

PHY 555 — Energy and Environment

PC3 — Carbon Capture & Storage – Solution Strategies

1 Orders of Magnitude

1. Obtain the total mass of the atmosphere, using the fact that $P_{\text{ground}} = \int_0^{\infty} \rho(z) g dz$.
2. Use atmospheric composition (N₂ : O₂ = 80:20) to get average molar mass of the atmosphere, then answer of first question to get mols in atmosphere. ppm and molar mass of carbon gives GtC.
3. 2200 GtCO₂ corresponds to 2200×12 /44=600GtC emitted. The atmospheric concentration increase 405–180=125 ppm correspond to an atmospheric carbon content increase of 268GtC. The difference (332 GtC, = 55% of total emissions) has been removed from the atmosphere through carbon sinks.
4. The saturation vapour pressure of CO₂ is P_{sat}=60 bar. The partial pressure of CO₂ in the atmosphere is P_{CO2}=400×10⁻⁶ bar. We use the chemical potential equilibrium between liquid and vapour (notice P₀ is P_{sat}, so P_i=P_{sat} when x=1)

$$\mu_l^0(T) + RT \ln x_i = \mu_v^0(T) + RT \ln \frac{P_i}{P_0} \Rightarrow x_i = \frac{P_i}{P_s}$$

leading to a surface concentration in water of $x = P_{CO2} / P_{sat} = 6.6 \text{ ppm}$

80% of Earth surface is covered with ocean, and taking first 100m, can get volume of water. Dissolved CO₂ corresponds to 660 GtCO₂.

5. Increasing partial pressure of CO₂ in the atmosphere → more CO₂ stored in water at equilibrium. But increasing temperature → increase saturation vapour pressure → decrease the amount of CO₂. Need also to take into account chemistry : more CO₂ increases pH, which shifts equilibrium with carbonates.
6. Average solar flux : 340W/m², Photosynthesis efficiency : 0.1%

Energy for CO₂ conversion into carbohydrates : 0.5 MJ/mol

Sequestration capabilities:
$$\frac{340 \times 10^4 \times 0.1 \times 3600 \times 24 \times 365.25 \times 8760}{500\,000 \times 44} \approx 10 \text{ tCO}_2/\text{ha}/\text{yr}$$

2 CO₂ Separation

1. Mixing operation, T and P are constant. Thermodynamic identities :

$$dU = \delta Q + \delta W = T dS - T S_{cr} - p dV = 0 \text{ (for a mixing operation)}$$

$$dG = -S dT - T S_{cr} + V dp = -T S_{cr} = d(N\mu) \text{ (change in chemical potential)}$$

Where S_{cr} is created entropy. The mixing operation is non-reversible, and the system evolves towards the minimum of the Gibbs free energy (which is also the entropy maximum).

In the initial state, one has:

$$G = \sum_i n_i \mu_i = \sum_i n_i \mu_i^0$$

And in final state:

$$G = \sum_i n_i \mu_i = n \sum_i x_i (\mu_i^0 + RT \ln x_i)$$

Therefore:

$$\Delta G = n \sum_i RT x_i \ln x_i = n RT (x \ln x + (1-x) \ln (1-x)) < 0 \quad (\text{as it should be})$$

The entropy creation in the mixture is

$$\Delta S_{\text{mix}} = -n R (x \ln x + (1-x) \ln (1-x)) > 0$$

2. The separation process releases heat and requires work:

$$Q \leq T \Delta S = -T \Delta S_{\text{mix}} \quad \text{and} \quad \Delta U = W + Q = 0$$

The minimal work is:

$$W \geq -n RT (x \log x + (1-x) \log (1-x))$$

Filtering n moles costs a work W and brings $x \times n$ moles of pure CO_2 , thus

$$W_{1\text{molCO}_2} = -RT \left(\log x + \frac{1-x}{x} \log (1-x) \right) \approx -RT (\log x - 1) \quad (\text{Eq. 2.3})$$

- Numerical application of above. $22 \text{ kJ/mol} = 0.13 \text{ kWh/kgCO}_2$
- The CO_2 concentration is now 20%, instead of 400 ppm. The energy is reduced 3 to 4 times less than before.
- The exhaust gas is made of almost pure CO_2 , thus removing the need for separation, but it implies cryogenic separation of air before combustion (with similar energetic cost). This also allows higher combustion temperatures, and thus a higher yield.
- The total energy required to capture 1 kg CO_2 from ambient air and the emissions due to the energy production is

$$W_{\text{tot}} = \frac{W_0}{\eta} (1 + W_{\text{tot}} \times I) \Rightarrow W_{\text{tot}} = \frac{W_0 / \eta}{1 - I \times W_0 / \eta}$$

3 Transport

- For an adiabatic compression (in open flow), $dH = \delta W$. For an ideal gas, $W = n C_p \Delta T$

Entropy conservation observed (adiabatic), so use Laplace relations to get

$$W = n \frac{\gamma R}{\gamma - 1} T_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] = \frac{\gamma}{\gamma - 1} P_1 V_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right]$$

Plug in values to get numerical answers.

It can be easily shown that adiabatic compression is more costly than isothermal compression, because the gas gets hotter and less compressible. Actual compressions processes usually use several compression stages, with intermediate inter-coolers (removal of heat).

2. The enthalpy variation in cooling followed by liquefaction reads

$$\Delta H = n(C_p \Delta T - L_f)$$

(beware, latent heat is given in kJ/kg whereas calorific capacities are in J/mol/K).

In the optimal case this enthalpy variation is provided by a Carnot cooling machine (heat pump) with an efficiency of :

$$r = \frac{W}{Q} = \frac{T_h}{T_l} - 1$$

3. Coal combustion produces 44/12 kg of CO₂ per kg of carbon, so 0.8*44/12 = 2.9 kg_{CO2}/kg. (h_v = 36MJ/kg). The CO₂ intensity of electricity production is (taking into account the plant yield)

$$I = \frac{M_{CO_2}}{M_c} \times \frac{0.8}{h_{v}} \times \frac{1}{\eta_p} \approx 2 \times 10^{-7} \text{ kg}_{CO_2} / J$$

In a first approximation, a molecule of CO₂ is produced for each molecule of oxygen. In exhaust gases one has x=0. to avoid partial combustion. Carbon dioxide minimal separation cost is (Eq. 2.3)

$$\Delta G = -RT(\log x - 1) = 7.18 \text{ kJ mol}_{CO_2}^{-1}$$

This gives per unit mass of produced CO₂

$$\Delta G = 163 \text{ kJ kg}_{CO_2}^{-1}$$

One can then sum up the energetic cost (per kg of CO₂) for separation and then either high pressure compression, or low pressure compression and liquefaction. One obtains a total of 633 kJ/kg for the first solution, and 469 kJ/kg for the second one. So carbon capture represents (in the most optimistic case) an energetic additional cost of 3.6 %. This limit is a fundamental thermodynamical limit that does not take into account the actual yield of the various processes.

Liquefaction and compression are relatively simple processes for which the yields are realistic. This is very different for the carbon separation for which the industrial processes deviate substantially from the thermodynamical limit.