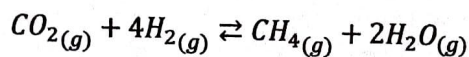


No documents allowed – All types of calculators allowed - All answers must be justified.

**Introduction**

This test investigates the possibility of producing methane  $CH_4(g)$  from renewable rather than fossil resources. The following reaction is considered in that objective:



The resources used are di-hydrogen ( $H_2$ ) and carbon dioxide ( $CO_2$ ).

Exercise 1 focuses on the production of di-hydrogen by electrolysis of water.

Exercise 2 concerns the capture of  $CO_{2(g)}$  produced by wood combustion.

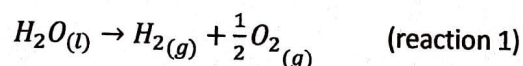
Exercise 3 studies the reaction of methanation to convert  $CO_{2(g)}$  and  $H_{2(g)}$  into  $CH_{4(g)}$

Exercise 4 explores different methods for storing methane.

The 4 exercises can be treated independently.

**Exercise 1 – Water electrolysis in alkaline medium**

Dihydrogen ( $H_2$ ) needed for the synthesis of methane can be produced by electrolysis of water, according to reaction 1 below, carried out at room temperature under alkaline conditions (pH = 14):



- 1.1- The two redox couples and the redox half-reactions associated are given in the redox data sheet. Specify the number of oxidation of the atoms undergoing the redox processes in each couple.
- 1.2- Schematically represent the device needed to implement the electrolysis of water (reaction 1). Indicate the direction of circulation of the electrons, the nature of each electrode (cathode, anode) and the reaction that occurs at each electrode.
- 1.3- Give the literal expressions of Nernst equation for the two redox couples, considering that the electrolysis is carried out under basic conditions.
- 1.4- Deduce the literal expression of the potential difference between the two electrodes,
- 1.5- Calculate the minimum voltage to be applied to the electrodes to make possible the electrolysis reaction. It will be considered here that the gases are both at standard pressure.

A production of  $1 \text{ m}^3$  of dihydrogen is considered at a pressure  $p = 1 \text{ bar}$  and a temperature  $T = 298 \text{ K}$ .

- 1.6- Calculate the mass of water required.
- 1.7- Calculate the amount of electricity consumed (in Coulomb).

## Exercise 2 – Capture and recovery of carbon dioxide from wood combustion

This exercise considers firstly the complete combustion of wood and the associated production of  $CO_{2(g)}$  in the fumes (paragraph 2.1) and secondly the capture of  $CO_2$  by absorption in pressurized water in paragraph 2.2. **Parts 2.1 and 2.2 can be treated independently.**

### 2.1- Wood combustion

The combustion of wood is a process where wood reacts at high temperature with air (80%  $N_2$ , 20%  $O_2$ ) to produce heat. Fumes are formed which mostly contain  $N_{2(g)}$ ,  $CO_{2(g)}$  and water<sub>(g)</sub>. **The other substances present in the fumes are neglected here. The simplified composition of wood is considered to be  $C_6H_{12}O_6$  and the combustion is considered to be operated under constant atmospheric pressure (1 bar).**

- 2.1.1- Write the combustion reaction of wood  $C_6H_{12}O_6$  with di-oxygen  $O_{2(g)}$
- 2.1.2- Calculate the variation of enthalpy of the reaction of combustion at 298 K with the formation of water in the vapor state.
- 2.1.3- If the combustion process is operated using a molar ratio of 50 moles of air (taken at 298 K) per mole of  $C_6H_{12}O_6$  (wood), calculate the molar fractions of the constituents in the fumes and verify that the molar fraction of  $CO_{2(g)}$  in the fumes is equal to 0.107.
- 2.1.4- Under these conditions, determine the flame temperature reached, defined as the temperature of the fumes at the outlet of the burner considered to be adiabatic.

### 2.2- Absorption / desorption of $CO_{2(g)}$ from wood combustion fumes

NOOOO!!!

In the objective to capture and recover  $CO_2$  from the combustion, a sorption / desorption process is used. The entire process (absorption and desorption steps) is operated at 298 K.

The fumes are introduced into a reactor containing liquid water and the pressure is increased to 50 bars to dissolve  $CO_2$  into water until thermodynamic equilibrium is reached between the aqueous solution and the gas mixture (absorption step). The other constituents of the fumes are not absorbed by water.

When the absorption equilibrium is reached, the desorption step is operated. The fumes are extracted from the reactor and the system is then allowed to re-equilibrate under a pressure of 1 bar and temperature of 298 K. At this stage, the gaseous phase is considered to contain only pure  $CO_2$ .

The liquid / vapor equilibrium of  $CO_2$  in water follows Henry's law given in the data sheet.

- 2.2.1- Define the 3 terms of Henry's law and specify their units.
- 2.2.2- Calculate the molar fraction of  $CO_{2(aq)}$  in water at the equilibrium of absorption of the fumes at 50 bars (fumes in which the molar fraction of  $CO_{2(g)}$  is 0.107).
- 2.2.3- Explain pure  $CO_{2(g)}$  can be recovered in the desorption stage when the pressure is brought back to 1 bar.
- 2.2.4- Calculate the mass of  $CO_2$  (in kg) that can be recovered under these conditions with a reactor containing  $1\text{ m}^3$  of water.

### Exercise 3 – Reaction of methanation

The reaction of methanation is a **homogeneous gas-phase reaction** where  $\text{CO}_2(\text{g})$  reacts with  $\text{H}_2(\text{g})$  to produce  $\text{CH}_4(\text{g})$  as shown in reaction 2:



This overall reaction 2 results actually from the combination of homogeneous gaseous reactions 3 and 4:



#### **Study of reaction 3 alone:**

Reaction 3 is carried out at  $400^\circ\text{C}$  (673 K).  
Its variation of enthalpy at 298 K is  $41.2\text{ kJ}\cdot\text{mol}^{-1}$ .

- 3.1- Calculate the variation of entropy of reaction 3 at 298 K.
- 3.2- What are the effects of temperature and pressure on the state of equilibrium of reaction 3?
- 3.3- Calculate the equilibrium constant  $K_3^0$  at 673 K (the influence of the heat capacities will be neglected).
- 3.4- Calculate the yield in CO (denoted  $r_3$ ) of reaction 3 at equilibrium at 673 K when the initial mixture contains 4 moles of  $\text{H}_2(\text{g})$  per mole of  $\text{CO}_2(\text{g})$ .

#### **Study of reaction 4 alone:**

- 3.5- Assuming an initial stoichiometric mixture (composed of 1 mole of  $\text{CO}(\text{g})$  and 3 moles of  $\text{H}_2(\text{g})$ ), establish the literal expression of the equilibrium constant of reaction 4 ( $K_4^0$ ) as a function of its methane yield (noted  $r_4$ ) and of the total pressure (noted  $p$ ).
- 3.6- The equilibrium constant  $K_4^0$  is equal to 58377 at 673 K. Verify that the yield  $r_4$  is between 0.95 and 0.99 when  $p = 1\text{ bar}$ .

#### **Study of overall reaction 2 (= 3 + 4):**

In practice, reaction 2 is carried out at 673 K under high pressure (10 bar), starting from a mixture containing 4 moles of  $\text{H}_2(\text{g})$  per mole of  $\text{CO}_2(\text{g})$ .

- 3.7- Explain (without calculations) the effect of pressure on reaction 2.
- 3.8- Explain (without calculations) how equilibrium 4 impacts equilibrium 3.  
What can be said about reaction 2? Deduce the composition of the mixture at equilibrium of reaction 2.

#### **Exercise 4 – Storage of methane for transportation**

Several techniques are being developed to store methane. These include cryogenic liquefaction of pure methane to produce LNG Liquefied Natural Gas (Part 4.1-) and solidification of methane hydrate (Part 4.2-). The two techniques are then compared in Part 4.3.

**Parts 4.1 and 4.2 can be treated independently.**

#### **4.1- Cryogenic storage of pure methane**

- 4.1.1- Calculate the temperature needed to liquefy pure methane under a pressure of  $p = 1$  bar.
- 4.1.2- Calculate under  $p = 1$  bar and  $\theta = 25$  °C the volume of gaseous methane corresponding to  $1 \text{ m}^3$  of liquefied methane at the temperature of  $-165$  °C.

#### **4.2- Storage of methane in the form of solid methane hydrate**

The isobaric ( $p = 1$  bar) equilibrium phase diagram of water (A) and methane (B) binary system is given in Fig. 1 of the appendix (which must be returned with your copy). The defined compound, denoted D in Fig. 1, corresponds to the methane hydrate.

- 4.2.1- Complete the diagram in Figure 1 by writing in the corresponding white rectangles the phases present in domains 2, 5 and 6.
- 4.2.2- Determine the formula of the defined compound D.
- 4.2.3- Considering a mixture M made of water (A) and methane (B) at a molar fraction  $x_B = 0,500$ 
  - a- Plot (directly on the appendix) the thermal analysis line obtained by cooling down the mixture from  $\theta_0 = +120$  °C à  $\theta_f = -20$  °C
  - b- Indicate on the graph the phases which appear or disappear at each change of slope, and give the variance in each part of the thermal analysis line.

The production of  $1 \text{ m}^3$  of methane hydrate is considered from mixture M at  $-20$  °C under  $p = 1$  bar. The volumetric mass of methane hydrate is given in the data sheet.

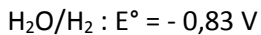
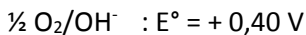
- 4.2.4- Calculate the number of moles of methane hydrate (defined compound D) in  $1 \text{ m}^3$  at  $-20$  °C under  $p = 1$  bar and the corresponding number of moles of water and methane.
- 4.2.5- Using the phase diagram of the appendix (Figure 1), calculate the total number of moles  $n_T$  (water + methane) of mixture M needed to produce  $1 \text{ m}^3$  of methane hydrate at  $-20$  °C under  $p = 1$  bar.

#### **4.3- Comparison of the two techniques**

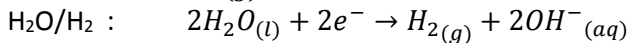
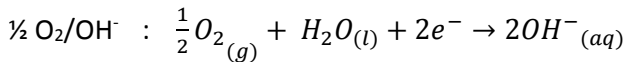
- 4.3- Compare the 2 techniques of storage with regards to the quantity of methane stored in 1 unit volume of liquefied methane or 1 unit volume of methane hydrate.

## Données :

### Oxydo-réduction :



Demi-réactions :



A (ampère) = C.s<sup>-1</sup> ; Constante de Faraday : F = 96 500 C.mol (d'e<sup>-</sup>)<sup>-1</sup>

Produit ionique de l'eau  $K_e = 10^{-14}$

### Autres données :

Constante de Henry pour le CO<sub>2</sub> :  $K_{H,\text{CO}_2} = 1,68 \cdot 10^8 \text{ Pa}$  à 25 °C

Masse molaire (g.mol<sup>-1</sup>) : O = 16 ; H = 1 ; C = 12 ;

### Données thermodynamiques :

	$\Delta_f H^\circ_{298} \text{ (kJ.mol}^{-1}\text{)}$	$S^\circ_{298} \text{ (J.K}^{-1}\text{.mol}^{-1}\text{)}$	$C_p \text{ (J.K}^{-1}\text{.mol}^{-1}\text{)}$
H <sub>2</sub> O <sub>l</sub>	-285,3	69,95	75,3
H <sub>2</sub> O <sub>g</sub>	-241,8	188,8	33,6
H <sub>2</sub> <sub>g</sub>	0	130,7	28,8
CH <sub>4</sub> <sub>g</sub>	-74,8	186,3	35,3
CO <sub>g</sub>	-110,5	197,7	29,1
CO <sub>2</sub> <sub>g</sub>	-393,5	213,8	37,1
N <sub>2</sub> <sub>g</sub>	0	191,6	29,1
O <sub>2</sub> <sub>g</sub>	0	205,2	29,4
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (s)	-1273,3	-	-

Equation de Clapeyron pour la vaporisation du méthane :

$$\ln p_{CH_4}^* = -\frac{1056}{T} + 9,37 \quad \text{avec } p^* \text{ en bar}$$

La masse volumique du méthane liquéfié à -165°C sous la pression  $p^\circ = 1 \text{ bar}$  est de 0,454 tonne par m<sup>3</sup>.

La masse volumique du composé défini (solide) d'hydrate de méthane à -20°C est de 0,900 tonne par m<sup>3</sup>.

Masse volumique de l'eau à température ambiante : 1 tonne par m<sup>3</sup>.

## Annexe à rendre avec la copie

Nom :                      Prénom :                      groupe :

Figure 1 : Diagramme isobare ( $p = 1 \text{ bar}$ ) du mélange binaire eau (A) – méthane (B).

