

Problem 5. The Second Law of thermodynamics applied to a chemical reaction

Consider a system, a chemical reactor in Fig. 1. Pressure p and temperature T inside the reactor are kept constant. There is no transfer of matter into or out of the system.

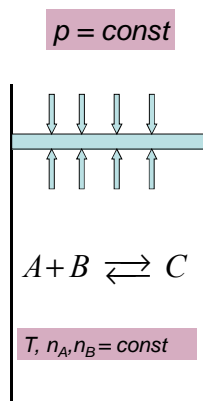


Fig. 1. Chemical reaction inside a reactor

According to the Second Law, every spontaneous process in such a reactor leads to the decrease of the Gibbs free energy, G_{system} , i.e. $\Delta G_{\text{system}} < 0$.

If the chemical reaction, e.g., $A + B = C$ (a), is the only process inside the reactor

$$\Delta G_{\text{System}} = \Delta G_{\text{Reaction}}(a) \Delta \xi(a) \quad (1)$$

$$\Delta \xi(a) = \Delta n_C = -\Delta n_A = -\Delta n_B$$

where $\Delta G_{\text{Reaction}}$ and $\Delta \xi$ are the Gibbs free energy and the extent of reaction (a), respectively, Δn_A , Δn_B , Δn_C are changes of the numbers of moles of A, B, C in the reaction (a).

-- Question 1.1. Relate $\Delta \xi$ to Δn_i of reactants and products of the following reaction



-- Question 1.2. Prove that, according to the Second Law, $\Delta G_{\text{Reaction}} < 0$ for any single spontaneous chemical reaction in the reactor (Fig.1).

Answer 1.1

Considering the chemical reaction: $\frac{1}{6} \text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$

$$\Delta x = \Delta n_{\text{CO}_2} = \Delta n_{\text{H}_2\text{O}} = -\Delta n_{\text{O}_2} = -6 \cdot \Delta n_{\text{C}_6\text{H}_{12}\text{O}_6}$$

Answer 1.2

According to the Second Law, for every spontaneous chemical process $\Delta G_{\text{system}} < 0$,

in which $\Delta G_{\text{system}} = \Delta G_{\text{reaction}} \cdot \Delta \xi$ so $\Delta G_{\text{reaction}} \cdot \Delta \xi < 0$

since in a spontaneous chemical process $\Delta \xi > 0$ (reagents \rightarrow products; $\Delta n_{\text{reagent}} < 0$ and $\Delta n_{\text{product}} > 0$)

$\Delta G_{\text{reaction}}$ must be negative ($\Delta G_{\text{reaction}} < 0$)

-- Question 2. The Gibbs free energy of the chemical reaction (a) is:

$$\Delta G_{\text{Reaction}} = \Delta G_{\text{Reaction}}^{\circ} + RT \ln \frac{[C]}{[A][B]} < 0 \quad (2)$$

where $[C]$, $[A]$, $[B]$ are time variant concentrations inside the reactor in the course of spontaneous reaction. Using the law of mass action, relate $\Delta G_{\text{Reaction}}$ to the ratio of rates of forward r_1 and reverse r_{-1} reaction (a). Consider both reactions as elementary ones.

Answer 2

We can affirm that: $r_1 = k_1 [A][B] \Rightarrow \frac{r_1}{k_1} = [A][B]$ and $r_{-1} = k_{-1} [C] \Rightarrow \frac{r_{-1}}{k_{-1}} = [C]$

replacing in the given equation of the Gibbs free energy we obtain:

$$\Delta G_{reaction} = \Delta G_{reaction}^0 + R T \ln \frac{[C][D]}{[A][B]} = \Delta G_{reaction}^0 + R T \ln \frac{r_{-1} \cdot k_1}{r_1 \cdot k_{-1}}$$

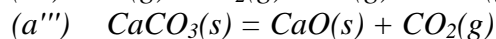
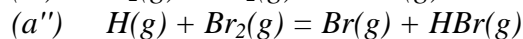
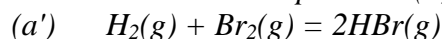
at equilibrium state $\Delta G_{reaction} = 0$ and $r_1 = r_{-1}$

replacing in the given equation of the Gibbs free energy we obtain:

$$0 = \Delta G_{reaction}^0 + R T \ln \frac{r_{-1} \cdot k_1}{r_1 \cdot k_{-1}} \Rightarrow \Delta G_{reaction}^0 = -R T \ln \frac{r_{-1} \cdot k_1}{r_1 \cdot k_{-1}} = -R T \ln \frac{k_1}{k_{-1}}$$

so we can write: $\Delta G_{reaction} = -R T \ln \frac{k_1}{k_{-1}} + R T \ln \frac{r_{-1} \cdot k_1}{r_1 \cdot k_{-1}} = R T \left(\ln \frac{r_{-1} \cdot k_1}{r_1 \cdot k_{-1}} - \ln \frac{k_1}{k_{-1}} \right) = R T \ln \frac{r_{-1}}{r_1}$

-- *Question 3.1. Derive the expression (2) for $DG_{reaction}$ of the following chemical transformations:*



-- *Question 3.2. For which of these reactions the relation between $DG_{Reaction}$ and r_1, r_{-1} derived in Problem 2 is valid?*

Answer 3.1

(a') For the reaction $H_2(g) + Br_2(g) = 2HBr(g)$

$$r_1 = k_1 [H_2][Br_2] \Rightarrow \frac{r_1}{k_1} = [H_2][Br_2] \quad \text{and} \quad r_{-1} = k_{-1} [HBr]^2 \Rightarrow \frac{r_{-1}}{k_{-1}} = [HBr]^2$$

$$\Delta G_{reaction} = \Delta G_{reaction}^0 + R T \ln \frac{[HBr]^2}{[H_2][Br_2]} = \Delta G_{reaction}^0 + R T \ln \frac{r_{-1} \cdot k_1}{r_1 \cdot k_{-1}} \quad \text{and} \quad \Delta G_{reaction}^0 = -R T \ln \frac{k_1}{k_{-1}}$$

so we can write $\Delta G_{reaction} = R T \ln \frac{r_{-1}}{r_1}$

(a'') For the reaction $H(g) + Br_2(g) = Br(g) + HBr(g)$

$$r_1 = k_1 [H][Br_2] \Rightarrow \frac{r_1}{k_1} = [H][Br_2] \quad \text{and} \quad r_{-1} = k_{-1} [Br][HBr] \Rightarrow \frac{r_{-1}}{k_{-1}} = [Br][HBr]$$

$$\Delta G_{reaction} = \Delta G_{reaction}^0 + R T \ln \frac{[Br][HBr]}{[H][Br_2]} = \Delta G_{reaction}^0 + R T \ln \frac{r_{-1} \cdot k_1}{r_1 \cdot k_{-1}} \quad \text{and} \quad \Delta G_{reaction}^0 = -R T \ln \frac{k_1}{k_{-1}}$$

so we can write $\Delta G_{reaction} = R T \ln \frac{r_{-1}}{r_1}$

(a''') For the reaction $CaCO_3(s) = CaO(s) + CO_2(g)$

$$r_1 = k_1 \quad \text{and} \quad r_{-1} = k_{-1} [CO_2] \Rightarrow \frac{r_{-1}}{k_{-1}} = [CO_2]$$

$$\Delta G_{reaction} = \Delta G_{reaction}^0 + R T \ln [CO_2] = \Delta G_{reaction}^0 + R T \ln \frac{r_{-1}}{k_{-1}}$$

Answer 3.2

The relation obtained in Answer 2 is valid only for (a') and (a'').

In (a''') there is an heterogeneous equilibrium where $CaCO_3$ and CaO are solids (the activity of pure solid = 1)

-- Question 4. The observed rate of chemical reaction, r_{obs} , is defined as $r_{obs} = r_1 - r_{-1}$.

Let reaction (a) proceed spontaneously. At a certain moment

$$r_{obs}/r_1 = 0.5, \quad [A] = 0.5 \text{ M}, [B] = 1 \text{ M}, [C] = 2 \text{ M}.$$

Find the equilibrium constant, K , of the reaction (a), $T = 298 \text{ K}$.

Answer 4

The observed rate is $r_{obs} = r_1 - r_{-1}$ and from the problem's data $\frac{r_{obs}}{r_1} = 0,5$

elaborating: $\frac{r_{obs}}{r_1} = \frac{r_1 - r_{-1}}{r_1} = \frac{r_1}{r_1} - \frac{r_{-1}}{r_1} = 1 - \frac{r_{-1}}{r_1} \Leftrightarrow 0,5 = 1 - \frac{r_{-1}}{r_1} \Rightarrow \frac{r_{-1}}{r_1} = 1 - 0,5 = 0,5$

from the definition of the reactions' rate, we can write: $\frac{r_{-1}}{r_1} = \frac{k_{-1}[C]}{k_1[A][B]} \Rightarrow \frac{k_1}{k_{-1}} = \frac{r_1[C]}{r_{-1}[A][B]}$

Considering that the K_{eq} is given by the ratio of the k :

at equilibrium state $r_{obs} = 0$ so $r_1 = r_{-1}$ by the law of mass action $K_{eq} = \left(\frac{[C]}{[A] \cdot [B]} \right)_{eq} = \frac{r_1 \cdot k_1}{r_{-1} \cdot k_{-1}} = \frac{k_1}{k_{-1}}$

from the data of the problem we know that $[A] = 0,5$; $[B] = 1$; $[C] = 2$ and we get $\frac{r_1}{r_{-1}} = \frac{1}{0,5} = 2$

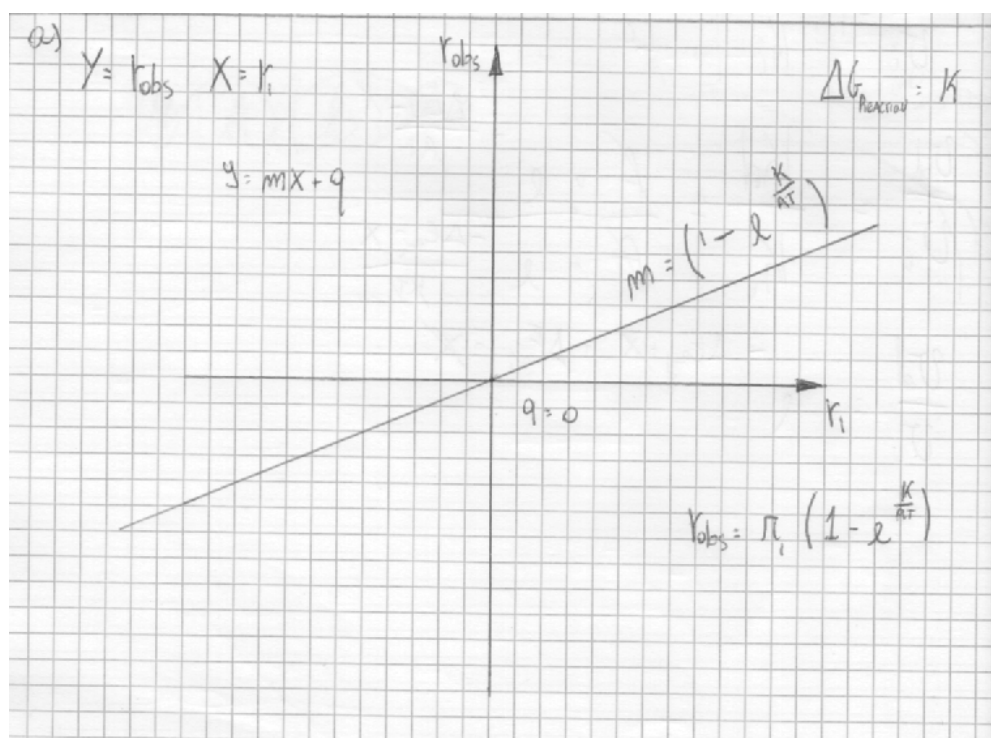
finally we can find: $K_{eq} = \left(\frac{[C]}{[A] \cdot [B]} \right)_{eq} = \frac{k_1}{k_{-1}} = \frac{r_1[C]}{r_{-1}[A][B]} = \frac{r_1}{r_{-1}} \cdot \frac{[C]}{[A][B]} = 2 \cdot \frac{2}{0,5 \cdot 1} = 8$

-- Question 5. Plot r_{obs} as a function of

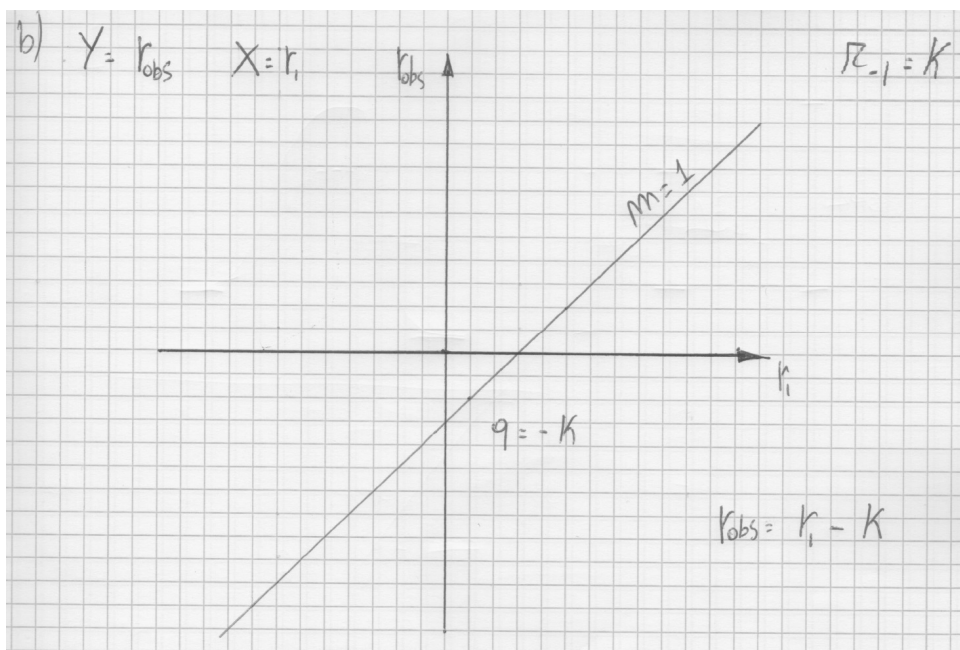
- r_1 , at $\Delta G_{Reaction} = const$;
- r_1 , at $r_{-1} = const$;
- $\Delta G_{Reaction}$, at $r_1 = const$.

Answer 5 Elaborating data we obtain:

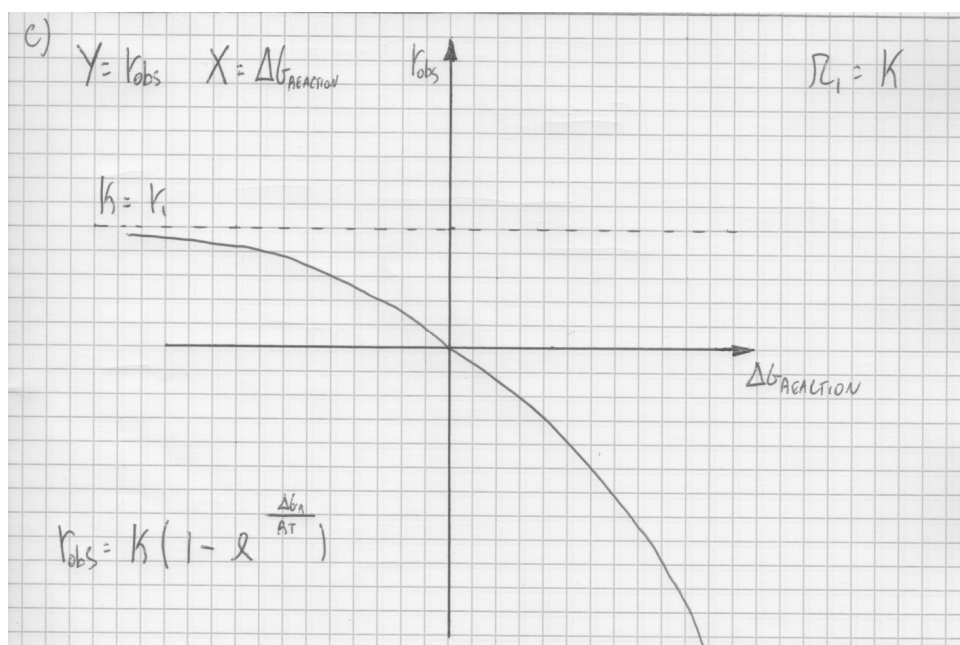
a)



b)



c)



-- Question 6. Which thermodynamic and kinetic parameters of a chemical reaction are influenced by a catalyst? Put plus (+) into the cell of the Table if a catalyst may cause a change of the corresponding parameter, (-) otherwise.

Answer 6

Table

r	r_1	r_1/r_{-1}	$\Delta G_{\text{reaction}}$	r/r_{-1}
+	+	-	-	-

Solution proposed by

Roberto Tinelli – Student – ITIS "L. dell'Erba" – Castellana Grotte – Italy