KINETICS OF THE OXIDATIVE DIMERIZATION REACTION OF METHANE

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Abstract

Oxidative dimerization of methane is one of the promising methods for synthesizing products of the petrochemical industry from natural gas, the main alternative to hydrocarbon raw materials. Currently, the demand for petrochemical products is increasing worldwide. The main demand is strong against vinyl chloride, polyethene, ethylene oxide, vinyl acetate, lavsan, etc. The main raw material for all the above-mentioned substances is ethylene. Currently, ethylene is mainly produced by the thermal decomposition of gasoline. The dynamic growth of demand for motor fuels is pushing to find another innovative way to obtain the main organic synthesis product. One such innovative method is the catalytic dimerization of methane to ethylene.

Keywords: synthesis of industrial products, catalytic dimerization, methane, dynamic growth, catalyst, X-ray phase analysis.
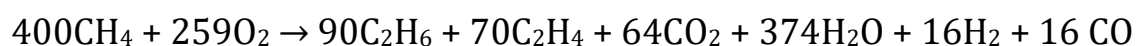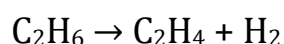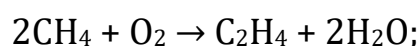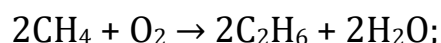
Introduction

Currently, ethylene extraction from methane is not established. The main reason for this is that the equipment for the process is not equipped and the optimal mode is not selected. It is necessary to study the kinetic laws of the reaction transition to determine the appropriate mode and equip the devices. Several works have been published [1-4] on the catalytic oxidative transformation of methane, and various absorbed catalysts have been proposed for the production of ethylene and ethane from methane.

The peculiarity of the methane oxidation condensation reaction is that in all known catalysts the reaction takes place at a high temperature and the process is strongly exothermic. In addition, the CH_4+O_2 mixture is highly explosive. At the same time, the activity and selectivity of catalysts are low.

In addition, the kinetics of the methane dimerization reaction in the catalysts of all studied literature $Bi_2O_3 \cdot 9\%$ K_2CO_3/Al_2O_3; 34% PbO/Al_2O_3; 4% $Na_2MoO_4*10\%Mn-O/SiO_2$ has not been fully studied without taking into account the processes involving catalysts. In the reactions with the mentioned catalysts, formal rank equations were used for the kinetic expression of the process. In all works, ethylene was obtained as the target product [5-9].

The formation of the target products of the methane dimerization reaction can be expressed by the following general equations:

$2CH_4 + O_2 \rightarrow 2C_2H_6 + 2H_2O$;

$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$;

$C_2H_6 \rightarrow C_2H_4 + H_2$

$400CH_4 + 259O_2 \rightarrow 90C_2H_6 + 70C_2H_4 + 64CO_2 + 374H_2O + 16H_2 + 16\ CO$

In this process, CO_2, CO and a small amount of C_3-C_4-hydrocarbons are formed as by-products.

It is known from the literature that catalysts containing oxides of Mn, Mo, Zr and rare earth elements (basic metals) have high catalytic activity for this process [10-16].

Materials and Methods

The catalytic activity of the catalyst was studied in a flow differential quartz reactor (P = 0.1 MPa, V_{cat} = 0.5 ml ÷ 2 ml, CH_4:O_2 = 2 ÷ 4, contact time 0.1-0.09 sec) in the temperature range 750-850 ℃.

Before and after the catalytic test, the spatial composition of the catalyst was determined by the X-ray phase analysis method with CuKa, λ=0.154187 nm (database: PCPDFWIN and POWDER CELL 2.4) radiation on a Shimadzu XRD-6000 diffractometer.

The morphology of the catalysts was studied using wave electron microscopy (ZEM) at Vegall LMU (Czech Republic). Also, the porous structure was established based on the analysis of the adsorption curves obtained by the method of chemisorption of nitrogen.

The surface area of the catalytic system S_{sol} was determined by the BET method, and the size of the micro- and mesopores was determined by the BJH method.

The study of the catalytic process of methane dimerization was carried out using the installation, the scheme of which is shown in Figure 1. The installation included a flow-type reactor from a quartz tube 650 mm long and 11 mm in diameter, partially filled with granular $(Na_2MoO_4)_x \cdot (Mn_2O_3)_y \cdot (ZrO_2)_z$ a catalyst with a grain size of 0.25-0.5 mm.

The gas mixture consisting of methane, oxygen and argon was supplied to the reactor inlet and contacted with a catalyst heated to 750-850 °C. The volume ratio of the ingredients of the $CH_4:O_2:Ar$ gas mixture was varied.
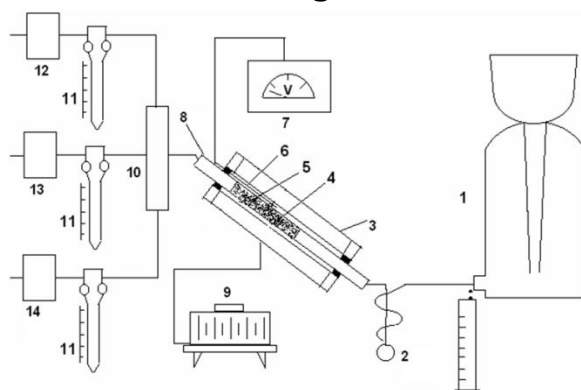
1-gasometer; 2-receiver; 3-tube furnace; 4-catalyst; 5-nozzle; 6-thermocouple; 7-voltmeter; 8 quartz reactor; 9-autotransformer; 10-displacer; 11-rheometer; 12-source of methane; 13-compressor; 14-source of inert gas (helium).

Figure 1. Scheme of a laboratory setup for oxidative dimerization of methane

The analysis of the gas mixture at the inlet and outlet of the reactor was carried out by the gas chromatographic method using gas chromatographs of the Gazokhrom 3101 and Tsvet 100, model 105 brands with thermal catalytic (TC) and thermally conductive (TCD) detectors, respectively. A steel chromatographic column 100 cm long and 0.3 cm in diameter was filled with activated carbon and was thermostated at 100 °C. Highly pure argon with a flow rate of 35 cm³/min was used as the carrier gas. The chromatograph was calibrated using an artificial model mixture, the composition of which was as close as possible to the composition of the natural gas used in the experiment.

Gas chromatographic studies have shown that the qualitative composition of gas mixtures at the inlet and outlet of the reactor contains methane, nitrogen, and lower saturated and unsaturated hydrocarbons. A typical chromatogram of the reaction mixture is shown in Figure 2.
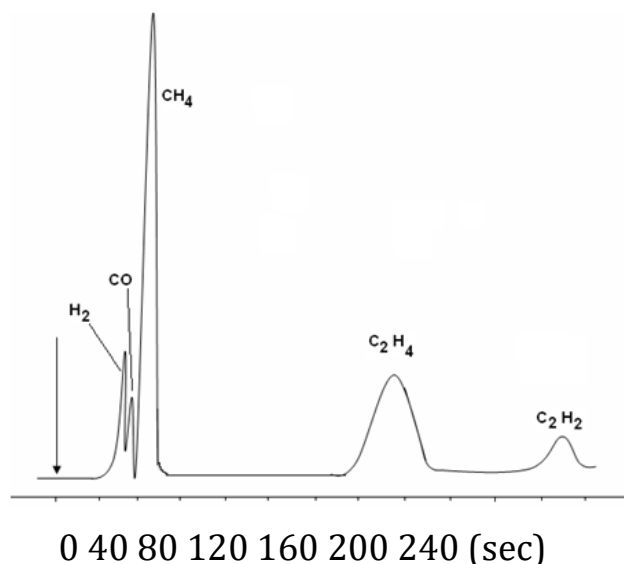

0 40 80 120 160 200 240 (sec)

Figure 2. Typical chromatogram of the reaction mixture obtained under the selected conditions.

To quantitatively determine the components of the gas mixture obtained as a result of the catalytic reaction, the method of absolute calibration (calibration) was applied and correction factors for the thermal conductivity detector (TCD) were established.

For this purpose, for each component of the mixture, a graph of the dependence of the area of the chromatographic peak (S) on the volume (V) of the gaseous substance was plotted [12]. Based on these calculations, a correction factor was established for each component. The volume concentration of each component in the sample was calculated using the formulas:

$$V_i = \frac{k_i S_i}{V} \cdot 100\% \text{ and } k_i = \frac{V_i}{S_i},$$

where V_i - the volume of the *i-th* component; k_i - поправочнction factor of the *i-th* component; *V*- the total volume of the mixture; S_i- peak area *i*-th component.

A non-additive synergistic effect is observed when adding combinations of other elements as promoters to one system. To study the nature of this effect, the physicochemical, textural and structural characteristics of the catalysts were studied. The results of the x-ray phase analysis show that when additives are added to the catalytic system, a defective solid solution containing oxygen vacancies is formed. And due to this, the activity of the catalytic system increases. Another reason for the increase in the activity of the catalytic system is the increase in the proportion of amorphous mesopores.

Results and Discussion

To establish the kinetic regularities of the catalytic conversion of CH_4 to C_2 hydrocarbons, the content of ethylene and ethane in the gas mixture at the reactor outlet was quantitatively determined using catalysts of various compositions. Based on the obtained data, the catalytic efficiency of the catalyst and methane conversion were evaluated. Table 1 shows the results of this experiment.

Table 1. Results of evaluating the catalytic activity of the studied systems

№	Catalyst	Methane conversion, %	Selectivity of C2 hydrocarbons, %	The yield of C2-hydrocarbons, %
1	$PbO\text{-}SnO_2/\alpha\text{-}Al_2O_3$	4,2	34,0	1,4
2	La_2O_3/SiO_2	23,8	42,0	10,0
3	$4\%NaCl\text{-}La_2O_3/SiO_2$	31,0	32,3	10,0
4	$13\%NaCl\text{-}17\%MnO_x/SiO_2$	26,6	28,6	7,6
5	$4\%NaCl\text{-}10\%MnO_x/SiO_2$	30,0	36,0	10,8
6	$4\%Na\text{-}10\%Mn\text{-}O/SiO_2$	20,1	34,8	7,0
7	$4\%Na_2MoO_4\text{-}10\%Mn\text{-}O/SiO_2$	39,6	47,1	18,6
8	$(Mn_2O_3)_x\cdot(Na_2MoO_4)_y\cdot(ZrO_2)_z$	52,6	81,4	42,8

The table shows that the highest catalytic activity, which manifests itself in the efficiency of methane conversion, was shown by our proposed catalyst with the composition $(Mn_2O_3)_x\cdot(Na_2MoO_4)_y\cdot(ZrO_2)_z$.

In this regard, our further studies were aimed at optimizing the molar composition of the gas mixture supplied to the catalyst zone and the flow conditions (temperature regime) of the catalytic process. The results of the experiment are presented in table 2.

Table 2. Dependence of methane conversion and selectivity of C_2 hydrocarbons on $CH_4:O_2$ molar ratio and temperature

T^l, ℃	$n^0_{CH_4}$, mol/s	$n^0_{O_2}$, mol/s	Methane conversion, %	output, %				
				C_2H_2	C_2H_4	CO	CO_2	C_2H_6
800	0,27	0,09	73,0	12,8	14,8	3,1	24,7	0,03
700	0,27	0,09	70,0	10,2	11,9	3,4	18,5	0,07
750	0,27	0,09	70,9	11,4	9,7	3,1	22,7	0,16
800	0,30	0,12	56,2	11,1	31,7	2,2	12,2	0,08
700	0,30	0,12	48,1	10,8	17,9	2,7	8,72	0,05
750	0,30	0,12	54,4	10,1	27,8	3,9	10,6	0,07
800	0,40	0,20	48,3	11,4	11,3	2,8	17,8	0,07
700	0,40	0,20	43,2	10,1	15,2	3,2	12,8	0,02
750	0,40	0,20	45,0	8,42	15,0	3,0	16,4	0,07
800	0,35	0,23	46,8	10,1	8,7	4,1	13,9	0,03
700	0,35	0,23	42,7	15,9	17,5	2,5	6,84	0,09
750	0,35	0,23	44,1	13,7	16,0	2,6	12,7	0,13

It follows from the obtained results that the optimal temperature regime for obtaining the target product - ethylene is 750 - 800 ℃, while the rate of supply of the gas mixture ingredients to the contact zone should be 0.30 mol/sec and 0.12 mol/sec for methane and oxygen, respectively.

According to the results of experimental studies, in the conversion of methane and oxygen, selectivity to ethane and ethylene increases with increasing temperature, and selectivity to carbon monoxide decreases. In this case, the selectivity to ethane begins to increase at a lower temperature than the selectivity to ethylene. This means that the primary product in the methane dimerization reaction is ethane, and ethylene is formed from its dehydrogenation [17-21].

The effect of diluting the reaction mixture with carbon dioxide and inert gases on the rate of the catalytic dimerization reaction of methane and the yield of the target product was studied. The obtained results are presented in Tables 3 and 4.

Table 3. Effect of carbon dioxide on the rate and yield of the target product of the catalytic dimerization reaction of methane

$CH_4:O_2:CO_2$	Conversion (%)		Selectivity (%)				
	CH_4	CO_2	H_2	CO_2	CO	C_2H_4	C_2H_6
3:1:0	52,6	-	6,2	13,4	16,8	62,4	19,0
3:1:1	57,2	-33,2	1,9	7,6	20,6	64,0	19,8
3:1:2	63,1	-14,0	2,6	4,1	21,0	66,2	20,7
3:1:2.5	57,1	-9,6	2,7	10,0	26,5	55,9	17,6
3:1:2.8	44,7	-1,6	3,3	3,1	70,4	45,0	11,5
3:1:3	42,7	2,0	3,1	-	92,6	32,2	5,2

The catalyst activity was tested in a quartz reactor on a fixed-bed catalyst (reactor length 650 mm, internal diameter 8 mm) at atmospheric pressure. 0.25g of catalyst was placed in the middle of the reactor. A thermocouple was installed in the middle of the catalyst layer on the outer wall of the reactor. Catalyst 10 from 25-30 ℃/min speed up to 800 ℃ in an argon atmosphere. Then 99.95% pure methane and oxygen were fed together into the reactor (CH_4:O_2=3:1). The effect of CO_2 was studied without changing the overall rate of gas flow [22-25].

As can be seen from the table above, the conversion of methane without the addition of carbon dioxide is 52.6% and the selectivity of ethylene is 62.4%. CH_4:O_2:CO_2 ratio from 3:1:0 to 3:1:2 mole ratio when carbon dioxide is added, conversion of methane from 52.6% to 63.1% selectivity to ethylene from 62.4% to 66.2%, selectivity to ethane From 19% to 20.7%, and selectivity to C_2-hydrocarbons increases from 81.4% to 86.9%. A further increase in the amount of carbon dioxide leads to a decrease in the above values. However, the selectivity of the exhaust gas increases. When we inject argon gas instead of carbon dioxide without changing the experimental conditions, the conversion of methane and the selectivity to C_2-hydrocarbons decrease as the amount of argon in the reaction mixture increases.

Table 4. Effect of dilution with inert gases on the catalytic dimerization reaction rate and target product yield of methane

CH_4:O_2:Ar	CH_4	Selectivity (%)				
		CO_2	H_2	CO	C_2H_4	C_2H_6
3:1:0	52,6	13,4	6,2	16,8	52,4	19,0
3:1:1	56,5	16,1	5,6	17,2	50,5	17,5
3:1:2	55,5	17,1	7,1	19,5	48,1	17,3
3:1:3	29,7	18,7	9,4	22,3	45,8	15,5
3:1:4	12,5	28,2	18,6	26,4	33,9	7,7

The dependence of the oxygen conversion on reagent contact time and temperature in the methane dimerization reaction was studied in the presence of a selected $(Mn_2O_3)_x \cdot (Na_2MoO_4)_y \cdot (ZrO_2)_z$ catalyst. The effect of temperature on oxygen conversion was studied when the volume ratio of reagents CH_4: air = 2:1, pressure P=0.1 MPa and temperature in the range of 700-800 ℃.
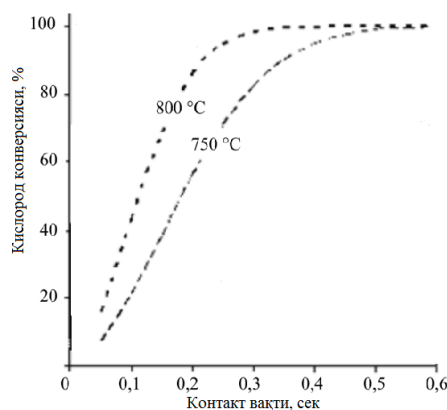
Figure 3. Dependence of oxygen conversion on reagent contact time and temperature at CH_4:air=2:1 and 0.1 MPa

As can be seen from the figure, deep conversion of oxygen is achieved in 0.6 sec at 750 ℃ and 0.3 sec at 800 ℃.

The effect of contact time and the ratio of reagents on oxygen conversion was studied in the range of 750-800 ℃, methane: air =6:1 ratio and pressure 0.1 MPa.

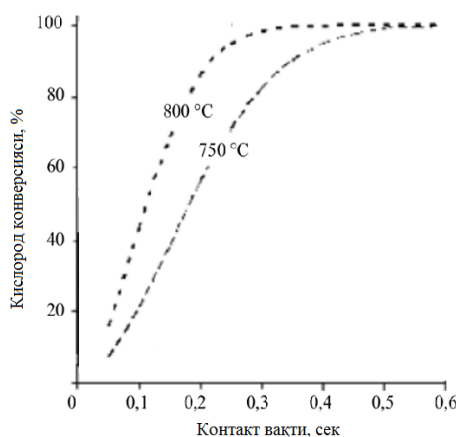Figure 4. Dependence of oxygen conversion on reagent contact time and temperature at CH_4:air=6:1 and 0.1 MPa

If we compare the results of the study of the contact time for oxygen conversion at different temperatures and at different ratios of reagents CH_4:air (1:3 and 1:6), it can be seen that the time to achieve complete conversion of oxygen decreases with an increase in the ratio of CH_4:air.

At 800 °C, the complete conversion time of oxygen is 0.25 sec when the ratio of reagents is 2:1, and it is 0.18 sec when the ratio is 6:1 at the same temperature. When the effect of pressure and ratio of reagents on the selectivity of the process is studied, the selectivity of the formation of an ethane-ethylene mixture decreases with increasing pressure.

As the volume ratio of reagents increases, the selectivity of the process increases slightly: the minimum selectivity is 56.4% when the ratio of reagents is 2:1, and 76.2% is reached when the ratio of reagents is 6:1.

It was of practical interest to establish the dependence of the yield of ethylene and ethane on the free volume of the reactor. For this, an experiment was carried out with a tubular reactor of various lengths, but with a constant volume filled with a catalyst. The results of the experiment are shown in Table 5.

Table 5. Results of a study on the reactor of various free volumes after the catalyst bed

T, ℃	$n^0_{CH_4}$, mol/s	$n^0_{O_2}$, mol/s	Выход, %			
			$V_{free\ volume}$ =45 cm³; V_{cat}= 0.5 cm³		$V_{free\ volume}$ = 25 cm³; V_{cat}= 0.5 cm³	
			C_2H_6	C_2H_4	C_2H_6	C_2H_4
800	0,312	0,267	15,4	17,1	26,2	5,3
800	0,402	0,2671	12,49	14,9	22,69	4,7
800	0,402	0,267	12,49	14,9	22,69	4,7
800	0,402	0,244	12,26	14,1	22,16	4,2
800	0,402	0,267	12,49	14,9	22,69	4,7
800	0,267	0,178	12,49	14,9	22,69	4,7
800	0,535	0,443	14,69	16,8	26,59	4,9
800	0,535	0,343	12,78	14,6	22,88	4,5
800	0,535	0,343	12,78	14,6	22,88	4,5
800	0,535	0,312	11,67	13,8	21,77	3,7

It can be seen from the table that, at a constant volume of the catalyst bed, with a decrease in the free volume of the reactor, the ethylene yield decreases, while the ethane yield increases. This effect is explained by the small volume of the reactor and, as a result, the decrease in the contact time.

Based on the foregoing, the conclusion follows: methane dimerization to ethane occurs on the catalyst surface.

In this case, the oxygen of the active centre of the catalyst, interacting with the methane molecule, forms an oxygen-carbon complex [Z·OCH$_3$], where Z is the active centre of the catalyst. The resulting complex interacts with the methane molecule, converting it to ethane. However, in the free volume of the reactor, ethane is converted into ethylene.

The least squares method was used to determine the activation energy of the process at different temperature intervals. Methane conversions and selectivity of C$_2$ hydrocarbons were calculated from the obtained kinetic parameters.

Table 6. Arrhenius parameters were calculated based on the kinetic regularities of the methane dimerization reaction and experimental data

№	reaction equation	Kinetic equation	Ea, kJ/mol
1	$2CH_4 + 1/2O_2 \rightarrow C_2H_6 + H_2O$	$W_1 = k_1 \cdot P^2_{CH_4} \cdot P_{O_2}$	49,86
2	$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O$	$W_2 = k_2 \cdot P_{C_2H_6} \cdot P_{O_2}$	41,42
3	$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$	$W_3 = k_3 \cdot P_{CH_4} \cdot P_{O_2}$	51,35
4	$C_2H_6 \rightarrow C_2H_4 + H_2$	$W_4 = k_4 \cdot P_{C_2H_6}$	41,46
5	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$W_5 = k_5 \cdot P_{CH_4} \cdot P_{O_2}$	44,85
6	$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$	$W_6 = k_6 \cdot P_{C_2H_4} \cdot P_{O_2}$	71,45
7	$CH_4 + O_2 \rightarrow CO + H_2O + H_2$	$W_7 = k_7 \cdot P_{CH_4} \cdot P_{O_2}$	92,11
8	$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2$	$W_8 = k_8 \cdot P_{C_2H_4} \cdot P_{H_2O}$	74,6
9	$CO_2 + H_2 \rightarrow CO + 4H_2O$	$W_9 = k_9 \cdot P_{CO_2} \cdot P_{H_2}$	26,47
10	$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	$W_{10} = k_{10} \cdot P_{C_2H_4} \cdot P_{O_2}$	57,59
11	$2CO + O_2 \rightarrow 2CO_2$	$W_{11} = k_{11} \cdot P_{CO} \cdot P_{O_2}$	27,23
12	$C_2H_6 + 2H_2O \rightarrow 2CO + 5H_2$	$W_{12} = k_{12} \cdot P_{C_2H_6} \cdot P_{H_2O}$	74,6

As can be seen from the data in Table 4, the formation of ethane from methane concerning methane is a 2nd order reaction (see reaction No. 1).

The results of the theoretical optimization of the methane catalytic dimerization reaction are presented in Table 7 below.

Table 7.Results of theoretical optimization of methane oxidative dimerization process

R, atm	$CH_4:O_2$, volume fraction	t, ℃	Time to reach 95% conversion of O2, sec	Selectivity of the process	
				C_2H_4 + C_2H_6, by %	C_2H_4, in %
		700	0,90	43,06	1,30
1	3:1	800	0,25	30,40	8,50
		1000	0,01	45,60	35,3
		700	0,50	42,52	0,77
1,7	3:1	800	0,09	28,40	5,24
		1000	0,01	39,00	31,6
		700	0,65	43,94	2,20
1	6:1	800	0,18	35,94	13,0
		1000	0,01	44,48	38,06

Conclusion

The process of catalytic dimerization of methane using catalysts based on alkali and alkaline earth metal salts containing molybdenum and manganese oxides has been studied.

It has been established that the catalytic conversion of methane occurs on the surface of a catalyst that adsorbs oxygen to form the active $[ZOCH_3]$ complex.

It has been shown that the catalytic conversion of methane can be accompanied by both the formation of ethane and ethylene. In this case, the proportion of ethylene in the free volume of the reactor increases in comparison with ethane, which allows the reaction of ethylene formation to proceed without oxygen and a catalyst.

The optimization of the catalytic process of methane dimerization was carried out, which showed that the process should proceed at a temperature of 750-800 °C at a controlled rate of supply of the reaction mixture of gases to the catalyst zone of 0.3 mol/sec CH_4 and 0.12 mol/sec O_2.

The phenomenological equations of the kinetics of the catalytic reaction of methane dimerization are compiled and the rate constants and Arrhenius parameters are calculated.

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