non fossil sources ?

About 5% only. From Wikipedia: "As of 2020, the majority of hydrogen (~95%) is produced from fossil fuels by steam reforming of natural gas and other light hydrocarbons, partial oxidation of heavier hydrocarbons, and coal gasification"

Part 4 Offshore wind and green hydrogen production

In this part, we will investigate the potential of offshore wind to produce the hydrogen needed for carbon-free steel-making. The first commercial floating offshore park, Hywind Scotland, was started in October 2017, 28 kilometers off Peterhead, Scotland. The farm has five 6 MW Siemens direct-drive turbines (type SWT-6.0-154), whose key parameters are given in table 1. The turbines were mounted on a ballast stabilized spar-buoy, with cartenary mooring drag embedded anchors (See figure 4, with Big Ben for scale).

32. Orders of magnitude: for cut-in wind speed (4 m/s) and average wind speed in the North Sea (10 m/s), estimate the power of the turbine

The wind power is

$$P = \frac{1}{2} \rho_{\text{air}} S v^3 \quad (\text{Eq. 4.1})$$

Under Betz condition, the turbine can extract a power

$$P = \frac{1}{2} C_p \rho_{\text{air}} S v^3, \quad \text{with} \quad C_p = \frac{16}{27} \quad (\text{Eq. 4.2})$$

For a cut-in wind power of 4 m/s , we obtain a power of 0,4MW . For the average wind speed of 10 m/s this rises to 6,3MW .

33. Under the Betz condition, compute the thrust on the rotor. Give the numerical value with the correct units.

The thrust on the rotor can be expressed from the slow-down of the wind (change of momentum of the air):

$$\vec{F} = -\frac{d\vec{p}_{\text{air}}}{dt} = -\rho_{\text{air}} S \vec{v} (\vec{v}_2 - \vec{v}_1) \quad (\text{Eq. 4.3})$$

Under Betz conditions:

$$v_2 = \frac{1}{3} v_1, \quad v = \frac{2}{3} v_1, \quad \Rightarrow \quad F = \frac{4}{9} \rho_{\text{air}} S v_1^2 \quad (\text{Eq. 4.4})$$

For a cut-in wind power of 4 m/s , we obtain a thrust of $1,5 \times 10^5 \text{ N}$. For the average wind speed of 10 m/s this rises to $9,4 \times 10^5 \text{ N}$.

34. The turbine is ballast stabilized (using a ‘‘Spar-buoy’’, a vertical tube) in the absence of wind. We consider a buoy whose structure has a mass of $m_B = 2300 \text{ tons}$ partially filled with a mass m_w of water (ballast). The total turbine mass is denoted $m_T = 1\,140 \text{ tons}$. Using the data from table 2 estimate the buoy volume V_B . Determine the maximum ballast mass m_w^{max} that can be filled into the buoy. We neglect the density of air compared to that of water:

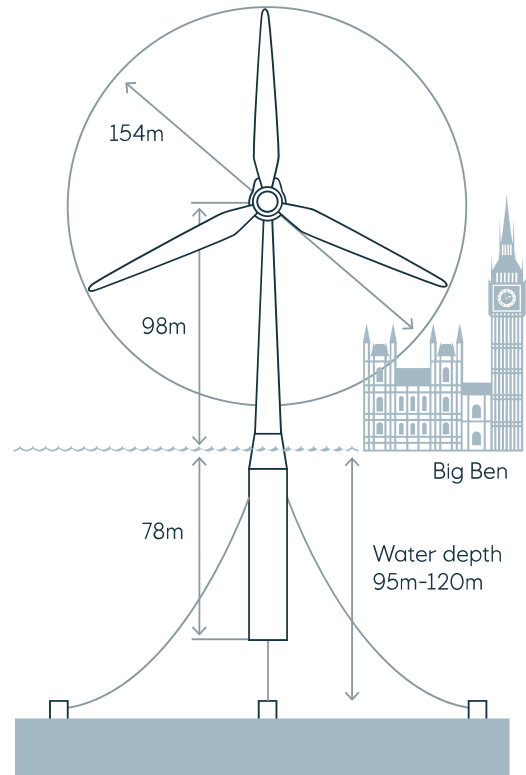


Figure 4: Design of the floating wind turbines equipping the Hywind Scotland floating wind farm.

The buoy volume is:

$$V_B = \pi r_B^2 \times h_B = 12\,880 \text{ m}^3 \quad (\text{Eq. 4.5})$$

The maximum ballast mass is then simply:

$$m_W^{\max} = \rho_{\text{water}} \times V_B = 12\,880 \text{ tons} \quad (\text{Eq. 4.6})$$

35. Determine the equilibrium condition in the absence of wind. What is the maximum ballast mass $m_W^{\text{eq,max}}$ at equilibrium?

The buoy results in an upward going force (Archimedes) corresponding to the opposite of the weight of the displaced water mass. The equilibrium condition reads:

$$\underbrace{m_B + m_T + m_W}_{\text{weight}} \leq \underbrace{m_W^{\max}}_{\text{buoyancy}} \Rightarrow m_W \leq m_W^{\max} - m_B - m_T = 9\,444 \text{ tons} \quad (\text{Eq. 4.7})$$

If the buoy is completely filled with water, the whole structure would sink.

36. We model the turbine mast (or tower) as a purely conical tube shape with a base radius $r_0 = 7.5 \text{ m}$ and a top radius $r(h) \equiv r_1 = 5 \text{ m}$. The radius evolves linearly with height:

$$r(z) = r_0 - \alpha \times z \quad \text{with} \quad \alpha = \frac{r_0 - r_1}{h} \quad (\text{Eq. 4.8})$$

Determine the mast volume V_M .

One has:

$$V_M = \int_0^h \pi r^2(z) dz = \pi \int_0^h (r_0^2 + \alpha^2 z^2 - 2\alpha r_0 z) dz = \frac{\pi h}{3} (r_0^2 + r_1^2 + r_0 r_1) \approx 2\,776 \text{ m}^3 \quad (\text{Eq. 4.9})$$

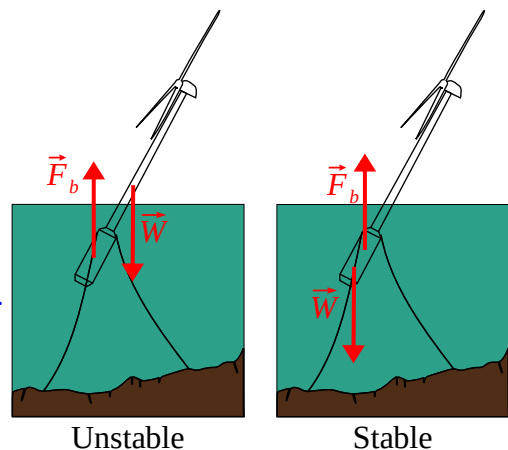
37. Determine the average density of the mast and compare it to that of water. What happens if, due to some external action, the whole turbine sinks a little into the sea?

$$\frac{V_M}{m_M} \approx 254 \text{ kg/m}^3 \quad (\text{Eq. 4.10})$$

The average density of the mast is lower (by a factor ~ 4) than that of water. In the case the turbine sinks a little in the sea, the buoyancy force increases, leading to an increased up-going reaction, which counteracts the moment. The vertical equilibrium of the turbine is stable.

38. Waves and other stimulation result in oscillations of the vertical axis of the turbine. Let's consider an inclination angle θ with respect to the vertical. Express the torque on the center of gravity of the turbine + empty buoy structure. Where should the center of gravity be located compared to the center of the buoy to reach a stable equilibrium? What is the role of the ballast?

At the center of gravity of the whole structure, the weight \vec{W} has no torque. The only remaining force is the buoyancy force \vec{F}_b . If the center of application of the buoyancy force is below the center of gravity (left), the torque will increase the inclination and the system



is unstable. The center of application of the buoyancy force should be below the center of gravity (right) to create a torque that opposes to the inclination.

The role of the ballast is precisely to lower the center of gravity of the structure below the center of application of the buoyancy force.

39. Assuming a uniform thickness of mast (s), one can show that the position of the center of gravity of the tower is given by :

$$OG = \frac{1}{M} \times \int OM dm = \frac{h}{3} \times \frac{r_0 + 2r_1}{r_0 + r_1} \quad (\text{Eq. 4.11})$$

We take the origin of the vertical coordinate O at sea level under normal floating conditions (see figure 4). The nacelle is at an altitude $z_N = +98$ m and the center of the buoy at an altitude $z_B = -39$ m. Determine the altitude of the center of gravity of the mast, then the altitude of center of gravity of the total turbine structure (mast + nacelle + blades + empty buoy) without ballast.

The mast total mass can be expressed as its circumference over the height:

$$M = s \times \rho \int 2\pi r(z) dz = 2\pi s \rho h \frac{(r_0 + r_1)}{2} \quad (\text{Eq. 4.12})$$

The position of the center of gravity is thus given by:

$$OG = \frac{1}{M} \times \int OM dm = \frac{h}{3} \times \frac{r_0 + 2r_1}{r_0 + r_1} \quad (\text{Eq. 4.13})$$

In general, it is lower than $h/2$. For $r_0 = r_1$ (cylinder), one obtains as expected:

$$OG = \frac{h}{3} \times \frac{3}{2} = \frac{h}{2}$$

In the current case the center of gravity of the mast is $z_M \approx 0.47 \times h = 38$ m. The center of gravity of the whole structure is:

$$z_G = \frac{z_M \times m_M + z_N \times (m_N + 3 \times M_{\text{blade}}) + z_B \times m_B}{m_M + m_N + 3 \times m_{\text{blade}} + m_B} = -5.6 \text{ m} \quad (\text{Eq. 4.14})$$

with total structure mass $m_S = m_M + m_N + 3 \times m_{\text{blade}} + m_B = 3\,440$ tons

40. We consider the buoy to be filled with a fraction x of water ($x \in [0, 1]$). Determine the position of the center of gravity of the structure + water and the position of application of the buoyancy force. Under which conditions for x does the turbine remain straight?

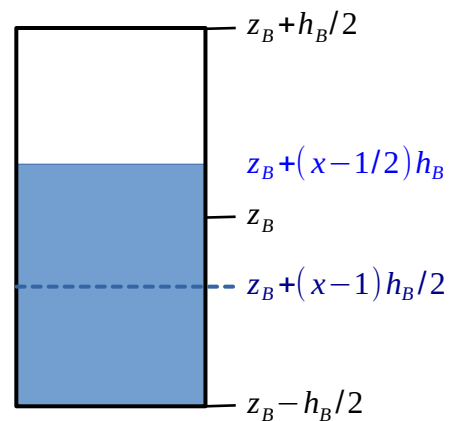
The mass of water in the buoy is

$$m_w(x) = x \times m_w^{\max}$$

with a center of gravity at $z_w(x) = (z_B + (x-1) \times h_B/2)$

thus the position of the center of gravity is given by:

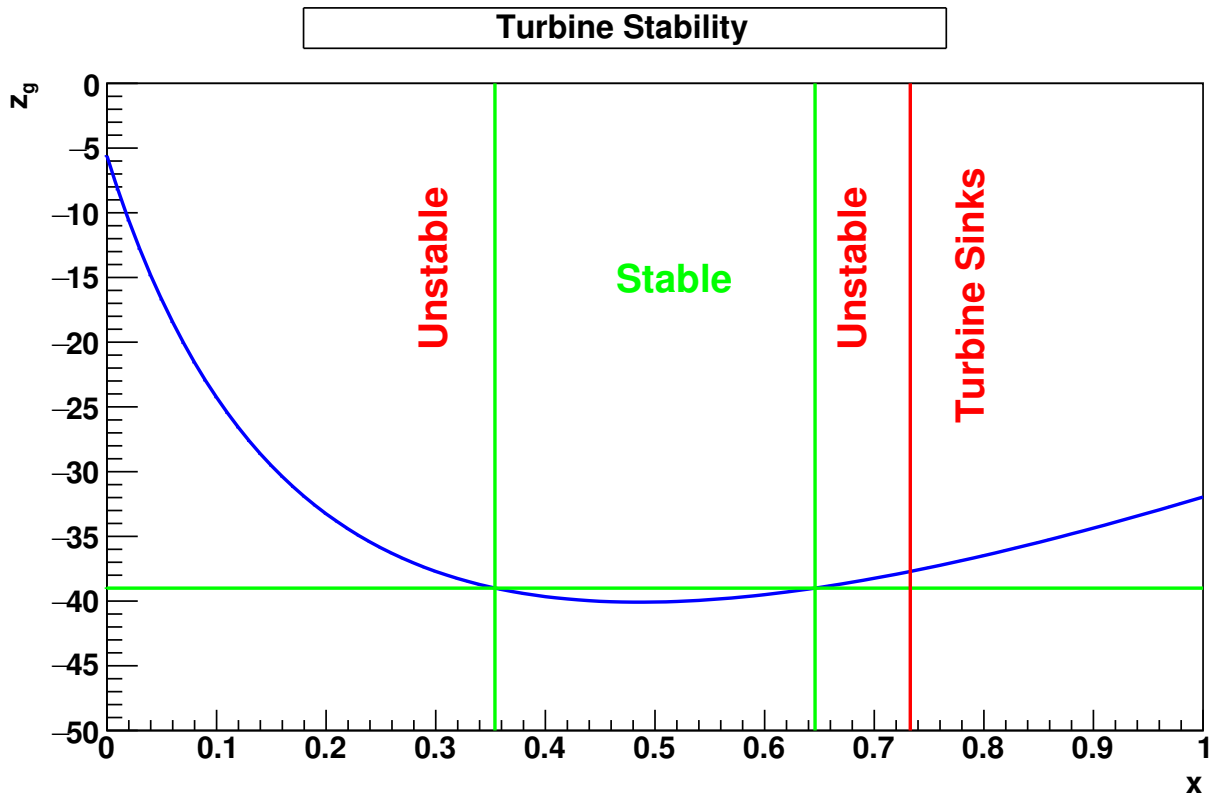
$$z_G(x) = \frac{z_G(0) \times m_S + (z_B + (x-1) \times h_B/2) \times x \times m_w^{\max}}{m_S + x \times m_w^{\max}} \quad (\text{Eq. 4.15})$$



The buoyancy force has a center of gravity which does not change with x :

$$z_b(x) = z_B \text{ (Eq. 4.16)}$$

In the case the buoy is filled with water, the weight of water and the buoyancy forces exactly compensate each other. We obtain the following curves:



The domain of stability is (graphically) $x \in [0,354; 0,646]$ with a best stability obtained from $x \approx 0,5$. This corresponds to a water mass of $\approx 6\,400$ tons and a total ballasted mass of $\approx 10\,000$ tons. Note that the literature indicates a total mass of $\approx 12\,000$ tons.

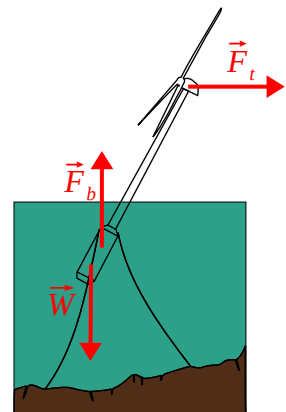
41. We assume that the equilibrium corresponds to $x \approx 0,5$. Determine the inclination angle of the turbine as function of wind speed.

The torque at the center of gravity of the structure has two components:

- Torque induced by the thrust: $F_t \times \cos \theta \times (z_N - z_G)$
- Torque induced by the buoyancy: $F_b \times \sin \theta \times (z_B - z_G)$

This results in an equilibrium conditions

$$\tan \theta = \frac{F_T (z_N - z_G)}{F_B (z_B - z_G)} \text{ (Eq. 4.17)}$$



The the equilibrium conditions with $x \approx 0,5$ gives $z_G = -40,1$ m thus $z_N - z_G = 138$ m and $z_B - z_G = 1,1$ m, The buoyancy and thrust can be expressed as:

- $F_B = \rho_{\text{water}} g V_B = 1,3 \times 10^8$ N
- $F_T = \frac{4}{9} \times \rho_{\text{air}} S v_1^2$

Thus the inclination angle is given by:

$$\tan\theta = 9.5 \times 10^{-3} \text{ rad} \times \left(\frac{v_1}{1 \text{ m/s}} \right)^2 = 0.54^\circ \times \left(\frac{v_1}{1 \text{ m/s}} \right)^2 \quad (\text{Eq. 4.18})$$

For a cut-in wind power of 4 m/s, we obtain an inclination angle of 8,7°. For the average wind speed of 10 m/s this rises to 54° which is not acceptable.

42. How can one reduce the inclination angle?

The important aspect is to lower the center of gravity. Increasing $z_B - z_G$ by just a factor of ~ 2 would result in much more acceptable values of the inclination angle. The easiest is to replace a fraction of the ballast by denser elements, such as stones.

Part 5 Constants relevant to the problem

Component	Molar Mass (g/mol)	$\Delta H_f^\circ(298)$ (kJ/mol)	$S^\circ(298)$ (J/(mol·K))	C_p (J/(mol·K))
CO ₂	44,010	-393,52	213,75	37,1
CO	28,011	-110,5	197,7	29,1
C	12,011	0	5,7	8,5
O ₂	32,00	0	205,2	29,4
H ₂ (g)	2,0	0	130,7	28,8
H ₂ O(g)	18,0	-241,8	188,8	33,6
Cu	63,54	0	33,2	24,2
Cu ₂ O(s)	143,09	-168,6	93,1	63,6
CuO(s)	79,54	-157,3	42,6	55,3
Fe	55,85	0	27,3	25,1
FeO(s)	71,85	-272,0	60,7	34,0
Fe ₂ O ₃ (s)	159,69	-824,2	87,4	103,9
Fe ₃ O ₄ (s)	231,54	-1118,4	146,4	143,4

Table 1: Standard Thermodynamical values of selected bodies. Data from https://www.engineeringtoolbox.com/standard-state-enthalpy-formation-definition-value-Gibbs-free-energy-entropy-molar-heat-capacity-d_1978.html

	Siemens SWT-6.0-154	GE Haliade-X
Blade Length	75 m	107 m
Blade mass	25 tons	55 tons
Rotor Diameter	154 m	218 m
Cut-in wind speed	4 m/s	3.5 m/s
Cut-out wind speed	25 m/s	28 m/s
Nominal power wind speed	13 m/s	
Rated rotor speed	Variable, 5-11 rpm	7.8 rpm
Hub Height	83 m	135 m
Tip height (offshore)	233 m	260 m
Nacelle width		11 m
Nacelle height		10.4 m
Nacelle length		20.6 m
Nacelle mass	360 tons	600 tons
Base diameter of steel mast	7.5 m	8.0 m
Top diameter		5.5 m
Length of steel mast	98 m	129 m
Tower mass	705 tons	2 555 tons
Total turbine mass	1140 tons	
Floating structure mass	10 500 tons	
Buoy height	78 m	
Buoy diameter	14.5 m	
Buoy steel mass	2 300 tons	
Buoy mass with ballast	10 000 tons	

Table 2: Properties of the Siemens SWT-6.0-154 and GE Haliade-X wind turbines

References:

- Hywind Scotland:
 - https://en.wikipedia.org/wiki/Hywind_Scotland
 - <https://www.equinor.com/energy/hywind-scotland>
 - <https://www.equinor.com/content/dam/statoil/documents/newsroom-additional-documents/news-attachments/brochure-hywind-a4.pdf>
 - <https://www.saipem.com/en/projects/hywind>
- Siemens SWT-6.0-154 turbine:
 - <https://www.siemensgamesa.com/products-and-services/offshore/wind-turbine-swt-6-0-154>