Exercices Series 1 (Introduction chapter)

Cl_2 / caustic soda NaOH electrolysis plant

a) From the 2 electrode half reactions occurring in the electrolysis of NaCl salt :

$2\ Cl^-$ ⇔ $Cl_2 + 2e^-$ (oxidation) E° = -1.36 V (vs NHE)

$2\ H_2O + 2e^-$ ⇔ $H_2 + 2\ OH^-$ (reduction) E° = -0.83 V (vs NHE)

write down the full cell reaction starting from NaCl, remembering that NaCl and NaOH are in aqueous solution (Na^+ aq, Cl^- aq., OH^- aq.)

NHE (Normal H_2 Electrode) is the absolute voltage scale we will introduce later.

b) From thermodynamic data tables, find the ΔH, ΔS and ΔG of this overall reaction, at 298K.

Compound	ΔH (formation) kJ/mol	S (formation) J/mol.K
H_2	0	130.6
Cl_2	0	223
H_2O	-285.8	70
Na^+ aq.	-240.35	59
Cl^- aq.	-167.08	56.5
OH^- aq.	-230.015	-10.8

c) Calculate the minimal voltage to apply to start the electrolysis reaction.

d) Verify how to link this voltage with the Gibbs free energy ΔG of the overall reaction, using Faraday's constant (F = 96'484 C/mol).

e) In reality, around 3 V is applied. Derive the efficiency of the process.

f) Where do you think the losses are ?

g) How many A (Amp) do you need to produce 1 kg Cl_2 in 1 hour ?
(molecular weight Cl_2 = 70.9 g/mol)

h) Using the values above, what is the theoretical minimal energy to produce 1 kg Cl_2?
And the effective energy, using 3 V?

i) World Cl_2 production is 58 Mt Cl_2/yr. How much electricity does this consume in total?
Compare this total electricity need to the world power production of 27'000 TWhe.

j) The average capacity factor of a Cl_2/NaOH production plant is 80% (= 8760 h/yr x 0.8 = 7008 h operating hours per year). Derive from this what is the total worldwide power installed (GWe) for world annual Cl_2 production. Considering there are 650 plants, what is the average power and production per plant?

k) Typical DC current applied in such a plant is 100'000 A for a current density of 0.25 A/cm^2. What is the active electrode area? And the number of cells in a plant?

l) How much H_2 as byproduct does such a plant produce per h ? Per yr ? Demonstrate your calculation by minimal 2 consistent approaches yielding the same result.

m) Considering the LHV (lower heating value) of H_2 as 3.05 kWh/m^3 or 33 kWh/kg, how much % energy is wasted in the process by not recovering the H_2 ? (It is usually vented!)

n) Considering that the annual world total production of H_2 is 80 Mt / yr, of which only 4% is obtained through electrolysis processes, what is the share of the world annual Cl_2 electrolytic production in this? Do you think this is green H_2 ?