Exercise Series 1 (Introduction chapter)

Cl_2 / caustic soda NaOH 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.

Answer:

$2\ NaCl + 2\ H_2O$ ⇔ $H_2 + Cl_2 + 2\ NaOH$
In solution :
$2\ Na^+ + 2\ Cl^- + 2\ H_2O$ ⇔ $H_2 + Cl_2 + 2\ Na^+ + 2\ OH^-$

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

Answer:

Filling in the numbers for the reaction, and since 2 Na^+ cancels out, we find :

ΔH (reaction) : 445.73 kJ / mol (endothermal, hence requires energy to drive the reaction from left to right)
ΔS (reaction) : 79 J/mol.K
T.ΔS : 23.542 kJ/mol (T = 298K)

ΔG (reaction) = ΔH – T.ΔS = **422.188 kJ/mol** (positive free enthalpy, hence the reaction is not spontaneous and needs energy input to drive it)

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

Answer:

-1.36 V + (-0.83 V) = **-2.19 V.**
Sign does not matter here. The applied voltage between the 2 electrode is minimally 2.19 V. It is + 2.19 V when applied between Cl_2 and H_2 electrode, and -2.19 V when applied between H_2 and Cl_2 electrode.

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

Answer :

ΔG = 422.188 kJ/mol
F = 96'484 C/mol
-2.19 V

Energy (Joule) equals Volts (V) x Charge (C).
The Faraday constant equals the charge of 1 mol of electrons :
1 e- = 1.6 10^{-19} C
x 1 mol = 6.02 10^{23} / mol
= 1 F = 96'484 C/mol
The charge transferred per mol (Cl_2 or H_2) of reaction equals 2 x F, since every Cl_2 or H_2 involves 2 electrons.
The link is therefore $\Delta G = - 2F.E°$
422'188 J/mol = - 2 x 96'484 C/mol x (-2.19 V)

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

Answer:
The voltage efficiency is in this case : 2.19 V / 3 V = **73%**

We made here the implicit assumption that every electron (flow of current) will lead to the production of Cl_2 and H_2, in other words that current efficiency or Faradaic efficiency is 100%. In reality, some electrons (5%) get lost into 'parasitic' side reactions. Taking those into account would then lower the power efficiency of the process to 73 % (voltage efficiency) x 95% (current efficiency) = 69.3%

f) Where do you think the losses are ?

Answer:

Apart from **parasitic** side reactions loss, the main loss stems from the voltage loss between 3V and 2.19 V, namely

- **Ohmic loss** of conduction in the electrolyte and electrodes and cabling
- **Overvoltage loss** at the electrodes (charge transfer and mass transfer)

These will be discussed in detail in class in coming weeks.

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)

Answer:

1000 g / 70.9 g/mol = 14.1 mol Cl_2 = 28.2 mol e-
Multiplying this by the Faraday constant F gives 2'721'692.5 C
Since A = C/s, we divide this charge by 3600 s (1 hour) to get **756 A** during 1 h.

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

Answer:

756 Ah x 2.19 V = **1665 Whe / kg Cl_2** theoretical minimum.
Effective : 756 Ah x 3 V = **2.268 kWhe/kg Cl_2**.

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

Answer:

2.268 kWhe / 1 kg Cl_2
=> multiplying for 58 Mton Cl_2 / yr gives **131.54 TWhe / yr**

Relating this to 27'000 TWhe world power production, the 131.5 TWhe consumed for world Cl_2 production equals 131.5 / 27'000 = **0.487 %.**

j) The average capacity factor of a Cl_2/NaOH production plant is 80% (= 8760 h/yr x 0.8 = 7008 h/yr operating time). 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?

Answer:

Power installed for all plants:
131.54 TWhe / 7008 h = **18.77 GWe**.
Since there are 650 plants, an average plant has 18.77 GWe / 650 = **28.88 MWe** installed power, producing 58 Mt Cl_2 /yr / 650 = **89.23 kt Cl_2/yr**.

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?

Answer:

100'000 A / 0.25 $A.cm^{-2}$ => 400'000 cm^2 = **4 m^2 electrodes**

- ⇨ Hence 28.88 MWe / 100 kA = 2.888 V
- ⇨ divided by 3 V per cell to give 288.8 / 3 = **96.3 cells** of 4 m^2 area in 1 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.

Answer 1 : via weight production ratio

89.23 kt Cl_2 / yr for 7008 h/yr operation gives 12842.46 kg Cl_2/h

Production of 1 mol Cl_2 gives also the production of 1 mol H_2.
With 70,9 g/mol Cl_2 and 2.016 g/mol H_2, the weight ratio Cl_2/H_2 = 70.9/2.016 = 35.17

Hence 89'230 t Cl_2 yield also 89'230 / 35.17 = **2537 t H_2/yr**
Or divided by 7008 h/yr : 12'733 kg Cl_2/h yield also 12'733 / 35.17 = **362 kg H_2/h**

Answer 2 : via current and Faraday constant

Charge passed through the plant in 1 hour :
= 100'000 A (C/s) x 96.3 cells x 3600 s/h = $3.466\ 10^{10}$ C
Divide this by 2.F to find the quantity of H_2 in moles (2 e- per 1 H_2) :
$3.466\ 10^{10}$ C / 96'484 C / mol / 2 = 179595 mol H_2
Multiplied with 2.016 g/mol H_2 gives **362 kg H_2/h**.

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!)

Answer:

362 kg H_2 /h equals 362 kg/h x 33 kWh/kg = 11'946 kWh/h = 11.946 MWh/h for 1 hour of production.
The plant consumes 28.88 MWe for 1 h in that time, i.e. 28.88 MWhe.
Hence 11.946 MWh (H_2) / 28.88 MWhe = **41.36%** of the electrical energy invested leaves the plant as vented H_2 energy !
Recovering back this H_2 energy in a fuel cell at 60% electrical efficiency would therefore recover 41.36% x 60% = 25% (7.17 MWhe) of the electrical energy needed in the plant !

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 Cl_2 electrolytic production in this? Do you think this is green H_2 ?

Answer:

For all 650 plants worldwide = 650 x 2537 t H_2/yr = 1.65 Mt H_2/yr.
This therefore corresponds to 1.65 / 80 = **2%** of the annual H_2 production.
Since 4% is of electrolytic origin, the caustic soda Cl_2 industry therefore accounts for half of the world electrolytic H_2 production (which is mostly not used!).

This is mostly not green H_2. Most of the electricity driving the Cl_2 plants are of fossil origin.
It is estimated that green H_2 is now <0.5% of total H_2 produced.