

## Final exam: around Nickel

Duration: 3 hours

No document allowed. Only « college » or « graphic » type calculators are authorized.

The 3 parts can be treated independently. The schedule of mark is given as an indication only. The data are given on page 6, on the back page of the phase diagram (page 5). This sheet is to be returned along with your copy.

### Exercise 1 : white gold

12 points

The numbers of moles will be given and / or calculated at  $\pm 0.01$  mol, the masses calculated at  $\pm 1$ g, the mass or mole fractions at  $\pm 0.01$ .

White gold is an alloy of gold and nickel that is very often used in jewelry, as an alternative to gold-palladium alloys, which are more ductile (malleable) but more expensive. Depending on nickel contents, white gold may have a color similar to that of platinum.

The Au-Ni solid-liquid isobaric equilibrium phase diagram where the compositions are expressed in mass fraction of Ni ( $X_{Ni}$ ), is given on page 5.

- 1) Indicate the nature of the phase(s) present in each numbered domain of the diagram. Name all equilibrium curves and zero variance points at fixed pressure (variance calculations must be detailed). The answers will be provided directly below the diagram
- 2) Two Au-Ni mixtures are prepared which composition (mass fraction) is respectively  $X_{Ni} = 0.15$  and  $X_{Ni} = 0.60$ . Each of these mixtures is heated to  $1500^{\circ}\text{C}$ , then cooled down to  $100^{\circ}\text{C}$ .  
Plot the thermal analysis curve obtained during the cooling of each mixture from  $1500^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ . Clearly indicate the (approximate) temperature value as well as the phases that appear or disappear at the slope changes.
- 3) 1 kg of the mixture at  $X_{Ni} = 0.60$  (mass fraction) is brought to  $1100^{\circ}\text{C}$ . What are the mass composition, the molar composition, the mass and the number of moles of each phase in presence?
- 4) It is desired to separate gold and nickel from 1 kg of mixture at  $X_{Ni} = 0.60$  (mass fraction). In this objective, the mixture is heated to  $1300^{\circ}\text{C}$  and subsequently cooled to  $1100^{\circ}\text{C}$ . The solid obtained is collected by filtration, then heated up to  $1400^{\circ}\text{C}$ . The liquid thereby obtained is cooled down to  $1200^{\circ}\text{C}$  and the new solid formed is collected.
  - a) What is the mass composition ( $X_{Ni}$ ) and the mass of the solid obtained? Conclusion?
  - b) What would be the mass composition and the maximum mass of solid that would be collected by a series of heating-cooling operations such as those described above?
  - c) What is the name of this purification technique?
- 5) What minimal mass of gold should be added to 1 kg of the melted mixture at  $X_{Ni} = 0.60$  (mass fraction) in order to obtain a single solid phase when cooling the new mixture at  $450^{\circ}\text{C}$ ?

6) Au-Ni alloys are particularly hard and brittle (breakable) in ranges of composition where Au and Ni are not fully miscible at the solid state.

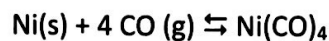
a) Explain in 2 lines the reasons that make such alloys breakable in these conditions ?

b) If a Au-Ni mixture is prepared at 700°C, what is the (approximate) range of mass concentration in Ni which can be recommended to produce a non-breakable alloy rich in gold ?

### **Exercise 2 : Nickel refining by the Mond process**

12 points

*Metals can be recovered from natural resources or from recycled materials. In both cases, they are mixed with many impurities. Refining operations are therefore necessary to obtain pure metals. For example, nickel of very high purity can be obtained using a treatment with carbon monoxide according to the following reaction:*



*where Ni(CO)<sub>4</sub> can be either liquid or gaseous depending on the temperature.*

*The forward reaction is called "carbonylation", and the reverse one is therefore a reaction of "decarbonylation".*

*Impurities do not react with CO under the same conditions, the reaction is very selective. Ni(CO)<sub>4</sub> produced is collected and treated to decompose it into very pure Ni (purity larger than 99.9%) following the reverse reaction.*

*The boiling temperature of Ni(CO)<sub>4</sub> is 316 K under 1 bar.*

*Assuming the influence of heat capacities can be neglected, the standard variation of Gibbs energy or free enthalpy of the reaction of carbonylation can be expressed as follows as a function of T :*

$$\text{For } T \leq 316 \text{ K : } \Delta_r G_T^0 = -190.4 + 0.508 \times T \text{ (in kJ.mol}^{-1}\text{, with T in K)}$$

$$\text{For } T \geq 316 \text{ K : } \Delta_r G_T^0 = -160.3 + 0.411 \times T \text{ (in kJ.mol}^{-1}\text{, with T in K)}$$

1) Find again the expression given for the standard free enthalpy variation of the carbonylation reaction as a function of temperature for temperatures above 316 K.

2) Calculate the standard variation of enthalpy of boiling of Ni(CO)<sub>4</sub> under a pressure of 1 bar at 316 K, denoted  $\Delta_{vap} \bar{H}_{316}^0$

*The carbonylation reaction is now carried out under a total pressure of 1 bar, at a temperature such that Ni(CO)<sub>4</sub> is gaseous.*

3) By calculating the variance, show that under these conditions the system is completely defined if the temperature is fixed.

Present a system of equations in agreement with this result.

4) In which temperature range would you recommend to carry out this reaction? Justify your answer (no calculation is necessary).

*The carbonylation reaction is now carried out 323 K.*

5) Establish the literal expression of the equilibrium constant of the reaction of carbonylation as a function of the yield in Ni(CO)<sub>4</sub>, in the case where the initial state is composed of the reactants alone under stoichiometric proportions. ✓

- 6) Verify that in this condition the yield in  $\text{Ni}(\text{CO})_4$  is between 98.0 and 98.1 %.
- 7) How would the yield be modified by introducing an excess of CO at the initial state? Justify your answer.
- 8) How would the yield be modified if Ni was in excess at the initial state? Justify your answer.

To produce fine nickel powder, the gaseous mixture containing the  $\text{Ni}(\text{CO})_4$  complex is heated to 573 K.

- 9) Calculate the equilibrium constant of the reverse reaction (decarbonylation) at this temperature. Conclusion?

### **Exercise 3 : use of nickel in an accumulator**

16 points

In aqueous solution, the metal ions may be in a major form that differs according to the pH of the solution. This is particularly the case of  $\text{Cd}^{2+}$  cadmium ions and  $\text{Ni}^{2+}$  nickel ions, species that may be involved in a redox process developed in a cadmium-nickel accumulator (that is to say a rechargeable cell). The latter is constituted of:

- a cadmium electrode  $\text{Cd}(\text{s})$  (electrode 1), involving a redox couple in which the cadmium is respectively at oxidation state [0] (metal cadmium) and [+ II];
- an inert metallic electrode covered with a deposit of  $\text{Ni}_2\text{O}_3(\text{s})$  (electrode 2), involving a redox couple in which the nickel is respectively at the oxidation state [+ II] and [+ III] (under the  $\text{Ni}_2\text{O}_3$  form);
- an aqueous solution of potassium hydroxide KOH at a concentration such that the pH of the solution is greater than 10.

#### **A] – About electrode 1**

- 1) Write the reaction of precipitation of  $\text{Cd}^{2+}$  in  $\text{Cd}(\text{OH})_2$  in basic medium.
- 2) Let  $S_0$  a solution of cadmium ions [II]  $\text{Cd}^{2+}$  equal to  $0.01 \text{ mol}\cdot\text{L}^{-1}$ . Show that at 25 °C there is precipitation for pH greater than or equal to pH = 8.

It is observed that, whatever the pH, and although it is not always the major species, the  $\text{Cd}^{2+}$  metal ion is always present in the solution.

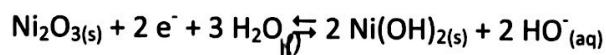
- 3) Calculate the real  $\text{Cd}^{2+}$  concentration of the  $S_0$  solution when the pH of the solution is 6, 8, 10 and 12, respectively. From which pH value, does the  $\text{Cd}^{2+}$  form represent less than 10% (in mole) of the cadmium species with the degree of oxidation [II]?
- 4) Write the half-equation of reduction of Cd (at the oxidation state [II]) to  $\text{Cd}(\text{s})$ , depending on whether the pH is above or below 8.

Since the  $\text{Cd}^{2+}$  species is always present in the solution, the Nernst potential of the cadmium electrode can be calculated at any time using the  $\text{Cd}^{2+}/\text{Cd}(\text{s})$  couple (unicity of the electrode potential), knowing that the standard reference potential of the  $\text{Cd}^{2+}/\text{Cd}(\text{s})$  couple is  $E^\circ_1 = -0.40 \text{ V}$ .

- 5) Express, depending on the pH of the aqueous solution, the potential  $E_1$  of the cadmium electrode for the  $S_0$  solution, according to whether the pH of the solution is higher or lower than pH = 8.

### B] – About electrode 2

For pH values greater than 10, the half-redox equation involving the Ni[III]/N [II] couple can be written as :



In these conditions, the standard reference potential of the  $\text{Ni}_2\text{O}_3(\text{s})/\text{Ni}(\text{OH})_2(\text{s})$  equals  $E^\circ_2 = +0.18 \text{ V}$ .

- ✓ 6) Justify in a few lines, that nickel with the degree of oxidation [II] is mainly in the form of the nickel hydroxide  $\text{Ni}(\text{OH})_2$ .
- ✓ 7) Give the expression of the Nernst potential  $E_2$  of the  $\text{Ni}_2\text{O}_3(\text{s})/\text{Ni}(\text{OH})_2(\text{s})$  as a function of the pH of the solution, under these basic conditions.

### C] Assembly of the accumulator

The two electrodes are now placed in an aqueous solution of potassium hydroxide (KOH, strong base) at  $10^{-2} \text{ mol.L}^{-1}$ , and electrically connected to each other.

- 8) Calculate the pH of the solution. Deduce the potentials of the 2 electrodes.
- 9) Which electrode is the positive terminal of the battery? Calculate its initial electromotive force (e.m.f.) (before it begins to flow). Does the e.m.f. depend on the concentration of the solution in KOH?
- ✓ 10) Write the global well-balanced redox reaction of the accumulator (balance of half-equations redox taking place on each electrode). Why is it not necessary to make use of a salt bridge in this accumulator?
- 11) This accumulator is now connected to an electrical receiver and delivers a current of 10 mA for 3 hours. Calculate the mass of  $\text{Ni}_2\text{O}_3$  that is then consumed, to within 1 mg.