

TD Series N°3
Second principle of thermodynamics

Exercise 01:

In an oven previously heated to 900°C, one mole of a solid substance taken at 25°C is introduced. Knowing that between 25°C and 900°C, this substance remains solid and that its molar heat at constant pressure is equal to 30 J.K⁻¹.mol⁻¹

1. Calculate the change in entropy of the solid.
2. Calculate the change in entropy exchanged between the furnace and the solid.
3. Deduce the entropy change created during heating.

Exercise 02 :

A kilogram of ice taken out of the refrigerator at -5°C is transported to a room at 25°C. It reaches equilibrium. Calculate the entropy created.

We give: $\Delta H^{\circ}_{\text{melt}, 273\text{K}}(\text{H}_2\text{O}, \text{s}) = 334 \text{ J.g}^{-1}$

The specific heats of mass are : $C_p(\text{H}_2\text{O}, \text{l}) = 18 \text{ J.g}^{-1}.\text{K}^{-1}$; $C_p(\text{H}_2\text{O}, \text{s}) = 9 \text{ J.g}^{-1}.\text{K}^{-1}$

Exercise 03:

Calculate the standard free enthalpy at 25°C (ΔG°) of the following reaction: $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$

Given that :

$$s^{\circ}_{298}(\text{NO}, \text{g}) = 50,34 \text{ u.e. ;}$$

$$s^{\circ}_{298}(\text{N}_2, \text{g}) = 45,77 \text{ u.e.}$$

$$s^{\circ}_{298}(\text{O}_2, \text{g}) = 49,00 \text{ u.e. ;}$$

$$\Delta H^{\circ}_{\text{f}, 298}(\text{NO}, \text{g}) = 21,6 \text{ kcal.mol}^{-1}$$

(Unit of entropy: u.e = cal.mol⁻¹.K⁻¹)

Exercise 04:

Consider the equilibrium: $\text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})} \rightleftharpoons \text{CO}_2_{(\text{g})} + \text{H}_2_{(\text{g})}$ $\Delta H = -10,2 \text{ Kcal}$

For which $K_p = 10$ at 690 K (ΔH is constant between 500 and 690 K)

a. In which direction does the equilibrium move?

- When the temperature increases,
- When the pressure decreases.

b. Calculate the equilibrium constant K_p at 500 K.

c. Calculate the partial pressures for each of the gases at equilibrium in a mixture initially prepared from 0.4 moles of CO and 0.2 moles of H₂O in a volume of 51 at 500 K.

d. Calculate:

- The equilibrium constant $K_{c, \text{at } 500 \text{ K}}$
- The standard free enthalpy ΔG° of the equilibrium at 690 K and 500 K.

Exercise 05:

A mixture initially comprising one mole of acetic acid **CH₃COOH** and one mole of methyl alcohol **CH₃OH**, evolve to a state of equilibrium for which the composition of the mixture is as follows: 0.3 mole of acid and alcohol 0.7 mole of ester (**CH₃COOCH₃**) and water.

a. Give the reaction of the mixture.

b. Calculate the constant K_c for this equilibrium.

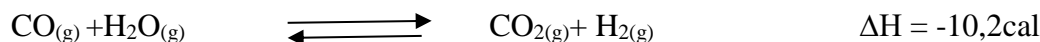
c. If the initial composition of the mixture is 2.5 moles of alcohol and 1 mole of acid, what will be the new composition of the mixture at equilibrium?

d. What factors need to be influenced, and how, to encourage the formation of (CH₃COOCH₃).

Chemical equilibrium

Exercise 01:

Consider the equilibrium:



For which $K_p = 10$ at 690 K (ΔH is constant between 500 and 690 K)

a. In which direction does the equilibrium move?

- When the temperature increases,
- When the pressure decreases.

b. Calculate the equilibrium constant K_P at 500 K.

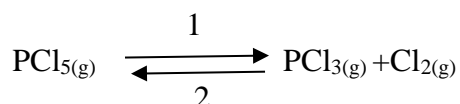
c. Calculate the partial pressures for each of the gases at equilibrium in a mixture initially prepared from 0.4 moles of CO and 0.2 moles of H_2O in a volume of 51 at 500 K.

d. Calculate:

- The equilibrium constant K_c at 500 K
- The standard free enthalpy ΔG° of equilibrium at 690 K and 500 K.

Exercise 02:

0.003 mol PCl_5 is introduced into a 0.5 L vessel at a temperature of 45°C . The total pressure is 194 mmHg when equilibrium is established.



Calculate: a- The mole fractions of each of the components at equilibrium.

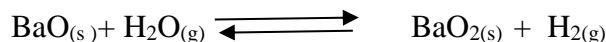
b- The partial pressures of these components in the mixture at equilibrium.

c- The equilibrium constant K_P .

d- In which direction does equilibrium move, if the volume of the container becomes equal to 1 liter, at the same temperature?

Exercise 03:

Consider the following reaction:



In which $K_p = 9.2$ at 700K, ($\Delta H = -10.3$ kcal).

a. Give the expression for K_P and calculate K_P at 530 K.

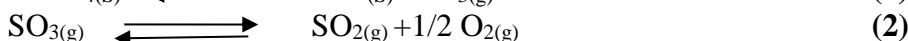
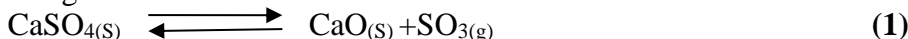
b. Write down the equilibrium condition.

c. Calculate the standard free enthalpy ΔG° of the equilibrium at 530 K.

d. Calculate the standard entropy ΔS° , assuming that ΔH° of the reaction is constant between 530K and 700K.

Exercise 04:

The following reactions are considered:



a. Calculate the change in standard free enthalpy of reactions (1) and (2) at 1400 K (enthalpies and entropies of formation are assumed to be independent of T).

Données	$\text{CaSO}_{4(s)}$	$\text{CaO}_{(s)}$	$\text{SO}_{3(g)}$	$\text{SO}_{2(g)}$	$\text{O}_{2(g)}$
ΔH_F° (kJ/mol)	-1432,7	-635,1	-395,8	-296,8	0
ΔS_F° (J/mol.K)	106,7	39,7	256,7	248,1	205,0

Calculate the constants K_{p1} and K_{p2} at 1400 K.

a. In which direction does equilibrium (2) move as the temperature increases?

b. A container which has been evacuated and into which calcium sulphate has been introduced is heated to 1400 K. What will be the values of the partial pressures of the **various constituents** of the gas mixture at equilibrium?

c. Which reaction should be considered at this temperature to describe the system at equilibrium? Evolution of $\frac{P_{\text{SO}_3}}{P_{\text{SO}_2}}$ with T.