

**TEST 1 – CHEMISTRY 2 (duration 1h30)**

Calculator allowed. No documents allowed. All answers must be justified.

It will be assumed that the gases behave as ideal gases.

For the calculations, take:  $R = 8.31 \text{ J.mol}^{-1}.\text{K}^{-1}$ ;  $1 \text{ atm} = 1.013 \text{ bar} = 1.013 \cdot 10^5 \text{ Pa}$ ;  $T_0 = 273 \text{ K} = 0 \text{ }^\circ\text{C}$

**Molar mass for atoms ( $\text{g.mol}^{-1}$ )**

<b>N</b>	<b>O</b>	<b>S</b>	<b>Zn</b>
14.0	16.0	32.1	65.4

Air is considered to contain (in mole) 80% of dinitrogen and 20% of dioxygen

**Equilibrium constants values (at 298 K)**

Acidity constants :  $K_{a1} (\text{H}_2\text{S} / \text{HS}^-) = 10^{-7}$

$K_{a2} (\text{HS}^- / \text{S}^{2-}) = 10^{-13}$

Compound	$\Delta_f H^\circ$ ( $\text{kJ.mol}^{-1}$ )	$S^\circ$ ( $\text{J.K}^{-1}.\text{mol}^{-1}$ )
Zn (s)	0	42
Zn (g)	123	150
<u>ZnS</u> (s)	-206	58
<u>ZnO</u> (s)	-351	44
O <sub>2</sub> (g)	0	205
<u>SO<sub>2</sub></u> (g)	-297	248

The solids are supposed to be fully immiscible.

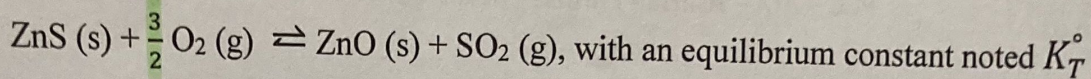
### ABOUT ZINC

Parts A, B, and C can be solved independently.

#### A. Roasting of ZnS (zinc sulphide, also named “blende”)

The main ore of zinc is the zinc sulphide ZnS of the blende type - from the German “blenden”, “to shine”. The preparation of zinc metal from blende is done in two steps. Here we focus on the first step, which is the preparation of zinc oxide according to a process called “roasting of ZnS”.

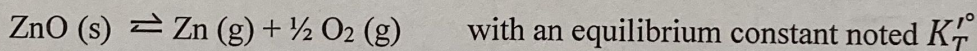
The corresponding reaction is, at 298 K :



1. Calculate the standard enthalpy change, standard entropy change, and standard free enthalpy change of the reaction at 298 K, and interpret the results obtained in each of these three calculations. What can be said about this reaction?
2. Indicate and justify briefly the influence on this reaction when equilibrium is reached of :
  - An increase in temperature at constant pressure
  - An increase in the total pressure at constant temperature
  - An isochore and isothermal addition of O<sub>2</sub>.
3. Expression of the equilibrium constant  $K_T^\circ$ 
  - 3.1. Calculate the variance for this reaction when the reactor contains initially some ZnS and some O<sub>2</sub> (in sufficient amount such that the equilibrium state is attained).
  - 3.2. Express  $K_T^\circ$  as a function of the activity of the reagents.
  - 3.3. Express  $K_T^\circ$  as a function of the following parameters only: P(O<sub>2</sub>), P(SO<sub>2</sub>), P° (reference pressure). Could we find back the value of the variance using this equation?
  - 3.4. Express  $K_T^\circ$  as a function of the following parameters only: n(O<sub>2</sub>), n(SO<sub>2</sub>), P°, P<sub>T</sub> (total pressure).

## B. Preparation of Zn

The second step of the process consists in reducing ZnO to Zn at an elevated temperature where Zn is gaseous (ZnO remains in the solid state). The reaction is as follows:



1. Assuming that the standard enthalpy and entropy change of this reaction are independent of temperature, find the temperature T such that  $K_T^{\prime\circ} = 0.088$ .
2. 1.00 mole of ZnO is introduced into a closed reactor of constant volume 200 L, previously under vacuum and maintained at temperature T. Calculate the final equilibrium pressure P and the remaining mass of ZnO.
3. Quantify the amount of heat exchanged between the chemical system and the reactor during this isothermal and isochoric reaction: should a heating or cooling system be provided to keep the temperature constant (justify)?

## C. pH of a hydrogen sulphide solution H<sub>2</sub>S (commonly used to dissolve blende)

1. H<sub>2</sub>S is a diacid: write the 2 successive acidity equations when H<sub>2</sub>S is introduced in water and express literally the acidity constants K<sub>a1</sub> and K<sub>a2</sub> as a function of the concentrations of the different species.
2. Assuming that the second acidity of H<sub>2</sub>S does not occur (given the low value of K<sub>a2</sub>), what would be the pH obtained by introducing 1.00x10<sup>-2</sup> mole of H<sub>2</sub>S in 1L of pure water (we will only consider the first acidity of constant K<sub>a1</sub> in this question)? Calculate the dissociation coefficient of H<sub>2</sub>S and justify *a posteriori* that the 2<sup>nd</sup> acidity can indeed be neglected.