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 11)

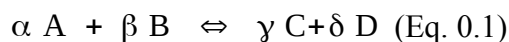**Note 3: Use green paper sheets for your answers.**

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*

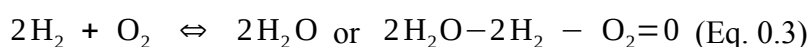We note that standard chemical reactions take the form:
$$\alpha\, A\ +\ \beta\, B\ \Leftrightarrow\ \gamma\, C + \delta\, D \quad \text{(Eq. 0.1)}$$
where A, B, C, D are chemical bodies and $\alpha, \beta, \gamma, \delta$ are the "**Stoichiometric coefficients**".
It can also be noted:
$$\sum v_i A_i = 0 \quad \text{(Eq. 0.2)}$$
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:
$$2\,H_2\ +\ O_2\ \Leftrightarrow\ 2\,H_2O \text{ or } 2\,H_2O - 2\,H_2\ -\ O_2 = 0 \quad \text{(Eq. 0.3)}$$
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**" $\Delta_r Q°$ is the "**reaction quantity**" $\Delta_r Q$ for "standard thermodynamic conditions" ($T° = 298\,K$, $P° = 1\,bar = 10^5\,Pa$).

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

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. $\Delta_r H(T) = \Delta_r H°$ and $\Delta_r S(T) = \Delta_r S°$. 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**" $\Delta H_f°$ 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:

$$2\,H_2 + O_2 \Leftrightarrow 2\,H_2O \qquad \Delta_r H° = 2\underbrace{\Delta H_f°(H_2O)}_{=-241,8} - 2\underbrace{\Delta H_f°(H_2)}_{=0} - \underbrace{\Delta H_f°(O_2)}_{=0} = -483,6\,kJ/mol$$

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:

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

For reactions occurring at constant temperature and pressure, $\Delta_r G°$ 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 $\Delta_r G°$ will correspond to reactions evolving towards the **right** (**increase** of ξ) while **positive** values of $\Delta_r G°$ will correspond to reactions evolving towards the **left** (**decrease** of ξ).

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

$$\Delta_r H° = 2\underbrace{\Delta H_f°(H_2O)}_{=-241,8} - 2\underbrace{\Delta H_f°(H_2)}_{=0} - \underbrace{\Delta H_f°(O_2)}_{=0} = -483,6\,kJ/mol$$

$$\Delta_r S° = 2\underbrace{S°(H_2O)}_{=188,8} - 2\underbrace{S°(H_2)}_{=130,7} - \underbrace{S°(O_2)}_{=205,2} = -90\,J/K/mol \qquad \text{(Eq. 0.7)}$$

$$\Delta_r G° = \Delta_r H° - T \times \Delta_r S° = (-483,6 + 0.090 \times T)\,kJ/mol$$

At low temperature, the reaction of the formation of water is spontaneous (negative reaction Gibbs energy). There exists a "dissociation" temperature $T = 483,6/0,090 = 5373\,K$ 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 $\Delta_r H = \Delta_r H°$.

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 :

$$\mu_i(T, P) = \mu_i° + RT \ln a_i$$

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 $P_i = x_i \times P_0$:

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

At constant temperature and pressure:

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

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

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

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

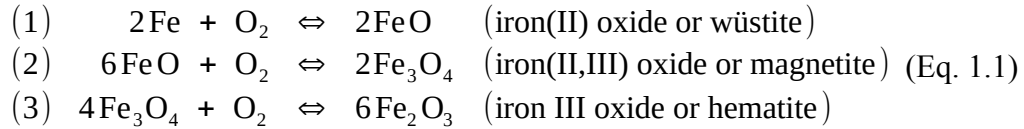$$0=dG=\Delta_r G\times d\xi \quad \Rightarrow \quad \Delta_r G=0$$

We then obtain:

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

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:

$$\begin{array}{lll}
(1) & 2\,Fe + O_2 \Leftrightarrow 2\,FeO & (\text{iron(II) oxide or wüstite}) \\
(2) & 6\,FeO + O_2 \Leftrightarrow 2\,Fe_3O_4 & (\text{iron(II,III) oxide or magnetite}) \\
(3) & 4\,Fe_3O_4 + O_2 \Leftrightarrow 6\,Fe_2O_3 & (\text{iron III oxide or hematite})
\end{array} \quad (\text{Eq. 1.1})$$

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 $\Delta_r G°(T) = A + B \times T$, when A and B are numerical values to be determined and T is the temperature in Kelvin.

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

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) ?

4. (*) How does this compare to $1\,kg$ of oil?

2. Temperature based reduction of iron oxides – Ellingham diagrams

5. (*) An Ellingham diagram is a diagram showing the value of $\Delta_r G°$ as function of temperature for various oxidation equations. By convention, all reaction equations are written for one mole of di-oxygen 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).

6. (**) Show that, at equilibrium the partial pressure of oxygen $P(O_2)$ is related to the standard reaction Gibbs free energy by the relation:

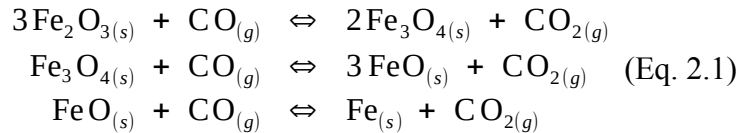$$\Delta_r G° = RT \ln P(O_2) \quad (\text{Eq. 1.2})$$

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

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

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

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?
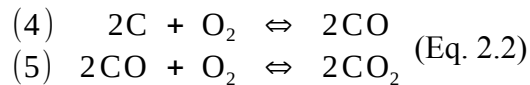
Part 2   Classical Steel production

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:

$$3\,Fe_2O_{3(s)} \; + \; CO_{(g)} \;\Leftrightarrow\; 2\,Fe_3O_{4(s)} \; + \; CO_{2(g)}$$
$$Fe_3O_{4(s)} \; + \; CO_{(g)} \;\Leftrightarrow\; 3\,FeO_{(s)} \; + \; CO_{2(g)} \quad \text{(Eq. 2.1)}$$
$$FeO_{(s)} \; + \; CO_{(g)} \;\Leftrightarrow\; Fe_{(s)} \; + \; CO_{2(g)}$$

10. (*) The carbon equilibrium is given by the chemical reaction: $C \; + \; CO_2 \;\Leftrightarrow\; 2\,CO$. This can be written as two different oxidation reactions:

$$\begin{array}{ll} (4) & 2\,C \; + \; O_2 \;\Leftrightarrow\; 2\,CO \\ (5) & 2\,CO \; + \; O_2 \;\Leftrightarrow\; 2\,CO_2 \end{array} \quad \text{(Eq. 2.2)}$$

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 $\Delta_r G°(T) = A + B \times T$, when A and B are numerical values to be determined and T is the temperature in Kelvin.

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

12. (***) We consider a carbon equilibrium $CO_2 + C \;\Leftrightarrow\; 2\,CO$ at a total pressure of 1 atmosphere. Compute the ratio of partial pressures $p(CO_2)/p(CO)$ 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:

$$\Delta_r G° = -RT \ln\left(\frac{P^2(CO)}{P(CO_2)}\right) \text{ and } P_{tot} = P(CO) + P(CO_2) \quad \text{(Eq. 2.3)}$$

13. (**) At what temperature is equilibrium reached?

14. (*) Why is carbon-based reduction more efficient that direct thermal reduction?

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?

2.   *Thermal balance*

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

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

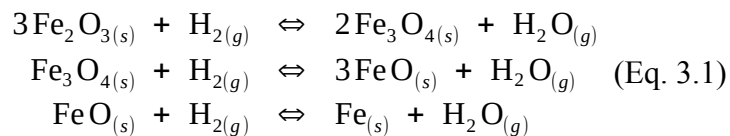Express these quantities in terms of kJ/kg of iron produced.

18. (***) A fraction of this heat is brought by the partial combustion of coke ($2C+O_2 \rightarrow 2CO$). 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.

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

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.

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

3. Carbon balance & conclusions

22. (*) Estimate the amount of emitted CO_2 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.

23. (*) In 2021, the IEA estimated the carbon intensity of steel production to be of the order of 1.4 tons emitted CO_2 per ton of produced steel. How does this value compare with our calculations?

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?

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:

$$3\,Fe_2O_{3(s)} \;+\; H_{2(g)} \quad \Leftrightarrow \quad 2\,Fe_3O_{4(s)} \;+\; H_2O_{(g)}$$
$$Fe_3O_{4(s)} \;+\; H_{2(g)} \quad \Leftrightarrow \quad 3\,FeO_{(s)} \;+\; H_2O_{(g)} \quad \text{(Eq. 3.1)}$$
$$FeO_{(s)} \;+\; H_{2(g)} \quad \Leftrightarrow \quad Fe_{(s)} \;+\; H_2O_{(g)}$$

25. (*) Add the hydrogen equilibrium $2\,H_2 + O_2 \;\Rightarrow\; 2\,H_2O$ to the Ellingham diagram.

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

27. (*) At what temperature can hydrogen reduce iron oxides?

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?

29. (**) As I 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.

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

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

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 1, with Big Ben for scale).
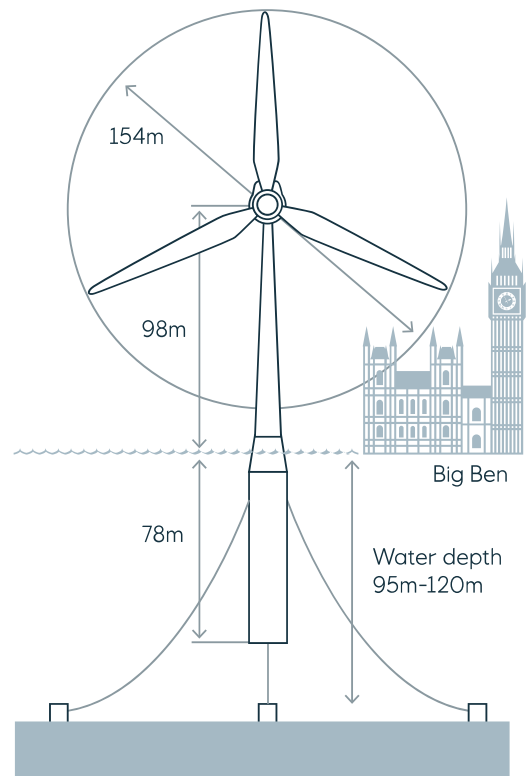
32. (*) Orders of magnitude: for cut-in wind speed ($4\,\mathrm{m/s}$) and average wind speed in the North Sea ($10\,\mathrm{m/s}$), estimate the power of the turbine

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

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 $m_B = 2300\,\mathrm{tons}$ partially filled with a mass m_W of water (ballast). The total turbine mass is denoted $m_T = 1\,140\,\mathrm{tons}$. 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 1: Design of the floating wind turbines equipping the Hywind Scotland floating wind farm.

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

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

$$r(z) = r_0 - \alpha \times z \quad \text{with} \quad \alpha = \frac{r_0 - r_1}{h} \quad \text{(Eq. 4.1)}$$

Determine the mast volume V_M.

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?

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?

39. (**) Treating the mast as a hollow cone with an external steel layer of uniform thickness (s), one can show that the position of the center of gravity of the tower is given by :

$$OG = \frac{1}{M} \times \int OM \, dm = \frac{h}{3} \times \frac{r_0 + 2r_1}{r_0 + r_1} \quad \text{(Eq. 4.2)}$$

We take the origin of the vertical coordinate O at sea level under normal floating conditions (see figure 1). 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.

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?

41. (***) We assume that the equilibrium corresponds to $x \approx 0.5$. Determine the inclination angle of the turbine as function of wind speed.

42. (***) How can one reduce the inclination angle?

Part 5 Constants relevant to the problem

Component	Molar Mass (g/mol)	$\Delta H_f°(298)$ (kJ/mol)	$S°(298)$ (J/(mol·K))	Cp (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
N_2	28,01	0	191,6	29,1
$H_2(g)$	2,0	0	130,7	28,8
$H_2O(g)$	18,0	-241,8	188,8	33,6
Cu	63,54	0	33,2	24,2
$Cu_2O(s)$	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
$Fe_2O_3(s)$	159,69	-824,2	87,4	103,9
$Fe_3O_4(s)$	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	
Property	**Value**
Blade Length	75 m
Blade mass	25 tons
Rotor Diameter	154 m
Cut-in wind speed	4 m/s
Cut-out wind speed	25 m/s
Nominal power wind speed	13 m/s
Rated rotor speed	Variable, 5-11 rpm
Hub Height	83 m
Tip height (offshore)	233 m
Nacelle width	
Nacelle height	
Nacelle length	
Nacelle mass	360 tons
Base diameter of steel mast	7.5 m
Top diameter	
Length of steel mast	98 m
Tower mass	705 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 turbine

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