PCC – AMERINSA - SCAN November 7th 2013

CHEMISTRY TEST # 1 **(duration: 1h30)**

No document is allowed. Only non-programmable ("college-type") calculators are authorized.

Answers should be qualified. <u>This paper must be returned with your copy.</u>

Constants and conversion: R=8.314 J.mol^{-1}.K^{-1} and $T_{0°C}$ = 273 K, 1 atm=760 torrs = 101325 Pa = 1.013 Bar.

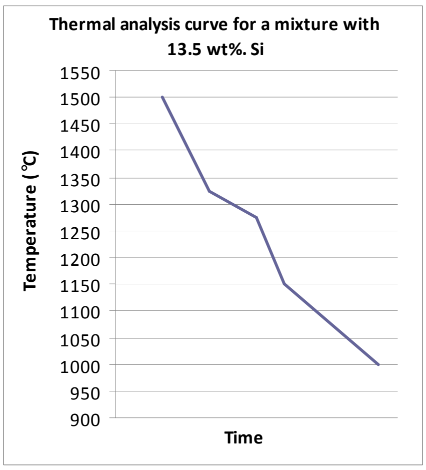
Vapors are considered as perfect gas.

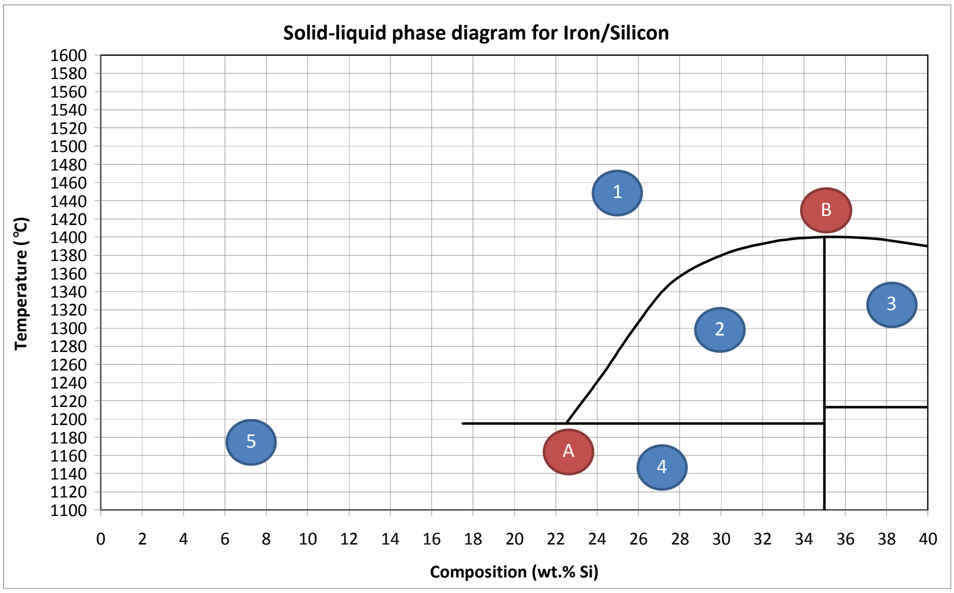
Number of moles will be calculated to within ±0.1 mol, mass to within ± 0.1 mass unit, percent to within 0.1 %

<u>Exercise I : Iron (Fe)/ Silicon (Si) solid-liquid phase diagram (13 points)</u>

Let's consider one part only of the iron/silicon phase diagram obtained while P = 1 atm (see below), where the composition is expressed in weight percent in Silicon (wt.% Si). Silicon and iron are only partially miscible. Here, in order to simplify the exercise, only the face-centered cubic system of iron (corresponding to the so-called « austenitic » phase) will be considered to qualify iron. The left-part of the phase diagram is missing but will be completed in question 2.

	Fe	Si
Molar mass (g.mol^{-1})	56.0	28.0
Crystalline structure (in the given temperature range)	Close-packed face centered cubic system, motif = 1 atom of Fe	Diamond-like face-centered cubic system motif = 2 atoms of Si
Atomic radius (nm)	0.126	0.111
Cell parameter (« Paramètre de maille ») (nm)	0.356	0.543





1/ Give the simplest possible formula for the defined component that can be found in the diagram. Specify 2 characteristics of this compound that are similar to the ones generally observed for a pure compound.

2/ At 1195°C – ε (i.e. at a temperature slightly lower than 1195°C), the maximum solubility of silicon in iron is observed for a composition of 30 **mol%** of Silicon. Using this value and the thermal analytical curve obtained when a mixture made of 13.5 **wt.%** of silicon is cooled from 1500°C to 1000°C, complete the left part of the phase diagram (we will consider that all equilibrium separation curves are linear). Then, deduce the value of the melting temperature of iron, and calculate the variance at this specific point.

3/ For each domain noted from 1 to 5 in the diagram, and for the two noteworthy points (A and B), give the number, physical state and (when possible) the composition of the phase(s); moreover compute the variance for the system (Variance calculations will be detailed). Give the specific name of A point, and the type of fusion exhibited by the B point.

4/ Let's consider 50 kg of a mixture of Fe and Si made of 30 **wt.% Si** :

a) Give the composition (wt.%) and the mass of each phase obtained at 1195°C - ε.

b) Plot the thermal analysis curve when cooling this mixture from 1500 to 1000°C. Give the values for temperatures when slope is changing, describe briefly the phenomenon/phenomena that explain(s) the change of slope, give the nature and the composition (in wt. %) of each phase which disappears or appears, as well as the variance on each curve segment.

c) How much of iron should be added to the given mixture at 1500°C, in order to obtain only one phase which composition is the maximum solubility of Si in Fe at 1150°C?

Bonus (1 point): Remembering of things past… (well, last year!)
Explain qualitatively why Fe and Si are only partially (and not fully) miscible.
In the domain where they are miscible, which solid solution do Fe and Si form: is it an inserted solid solution ("solution solide d'insertion") or substitutional solid solution ("solution solide de substitution")? Justify your answer. (Recall : solid solution in general are formed by diffusion of atoms)

Exercise II : Water/pinene mixture (5.5 points)

Oil of turpentine ("essence de térébenthine"), obtained from the resin collected from live trees such as pines, have found various industrial end uses such as solvent (for thinning oil-based paints, or producing varnishes) and as raw material for the chemical industry. The major component of oil of turpentine is pinene, which formula is $C_{10}H_{16}$ and which is a liquid at room temperature and atmospheric pressure (the other minor components will be neglected in the following part).

The following relationships laying the temperature T (in K) to the saturation vapor pressure of both pinene and water P* (in Pa) are given below:

For pinene: Formula $C_{10}H_{16}$, (Molar mass = 136g/mol) : $\log_{10} P^*_{pinene} = 9.95 - 2115.21/T$

For water: Formula H_2O, (Molar mass = 18g/mol) : $\log_{10} P^*_{water} = 10.70 - 2124.34/T$

The liquid-vapor phase diagram for water/pinene mixtures, where the total pressure is 101325 Pa, presents a heteroazeotropic point which coordinates are:

(θ = 95 °C, x (mol fraction in pinene) = 0.16)

1/ Oil of turpentine is actually toxic, and the maximum safe concentration in air is $5 g.m^{-3}$. Is it actually safe to work in a closed-room at 25°C if one were to expose oil of turpentine to air? Which solution(s) to this issue do you suggest then (other than using another chemical)?

2/ Calculate the entropy change of vaporization, when P=101325 Pa, for water and pinene, respectively. Comment the values.

3/ Whatever the temperature and the composition of the water/pinene liquid mixture are, the isobaric diagram (for P=101325 Pa) do not present any monophasic domain at the liquid state.

a) Explain qualitatively such a behavior in the case of water and pinene, and suggest a method for extracting oil of turpentine.

b) For any heterogeneous mixture of liquid at boiling, demonstrate that there is only one possible value for the temperature.

c) Indicate the coordinates of the noteworthy points of the diagram where the system is invariant.

4/ What is the ratio of the mass of pinene to the mass of water of the mixture which is collected by distillation performed at P=101325 Pa?

5/ Which minimum mass of water should be used if one were to collect 1 kg of pinene by distillation?

Exercise III : Ideal liquid solutions (1.5 points)

In a container initially emptied of air, one introduces a mixture of 2 gaseous pure compounds, noted as A and B respectively, such that the molar composition in A is 0.4. This mixture is compressed while the temperature T is kept constant (isothermal compression). By the way, at this temperature, the saturation vapor pressures are such that: $P_A^* = 0.4$ atm and $P_B^* = 1.2$ atm.

1/ Define what a so-called "ideal solution" is.

2/ Calculate the composition of the very first droplet of liquid which appears upon compression and the total pressure which results in this equilibrium state. Justify the overall demonstration.