

Carrying out thermodynamic calculations and definition of the main reactions of decomposition of vapours of ethyl alcohol

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Abstract. Thermodynamic opportunities of course of chemical reactions of decomposition of the vapors of ethyl alcohol necessary at development of devices where these reactions will take place are considered. The entalpiyny method of calculation of constants of balance of probable chemical reactions is given in the Excel editor. Independent reactions of process of oxidation are defined. By result of thermodynamic calculation of each reaction schedules of dependence of a constant of balance on environment temperature from which follows are constructed that one reactions proceed until the end of aside formation of the final products, and others are improbable or impossible. The analysis of the received results shows that reactions of oxidation will successfully proceed in the established directions, and for an intensification of process of decomposition it is necessary to provide a supply of some energy which quantity will be sufficient for oxidation of vapors of ethyl alcohol. Results of calculations showed good convergence with programs of thermodynamic calculations like "Aster – 4" and "TERRA".

1. Introduction

Problem of pollution of atmospheric air – one of the most serious global problems which the mankind faced. Danger of pollution of the atmosphere – that harmful substances get to clean air, pernicious for live organisms.

Gravity of the environmental problems connected with pollution of the atmosphere is illustrated by the following statistical data: only 15% of urban population of Russia breathe rather clean air. In 125 cities of the Russian Federation the exceeding maximum concentration limits of concentration of pollution of the atmosphere are annually fixed at 5-10 times [1]. Hit in it uncharacteristic physical, chemical and biological substances in the course of activity of the person is the main reason for air pollution.

In the course of production of medicinal substances, there is a need of cleaning of organized emissions in environment of vapors of various organic substances which are emitted as in synthesis processes, and processings of a number of chemicals. The main share of pollution of the atmosphere belongs to drying processes. The dividing systems representing two-level cleaning of dust fractions most often don't provide cleaning of a steam phase. There is a need of the solution of a question of cleaning of organized atmospheric emissions of vapors of organic chemistry.

For successful fight against similar pollution it is necessary to know as physical and chemical properties of the substances deleted from production volume, and the thermodynamic opportunities of course of chemical reactions necessary at development of devices where these reactions will take place.

This work is also devoted to the thermodynamic analysis of chemical catalytic reactions of decomposition of vapors of ethyl alcohol and definition of the main reactions.

2. Calculated part

The chemical thermodynamics considers interrelations between work and energy in relation to chemical transformations. As chemical transformation usually is followed by release or absorption of a certain amount of heat, it submits to the fundamental principles (beginnings) of thermodynamics. The chemical thermodynamics defines, first of all, conditions (such as temperature and pressure) courses



of chemical reactions and equilibrium states which they reach [2].

For carrying out thermodynamic calculations it is necessary from possible reactions to define independent reactions of process of oxidation of ethyl alcohol.

For calculation of thermodynamic parameters of process of oxidation of ethyl alcohol balance reactions were made:

- 1) $C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O$;
- 2) $C_2H_5OH \rightarrow C_2H_2 + H_2\uparrow$;
- 3) $C_2H_5OH \rightarrow CH_4 + H_2O + C$;
- 4) $C_2H_5OH \rightarrow CH_4 + CO + H_2\uparrow$;
- 5) $C_2H_5OH \rightarrow C_2H_4 + H_2O$;
- 6) $C_2H_5OH \rightarrow C_2H_2 + H_2O + H_2\uparrow$.

Number of independent reactions equally to number of substances (C_2H_5OH , O_2 , CO_2 , H_2O , C_2H_2 , H_2 , CH_4 , C_2H_4 , C) in system minus number of diverse atoms (to H_2 , O_2 , C) of which reagents are formed, i.e. the number of independent reactions is equal to six ($9-3=6$) [2]. Therefore, all presented reactions are independent.

Thermodynamic calculations were implemented on a method of calculation of the balance [3] considering dependence $\Delta H = f(T)$, by means of which $lgK_p = f(T)$, and ΔH , lgK_p in the range of temperatures $0 \div 100$ °C are counted.

Influence of temperature on a constant of balance is described by Vant Hoff's equation [4].

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^0}{RT^2} \quad (2)$$

where, ΔH^0 – standard thermal effect of reaction; R – universal gas constant; T – temperature is °K; K_p – a balance constant.

In case of exact calculation and at big temperature intervals the equation (2) considers dependence of thermal effect of reaction on temperature. For this purpose we will substitute the equation

$$\Delta C_p = \Delta a + \Delta b \cdot T + \Delta c' \cdot T^2 \quad (3)$$

in the equation of the law of Kirchhoff [5].

Integrating, we will receive: in a final formula:

$$\left(\frac{d(\Delta H)}{dT} \right) \cdot p = \Delta C_p \quad (4)$$

$$\Delta H_T = \Delta H^0 + \Delta a \cdot T + \frac{\Delta b \cdot T^2}{2} + \frac{\Delta c \cdot T^3}{3} - \frac{\Delta c'}{T} \quad (5)$$

Combining the equation (2) with the equation (4) and integrating, we will receive the equation in technical system of coordinates:

$$\lg K_p = \frac{-\Delta H^0}{2.303 \cdot R \cdot T} + \frac{\Delta a}{R} \cdot \lg T + \frac{\Delta b \cdot T}{2.303 \cdot 2 \cdot R} + \frac{\Delta c \cdot T^2}{2.303 \cdot 6 \cdot R} + \frac{\Delta c' \cdot T^{-2}}{2.303 \cdot 2 \cdot R} + J''$$

According to the equation of an isobar of chemical reaction

$$\Delta G_T = -R \cdot T \cdot \ln K_p = -2.303 \cdot R \cdot T \cdot \lg K_p \quad (6)$$

$$\Delta G_T = \Delta H^0 - \Delta a \cdot T \cdot \ln T - \frac{\Delta b \cdot T^2}{2} - \frac{\Delta c \cdot T^3}{6} - \frac{\Delta c' \cdot T}{2} + J \cdot T \quad (7)$$

where, $J = -2.303 \cdot R \cdot J''$.

In the equations 3 – 6 unknown sizes are Δa , Δb , Δc , $\Delta c'$, ΔH_{298} , ΔG_{298} , ΔH^0 , J , which are in compliance of the equations:

$$\Delta H_{298} = \sum \Delta H_{298(npo\delta)} - \sum \Delta H_{298(ucx)} \quad (8)$$

$$\Delta G_{298} = \sum \Delta G_{298(npo\delta)} - \sum \Delta G_{298(ucx)} \quad (9)$$

$$\Delta a = \sum \Delta a_{(npo\delta)} - \sum \Delta a_{(ucx)} \quad (10)$$

$$\Delta b = \sum \Delta b_{(npo\delta)} - \sum \Delta b_{(ucx)} \quad (11)$$

$$\Delta c = \sum \Delta c_{(npo\delta)} - \sum \Delta c_{(ucx)} \quad (12)$$

$$\Delta c' = \sum \Delta c'_{(npo\delta)} - \sum \Delta c'_{(ucx)} \quad (13)$$

Coefficients a , b , c , c' and ΔH_{298} , ΔG_{298} undertake taking into account the stekhiometricheskikh of coefficients of the equation of the counted reactions. For stay ΔH^0 , which are an extrapolation constant we will substitute in the equation (2) values Δa , Δb , Δc , $\Delta c'$ at $T=298$ °K and ΔH_{298} we will receive in case of high temperatures:

$$\Delta H^0 = \Delta H_{298} - \left(\Delta a \cdot 298 + \frac{\Delta b}{2} \cdot 298^2 + \frac{\Delta c}{3} \cdot 298^3 - \frac{\Delta c'}{298} \right) \quad (14)$$

For finding of J we will substitute values ΔH^0 (the equation 14), ΔG_{298} and $T = 298$ °K in the equation (7), we will receive

$$J = \frac{(\Delta G_{298} - \Delta H^0)}{T} + \Delta a \cdot \ln T + \frac{\Delta b \cdot T}{2} + \frac{\Delta c \cdot T^2}{6} + \frac{\Delta c' \cdot T^{-2}}{2} = \frac{(\Delta G_{298} - \Delta H^0)}{298} + \Delta a \cdot 5.69 + \Delta b \cdot 149 + \Delta c \cdot 14801 + \Delta c' \cdot 5.63 \cdot 10^{-6} \quad (15)$$

We will substitute values 8 – 15 in 5 and we will receive:

$$\lg K_p = \frac{-\Delta H^0/T + \Delta a \cdot 2.3 \cdot \lg T + 0.5 \cdot \Delta b \cdot T + 0.5 \cdot \Delta c' \cdot T^{-2} + J''}{2.303 \cdot R} \quad (16)$$

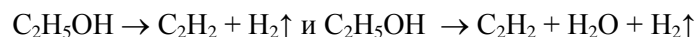
It is known that thermodynamic parameters share on extensive and intensive. The sizes proportional to weight (or to amount of substance) the considered thermodynamic system, carry to extensive, it is volume, internal energy, an enthalpy, etc., intensive sizes don't depend on the mass of thermodynamic system. It, for example, temperature and pressure.

3 Results

By result of thermodynamic calculation of each reaction schedules of dependence of a constant of balance of $\lg K_p$ on environment temperature which are represented in figure 1 were constructed.

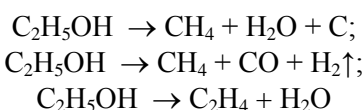
Reactions of decomposition can go in several directions. Everything depends on energy which is applied to these processes.

From figure 1 it is visible that reactions:



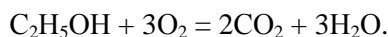
aren't feasible as have negative value of a constant of balance of $\lg K_p$ and course of reaction towards formation of products it is impossible.

Following reactions:



have low probability of course towards formation of products.

Reaction with high probability of course until the end of aside formation of the final products the following:



After the analysis of schedules of dependence of a constant of balance on temperature of the environment the directions of decomposition of reactions were defined.

From schedules it is visible that one reactions proceed until the end of aside formation of the final products, and others are improbable or impossible.

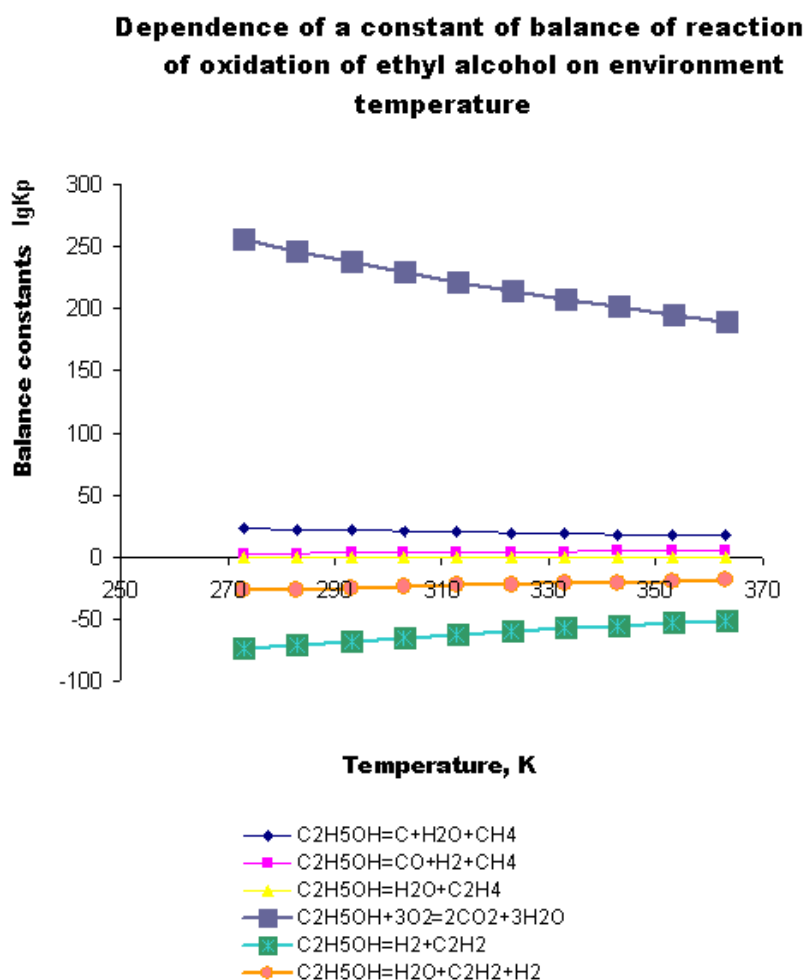


Figure 1. Dependence of a constant of balance of reaction of oxidation of ethyl $\lg K_p$ alcohol on environment temperature.

The analysis of the received results allows to draw a conclusion that reactions of oxidation will successfully proceed in the established directions, and for an intensification of process of decomposition it is necessary to provide a supply of some energy which quantity will be sufficient for oxidation of vapors of alcohol, thereby minimizing technological emission on a steam component in environment.

4. Conclusion

As a result of the conducted research thermodynamic calculation of possible reactions of oxidation of alcohol was considered. Independent reactions of process of oxidation are defined. Thermodynamic calculations of process of oxidation of ethyl alcohol are carried out (balance constants, Gibbs's energy). The entalpiyny method of calculation of constants of balance of chemical reactions is given in the Excel editor. Results of calculations showed good convergence with programs of thermodynamic

calculations like "Aster – 4" and "TERRA" [6, 7].

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