CHEMISTRY TEST # 1 (1h30)

Any type of calculator allowed

The 2 exercises can be treated independently - All answers must be justified.
For all numerical applications, take: R=8.314 J.mol^{-1}.K^{-1}; T (K) = Θ(°C) + 273 K
1 atm = 760 Torr = 101325 Pa = 1,013 bar. P° = 1 bar
All gases may be considered as ideal

Exercise I – Thermochemistry – Magnesium oxide (7 points)

We want to determine the standard molar enthalpy of oxidation of solid magnesium $\Delta_{Oxy}H°_{298}$.

1- Write the chemical reaction of oxidation of solid magnesium $Mg_{(s)}$ that results in the formation of magnesium oxide $MgO_{(s)}$.

2- In order to determine the standard molar enthalpy of oxidation of magnesium, it is possible to carry out successively the following two reactions in an adiabatic calorimeter:

R_1 : $Mg_{(s)} + 2H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$ Standard molar enthalpy of reaction R_1 $\Delta_{r1}H°_{(T)}$ = - 435 kJ.mol^{-1}

R_2 : $MgO_{(s)} + 2H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_2O_{(l)}$ Standard molar enthalpy of reaction R_2 $\Delta_{r2}H°_{(T)}$ = - 88.3 kJ.mol^{-1}

It will be assumed that the work related to the outside pressure can be neglected. $W_p = 0$ $W'_n = 0$

a) Recall the principle of operation of an adiabatic calorimeter.

b) What type of reactions are R_1 and R_2 ?

c) After defining the thermodynamic system, establish the energy balance of the system.

d) To carry out reaction R_2, 0.1 mol of magnesium oxide is introduced into the calorimeter in 100 g of acidified water ($[H^+]$ = 2.0 mol.L^{-1}). The initial temperature is 25 ° C. Determine the final temperature reached in the calorimeter

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a) Using a method of your choice (Hess cycle, or combination of chemical reactions), give the expression of the standard molar enthalpy of oxidation of magnesium $\Delta_{Oxy}H°_{298}$ according to the data of the exercise.

b) Calculate the value of the standard molar enthalpy of oxidation of magnesium $\Delta_{Oxy}H°_{298}$.

c) What is the physical meaning of the enthalpy of this reaction?

Data :

The heat capacity of the obtained solutions is the same as the heat capacity of pure water.
Heat capacity of water: Cp_{water} = 4.18 J.K^{-1}.g^{-1}.
Water equivalent of the calorimeter: μ = 60.0 g.
$\Delta_fH°_{298}$ $H_2O(l)$ = -285 kJ.mol^{-1} M_O = 16.0 g.mol^{-1} M_{Mg} = 24.3 g.mol^{-1}

Exercise II – Chemical equilibria – Germanium oxide (13 points)

Parts A and B are independent

This exercise studies the reduction of germanium oxide GeO by carbon monoxide $CO_{(g)}$. Carbon monoxide can participate in another chemical equilibrium that is firstly studied in part A below.

Part A: *At high temperature*, graphite $C_{graphite\ (s)}$ as a solid can react with carbon dioxide $CO_{2\ (g)}$ to produce carbon monoxide $CO_{(g)}$ according to the following equilibrium

A1)
$$C_{graphite\ (s)} + CO_{2\ (g)} \leftrightarrows 2\ CO_{(g)} \qquad\qquad \text{(i)}$$
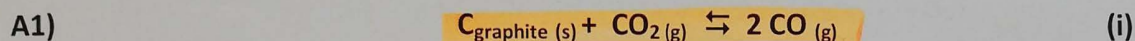
A1a) Is this equilibrium sensitive to pressure? Why ? How would the total pressure qualitatively evolve when the equilibrium is established at a constant volume from an initial state made of $C_{graphite\ (s)}$ and $CO_{2(g)}$?

A1b) What is the variance of the system at equilibrium? What conclusion can you make?

A1c) Knowing that the equilibrium is established from an initial state containing 1 mole of $CO_{2\ (g)}$ and an excess of $C_{graphite\ (s)}$, establish the expression of the equilibrium constant $K°_{(T)}$ as a function of the degree of conversion of CO_2, α $(0 < \alpha < 1)$, and the total pressure P_t of the gas mixture.

A2) At a temperature $T_1 = 1330$ K under a total pressure $P_t = 1$ bar, the degree of conversion α of $CO_{2\ (g)}$ is equal to 0.997, indicating that most of the CO_2 is converted into CO.

A2a) Use this information to calculate the equilibrium constant $K_{(i)}°_{1330}$.

A2b) Calculate $K_{(i)}°_{1330}$ using the thermodynamic data given in the table below.

A2c) Explain the difference between the numerical values of the equilibrium constant thus calculated.

Part B: The reduction of $GeO_{(s)}$ by carbon monoxide $CO_{(g)}$ is now studied at a temperature of $T_2 = 950$ K (*reaction (i) doesn't occur at this temperature*).

B1) A reactor of 30 L (**constant volume**) is completely emptied prior to introducing 10 moles of carbon monoxide $CO_{(g)}$ and allowing the following equilibrium (ii) to establish at $T_2 = 950$ K. The numerical value of the corresponding equilibrium constant at 950 K is $K_{(ii)}°_{950} = 1.0$.

$$2\ CO_{(g)} \leftrightarrows CO_{2\ (g)} + C_{(s)} \qquad\qquad \text{(ii)}$$
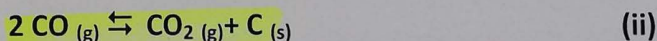
B1a) Calculate at equilibrium, the numbers of moles of all the constituents (n_{CO}, n_{CO_2}, n_C) and the partial pressures of the gaseous constituents (P_{CO}, P_{CO_2}).

B1b) Show that the following relationship applies at any time: $n_{CO} + 2\ n_{CO_2} = 10$.

B2) 10 moles of germanium monoxide $GeO_{(s)}$ are added to the system thus obtained at equilibrium (ii) in order to study the reduction of $GeO_{(s)}$ according to equation (iii). The numerical value of the corresponding equilibrium constant at 950 K is $K_{(iii)}^{0}\,_{950} = 0.8$.

$$GeO_{(s)} + CO_{(g)} \leftrightarrows Ge_{(s)} + CO_2\,(g) \qquad (iii)$$
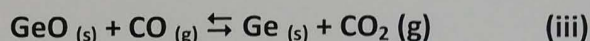
B2a) According to the numerical value of the variation of free enthalpy ΔG, is it possible to reduce GeO in Ge following the forward reaction of equilibrium (iii)?

B2b) What is the variance of the system when both equilibria (ii) and (iii) are achieved? What conclusion(s) can you make?

B2c) What is the influence of temperature on equilibrium (iii)? Justify your answer.

B3) To achieve favorable conditions for the reduction of $GeO_{(s)}$ while maintaining the temperature constant at 950 K, the volume of the reactor is modified to a value V 'to be determined. Both equilibria (ii) and (iii) are then established and their equilibrium constants both apply.

B3a) Deduce the relationship between the new pressure of CO at equilibrium (noted P'_{CO}) and the two equilibrium constants.

B3b) Describe the state of the system by calculating the new partial pressures (P'_{CO}, P'_{CO_2}), the total pressure P'_t, the numbers of moles (n'_{CO}, n'_{CO_2}) and the new volume V'.

Data :

Substance (physical state))	$\Delta_f H^{\circ}_{298}$ (kJ.mol^{-1})	S°_{298}(J.K^{-1}.mol^{-1})
$C_{graphite\,(s)}$	0	5.8
$CO_{(g)}$	-110.4	197.7
$CO_{2\,(g)}$	-393.5	213.7
GeO (s)	-255.0	73.0
Ge (s)	0	21.0