

Analysis of the chemical equilibrium of combustion at constant volume

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Abstract: *Determining the composition of a mixture of combustion gases at a given temperature is based on chemical equilibrium, when the equilibrium constants are calculated on the assumption of constant pressure and temperature.*

In this paper, an analysis of changes occurring when combustion takes place at constant volume is presented, deriving a specific formula of the equilibrium constant. The simple reaction of carbon combustion in pure oxygen in both cases (constant pressure and constant volume) is next considered as example of application, observing the changes occurring in the composition of the combustion gases depending on temperature.

Key Words: *mathematical modeling, combustion, chemical equilibrium, thermodynamic properties, internal energy*

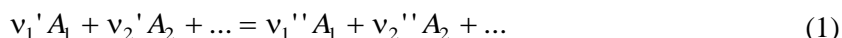
1. INTRODUCTION

The mathematical modeling of the chemical reactions usually regards their behavior in reactors where processes are steady, so that the temperature and pressure are constant. The composition of the reaction products at equilibrium is determined by the law of mass action using the equilibrium constants which take into account a constant pressure.

However, there are cases when the reaction is carried out at constant volume (for example, combustion in a piston engine cycle). We will show that, at constant volume, the expressions of equilibrium constant differ from those which are specific to reactions at constant pressure. The influence of the mathematical model changes on the composition of the combustion products, depending on the combustion temperature, will be analyzed in this paper.

2. LAW OF MASS ACTION

We will refer to the law concerning the chemical equilibrium. For a chemical reaction of the form



the law of the mass action can be expressed by the equation:

$$K_C = \frac{\prod_i C_i^{\nu_i''}}{\prod_i C_i^{\nu_i'}} \quad (2)$$

where K_C = equilibrium constant in terms of concentrations

C_i = concentrations of species []_{*i*}.

ν_i = stoichiometric coefficients

A similar expression of equilibrium constant can be derived in terms of pressures or molar fractions.

The last shows a special interest, since it can be expressed as a function of thermodynamic properties of the reaction participants:

$$K_X = \frac{\prod_i X_i^{\nu_i''}}{\prod_i X_i^{\nu_i'}} \quad (3)$$

where K_X = equilibrium constant in terms of molar fractions (used for reactions in gas phase).

X_i = molar fraction of species []_{*i*}.

It is well known that, for the reactions occurring at constant pressure and temperature, the chemical equilibrium is reached then when the Gibbs free energy of the given system gets minim:

$$\text{equilibrium} \Big|_{p,T} \Rightarrow G_{\text{sys}} = \min \Rightarrow dG_{\text{sys}} = 0 \quad (4)$$

which is equivalent to the condition:

$$\sum_i (G_i)_R = \sum_i (G_i)_P \quad (5)$$

where $(G_i)_R$, $(G_i)_P$ = Gibbs free energies of species []_{*i*} of reactants and of reaction products respectively, the thermodynamic function G being defined by the expression

$$G = U + pV - TS \quad (6)$$

wherein U = internal energy, S = entropy, p = pressure, T = absolute temperature, V = volume.

By processing equation (5), an explicit formula of the equilibrium constant in terms of molar fractions is derived, which is very useful for the reactions in gas phase occurring at constant pressure and temperature [1], [2]:

$$K_X \Big|_p = \left(\frac{p}{p_0} \right)^{\left(\Delta \sum_i \nu_i \right)_r} \cdot \exp \left[- \frac{(\Delta \bar{G})_r}{RT} \right] \quad (7)$$

where p_0 = standard reference pressure, $p_0 = 1.013$ bar, then

$$(\Delta \bar{G})_r = \sum_i (\bar{G})_P - \sum_i (\bar{G})_R \quad (8)$$

$$\left(\Delta \sum_i \nu_i \right)_r = \sum_i (\nu_i)_P - \sum_i (\nu_i)_R \quad (9)$$

and R = universal gas constant, $R = 8.314$ kJ/kmol.K, notation [] referring to the "molar" quantities.

3. EQUILIBRIUM CONSTANT AT CONSTANT VOLUME

In what follows, a similar formula of the equilibrium constant will be derived, but for a reaction taking place at constant volume. Accordingly, under the 1st law of *Thermodynamics*, the thermal effect of the reaction is related to the change in internal energy of the system:

$$\delta Q = dU \Rightarrow Q_r = \sum_i (U_i)_P - \sum_i (U_i)_R = (\Delta U)_r \quad (10)$$

On the other hand, according to the 2nd law, the total (universal) entropy system+surroundings must increase:

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr} \geq 0 \quad (11)$$

Using the notation $\Delta S_{syst} = (\Delta S)_r$ (where []_r means “reaction”) and taking into account that:

$$\Delta S_{surr} = -\frac{Q_r}{T_0} \quad (12)$$

one deduces from (11) the equation:

$$(\Delta S)_r - \frac{Q_r}{T_0} \geq 0 \Rightarrow Q_r - T_0 \cdot (\Delta S)_r \leq 0 \quad (13)$$

Since the reaction is considered to take place at constant volume and constant temperature T equal to that of the surroundings, by applying (10), the above inequality becomes:

$$(\Delta U)_r - T \cdot (\Delta S)_r \leq 0 \quad (14)$$

According to the definition of Helmholtz free energy:

$$F = U - TS \Rightarrow dF = dU - T \cdot dS \quad (T = \text{const.}) \quad (15)$$

the condition (14) reduces to

$$dF \leq 0 \quad (16)$$

At equilibrium, the Helmholtz free energy reaches its minimum value:

$$F_{eq} = \min \Rightarrow (\Delta F)_r|_{eq} = 0 \quad (17)$$

Under these circumstances, similarly to equation (7), the equilibrium constant for the reactions taking place at constant volume and temperature will have the expression:

$$K_X|_V = \left(\frac{p}{p_0}\right)^{-\left(\Delta \sum_i \nu_i\right)_r} \cdot \exp\left[-\frac{(\Delta \bar{F})_r}{RT}\right] \quad (18)$$

The above equation can be processed as below, considering the relation between the free energies:

$$(\Delta \bar{F})_r = \sum_i (v_i \bar{F}_i)_P - \sum_i (v_i \bar{F}_i)_R \quad (19)$$

$$\sum_i v_i \bar{F}_i = \sum_i (v_i \bar{G}_i - v_i RT) = \sum_i v_i \bar{G}_i - RT \sum_i v_i \quad (20)$$

$$(\Delta \bar{F})_r = \left[\sum_i (v_i \bar{G}_i)_P - \sum_i (v_i \bar{G}_i)_R \right] - RT \left(\Delta \sum_i v_i \right)_r \quad (21)$$

$$(\Delta \bar{F})_r = (\Delta \bar{G})_r - RT \left(\Delta \sum_i v_i \right)_r \quad (22)$$

where $\left(\Delta \sum_i v_i \right)_r$ is given by (9).

By replacing in (18), the formula of the equilibrium constant for the reactions at constant volume is found:

$$K_X|_V = \left(\frac{p}{p_0} \right)^{-\left(\Delta \sum_i v_i \right)_r} \cdot \exp \left[-\frac{(\Delta \bar{G})_r}{RT} + \left(\Delta \sum_i v_i \right)_r \right] \quad (23)$$

or, by comparing to (7):

$$K_X|_V = K_X|_p \cdot \exp \left(\Delta \sum_i v_i \right)_r \quad (24)$$

where the pressure p in (23) is the final pressure obtained when a chemical reaction at constant volume reaches its equilibrium.

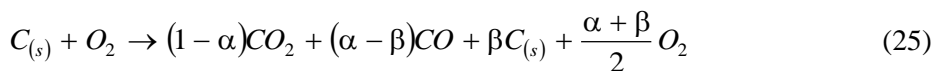
It can be observed that, for a reaction showing a difference between the total number of moles of reactants and the reaction products, the equilibrium constant at constant volume is different from that at constant pressure.

Thus:

- if the total number of moles of reaction products exceeds the total number of moles of reactants, then the reaction constant at constant volume is higher than in the case of constant pressure, hence the equilibrium shifts to products forming;
- if the total number of the reaction products moles is less than the total number of the reactants moles, then the reaction constant at constant volume is lower than in the case of constant pressure, hence the equilibrium shifts to the reactants.

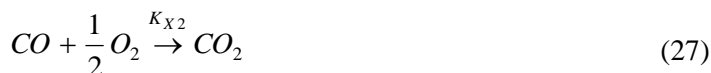
4. EXEMPLIFICATION FOR THE CASE OF COMBUSTION OF CARBON IN OXYGEN

Let's consider the chemical reaction of combustion of pure carbon (graphite) in oxygen, wherein products of incomplete combustion are present as well. Globally, this can be described by the equation:



The composition of combustion products at various temperatures will be analyzed by comparison, considering the chemical equilibrium separately, at constant pressure and constant volume.

The equations of simple reactions leading to overall reaction (25) are:



For the above reactions, the equilibrium constants in molar fractions will be considered, ignoring the solid phase:

$$K_{X1} = \frac{X_{CO}}{X_{O_2}^{1/2}} \Rightarrow X_{CO} = K_{X1} X_{O_2}^{1/2} \quad (28)$$

$$K_{X2} = \frac{X_{CO_2}}{X_{CO} X_{O_2}^{1/2}} \Rightarrow X_{CO_2} = K_{X2} X_{CO} X_{O_2}^{1/2} \quad (29)$$

By adding the normation equation:

$$X_{CO} + X_{CO_2} + X_{O_2} = 1 \quad (30)$$

the system of equations which determines the molar fractions of combustion products in gas phase will be found.

By solving the system, one yields:

$$X_{O_2} = \left[\frac{-K_{X1} + \sqrt{K_{X1}^2 + 4(1 + K_{X1}K_{X2})}}{2(1 + K_{X1}K_{X2})} \right]^2 \quad (31)$$

$$X_{CO} = K_{X1} \left[\frac{-K_{X1} + \sqrt{K_{X1}^2 + 4(1 + K_{X1}K_{X2})}}{2(1 + K_{X1}K_{X2})} \right] \quad (32)$$

$$X_{CO_2} = K_{X1}K_{X2} \left[\frac{-K_{X1} + \sqrt{K_{X1}^2 + 4(1 + K_{X1}K_{X2})}}{2(1 + K_{X1}K_{X2})} \right]^2 \quad (33)$$

Formulas (31), (32) and (33) determine the composition of the combustion products of (25) at equilibrium, at a given temperature and pressure, depending on the equilibrium constants.

These equilibrium constants will be computed in the following at both reaction conditions: constant pressure and constant volume.

Calculation of the equilibrium constants for the reaction at constant pressure $p = p_0$

The equilibrium constants K_{X1} , K_{X2} will be determined by using formula (7), that is:

$$K_{X1} = \exp \left(- \frac{\sum_i (v_i \bar{G}_i)_P^T - \sum_i (v_i \bar{G}_i)_R^T}{RT} \right) = \exp \left(- \frac{\bar{G}_{CO}^T - \frac{1}{2} \bar{G}_{O_2}^T}{RT} \right) \quad (34)$$

$$K_{X2} = \exp \left(- \frac{(\Delta \bar{G})_r^T}{RT} \right) = \exp \left(- \frac{\bar{G}_{CO_2}^T - \bar{G}_{CO}^T - \frac{1}{2} \bar{G}_{O_2}^T}{RT} \right) \quad (35)$$

The composition of the reaction products will be analyzed at 3 temperatures: 1000 K, 2000 K and 3000 K.

The thermodynamic data are taken from [3], [4] and [5] and the values of the computed equilibrium constants are presented in tables 1, 2 and 3.

The total number of the combustion products moles in the gas phase which occurs in equation (25) is:

$$\left(\sum_i v_i \right)_{P(g)} = 1 - \alpha + \alpha - \beta + \frac{\alpha + \beta}{2} = \frac{2 + \alpha - \beta}{2} \quad (36)$$

so that the molar fractions of corresponding components can be expressed as:

$$X_{CO_2} = \frac{2(1 - \alpha)}{2 + \alpha - \beta}, \quad X_{CO} = \frac{2(\alpha - \beta)}{2 + \alpha - \beta}, \quad X_{O_2} = \frac{\alpha + \beta}{2 + \alpha - \beta} \quad (37)$$

One yields for α and β :

$$\alpha = \frac{2X_{O_2} + X_{CO}}{2X_{CO_2} + X_{CO} + 2X_{O_2}}, \quad \beta = \frac{2X_{O_2} - X_{CO}}{2X_{CO_2} + X_{CO} + 2X_{O_2}} \quad (38)$$

The following notations will be used in the next:

$$(\Delta \bar{G})_r^T = \sum_i (v_i \bar{G}_i)_P^T - \sum_i (v_i \bar{G}_i)_R^T \quad (39)$$

$$\begin{aligned} (\Delta \bar{G})_r^T &= (\Delta \bar{G})_r^0(T) + \sum_i [v_i \Delta \bar{H}_i(T_0, T)]_P - \sum_i [v_i \Delta \bar{H}_i(T_0, T)]_R - \\ &- T \left\{ \sum_i [v_i \Delta \bar{S}_i^0(T_0, T)]_P - \sum_i [v_i \Delta \bar{S}_i^0(T_0, T)]_R \right\} \end{aligned} \quad (40)$$

$$(\Delta \bar{G})_r^0(T) = (\Delta \bar{H})_r^0 - T(\Delta \bar{S})_r^0 \quad (41)$$

$$\Delta \bar{H}_i(T_0, T) = \int_{T_0}^T (\bar{c}_p)_i(T) \cdot dT \quad (42)$$

$$\Delta \bar{S}_i^0(T_0, T) = \int_{T_0}^T (\bar{c}_p)_i(T) \cdot \frac{dT}{T} \quad (43)$$

Tab.1 – Standard enthalpy and entropy of formation and combustion of CO [4], [5]

Thermochemical data	$(\Delta\bar{H})_r^0$ [kJ/kmol]	$(\Delta\bar{S})_r^0$ [kJ/kmol.K]
Formation CO	-110530	-62.9
Combustion CO	-283000	-86.3

Tab.2 – Enthalpy and entropy variation for species present in the reactions of formation and combustion of CO within temperature range (T_0, T) (data taken from [3])

Temperature \rightarrow	$T_1 = 1000$ K	$T_2 = 2000$ K	$T_3 = 3000$ K
$\Delta\bar{H}_{O_2}(T_0, T)$ [kJ/kmol]	22700	59170	98010
$\Delta\bar{S}_{O_2}^0(T_0, T)$ [kJ/kmol.K]	38.5	63.6	79.4
$\Delta\bar{H}_{CO}(T_0, T)$ [kJ/kmol]	21690	56740	93510
$\Delta\bar{S}_{CO}^0(T_0, T)$ [kJ/kmol.K]	36.8	61.0	75.9
$\Delta\bar{H}_{CO_2}(T_0, T)$ [kJ/kmol]	33400	91440	152800
$\Delta\bar{S}_{CO_2}^0(T_0, T)$ [kJ/kmol.K]	55.5	95.5	120.4

Tab.3 – Calculation of equilibrium constants for reactions of formation and combustion of CO at constant pressure

Temperature \rightarrow	$T_1 = 1000$ K	$T_2 = 2000$ K	$T_3 = 3000$ K
$[(\Delta\bar{G})_r]_{CO}^0$ [kJ/kmol]	-47630	15270	78170
$[(\Delta\bar{G})_r]_{CO_2}^0$ [kJ/kmol]	-196700	-110400	-24100
$[(\Delta\bar{G})_r]^Y_{CO}$ [kJ/kmol]	-54840	-15975	14075
$[(\Delta\bar{G})_r]^Y_{CO_2}$ [kJ/kmol]	-195790	-110685	-28215
K_{X1}	732.2	2.614	0.569
K_{X2}	$1.69 \cdot 10^{10}$	777.9	3.099

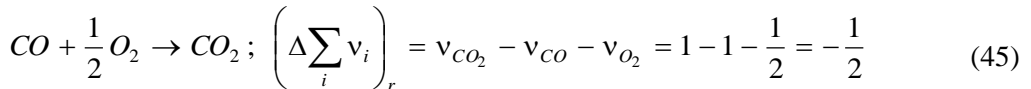
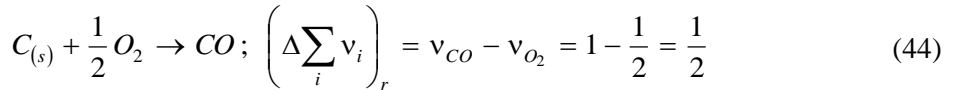
The results from table 3 will be introduced in (31), (32), (33) and (38) and the values presented in table 4 will be obtained.

Tab.4 – Composition of gases resulted from carbon combustion at 3 temperatures and constant pressure

Temperature →	$T_1 = 1000 \text{ K}$	$T_2 = 2000 \text{ K}$	$T_3 = 3000 \text{ K}$
X_{O_2}	$8.08 \cdot 10^{-14}$	$4.64 \cdot 10^{-4}$	0.257
X_{CO}	$2.08 \cdot 10^{-4}$	0.056	0.289
X_{CO_2}	0.9998	0.943	0.454
α	0.0001	0.0294	0.4695
β	-0.0001	-0.0285	0.1323

Calculation of the equilibrium constants for the reaction at constant volume and final pressure $p = p_0$

For the application of formula (24), the variation of the moles number (gas phase) will be computed in the two simple reactions (formation and combustion of CO):



By applying formula (24) to the equilibrium constants from table 3, the values presented in table 5 will be found:

Tab.5 – Composition of gases resulted from carbon combustion at 3 temperatures and constant volume

Temperature →	$T_1 = 1000 \text{ K}$	$T_2 = 2000 \text{ K}$	$T_3 = 3000 \text{ K}$
K_{X1}	1207.2	4.309	0.938
K_{X2}	$1.02 \cdot 10^{10}$	471.8	1.880
X_{O_2}	$8.09 \cdot 10^{-14}$	$4.47 \cdot 10^{-4}$	0.207
X_{CO}	$3.43 \cdot 10^{-4}$	0.091	0.427
X_{CO_2}	0.9997	0.908	0.366
α	$1.72 \cdot 10^{-4}$	0.0482	0.535
β	$-1.72 \cdot 10^{-4}$	-0.0473	-0.0078

In figures 1, 2 and 3, the variation of the molar fractions of O_2 , CO and CO_2 with temperature is plotted, by comparison – at constant pressure and at constant volume.

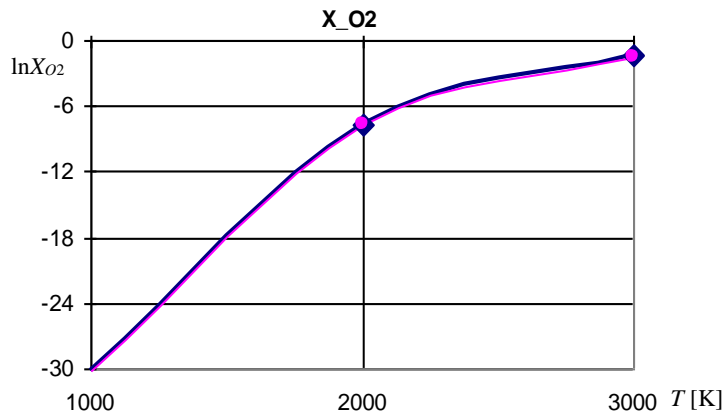


Fig. 1 – Variation of O₂ percentage in combustion gas mixture with temperature by comparison, at constant pressure and constant volume

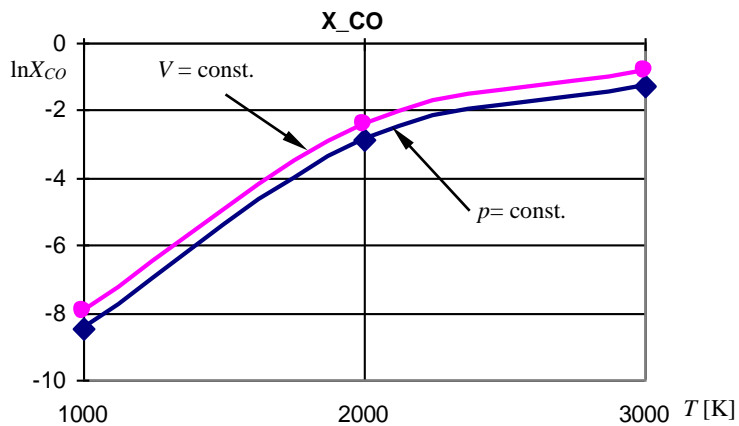


Fig. 2 – Variation of CO percentage in combustion gas mixture with temperature by comparison, at constant pressure and constant volume

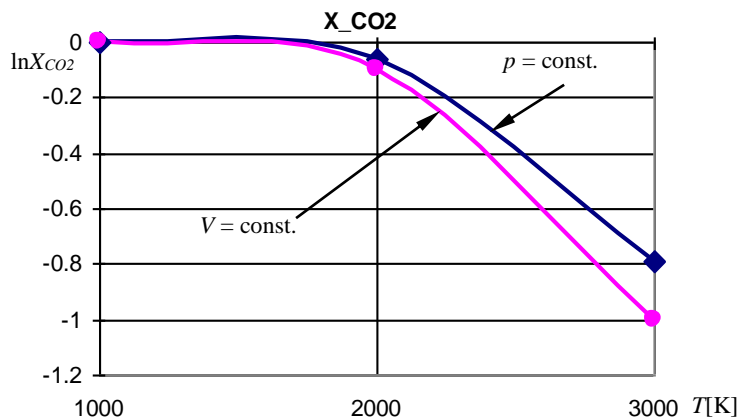


Fig. 3 – Variation of CO₂ percentage in combustion gas mixture with temperature by comparison, at constant pressure and constant volume

5. CONCLUSIONS AND COMMENTS ON THE RESULTS

By analyzing the data shown in the presented tables and diagrams, the following observations come out:

- 1) The percentage of unconsumed oxygen in the combustion gases is almost the same in both models (constant pressure and constant volume, respectively). However, the amount of unconsumed oxygen increases along with the combustion temperature.
- 2) The percentage of CO in the combustion gases is higher in the case of constant volume and increases along with the combustion temperature. In other words, the combustion at constant volume is more polluting than at constant pressure.
- 3) The percentage of CO₂ obtained by combustion at constant volume is lower than at constant pressure, the differences rising along with the combustion temperature.
- 4) In tables 4 and 5, small negative values of coefficient β can be observed, which means that, in fact, more than 1 mole of carbon gets in the reaction. However, at constant pressure (table 4), one observes that at 3000 K, $\beta = 0.1323$, which shows traces of smog in the combustion products. According to this model, at constant volume, no smog is present in the composition of the combustion products.
- 5) Increasing of the percentage of incomplete combustion products along with the temperature rise is in agreement with Le Chatelier principle, which states that, in the case of exothermic reactions, a temperature rise shifts the equilibrium towards the reactants.

Based on the above analysis, we can conclude that in the case of the carbon combustion in pure oxygen, at low temperatures, no significant differences between the results given by the models of equilibrium at constant pressure and constant volume occur, while at higher temperatures (as usual combustion processes with energetic effects happen), combustion at constant volume changes the weight of incomplete reaction products. In the case of the carbon combustion in oxygen at constant volume, when comparing to the constant pressure condition, the equilibrium moves according to the variation of the moles number in the simple reactions. Thus:

- at formation of CO, the variation of the moles numbers is positive, equilibrium shifts to the right;
- at combustion of CO, the variation of the moles numbers is negative, equilibrium shifts to the left.

It is also expected that other features of combustion (heat released, energetic efficiency, flammability limits versus air/fuel ratio and others) in the case of the combustion at constant volume will be affected by adopting the model of constant volume equilibrium, different from that of constant pressure.

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