

Yuri I. Pyatnitsky and Peter E. Strizhak

CALCULATING EQUILIBRIUM AND SIMULATING KINETICS OF
HETEROGENEOUS CATALYTIC REACTIONS

Kyiv – 2018

Calculating equilibrium and simulating kinetics of heterogeneous catalytic reactions
© 2018 Yuri I. Pyatnitsky and Peter E. Strizhak

Contents

Preface	4
1. Calculation of equilibrium constants	5
1.1. Simplified method of an equilibrium constant calculation	5
1.2. Calculation of equilibrium constant for arbitrary temperatures	6
1.3. Example of calculation for the methanol synthesis reaction	7
1.4. Computer calculation of equilibrium constants by <i>Microsoft Excel</i>	8
2. Calculation of equilibrium composition of the gas-phase chemical reactions	11
2.1. Calculation of equilibrium composition for methanol synthesis process	11
2.1.1. Method 1 of an equilibrium state calculation	11
2.1.2. Method 2 of an equilibrium state calculation	13
2.2. Calculation of equilibrium composition for ethanol steam reforming	16
2.2.1. Method 1 of an equilibrium state calculation	17
2.2.2. Method 2 of an equilibrium state calculation	19
3. Kinetic simulating of heterogeneous catalytic reactions in a plug-flow reactor	22
3.1. Isothermal reactor	23
3.2. Adiabatic reactor	28
4. Kinetic simulating of heterogeneous catalytic reactions in a gradientless reactor	30
4.1. Reaction occurring without change of a molecule number	30
4.2. Reaction occurring with change of a molecule number	32
4.2.1. CO oxidation by oxygen	32
4.2.2. Ammonia synthesis	34
4.2.3. Fischer-Tropsch process	38
5. Kinetic simulating of gas-phase homogeneous reactions	46
5.1. NO-O ₂ -NO ₂ system	46
5.1.1. Differentiation by a reactor volume	46
5.1.2. Differentiation by a residence time	48
5.2. Oxidative coupling of methane	50
6. Simulating of auto-oscillating reactions	55
6.1 Heterogeneous catalytic reaction with Langmuir-Hinshelwood mechanism in a gradientless reactor	55
6.2. Reaction between CO and NO on platinum	57
7. Simulating of thermo-programmed reactions	59
7.1. Thermoprogrammed desorption	59
7.2. Thermoprogrammed reactions	62
7.2.1. Thermoprogrammed reactions with participation of nitrogen and hydrogen atoms adsorbed on iron catalyst	62
7.2.2. Thermoprogrammed reduction of an oxide catalyst by hydrogen	64
Appendix	67
References	70

Preface

In a practice of investigation and application of the gas-phase chemical reactions, we often face a problem of calculation of equilibrium composition of the reaction mixture for given reaction conditions. A solution to the problem consists of two main stages:

- Determination of numerical values of reaction equilibrium constants.
- Calculation of equilibrium composition of the reaction mixture for given reaction conditions such as temperature, pressure, initial composition of the reaction mixture.

Present textbook is devoted to the solution of these problems with help of computer methods.

We also consider some simplest, as possible, ways of computer kinetic simulating of the gas-phase heterogeneous catalytic reactions as well as some homogeneous reactions.

The textbook may be useful for students, postgraduates and scientists specialized in chemistry.

1. Calculation of equilibrium constants

The equilibrium constant of a chemical reaction can be represented as:

$$K_p = e^{-\frac{\Delta G^0}{RT}} = e^{-\frac{\Delta H^0 + T\Delta S^0}{RT}} \quad (1)$$

or in the logarithmic form as:

$$\ln K_p = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (2)$$

where ΔG^0 , ΔH^0 and ΔS^0 are a change of standard free reaction energy, enthalpy, and entropy, respectively; T is temperature (K); R is the gas constant.

Values of the thermodynamic parameters of reactions (ΔH^0 and ΔS^0) can be calculated on the basis of the reference values of enthalpy formation and entropy of individual compounds in a reaction stoichiometric equation. This allows calculating a composition of the reaction mixture. For cases, when several reactions carried out simultaneously, such evaluations often are difficult to perform without using some means. One of such means, that is enough simple and, at the same time, effective, is proposed in the present textbook.

The means of a steady-state simulating of chemical reactions are considered also for the cases when kinetic equations of the reactions or their mechanism are known. The main attention is devoted to heterogeneous-catalytic reactions, which play the great role in chemical industry and environmental protection.

Note, that only gas-phase reactions are considered in this textbook. It is accepted that the gases are in the ideal state that corresponds to the classic equation $PV = RT$. This approximation is usually good at the pressures up to 50 atm and at the room temperature and higher. These conditions are typical for the most of gas-phase heterogeneous catalytic processes.

For real gases, a fugacity is used instead of a pressure in the thermodynamic equations. Methods of the evaluation of a fugacity may be found, for example, in [1-3].

1.1. Simplified method of an equilibrium constant calculation

For estimated calculations of the equilibrium constants at given temperatures, it is often used the simplified method of the K_p evaluation using the reaction enthalpy and entropy values for standard conditions (1 atm, 298 K):

$$K_p = e^{-\frac{\Delta H_{298}^0}{RT} + \frac{\Delta S_{298}^0}{R}} \quad (3)$$

For example, let us consider such calculation for the methanol synthesis reaction:



Values of the equilibrium constants of the reaction (I), calculated by Eq.(3) for different temperatures, are shown below. For their calculation, it was used the referenced data on the standard entropy of the reaction components (CO, H₂, CH₃OH) and their standard enthalpy formation [4]. Referenced data [4] were used also in other examples of this textbook.

As seen from Table 1, simplified calculation gives enough large *большие* errors at elevated temperatures in comparison with the "exact" calculation when temperature dependence of entropy and enthalpy is taking to account.

Table 1.

T, K	«Exact» calculation (equation (1))		Simplified calculation (equation (3))	
	$\ln K_p$	K_p, atm^{-2}	$\ln K_p$	K_p, atm^{-2}
298	10,1915	$2,67 \cdot 10^{+04}$	10,1915	$2,67 \cdot 10^{+04}$
300	9,9490	$2,09 \cdot 10^{+04}$	9,9477	$2,09 \cdot 10^{+04}$
400	0,6718	1,96	0,8645	$2,37 \cdot 10^{+00}$
500	-5,2476	$5,26 \cdot 10^{-03}$	-4,5853	$1,02 \cdot 10^{-02}$
600	-9,1989	$1,01 \cdot 10^{-04}$	-8,2186	$2,70 \cdot 10^{-04}$
700	-12,0887	$5,62 \cdot 10^{-06}$	-10,8138	$2,01 \cdot 10^{-05}$
800	-14,2152	$6,71 \cdot 10^{-07}$	-12,7602	$2,87 \cdot 10^{-06}$

900	-15,9481	1,19 10 ⁻⁰⁷	-14,2740	6,32 10 ⁻⁰⁷
1000	-17,3551	2,90 10 ⁻⁰⁸	-15,4851	1,88 10 ⁻⁰⁷

But, the question remains how to calculate equilibrium constants for arbitrary temperatures not only for tabulated ones. Below we describe the known procedure that allows resolving this problem.

1.2. Calculation equilibrium constant for arbitrary temperatures

Dependence of the reaction enthalpy on temperatures is expressed by the Kirchoff law:

$$\Delta H_T^o = \Delta H_o^o + \int_o^T \Delta C_p dT \quad (4)$$

and the entropy by

$$\Delta S_T^o = \int \frac{\Delta C_p}{T} dT \quad (5)$$

where ΔC_p is a change of heat capacity as a result of the reaction.

Dependence of the ΔC_p value on temperature can be expressed as follows. The widespread temperature dependence of heat capacity of individual substances is the equation:

$$C_p = a + bT + cT^2 \quad (6)$$

where a , b and c are empirical constants.

Accordingly, for a chemical reaction:

$$\Delta C_p = \Delta a + \Delta bT + \Delta cT^2 \quad (7)$$

Substitution Eq.(7) into Eq.(4) and (5) with their subsequent integration gives:

$$\Delta H_T^o = \Delta H_o^o + \Delta aT + \frac{\Delta b}{2}T^2 + \frac{\Delta c}{3}T^3 \quad (8)$$

$$\Delta S_T^o = \Delta a \ln T + \Delta bT + \frac{\Delta c}{2}T^2 + I' \quad (9)$$

(I' is integration constant)

Substitution Eq.(8) and Eq.(9) into Eq.(2) gives:

$$\ln K_p = -\frac{\Delta H_o^o}{RT} + \frac{\Delta a}{R} \ln T + \frac{\Delta b}{2R}T + \frac{\Delta c}{6R}T^2 + I \quad (10)$$

(I is equal to $I' - \Delta a/R$).

For calculation of an equilibrium constant, the numerical values of constants Δa , Δb , Δc , ΔH_o^o and I in Eq. (10) are needed. The following procedure for the constant finding, composed of the several stages, are used:

1. Calculation of coefficients Δa , Δb , Δc . Firstly, values of $\Delta C_{p,i}$ are calculated for the tabulated in [4] temperatures T_1 , T_2 , and T_3 . Then, the following system of algebraic equations are composed:

$$\begin{aligned} \Delta C_{p,1} &= \Delta a + \Delta bT_1 + \Delta cT_1^2 \\ \Delta C_{p,2} &= \Delta a + \Delta bT_2 + \Delta cT_2^2 \\ \Delta C_{p,3} &= \Delta a + \Delta bT_3 + \Delta cT_3^2 \end{aligned} \quad (11)$$

A solution of this system allows finding numerical values of Δa , Δb , Δc . For finding a solution, it is convenient to use determinates:

$$\Delta a = Det_1/Det; \Delta b = Det_2/Det; \Delta c = Det_3/Det,$$

where

$$Det = \begin{vmatrix} 1 & T_1 & T_1^2 & \Delta C_{p,1} \\ 1 & T_2 & T_2^2 & \Delta C_{p,2} \\ 1 & T_3 & T_3^2 & \Delta C_{p,3} \end{vmatrix}; Det_1 = \begin{vmatrix} T_1 & T_1^2 \\ T_2 & T_2^2 \\ T_3 & T_3^2 \end{vmatrix}; Det_2 = \begin{vmatrix} 1 & T_1^2 \\ 1 & T_2^2 \\ 1 & T_3^2 \end{vmatrix}; Det_3 = \begin{vmatrix} 1 & T_1 \\ 1 & T_2 \\ 1 & T_3 \end{vmatrix}$$

2. Calculation of ΔH_o^o . Substitution values ΔH_T^o (referenced data), Δa , Δb , Δc for each chosen temperature (T_1 , T_2 , T_3) into Eq.(8) gives equations:

$$\begin{aligned} \Delta H_{T_1}^o &= \Delta H_o^o + \Delta aT_1 + \frac{\Delta b}{2}T_1^2 + \frac{\Delta c}{3}T_1^3 \\ \Delta H_{T_2}^o &= \Delta H_o^o + \Delta aT_2 + \frac{\Delta b}{2}T_2^2 + \frac{\Delta c}{3}T_2^3 \\ \Delta H_{T_3}^o &= \Delta H_o^o + \Delta aT_3 + \frac{\Delta b}{2}T_3^2 + \frac{\Delta c}{3}T_3^3 \end{aligned} \quad (12)$$

Then, it is found ΔH_o^o for each temperature T_1 , T_2 , T_3 and the average value of the obtained ΔH_o^o values.

3. Calculation of constants I. The obtained values Δa , Δb , Δc , ΔH_o° and reference values of the equilibrium constants K_p for given temperatures are placed into Eq.(10), after that we have equations:

$$\begin{aligned} \ln K_{p,1} &= -\frac{\Delta H_o^\circ}{RT_1} + \frac{\Delta a}{R} \ln T_1 + \frac{\Delta b}{2R} T_1 + \frac{\Delta c}{6R} T_1^2 + I_1 \\ \ln K_{p,2} &= -\frac{\Delta H_o^\circ}{RT_2} + \frac{\Delta a}{R} \ln T_2 + \frac{\Delta b}{2R} T_2 + \frac{\Delta c}{6R} T_2^2 + I_2 \\ \ln K_{p,3} &= -\frac{\Delta H_o^\circ}{RT_3} + \frac{\Delta a}{R} \ln T_3 + \frac{\Delta b}{2R} T_3 + \frac{\Delta c}{6R} T_3^2 + I_3 \end{aligned} \quad (13)$$

Each equation is solved relatively to I_i , then, the average value of the obtained values I_i is found.

Substitution numerical values of all found coefficients to Eq.(10) gives an equation for the equilibrium constant as a function of a single variable which is temperature. Obtained equation allows calculating equilibrium constants for any temperature in the range of $T_1 - T_3$ or close to it.

Below, we give the example of using the described procedure for calculation of numerical values of coefficients in Eq.(10).

1.3. Example of calculation for the methanol synthesis reaction

The commercial reaction of the methanol synthesis proceeds by the overall stoichiometric equation:
 $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$ (I)

Table 2 lists the thermodynamic properties of the reaction participants [4].

Table 2. Thermodynamic properties of H_2 , CO , and CH_3OH

Substance	C_p° , cal/(mol K)			S° , cal/(mol K)			ΔH_f° , kcal/mol		
	500K	600K	700K	500K	600K	700K	500K	600K	700K
H_2	6.993	7.008	7.035	34.809	36.085	37.167	0	0	0
CO	7.12	7.28	7.45	50.93	52.24	53.38	-26.30	-26.33	-26.41
CH_3OH	14.22	16.02	17.62	63.58	66.33	68.92	-49.57	-50.21	-50.75

Using these data, the following reaction parameters are calculated:

$$\begin{aligned} \Delta C_p^\circ &= C_{p,\text{CH}_3\text{OH}}^\circ - C_{p,\text{CO}}^\circ - 2 C_{p,\text{H}_2}^\circ \\ \Delta S^\circ &= S_{\text{CH}_3\text{OH}}^\circ - S_{\text{CO}}^\circ - 2 S_{\text{H}_2}^\circ \\ \Delta H^\circ &= \Delta H_{f,\text{CH}_3\text{OH}}^\circ - \Delta H_{f,\text{CO}}^\circ - 2 \Delta H_{f,\text{H}_2}^\circ \end{aligned} \quad (14)$$

The calculated values, as well as the reaction equilibrium constants at different temperatures, are presented in Table 3.

Table 3. Thermodynamic parameters of the methanol synthesis reaction

T, K	ΔC_p° , cal/(mol K)	ΔS° , cal/(mol K)	ΔH° , cal/mol	K_p , atm ⁻²	$\ln K_p$
500	-6.886	-56.968	-23270	$5.26 \cdot 10^{-3}$	-2.2788
600	-5.276	-58.080	-23880	$1.01 \cdot 10^{-4}$	-3.9948
700	-3.900	-58.794	-24340	$5.63 \cdot 10^{-6}$	-5.2497

Substitution ΔC_p° values into Eq.(10) gives the equations:

$$\begin{aligned} -6.886 &= \Delta a + \Delta b \cdot 500 + \Delta c \cdot 500^2 \\ -5.276 &= \Delta a + \Delta b \cdot 600 + \Delta c \cdot 600^2 \\ -3.900 &= \Delta a + \Delta b \cdot 700 + \Delta c \cdot 700^2 \end{aligned} \quad (15)$$

Joint resolution of these equations gives: $\Delta a = -18.446$; $\Delta b = 0.02897$; $\Delta c = -1.17 \cdot 10^{-5}$.

Substitution of obtained numerical values Δa , Δb , Δc and ΔH° into Eq.(11) gives the following equation system:

$$\begin{aligned} -23270 &= \Delta H_o^\circ - 18.446 \cdot 500 + \frac{0.02897}{2} 500^2 - \frac{1.17 \cdot 10^{-5}}{3} 500^3 \\ -23880 &= \Delta H_o^\circ - 18.446 \cdot 600 + \frac{0.02897}{2} 600^2 - \frac{1.17 \cdot 10^{-5}}{3} 600^3 \\ -24340 &= \Delta H_o^\circ - 18.446 \cdot 700 + \frac{0.02897}{2} 700^2 - \frac{1.17 \cdot 10^{-5}}{3} 700^3 \end{aligned} \quad (16)$$

Solution of this system are: $\Delta H^\circ_{\text{o}}(500) = -17181$; $\Delta H^\circ_{\text{o}}(600) = -17185$; $\Delta H^\circ_{\text{o}}(700) = -17188$. Average value $\Delta H^\circ_{\text{o,aver}}$ is equal to -17184.

Substitution of values $\Delta H^\circ_{\text{o,сред}}$, Δa , Δb , Δc , $\ln K_p$ (Table 3) and $R = 1.9872$ cal/(mol K) in Eq.(13), gives: $I_1 = 31.7446$; $I_2 = 31.7473$; $I_3 = 31.7460$; average value 31.7459.

Finally, substitution values of all found coefficients into Eq.(10) gives the resultant dependence of the equilibrium constants of the methanol synthesis reaction on temperature:

$$\ln K_I = \frac{8647.5}{T} - 9.2824 \ln T + 7.2892 \cdot 10^{-3} T - 9.8128 \cdot 10^{-7} T^2 + 31.7459 \quad (17)$$

All noted above evaluations may be computerized as described in the next subsection.

1.4. Computer calculation equilibrium constants by Microsoft Excel

The evaluation of the coefficients in Eq.(10) with the subsequent calculation of the equilibrium constants K_p can be enough easy carried out in the programming environment of the *Microsoft Excel*.

The Excel file creation is described below for the methanol synthesis reaction in detail to be available even for beginners:

1. The chosen temperatures and referenced data for reaction participants are placed, for example, in the cells from A5 to J7 (A5:J7).
2. The cells B9:D11 contain formulas for calculation of the change of the reaction heat capacity, entropy and enthalpy according to the Eqs (14). For their evaluation, the formula =H5-E5-2*B5 is recorded to the cell B9, after that it is copied to the cells B9:D11.
3. The next step is an evaluation of the coefficients Δa , Δb and Δc according to Eqs. (15) with help of determinates Det, Det₁, Det₂ and Det₃ (see subsection 1.2). To form the determinates, the unities are recorded to the cells B13:B15; B17:B19; F17:F19; the formula =A5 is written to the cells C13, G13, G17 and then copied to C14:C15; G14:G15; G18:G19, respectively; the formula =A5^2 is written to the cells D13, H13, D17 and then copied to D14:D15; H14:H15; D18:D19, respectively; the formula =B9 is written to the cells F13, C17, H17 and then copied to F14:F15; C18:C19; H18:H19, respectively. The formulas for evaluation of the generated determinates =MDETERM(B13:D15); =MDETERM(F13:H15); =MDETERM(B17:D19); =МОПРЕД(F17:H19) are written to the cells C16, F16, B20, F20, respectively. As a result, the numerical values of the corresponding determinates appear in the cells C16, F16, B20, F20. Finally, the numerical values of coefficients Δa , Δb and Δc appear in the cells H16, D20, H20 after the formulas =F16/\$C\$16, =B20/\$C\$16, =F20/\$C\$16 were written to these cells.
4. The next step is the evaluation of the average values of $\Delta H^\circ_{\text{o,aver}}$ according to Eq. (16). To do it, the formula =D9-(\$H\$16*A5+\$D\$20/2*A5^2+\$H\$20/3*A5^3) is written to the cell C22. Copying this formula to the cells C23:C24 gives separate $\Delta H^\circ_{\text{o}}$ values. The average value of $\Delta H^\circ_{\text{o}}$ can be found in the cell C25 after the formula =AVERAGE(C22:C24) was written to this cell.
5. The coefficient I in Eq.(10) is calculated according to Eqs.(13). The formula =E9-(\$C\$25/A5+\$H\$16*LN(A5)+\$D\$20/2*A5+\$H\$20/6*A5^2)/\$G\$1 is written to the cell G22 and then it is copied to the cells G23: G24. The entry of the formula = AVERAGE (G22:G24) gives the desired value of coefficient I .

The cells A28, B28, C28, D28 and E28 contain formulas =-C25/G1, =H16/G1, =D20/2/G1, =H20/6/G1 and =G25, respectively; coefficient values in the following equation one may see on a computer monitor.

$$\ln K_I = \frac{8647.5}{T} - 9.2824 \ln T + 7.2892 \cdot 10^{-3} T - 9.8128 \cdot 10^{-7} T^2 + 31.7459$$

Table 4 may serve as verification of the created file version.

Table 4. View of the *Excel* file for calculation of the equilibrium constants of the methanol synthesis reaction

	A	B	C	D	E	F	G	H	I	J
1		CO + 2H2 = CH3OH			R(cal/(mol K)	1.9872				
2	Dimensions of Cpo, and So are cal/(mol K), ΔHfo is cal/mol									
3			H2			CO			CH3OH	
4	T, K	Cpo	So	ΔHfo	Cpo	So	ΔHfo	Cpo	So	ΔHfo
5	500	6.993	34.809	0	7.12	50.93	-26300	14.22	63.58	-49570
6	600	7.008	36.085	0	7.28	52.24	-26330	16.02	66.33	-50210
7	700	7.035	37.167	0	7.45	53.38	-26410	17.62	68.92	-50750
8	T, K	ΔCpo	ΔSo	ΔHo						
9	500	-6.89	-56.968	-23270						
10	600	-5.28	-58.080	-23880						
11	700	-3.90	-58.794	-24340						
12	Calculation Δa, Δb and Δc									
13		1	500	250000		-6.89	500	250000		
14	Det	1	600	360000	Det1	-5.28	600	360000		
15		1	700	490000		-3.90	700	490000		
16		Det =	2000000		Det1 =	-36892000	Δa =	-18.446		
17		1	-6.89	250000		1	500	-6.89		
18	Det2	1	-5.28	360000	Det3	1	600	-5.28		
19		1	-3.90	490000		1	700	-3.90		
20	Det2 =	57940,00	Δb =	0.02897	Det3 =	23.40	Δc =	-1.17E-05		
21	Calculation ΔH _o ^o					Calculation I constant				
22	ΔH _{oo} (500) =		-17181		I (500) =		31.7446			
23	ΔH _{oo} (600) =		-17185		I (600) =		31.7473			
24	ΔH _{oo} (700) =		-17188		I (700) =		31.7460			
25	ΔH _o ^o (average) =		-17184		I (average) =		31.7459			
26	Coefficients in the equation Kp = f(T)									
27	-ΔH _o ^o /R	Δa/R	Δb/2R	Δc/6R	I					
28	8647.5	-9.2824	7.2892E-03	-9.8128E-07	31.7459					

It is important that described file may be easily reconstructed for any other chemical reaction following the next actions:

- to put in the corresponding cells the referenced data for new reaction (as appropriate, it is easy to increase or decrease the number of reaction participants);
- to reprogram formulas for ΔC_p^o , ΔS^o and ΔH_o evaluations in accordance with the stoichiometric equation of new reaction.
- the rest of the file remains invariable thus the transition to the new reaction may be easily done that is the great merit of the proposed way of calculation.

Let us consider the transformation of the file for the reaction of water shift:



The upper part of the new file is shown in Table 5.

The thermodynamic referenced data for H₂, CO, CO₂, and H₂O are placed to the B5:M7 cells, the formula =H5+B5-E5-K5 is placed to the B9 cell, after that, it is copied to the B9:D11 cells. As a result, we obtain the following values coefficients in Eq.(10) for the water shift reaction (II):

$-\Delta H_o^o/R$	$\Delta a/R$	$\Delta b/2R$	$\Delta c/6R$	I
4990,7	-0,5193	2,3878 10^{-3}	-5,3677 10^{-7}	-2,9441

The equation for the equilibrium constant as a function of temperature is as follows:

$$\ln K_{II} = \frac{4990,7}{T} - 0,5193 \ln T + 2,3878 \cdot 10^{-3} T - 5,3677 \cdot 10^{-7} T^2 - 2,9441 \quad (21)$$

For one more reaction which we use below



the equation for the equilibrium constant may be obtained by the same way:

$$\ln K_{III} = \frac{3656,8}{T} - 8,7631 \ln T + 4,9014 \cdot 10^{-3} T - 4,4451 \cdot 10^{-7} T^2 + 34,6900 \quad (22)$$

(dimension of K_{III} is atm⁻²).

2. Calculation of equilibrium composition of the gas-phase chemical reactions

Let's consider in detail the calculation of the equilibrium composition of a reaction mixture for the For наглядности рассмотрим детально calculation равновесного состава реакционной смеси for concrete reaction systems.

2.1. Calculation of equilibrium composition for methanol synthesis process

Conversion of synthesis gas to methanol over commercial Cu-containing catalysts proceeds by quite an unusual reaction scheme. Methanol is generated directly not from CO, but as a result of the CO₂ hydrogenation:



Therefore, initial reaction mixture must contain some amount of CO₂. Its consumption is compensated by the water gas shift:



Sum of the Eq.(II) and Eq.(III) is the overall chemical equation of the methanol synthesis process (Eq.(I)). But, the proper calculation of the equilibrium reaction mixtures is necessary to realize by the Eqs.(II, III),

In the equilibrium state at constant pressure, the equations for constant equilibrium may be written as:

$$K_{II} = \frac{P_{\text{CO}_2, \text{eq}} P_{\text{H}_2, \text{eq}}}{P_{\text{CO}, \text{eq}} P_{\text{H}_2\text{O}, \text{eq}}} = \frac{m_{\text{CO}_2, \text{eq}} m_{\text{H}_2, \text{eq}}}{m_{\text{CO}, \text{eq}} m_{\text{H}_2\text{O}, \text{eq}}}$$

$$K_{III} = \frac{P_{\text{CH}_3\text{OH}, \text{eq}} P_{\text{H}_2\text{O}, \text{eq}}}{P_{\text{CO}_2, \text{eq}} P_{\text{H}_2, \text{eq}}^3} = \frac{m_{\text{CH}_3\text{OH}, \text{eq}} m_{\text{H}_2\text{O}, \text{eq}}}{P^2 m_{\text{CO}_2, \text{eq}} m_{\text{H}_2, \text{eq}}^3}$$

where P is total pressure; $P_{i, \text{eq}}$ is equilibrium partial pressure of the reaction component, $m_{i, \text{eq}}$ is equilibrium mole fraction of the component.

Below, we consider two methods of the calculation of equilibrium composition of the reaction mixture at given initial conditions.

2.1.1. Method 1 of an equilibrium state calculation

The equilibrium composition for the concerned totality of the chemical equations can be можно determined by the solution of the following system of the algebraic equations:

$$K_2 = \frac{m_{\text{CO}_2} m_{\text{H}_2}}{m_{\text{CO}} m_{\text{H}_2\text{O}}} \quad (23)$$

$$K_3 = \frac{m_{\text{CH}_3\text{OH}} m_{\text{H}_2\text{O}}}{P^2 m_{\text{CO}_2} m_{\text{H}_2}^3} \quad (24)$$

$$b_m = m_{\text{CO}_2} + m_{\text{CO}} + m_{\text{H}_2} + m_{\text{CH}_3\text{OH}} + m_{\text{H}_2\text{O}} + m_i = 1 \quad (25)$$

$$b_C = m_{\text{CO}_2, o} + m_{\text{CO}, o} + m_{\text{CH}_3\text{OH}, o} = (m_{\text{CO}_2} + m_{\text{CO}} + m_{\text{CH}_3\text{OH}}) \alpha \quad (26)$$

$$b_O = 2 m_{\text{CO}_2, o} + m_{\text{CO}, o} + m_{\text{CH}_3\text{OH}, o} + m_{\text{H}_2\text{O}, o} = (2 m_{\text{CO}_2} + m_{\text{CO}} + m_{\text{CH}_3\text{OH}} + m_{\text{H}_2\text{O}}) \alpha \quad (27)$$

$$b_H = 2 m_{\text{H}_2\text{O}, o} + 2 m_{\text{H}_2, o} + 4 m_{\text{CH}_3\text{OH}, o} = (2 m_{\text{H}_2\text{O}} + 2 m_{\text{H}_2} + 4 m_{\text{CH}_3\text{OH}}) \alpha \quad (28)$$

$$b_i = m_{i, o} = m_i \alpha \quad (29)$$

Here m_i is mole fractions in the equilibrium state; indexes "o" correspond to the initial mole fractions.

Equations b_m , b_i , b_C , b_O , and b_H are the balance equations on the mole fractions of the reaction participants; an inert gas; atoms of carbon, oxygen and hydrogen, respectively. Parameter α designates the ratio of a current gas mixture volume to volume in the initial state (when a total number of the molecules do not change due to the reaction, $\alpha = 1$; at decreasing the molecule $\alpha < 1$, at increasing $\alpha > 1$).

The current mole fractions (6 in all) and α are the variable quantities in equations (23)-(29). The calculation of the mentioned variables can be done with help of the *Mathematica* software (*Wolfram Research, Inc.*).

Firstly, we make some preliminary remarks on the program compilation within the *Mathematica* framework:

- The built-in *Mathematica* commands begin from capital letters, also the commands contain square and curly brackets. Therefore, the own indications should be begun from the lowercase letters, and round brackets should be used in the self-made formulas.
- Any comments may be made as (**comment**).

Now, we consider the program for solution of the system (23-29) in the *Mathematica* framework. After *Mathematica* is launched, we write in the first cell of the program file the following initial parameters:

```
tC = 200; tK = tC + 273; p = 50; mCO2o = 0.1;
mCOo = 0.28;
mH2o = 0.58;
mCH3OHo = 0;
mH2Oo = 0;
mlo = 1-mCH3OHo - mCO2o - mCOo - mH2o - mH2Oo;
```

Here tC is temperature, °C; tK is temperature, K; p is total pressure, atm.

We use here and below mainly *InputForm* of the cells. It is the simplest form, besides, in this case, the cell content can be directly copied from this textbook file to the *Mathematica* file.

For calculation, it is necessary to select the cell and to press Shift+Enter.

Then, we show the formulas for calculation natural logarithms of the equilibrium constants according to Eq.(21) and Eq.(22), and formulas for conversion of logarithms to the numerical values of equilibrium constants:

```
Ink2=N[4990.7/tK-0.51931 Log[tK] +2.3878 10^-3 tK - 5.3677 10^-7 tK^2 - 2.9441];
Ink3=N[3656.8/tK-8.7631 Log[tK] +4.9014 10^-3 tK - 4.4451 10^-7 tK^2 +34.6900];
k2 = N[E^Ink2];
k3 = N[E^Ink3];
```

Some comments to writing the formulas are as follows:

- a multiplication sign may be writing as asterisk (*) as well it may be designated by a gap;
- Command Log[x] evaluates natural logarithm of x while command Log[10,x] evaluates decimal logarithm; основанием e (), команда for десятичного логарифма имеет вид; E is command for entry of the e number (2.71828);
- If the semicolon is placed at the end of a command, the result of an evaluation is not visible. If the semicolon is absent, we can see the result of an evaluation.

Then, we write the command for calculation of the numerical values of the variables in the equilibrium state, namely, mole fractions and the α coefficient, denoted here as **a**:

```
NSolve[{k2==(mCO2 mH2)/(mCO mH2O), k3==(mCH3OH mH2O)/(p^2 mCO2 mH2^3),
mCH3OH+mCO+mCO2+mH2+mH2O+mI==1,
mCO2o+mCOo+mCH3OHo==(mCO2+mCO+mCH3OH) a, mCOo+mH2Oo+2
mCO2o+mCH3OHo==(mCO+mH2O+2 mCO2+mCH3OH) a, 2 mH2Oo+2 mH2o+4
mCH3OHo==(2 mH2O+2 mH2+4 mCH3OH) a, mlo==ml a},
{mCO2,mH2,mCH3OH,mH2O,mCO,mI,a}]
```

This command contains Eqs.(23)-(29), adopted to *Mathematica*, the initial parameters and the calculated variables. We do not placed semicolon at the end of the command, thus, we can see the next results of calculation:

```
{mCO2 → 0.437493 +0.101949 ™, mH2 → 1.14149 +0.538229 ™, mCH3OH → -
0.215382-0.419501 ™, mH2O → -0.380569-0.185849 ™, mCO → -0.00580096-
0.0012684 ™, mI → 0.0227694 -0.0335601 ™, av → 0.553756 +0.816187 ™},
{mCO2 → 0.437493 -0.101949 ™, mH2 → 1.14149 -0.538229 ™, mCH3OH → -
0.215382+0.419501 ™, mH2O → -0.380569+0.185849 ™, mCO → -
0.00580096+0.0012684 ™, mI → 0.0227694 +0.0335601 ™, av → 0.553756 -
0.816187 ™},
{mCO2 → 0.174383, mH2 → 0.258491, mCH3OH → 0.380665, mH2O → 0.00175011,
mCO → 0.114258, mI → 0.0704532, av → 0.567753},
{mCO2 → -0.440087, mH2 → -3.48958, mCH3OH → 3.39374, mH2O → 1.21884,
mCO → 0.00558942, mI → 0.311499, av → 0.128411},
{mCO2 → 0.26158 -0.0706346 ™, mH2 → -0.10928+0.300889 ™, mCH3OH → 0.818134
-0.357234 ™, mH2O → 0.00204702 -0.000812188 ™, mCO → -0.077932+0.156371
™, mI → 0.105451 -0.0285787 ™, av → 0.353369 +0.0957684 ™},
```

{mCO₂ → 0.26158 + 0.0706346 TM, mH₂ → -0.10928 - 0.300889 TM, mCH₃OH → 0.818134 + 0.357234 TM, mH₂O → 0.00204702 + 0.000812188 TM, mCO → -0.077932 - 0.156371 TM, mI → 0.105451 + 0.0285787 TM, a_v → 0.353369 - 0.0957684 TM}}

The sole solution that satisfy a physical meaning is marked above by the bold font. Indeed, all mole fractions are in the range from 0 to 1, and their sum is equal to 1.

2.1.2. Method 2 of an equilibrium state calculation

Below, we consider another method of an equilibrium composition finding. This method is universal and suitable for any number and any complexity of chemical equations.

Let us imagine that some chemical reactions occur over a heterogeneous catalyst in an ideal plug-flow reactor. The concept of the proposed method of the equilibrium composition calculation consists of the following considerations. It is made up the system of the differential equations; the solution of this system gives the dependence of the reaction mixture composition on, for example, a catalyst mass. At some catalyst quantity, the reactions come to a practically equilibrium state at the definite composition of the reaction mixture. Thus, we obtain the solution of the assigned task.

Below, we consider, for determinacy, the composition of the differential equations for reactions (II) and (III).

Let us take the following denominations:

P is total pressure and P_i are component partial pressures;

m_i are component mole fractions;

F is a total feed of reaction mixture, mol/time;

F_i is feed of reaction component, mol/time;

t is time;

g is catalyst mass.

r_j are reaction rates, mol/(time · catalyst mass).

$\nu_i^{(j)}$ is the stoichiometric coefficient of i -component in j -reaction.

For the steady-state conditions in a plug-flow reactor, we can write:

$$r_2 = \frac{dn_i^{(2)}}{dg} \frac{1}{t} \frac{1}{\nu_i^{(2)}} = \frac{dF_i^{(2)}}{dg} \frac{1}{\nu_i^{(2)}} \quad (30)$$

$$r_3 = \frac{dn_i^{(3)}}{dg} \frac{1}{t} \frac{1}{\nu_i^{(3)}} = \frac{dF_i^{(3)}}{dg} \frac{1}{\nu_i^{(3)}} \quad (31)$$

where upper indexes are accepted reaction numbers).

Taking these equations into account, one may receive the following equations for each separate component:

$$\frac{dF_{CO_2}}{dg} = \frac{dF_{CO_2}^{(2)}}{dg} + \frac{dF_{CO_2}^{(3)}}{dg} = r_2 - r_3 \quad (32)$$

$$\frac{dF_{H_2}}{dg} = \frac{dF_{H_2}^{(2)}}{dg} + \frac{dF_{H_2}^{(3)}}{dg} = r_2 - 3 r_3 \quad (33)$$

$$\frac{dF_{CH_3OH}}{dg} = \frac{dF_{CH_3OH}^{(3)}}{dg} = r_3 \quad (34)$$

$$\frac{dF_{H_2O}}{dg} = \frac{dF_{H_2O}^{(2)}}{dg} + \frac{dF_{H_2O}^{(3)}}{dg} = -r_2 + r_3 \quad (35)$$

$$\frac{dF_{CO}}{dg} = \frac{dF_{CO}^{(2)}}{dg} = -r_2 \quad (36)$$

$$\frac{dF_{inert}}{dg} = 0 \quad (37)$$

It should be noted that the feed of an inert gas is constant because it is not formed or consumed. For reactions carried out with a change of the total molecules number (in our case, the reaction (III), it is necessary to take into account also a change of a total feed due to a reaction. In our case, this change is expressed as:

$$\frac{dF}{dg} = \sum \frac{dF_i}{dg} = -2 r_3 \quad (38)$$

Taking into account that

$$F_i = F m_i \quad (39)$$

We obtain:

$$\frac{dF_i}{dg} = \frac{d(F m_i)}{dg} = m_i \frac{dF}{dg} + F \frac{dm_i}{dg} = m_i (-2 r_3) + F \frac{dm_i}{dg} \quad (40)$$

and

$$\frac{dm_i}{dg} = \frac{1}{F} \left(\frac{dF_i}{dg} + m_i 2 r_3 \right) \quad (41)$$

Using Eqs.(32)-(37), we obtain finally the system of differential equations:

$$\frac{dm_{CO_2}}{dg} = \frac{r_2 - r_3 + m_{CO_2} 2 r_3}{F} \quad (42)$$

$$\frac{dm_{H_2}}{dg} = \frac{r_2 - 3 r_3 + m_{H_2} 2 r_3}{F} \quad (43)$$

$$\frac{dm_{CH_3OH}}{dg} = \frac{r_3 + m_{CH_3OH} 2 r_3}{F} \quad (44)$$

$$\frac{dm_{H_2O}}{dg} = \frac{-r_2 + r_3 + m_{H_2O} 2 r_3}{F} \quad (45)$$

$$\frac{dm_{CO}}{dg} = \frac{-r_2 + m_{CO} 2 r_3}{F} \quad (46)$$

$$\frac{dm_{inert}}{dg} = \frac{m_{inert} 2 r_3}{F} \quad (47)$$

$$\frac{dF}{dg} = -2 r_3 \quad (48)$$

The numerical solution of the system (42)-48) can be made with help of the *Mathematica* program.

Below, we describe in detail how to receive the solution using the *Mathematica*.

The given initial conditions can be written as

tC=200;
tK = tC+273;
p=50;
fo =0.1;
mCO2o=0.10;
mCOo=0.28;
mH2o=0.58;
mCH3OHo=0;
mH2Oo=0;
mlo=1-mCO2o-mCOo-mH2o-mCH3OHo-mH2Oo;

Next, we write the formulas for calculation of the equilibrium constants:

lnk2= N[4990.7/tK-0.5193 Log[tK]+2.3878 10^-3 tK-5.3677 10^-7 tK^2-2.9441];
lnk3=N[3656.8/tK-8.7631 Log[tK]+4.9014 10^-3 tK-4.4451 10^-7 tK^2+34.6900];
k2=N[E^lnk2];
k3=N[E^lnk3];

To set the dependence of the reaction rates on the reaction component concentrations, the Guldberg-Waage law of mass action can be used. Basing on this law with some simplification, we can write

$$r_2 = k_{2+} m_{CO} m_{H_2O} - k_{2-} m_{CO_2} m_{H_2}$$

$$r_3 = k_{3+} P^2 m_{CO_2} m_{H_2}^3 - k_{3-} m_{CH_3OH} m_{H_2O}$$

where k_{2+} and k_{3+} are the rate constants of the direct reactions, k_{2-} and k_{3-} are the rate constants of the reverse reactions. Between rate constants and equilibrium constants must be relation:

$$K_2 = \frac{k_{2+}}{k_{2-}}; K_3 = \frac{k_{3+}}{k_{3-}}$$

To reduce equations, let us accept that the rate constants of the reverse reactions are equal to 1, then numerical values of the rate constants of the direct reactions will be equal to the corresponding equilibrium constants. Taking this into account, the equations for the reaction rates in *Mathematica* format can be written as

r2 = k2 mCO[g] mH2O[g]- mCO2[g] mH2[g];
r3 = k3 mCO2[g] p^2* mH2[g]^3 - mCH3OH[g] mH2O[g];

Mole fractions are introduced as **mi[g]**. This means that mole fractions are a function of the catalyst mass **g** variable.

To the next cell, we introduce the fixed catalyst mass **gt**. The **gt** value is arbitrary, it should be sufficient for the reaction system transition to an equilibrium state.

gt=10000;

The next cell is aimed for the solution of the above system of differential equations.

```
sol=NDSolve[{mCO2'[g]==(r2-r3+mCO2[g] 2 r3)/f[g], mH2'[g]==(r2-3 r3+mH2[g] 2 r3)/f[g],
mCH3OH'[g]==(r3+mCH3OH[g] 2 r3)/f[g], mH2O'[g]==(-r2+r3+mH2O[g] 2 r3)/f[g],
mCO'[g]==(-r2+mCO[g] 2 r3)/f[g], ml'[g]==(ml[g] 2 r3)/f[g], f'[g]==- 2 r3,
mCO2[0]==mCO2o, mH2[0]==mH2o, mCH3OH[0]==mCH3OHo, mH2O[0]==mH2Oo,
mCO[0]==mCOo, ml[0]==mlo, f[0]==fo}, {mCO2, mH2, mCH3OH, mH2O, mCO, ml, f},
{g, 0, gt}];
```

Some explanations of the last cell entries are as follows:

- **mi'[g]** are derivatives of the component mole fractions individual of g;
- **f'[g]** is derivatives of the total feed of g;
- **mi[0] == mio** are the formulas which define the initial conditions with numerical values given in the first cell;
- **{mCO2, mH2, mCH3OH, mH2O, mCO, mi, f}** is the list of the used variables which are functions of g;
- **{g, 0, gt}** is independent variable, its initial and finite quantity, respectively.

Now, we can find the finite values of the component mole fractions, which are reached at given catalyst mass **gt**. To do it, the following cell is used

```
mCO2g=mCO2[gt]/.sol
mH2g=mH2[gt]/.sol
mCH3OHg=mCH3OH[gt]/.sol
mH2Og=mH2O[gt]/.sol
mCOg=mCO[gt]/.sol
mlg=ml[gt]/.sol
fg=f[gt]/.sol
```

The result of calculation appears at the display in out cells after pressing Shift+Enter:

```
{0.174383}
{0.258491}
{0.380665}
{0.00175011}
{0.114258}
{0.0704532}
{0.0567753}
```

These are the values of the mole fractions of the CO₂, H₂, CH₃OH, H₂O, CO and inert gas, respectively, and the total feed at the reactor outlet.

The sum of all mole fractions

```
mCO2g+mH2g+mCH3OHg+mH2Og+mCOg+mlg
```

are equal to 1.

```
{1.}
```

This confirms the calculation validity.

The following cell is used for test whether obtained values of the mole fractions are equilibrium:

```
k2/((mCO2g mH2g)/(mCOg mH2Og))
k3/((mCH3OHg mH2Og)/(p^2 mCO2g mH2g^3))
```

The calculation of this cell gives:

```
{1.}
{1.}
```

Thus, the reaction system reached the thermodynamic equilibrium.

The figure at the end of the present subsection demonstrates the image of the *Mathematica* file after its evaluation.

The results obtained by the method 1 and method 2 are the same as it may be verified. In contrast to the first algebraic method 1, the proposed method 2 allows easy obtain just one solution. Besides, the method 2 give the possibility to calculate not only the equilibrium state but also to perform the reaction simulating if the kinetic equations of the reactions are known. The examples of such simulating will be given in the following sections of the present textbook.

```

In[1]:= tC = 200; tK = tC + 273; p = 50; fo = 0.1;
mCO2o = 0.10; mCOo = 0.28; mH2o = 0.58;
mCH3OHo = 0; mH2Oo = 0;
mIo = 1 - mCO2o - mCOo - mH2o - mCH3OHo - mH2Oo;

In[5]:= lnk2 = N[4990.7 / tK - 0.5193 Log[tK] + 2.3878 × 10^-3 tK - 5.3677 × 10^-7 tK^2 - 2.9441];
lnk3 = N[3656.8 / tK - 8.7631 Log[tK] + 4.9014 × 10^-3 tK - 4.4451 × 10^-7 tK^2 + 34.6900];
k2 = N[E^lnk2]; k3 = N[E^lnk3];

In[8]:= r2 = k2 mCO[g] mH2O[g] - mCO2[g] mH2[g];
r3 = k3 mCO2[g] p^2 + mH2[g]^3 - mCH3OH[g] mH2O[g];

In[10]:= gt = 10000;

In[11]:= sol = NDSolve[{mCO2'[g] == (r2 - r3 + mCO2[g]^2 r3) / f[g], mH2'[g] == (r2 - 3 r3 + mH2[g]^2 r3) / f[g],
mCH3OH'[g] == (r3 + mCH3OH[g]^2 r3) / f[g], mH2O'[g] == (-r2 + r3 + mH2O[g]^2 r3) / f[g],
mCO'[g] == (-r2 + mCO[g]^2 r3) / f[g], mI'[g] == (mI[g]^2 r3) / f[g], f'[g] == -2 r3, mCO2[0] == mCO2o,
mH2[0] == mH2o, mCH3OH[0] == mCH3OHo, mH2O[0] == mH2Oo, mCO[0] == mCOo, mI[0] == mIo, f[0] == fo},
{mCO2, mH2, mCH3OH, mH2O, mCO, mI, f}, {g, 0, gt}];

In[12]:= mCO2g = mCO2[gt] /. sol
mH2g = mH2[gt] /. sol
mCH3OHg = mCH3OH[gt] /. sol
mH2Og = mH2O[gt] /. sol
mCOg = mCO[gt] /. sol
mIg = mI[gt] /. sol
fg = f[gt] /. sol

Out[12]= {0.174383}
Out[13]= {0.258491}
Out[14]= {0.380665}
Out[15]= {0.00175011}
Out[16]= {0.114258}
Out[17]= {0.0704532}
Out[18]= {0.0567753}

In[19]:= mCO2g + mH2g + mCH3OHg + mH2Og + mCOg + mIg
Out[19]= {1.}

In[20]:= k2 / ((mCO2g mH2g) / (mCOg mH2Og))
k3 / ((mCH3OHg mH2Og) / (p^2 mCO2g mH2g^3))
Out[20]= {1.}
Out[21]= {1.}

```

2.2. Calculation of equilibrium composition for ethanol steam reforming

As one more example, let us consider the calculation of the equilibrium concentrations for the ethanol steam reforming process which is a promising way of the hydrogen production from the renewable source:



The catalytic process of the ethanol reforming includes usually the following main reactions:



and some side reactions:





Table 6 shows numerical values of the coefficients in Eq.(10) for the mentioned reactions. The coefficients calculated by the procedure described in the subsections 1.3 and 1.4 with help of the reference data for 500, 700 and 900 K (see Appendix in this textbook).

Table 6. Coefficients in Eq.(10) for reactions (I)-(V).

№	$\Delta H_0^\circ/R$	$\Delta a/R$	$\Delta b/2R$	$\Delta c/6R$	I
I	7403.1	3.6499	$-3.0747 \cdot 10^{-03}$	$4.5290 \cdot 10^{-07}$	-9.2040
II	19733.0	11.9026	$-9.4756 \cdot 10^{-03}$	1.243410^{-06}	-34.1611
III	-5046.6	-0.2243	$1.8820 \cdot 10^{-03}$	$-3.9629 \cdot 10^{-07}$	-4.6727
IV	-2814.4	2.9225	$-4.0383 \cdot 10^{-03}$	$7.3386 \cdot 10^{-07}$	-2.8618
V	22547.4	8.9801	$-5.4373 \cdot 10^{-03}$	$5.0951 \cdot 10^{-07}$	-31.2993

As for the process of the methanol synthesis, we consider the calculation of an equilibrium state by two methods.

2.2.1. Method 1 of an equilibrium state calculation

Equilibrium composition for the considered aggregate of the chemical equations (I)-(V) can be found by the solution of the following algebraic equation system:

$$K_1 = \frac{P m_{Ac} m_{H_2}}{m_{Et}} \quad (49)$$

$$K_2 = \frac{P^3 m_{CO}^2 m_{H_2}^3}{m_{Ac} m_{H_2O}} \quad (50)$$

$$K_3 = \frac{m_{CO} m_{H_2O}}{m_{CO_2} m_{H_2}} \quad (51)$$

$$K_4 = \frac{P m_{CO} m_{CH_4}}{m_{Ac}} \quad (52)$$

$$b_m = m_{Et} + m_{H_2O} + m_{Ac} + m_{H_2} + m_{CO} + m_{CO_2} + m_{CH_4} + m_I = 1 \quad (53)$$

$$b_C = 2 m_{Et,o} + 2 m_{Ac,o} + m_{CO,o} + m_{CO_2,o} + m_{CH_4,o} = (2 m_{Et} + 2 m_{Ac} + m_{CO} + m_{CO_2} + m_{CH_4}) \alpha \quad (54)$$

$$b_O = m_{Et,o} + m_{H_2O,o} + m_{Ac,o} + m_{CO,o} + 2 m_{CO_2,o} = (m_{Et} + m_{H_2O} + m_{Ac} + m_{CO} + 2 m_{CO_2}) \alpha \quad (55)$$

$$b_H = 6 m_{Et,o} + 2 m_{H_2O,o} + 4 m_{Ac,o} + 2 m_{H_2,o} + 4 m_{CH_4,o} = (6 m_{Et} + 2 m_{H_2O} + 4 m_{Ac} + 2 m_{H_2} + 4 m_{CH_4}) \alpha \quad (56)$$

$$b_I = m_{I,o} = m_I \alpha \quad (57)$$

Above, we do not take into account the equation of the equilibrium constant of the reaction (V) because this reaction is not independent (the chemical equation of the reaction (V) can be obtained by the algebraic subtraction of reaction (IV) from reaction (II)).

Equations b_m , b_i , b_C , b_O , and b_H are the balance equations of the reaction mixture components; atoms of carbon, oxygen, hydrogen and inert gas, respectively; indexes "o" correspond to the initial mole fractions; parameter α designates the ratio of a current gas mixture volume to volume in the initial state (when total number of the molecules do not change due to reaction, $\alpha = 1$; at decreasing the molecule $\alpha < 1$, at increasing $\alpha > 1$).

The current mole fractions and α are the variable quantities in equations (49)-(57). The calculation of these variables will be done by the *Mathematica* program. The first cell of the program file contains the chosen initial parameters:

```
tC =300;
tK = tC + 273;
p = 1;
mEto = 0.12;
mH2Oo=0.4;
```

Thank You for previewing this eBook

You can read the full version of this eBook in different formats:

- HTML (Free /Available to everyone)
- PDF / TXT (Available to V.I.P. members. Free Standard members can access up to 5 PDF/TXT eBooks per month each month)
- Epub & Mobipocket (Exclusive to V.I.P. members)

To download this full book, simply select the format you desire below

