CHEMISTRY TEST # 1 (1h30)

The 2 exercises can be treated independently - All answers must be justified.
No document allowed. – Only "College" type calculators are allowed.

For all numerical applications, take: R=8.314 J.mol^{-1}.K^{-1}; T_0 = 273 K = 0°C; 1 bar = 10^5 Pa.
All gases may be considered as ideal.

Exercise I – About the effects of an atmosphere too rich in CO_2 (≈10 points)

Data: Self-ionization of water at 298K: $K_e = 10^{-14,0}$

Compound	Physical state	$\overline{\Delta_f H^0_{298}}$ $(kJ.mol^{-1})$	$\overline{S^0_{298}}$ $(J.K^{-1}.mol^{-1})$
$CaCO_3$	solid	-1207.1	88.7
Ca^{2+}	Ion in solution	-542.8	- 53.1*
CO_3^{2-}	Ion in solution	-677.1	-56.9*

* The partial molar entropies of the ions in solution are defined on an arbitrary scale in which the standard entropy of the $H^+_{(aq)}$ ions is taken equal to zero at all temperatures. As a result, they can be negative or positive. They reflect how the ions organize the water molecules around them in the solution.

The carbon dioxide (CO_2) of the atmosphere can dissolve in water, especially seawater. The resulting acidification affects the solubility of calcium carbonate ($CaCO_3$) in water, which could have a heavy impact on the survival of marine calcareous organisms in the seas and oceans, as the following calculations will show.

Let's consider the equilibrium of dissolution of calcium carbonate $CaCO_3$ in water, at temperature T and under pressure P° = 1 bar:

$$CaCO_{3\,(s)} \rightleftarrows Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \qquad \text{(R0)}$$

1- Express the solubility product of $CaCO_3$, noted K_S (the standard concentration is noted $C° = 1.00\,mol.L^{-1}$).
2- Calculate the standard free enthalpy change $\Delta_R G_T^0$ for this reaction at T = 298K.
3- Calculate pK_S for this reaction at 298K (reminder: $pK_S = -log(K_S)$).
4- Compare the calculated value to the experimental one determined at 298K: $pK_S = 8,35$.

In the rest of the exercise, you will use the experimental value $pK_S = 8,35$.

The solubility of $CaCO_3$ represents the maximum quantity (in mol) of this solid which can dissolve in one liter of water at temperature T.

5- Calculate the solubility of $CaCO_3$ in water at 298K, noted *s*, considering that the only species during the dissolution are $Ca^{2+}{}_{(aq)}$ and $CO_3^{2-}{}_{(aq)}$.

In reality, the following equilibria also occur in aqueous solution :

$$CO_{2\,(aq)} + 2H_2O \rightleftarrows HCO_3^-{}_{(aq)} + H_3O^+{}_{(aq)} \qquad \text{(R1) with at 298K:} \quad pK_{a1} = 6.35$$

$$HCO_3^-{}_{(aq)} + H_2O \rightleftarrows CO_3^{2-}{}_{(aq)} + H_3O^+{}_{(aq)} \qquad \text{(R2) with at 298K:} \quad pK_{a2} = 10.4$$

6- Justify qualitatively, in maximum two lines, that the dissolution of CO_2 in the ocean leads to a decrease of pH.
7- Express the acidity constants K_{a1} and K_{a2} as a function of the concentration of the involved species and $C°$.

8- On a pH scale, indicate the domains of predominance of the following species $CO_{2(aq)}$, $HCO_3^-{}_{(aq)}$ and $CO_3^{2-}{}_{(aq)}$, at 298K (species 1 is considered to be predominant compared to species 2 when their concentrations are such that : [1] > 10 × [2]).

Solubility of $CaCO_3$ is actually written: $s = [Ca^{2+}] = [CO_{2\,(aq)}] + [HCO_3^-{}_{(aq)}] + [CO_3^{2-}{}_{(aq)}]$

9- Using the previous relation, show that the solubility s of $CaCO_3$ satisfies the following relation: $s^2 = [Ca^{2+}]^2 = A \times \left\{ \frac{[H_3O^+]^2}{B} + \frac{[H_3O^+]}{C} + 1 \right\}$ and express the A, B and C constants as a function of K_{a1}, K_{a2}, K_S and $C°$.

pH of seawater is included between 8.1 and 8.3.

10- In what chemical form is found CO_2 dissolved in the oceans? How can the expression of s^2 be thus simplified?

11- We then note s' the solubility of $CaCO_3$ in seawater, and $ps' = -\log\left(\frac{s'}{C°}\right)$. Determine the equation of variation of ps' as a function of the pH.

12- Calculate the solubility of $CaCO_3$ noted s' at pH = 8.2.

13- Comment on the effect of an increase in carbon dioxide concentration on calcareous organisms (mainly made of $CaCO_3$) in the ocean.

Exercise II – Formation of magnesium hydroxide (≈10 points)

Data : Molar mass ($g.mol^{-1}$) Mg : 24.3 O : 16.0 H : 1.0

Questions 5 and following can be answered even if you have not answered questions 2 to 4

Magnesium oxide, a solid which formula is MgO, can react with gaseous water to form magnesium hydroxide, a solid which formula is $Mg(OH)_2$. The two solids are not miscible.

1- Write the chemical reaction of formation of $Mg(OH)_2$.
2- Calculate the variance of the system at equilibrium. Comment on the found value.

In a vessel of constant volume V = 10.0 liters, a mass m = 49.57 g of magnesium oxide (whose volume is negligible in front of V) is introduced. After evacuation of the possible gases, the whole is brought to the temperature θ = 150 ° C. A number of moles n of water is then introduced very gradually. At the temperature θ, the total pressure at equilibrium is p_E = 1.00 bar.

Moreover, the saturation vapor pressure of water at temperature θ is p_S = 5.06 bar.

3- Justify, in 2 lines, that no liquid water can be formed under these experimental conditions.
4- Show that there is no $Mg(OH)_2$ in the container if we introduce n = 0.222 moles of water.
5- What minimum quantity n_{min} of water must be introduced so that $Mg(OH)_2$ can be formed?
6- What is the maximum amount n_{max} of water that can be added while keeping the equilibrium state?
7- a. Plot the representative curve of P = f (n), for n varying from 0 to 2 moles.
(To answer question 10 on the same graph: make sure that the pressure can go up to 5.5 bars, and the quantity of water n up to 4 moles).
   b. Indicate clearly on the curve the numbers of moles of water n and the pressures at the limits of each domain.
   c. Specify the compounds that are present in the various domains of the curve.
8- What is the quantity of material of each component (in number of moles) of the system when :
   a. n = 1,00 mole of gaseous water is added?
   b. n = 2,00 moles of gaseous water were added?
9- How much minimum water n_{min}' must be added to observe the formation of liquid water?
10- Complete the representative curve P = f (n), for n varying from 0 to 4 moles.