# Chemistry 2 Test N° 1 (Duration 1h30)

*No document allowed. Only TI 30 « collège » type calculators are authorized.*

The 2 parts can be solved independently

*The marking-scheme is for information only.*

*Each answer has to be justified*

Data : R=8.314 $J.mol^{-1}.K^{-1}$ et $T_{0°C}$ = 273 K, 1 atm=760 torrs = 101325 Pa

## Exercise I : Ideal solution (10 points)

For microelectronic applications, silicium with a high degree of purity is required. A step of the process is the separation of dichlorosilane ($SiH_2Cl_2$, compound A) from trichlorosilane ($SiHCl_3$, compound B). The isobaric experimental phase diagram has to be joined to your copy.

**1) Course** : Recall the definition of an ideal solution, and give the expression of the chemical potential of a liquid in ideal solution as a function of the chemical potential of the pure liquid at the same temperature.

**2) Pure substance**

**a)** By using the equation of Clapeyron as well as the appropriate assumptions, demonstrate that it is possible to express the saturated vapor pressure of both compounds according to : $LnP^* = -A/T + B$ (T en K)

**b)** Give the corresponding numerical expression for each compound, the pressure being in atm.

**3) Shape of the phase diagram :**

**a)** Indicate what the particular points of the diagram correspond to.

**b)** Indicate the name of both curves of the diagram.

**c)** Does the X-axis of the diagram correspond to the molar fraction of A or B ? Which compound is the most volatile one?

**d)** For $\Theta$= 15°C and $\Theta$= 25°C, compute (within $10^{-3}$ USI) the compositions x and y of the liquid and vapor phases in equilibrium, respectively. Plot the corresponding points on the diagram, and comment on the assumption of « ideal solution ».

**4) Distillation of a mixture (100 moles of initial molar composition : 80 mol % of $SiHCl_3$)**

**a)** Based on the experimental results, describe the state of the mixture when heated up to 27.5°C (number of phases, number of moles in each phase (calculated within 0.1 mol)).

**b)** Using fractionated distillation, explain how it is possible to carry out a separation of the initial mixture.

**c)** Which compound does form the distillate and what is the temperature of the vessel (bouilleur) ?

**d)** Position of the feed tray (plateau d'alimentation): Using the graph, estimate the minimal number of plates of the column i) between the feed tray and the column head and ii) between the feed tray and the column bottom(pied de colonne) for a good separation of both compounds.

***Data :***

Molar masses ($g.mol^{-1}$) : H= 1 ; Cl= 35.5 ; Si = 28.

Dichlorosilane (A) : saturated vapor pressure 1.5 atm at 21°C ; boiling point : 8.4°C under 1.0 atm.

Trichlorosilane (B) : saturated vapor pressure 0.526 atm at 14.5°C , boiling point : 31.8°C under 1.0 atm.

**Exercise II : Solid-liquid equilibrium (10 points)**

Data :

Molar masses expressed in $g.mol^{-1}$ : K = 39.0 ; Cl = 35.5 ; Na = 23.0.

The isobaric phase diagram (p = 1 bar) for the solid-liquid equilibrium of the binary mixtures NaCl – KCl is characterised by :

- solid NaCl and solid KCl non miscible at room temperature
- partial miscibility of NaCl and KCl that form solid solutions $\alpha$ and $\beta$ in the solid state from 200°C to 500°C. Solubility limits of $\alpha$ and $\beta$, expressed in molar fractions of KCl are supplied in the table below:

| $\theta$ (°C) | 200 | 325 | 400 | 450 | 475 | 500 |
|---|---|---|---|---|---|---|
| $\alpha$ * | 0.020 | 0.05 | 0.080 | 0.130 | 0.175 | 0.350 |
| $\beta$ * | 0.960 | 0.900 | 0.825 | 0.705 | 0.600 | 0.350 |

* expressed in molar fractions of KCl.

- from 600°C to 810°C, the solid-liquid equilibrium has the same shape as a liquid-vapor equilibrium with positive azeotrope, the coordinates of the azeotrope being $x_{KCl}$ = 0.50 and $\theta$ = 658°C
- melting points of NaCl and KCl under p = 1 bar are respectively 808°C and 772°C.

**Questions** :

1) Plot the isobaric phase diagram (p = 1 bar) for the solid-liquid equilibrium of the NaCl – KCl binary mixtures with the data supplied. Only the approximate shape of the solidus and liquidus curves has to be plotted.
2) On the figure, specify the nature of the phases in each domain of the diagram, the names of the equilibrium curves and of the characteristic points.
3) In the solid state, in which precise range of temperature, are NaCl and KCl miscible in any proportion?
4) Give the compositions and the temperatures corresponding to a nil variance, under fixed pressure.

An equimolecular mixture is cooled from 800 to 200°C under p = 1 bar.

5) Plot the thermal analysis curve, and indicate the variance (for fixed p), as well as the nature of the phases that appear or disappear when cooling. Which particular relation(s) between some molar fractions can turn out (appear) upon cooling ?

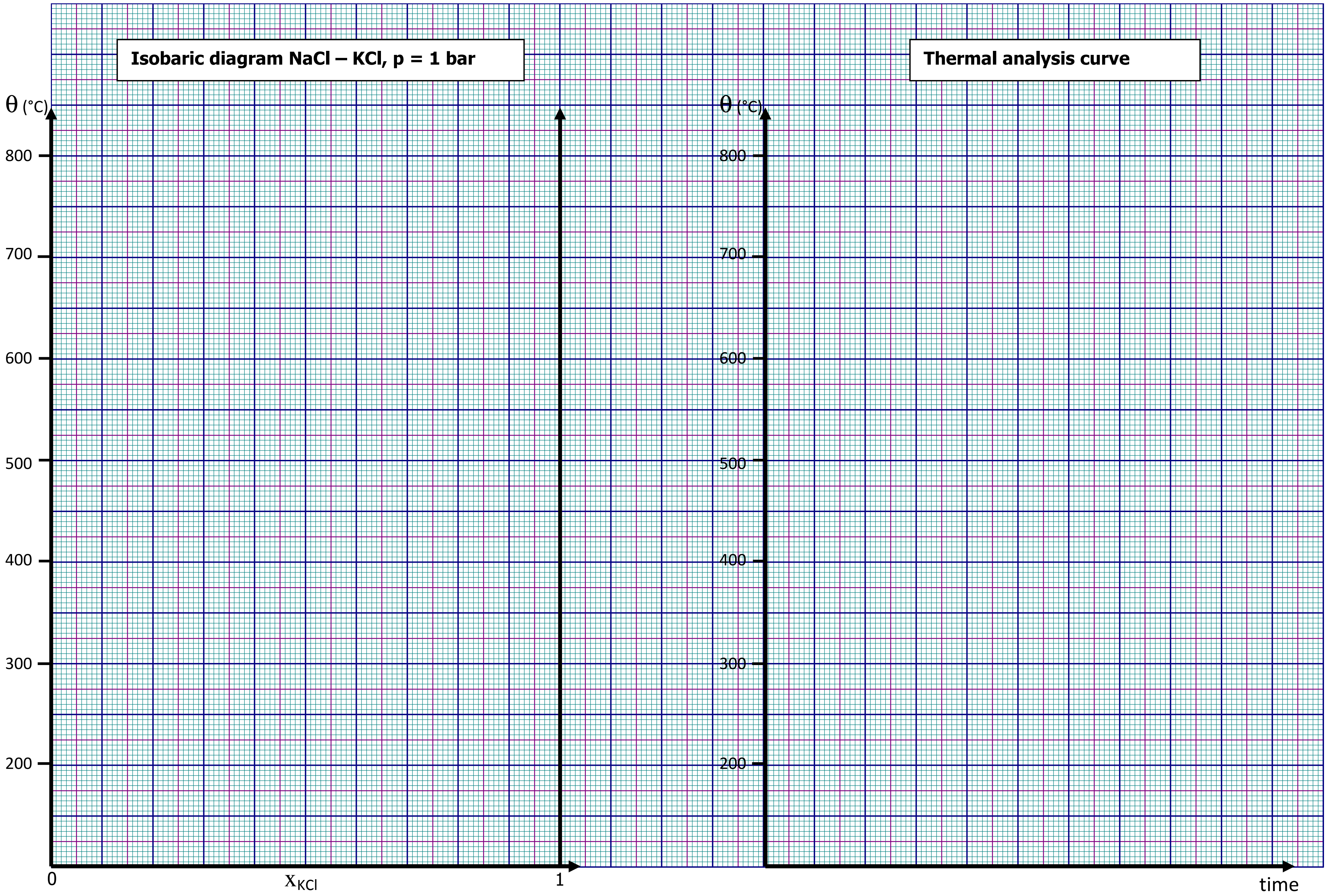
The mass of the mixture is 1 kg.

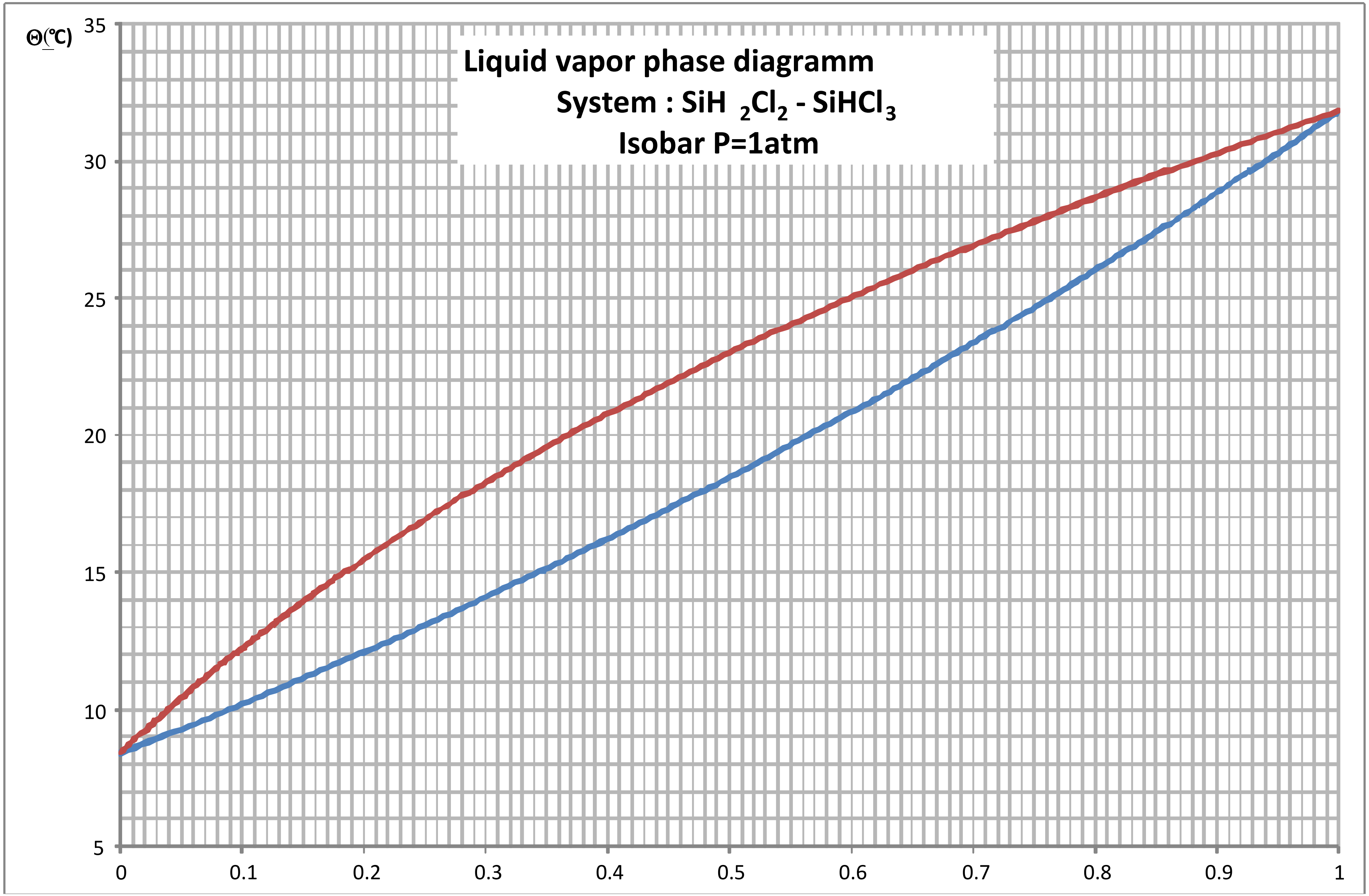
6) Find the masses of $\alpha$ and $\beta$ at 400°C.
7) Theoretically, which amount of KCl should be added to this mixture to obtain one solid phase only ?

The figure has to be returned with the copy.

NAME :

GROUP :


Isobaric diagram NaCl – KCl, p = 1 bar
θ (°C)
800
700
600
500
400
300
200
0
$x_{KCl}$
1
Thermal analysis curve
θ (°C)
800
700
600
500
400
300
200
time



Θ(℃)
Liquid vapor phase diagramm
System : SiH 2Cl2 - SiHCl3
Isobar P=1atm
35
30
25
20
15
10
5
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1