Chemistry 2
Test n°2. Duration 1h30

No document allowed – only TI30 type calculators are authorized
The 2 exercises can be solved independently. The schedule of mark is indicative.

Data   T$(K) = \theta(°C)+273$ $P^0 = 1bar$ $R = 8.314\ J.mol^{-1}.K^{-1}$

I- Homogeneous equilibrium in gaseous phase : Dissociation of phosgene (11.5 pts)

Compounds	$\Delta_f H^0_{(298)}$ (kJ.mol^{-1})	$S^0_{f(298)}$ (J.mol^{-1} K^{-1})	C_p (J.mol^{-1} K^{-1})
COCl$_{2(g)}$	-220.1	283.8	57.0
CO$_{(g)}$	-110.5	197.7	29.1
Cl$_{2(g)}$	0	223.1	33.9

In gaseous phase, phosgene COCl$_2$ can dissociate into carbon monoxide (CO) and chlorine (Cl$_2$).

1. Write the equation of the corresponding chemical equilibrium.

A] Lecture questions.
Let's consider as the chemical system a mixture of the 3 compounds, initially at equilibrium at 25°C.
2. How would the reaction evolve if:
- Temperature was increased, at constant pressure? Qualify.
- Volume was decreased, at constant temperature? Qualify.

3. Give the literal expression of the change in enthalpy $\Delta_r H^0_{(T)}$ and the change in entropy $\Delta_r S^0_{(T)}$ of dissociation of phosgene, as a function of the respective values at 25°C and the heat capacities at constant pressure.
4. Show that in a range of temperature between 25°C and 427°C, the previous expressions can be approximated to the values at 25°C. <u>These approximations will be used in the following parts of the exercise.</u>

B] Study of the equilibrium at $\theta_1 = 400$ °C.

5. Calculate K$_{p(400°C)}$ (in bars, to within 10^{-3}).
6. Starting from phosgene only, express the dissociation degree of phosgene (α) as a function of the equilibrium constant K$_P$ and the total pressure P$_T$. Calculate the value of α at 400°C under P$_T$ = 1 bar.
7. Give the literal expression for the variance of the system at equilibrium, define each parameter and calculate the value in the situation of question 6.
8. Show that the value calculated for the variance is consistent with a set of equations between intensive parameters.
9. Determine the condition on the total pressure P$_T$ so that the dissociation degree α would be smaller than 0.25.

C] Shift of the reaction under isothermal conditions ($\theta_1 = 400°C$).
A container which volume is adjustable is initially emptied from any gas. Then, n$_0$ = 1 mole of phosgene is introduced at $\theta_1 = 400°C$ until the pressure P_T reaches 1 bar (state a). Once the equilibrium is reached under a total pressure maintained constant, the volume occupied by the gaseous mixture is referred as V$_b$ (state b). Then a two-steps process is considered: first, a volume V$_{Cl2}$ of gaseous chlorine, measured at the same temperature ($\theta = 400°C$) and under a pressure of P = 1 bar, is added into the container. Second, the system is compressed so that the volume recovers the value V$_b$. We want to determine the total pressure P_T' finally attained when the chemical equilibrium is again reached (state c).

10. Give a clear material balance in the form of a table of advancement ("tableau d'avancement"), considering the 3 different stages of the chemical system: *i)* the initial state (state a), *ii)* the intermediary

equilibrium state (state b) and *iii)* the equilibrium finally reached after chlorine was added (state c). The degree of progress of the reaction, between states b and c, will be denoted x' (« avancement de la réaction »).

11. Give the literal expression of the P_T'/P_T ratio as a function of x'.

12. Using the expression of $Kp_{(400°C)}$, determine the numerical values of x' (degree of progress of the reaction) and the total pressure P_T' obtained at state c

13. Compared to the amount of phosgene initially introduced into the container, calculate the dissociation degree α' finally observed. Was the direction which reaction has shifted predictable?

II Hydrates of Cadmium sulfate (8.5 pts) *(Many questions are independent)*

The enthalpy and entropy changes will be considered as independent on temperature.

Herein systems based on cadmium sulfate $CdSO_4$ and different hydrates in equilibrium with gaseous water are studied.
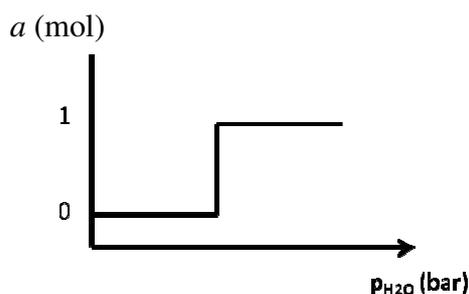

Figure 1

	$\Delta_f H^0_{(298)}$ (kJ.mol^{-1})	$S^0_{f\,(298)}$ (J.mol^{-1}.K^{-1})
$CdSO_4$ (s)	-932.4	122.9
$CdSO_4.H_2O$ (s)	-1238.4	153.9
$CdSO_4.8/3H_2O$ (s)	-1727.7	229.4
H_2O (g)	-241.3	198.3

$M_{CdSO4} = 208.5$ g.mol^{-1} /$M_{H2O} = 18.0$ g.mol^{-1}

Table 1

One way to trap gaseous water consists in taking advantage of the hydration reaction of a salt such as $CdSO_4$ (initially hydrated or not) into higher hydration states. Let's define as *a* the number of moles of water molecules in the <u>condensed state</u> per mole of $CdSO_4$.

1. Under isothermal conditions (77°C) the variation of *a* as a function of p_{H2O} for the equilibrium between $CdSO_4$ and $CdSO_4,H_2O$ is shown in Figure 1.

a) Write the corresponding equilibrium. Calculate the partial pressure p_{H2O} at equilibrium at 77°C.

b) Explain the variation of *a* shown in Fig.1. On each part of the curve, what are the chemicals present in the system?

c) Determine the variance of the system at equilibrium by two different means. Deduce whether the condensed state corresponds to a solid solution.

2. Three different solid forms of $CdSO_4$ have been identified (see Table 1).

a) Write the 3 different chemical equilibria involving the different solids. Give the literal expressions of the respective equilibrium constants. Can the three solids coexist (justify your answer)?

At 25°C, an equilibrium involving the two hydrated forms may establish with a total pressure of 0.067 bar.

b) What would happen to a sample of $CdSO_4.8/3H_2O$ in contact with the air at room temperature, knowing that the saturation vapor pressure of water $p*_{vap}(H_2O)$ is 0.038 bar at 25°C?

c) 200 mg of $CdSO_4.8/3H_2O$ are introduced in a 10 mL vial initially emptied from air. Calculate the number of moles of each compound at equilibrium at 25°C.

d) At which temperature should the system be heated to get $p_{H2O} = 0.345$ bar at equilibrium?

e) Under constant $p_{H2O} = 0.345$ bar, the temperature of the initial system is increased from 25°C to 200°C per steps of 25°C, with long enough time intervals to allow the equilibrium to be reached at each temperature. Determine the successive temperatures of dehydration of the hydrates.

f) By analogy with Fig. 1, indicate schematically the change of *a* as a function of the temperature (from 25 to 200°C) under isobaric conditions p = 0.345 bar.