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Mathematical Equations of Thermodynamic Probability of Thermal Decomposition of Ammonia

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Annotation: Technical solutions have been developed to create a technology for obtaining calcium cyanamide from lime, carbonate anhydride and industrial ammonia. A technological scheme for obtaining nitrogen fertilizer and an effective defoliant - calcium cyanamide has been developed and the optimal technological parameters of the process at the pilot plant an experimental batch of calcium cyanamide was produced.
Keywords: Carbon dioxide, ammonia, expander gas, calcium cyanamide, off-gases.

I. INTRODUCTION

The basis of thermodynamic calculations of the thermal decomposition of ammonia were given below, derived by us mathematically by multiplying by the reduced coefficient 4.184, the results of thermodynamic calculations were converted from the metric system of measures to the international SI system.

1) In accordance with the Hess law, the change in the enthalpy of reaction is determined under standard conditions:

$$\Delta H^o_{298} = \sum \Delta H^o_{пр} - \sum \Delta H^o_{и.в.} = [(0{,}5\Delta H^o_{N2} + 1{,}5\Delta H^o_{H2}) - (\Delta H^o_{(NH3)}] \cdot 10^3 \text{cal/mol}$$

2) From the following expression, the thermal effect of the reaction is determined at 298 K:

$$Q_{298} = -\Delta H^o_{298} \text{cal/mol}$$

3) For standard conditions, we calculate the absolute value of entropy using the equation

$$\Delta S^o_{298} = \sum \Delta S^o_{пр} - \sum \Delta S^o_{и.в.} = (0{,}5\Delta S^o_{N2} + 1{,}5\Delta S^o_{H2}) - \Delta S^o_{NH3}, \text{ cal/mol.deg}$$

4) At a temperature of 298 K, the change in the Gibbs energy is:

$$\Delta G^o_{298} = \Delta H^o_{298} - T^* \Delta S^o_{298}, \text{ cal/mol}$$

5) According to the Kirchhoff equation, the dependence of the true molar isobaric heat capacity of the reagents on temperature is determined:

$$\Delta C^o_p = \Delta a + \Delta b^* T + c^1/T^2,$$

where: Δa, Δb, Δc1 - constant coefficients of the equation are defined as the algebraic difference of the corresponding parameters of the reaction products and initial substances, taking into account their stoichiometric coefficients;

where: T is the temperature in degrees Kelvin.

5.1 $\Delta a = \sum \Delta a_{пр} - \sum \Delta a_{и.в.} = (0{,}5\Delta a_{N2} + 1{,}5\Delta a_{H2}) - \Delta a_{NH3}$

5.2 $\Delta b = \sum \Delta b_{пр} - \sum \Delta b_{и.в.} = (0{,}5\Delta b_{N2} + 1{,}5\Delta b_{H2}) - \Delta b_{NH3}$

5.3 $\Delta c^1 = \sum \Delta c^1_{пр} - \sum \Delta c^1_{и.в.} = (0{,}5\Delta c^1_{N2} + 1{,}5\Delta c^1_{H2}) - \Delta c^1_{NH3}$

6) The integration constant of the equation for the dependence of the change in the enthalpy of the reaction on temperature is calculated by the formula:

$$\Delta H^o_0 = \Delta H^o_{298} - \Delta a^* 298 + \Delta b^* 298^2/2 + \Delta c^1/298$$

7) For different temperatures, the change in the enthalpy of the components is calculated by the following formula:

$$\Delta H^o_T = \Delta H^o_0 + \int_{298}^{T} \Delta C^o_p dT = \Delta H^o_0 + \int_{298}^{T} (\Delta a + \Delta b \cdot T + \Delta C^1/T^2) dT$$

After integrating this expression, we have the following formula:

$$\Delta H^o_T = \Delta H^o_0 + \Delta a^* T + \Delta b^* T^2/2 - \Delta C^1/T$$

8) The thermal effect of a chemical reaction at different temperatures is determined as follows:

$$Q_{PT} = -\Delta H^o_T, \text{ cal/mol}$$

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9) According to the Vant Hoff's isobar equation, the dependence of the equilibrium constant of a chemical reaction on temperature is determined:

$$dlnK_{PT}/dT = \Delta H^{o}_{T}/R*T^{2}$$

Where:

$$dlnK_{PT} = (\Delta H^{o}_{T}/R*T^{2})dT$$

or:

$$dlnK_{PT} = \Delta H^{o}_{T}/(R*T)$$

10) The decimal logarithm of the equilibrium constant of a chemical reaction is calculated by the formula at a temperature of 298K:

$$lgK_{P298} = -\Delta G^{o}_{298}/R{\cdot}298$$

11) The integration constant of the decimal logarithm dependency equation is found by the equation:

$$K_0 = lgK_{P298}+\Delta H^{o}_{0}/(4{,}576*lg298)-(\Delta a*lg298)/1{,}987)-(\Delta b*lg298)/9{,}150)-\Delta c^{/}/(9{,}150*lg298^{2})-(\Delta c^{/}*lg298^{2})/27{,}45$$

12) The value of the decimal logarithm of the equilibrium constant of a chemical reaction is determined by the formula:

$$lgK_{PT} = -\Delta H^{o}_{0}/(4{,}576*T)+(\Delta a*lgT)/1{,}987)+$$
$$+(\Delta b*lgT)/9{,}150)*\Delta c^{1}/(9{,}150*T^{2})+(\Delta c^{/}*298^{2})/27{,}45+K^{o}_{0}$$

13) The value of the change in the Gibbs's energy of a chemical reaction depending on the temperature of the solution:

$$\Delta G^{o}_{T} = -R*T*lgK^{o}_{PT} = -4{,}576*T*lgK^{o}_{PT},\ cal/mol$$

The C++Builder 6 computer program for calculating the thermodynamic decomposition probability was as follows:

```
//---------------------------------------------------------------------------

#include <vcl.h>

#include <math.h>

#pragma hdrstop

#include "Unit1.h"

//---------------------------------------------------------------------------

#pragma package(smart_init)

#pragma resource "*.dfm"

TForm1 *Form1;

//---------------------------------------------------------------------------

__fastcall TForm1::TForm1(TComponent* Owner)

: TForm(Owner)

{

}

//---------------------------------------------------------------------------

void __fastcall TForm1::Button1Click(TObject *Sender)

{

double n1=1, n2=0, n3=0, n4=0, H1=-10980, H2=0,

H3=0, H4=0, n5=0.5,n6=1.5, n7=0, n8=0, H5=0, H6=0,

H7=0, H8=0, S1=46.047, S2=0,S3=0, S4=0, S5=45.77,

S6=31.195, S7=0, S8=0, A1=7.122, A2=0,A3=0, A4=0,
```

```
A5=6.663, A6=0, A7=0, A8=0, B1=0.00609, B2=0, B3=0,

B4=0, B5=0.001021,B6=0.000779, B7=0, B8=0,

C11=-39900, C12=0, C13=0,C14=0, C15=0, C16=11900,

C17=0, C18=0, T=298, T1=373, K1=4.576,K2=1.987,

K3=9.150, K4=27.45,DHO298, DS298, GO298, DA, DB,

DC1, DCPT1,HO, DHTO1, LOGKP298, KO, LOGKPT1, DGOT1;


DHO298 = (n5 * H5 + n6 * H6 + n7 * H7 + n8 * H8) - (n1 * H1 + n2 * H2 + n3 * H3 + n4 *H4);

DS298 = (n5 * S5 + n6 * S6 + n7 * S7 + n8 +S8) - (n1 * S1 + n2 * S2 + n3 *S3 + n4 * S4);

GO298 = DHO298 * (T * DS298);

DA = (n5 * A5 + n6 * A6 + n7 * A7 + n8 *A8) - (n1 *A1 + n2 * A2 + n3 * A3 + n4 *A4);

DB = (n5 * B5 + n6 * B6 + n7 * B7 + n8 *B8) - (n1 *B1 + n2 * B2 + n3 * B3 + n4 *B4);

DC1 = (n5 * C15 + n6 * C16 + n7 * C17 + n8 *C18) - (n1 *C11 + n2 * C12 + n3 * C13 + n4 *C14);

DCPT1 =float (DA + DB * T1 +DC1) / float(T1 * T1);

HO = float (DHO298 - DA * T -(DB * (T * T))) / float (2- DC1 / T);
DHTO1 = HO + DA * T1 +(DB * (T * T)) - float (2- DC1 / T1);
LOGKP298 = log10(fabs(- GO298 / float(K1 * T)));
KO = LOGKP298 + float (HO) / float((K1 *T) - (DA * (log10(T))) / float( K2 - (DB * T1)) / float (K3 + DC1) / float(K3 * (T1 *
T1)));
LOGKPT1 = log10(fabs(- HO / (K1 * T1 ) + (DA * log10(T1)) / K2 + (DB * T1) / (K3 * (T * T)) + KO));

DGOT1 = - K1 * T1 * LOGKPT1;
StringGrid1->Cells[0][0]=FloatToStrF(DHO298,ffFixed,15,2);
StringGrid1->Cells[1][0]=FloatToStrF(DS298,ffFixed,15,2);
StringGrid1->Cells[2][0]=FloatToStrF(GO298,ffFixed,15,2);
StringGrid1->Cells[3][0]=FloatToStrF(DA,ffFixed,15,2);
StringGrid1->Cells[4][0]=FloatToStrF(DB,ffFixed,15,2);
StringGrid1->Cells[5][0]=FloatToStrF(DC1,ffFixed,15,2);
StringGrid1->Cells[6][0]=FloatToStrF(DCPT1,ffFixed,15,2);
StringGrid1->Cells[7][0]=FloatToStrF(HO,ffFixed,15,2);
StringGrid1->Cells[8][0]=FloatToStrF(DHTO1,ffFixed,15,2);
StringGrid1->Cells[9][0]=FloatToStrF(LOGKP298,ffFixed,15,2);
StringGrid1->Cells[10][0]=FloatToStrF(KO,ffFixed,15,2);
StringGrid1->Cells[11][0]=FloatToStrF(LOGKPT1,ffFixed,15,2);
StringGrid1->Cells[12][0]=FloatToStrF(DGOT1,ffFixed,15,2);
}

        //---------------------------------------------------------------------------
```

According to the above program, a number of calculations were made, changing 122 temperature values from 373 to 1473K in increments of 100 degrees.

The results obtained are presented in Tables 1-4:

Table 1

Values of thermal effect, entropy and change of Gibbs energy for the reaction of ammonia decomposition under standard conditions

Qp 298		DS 298		GO 298	
Cal/mol	J/mol	Cal/mol	J/mol	Cal/mol	J/mol
-10980	-4594,32	23,635	98,889	+3936,77	+16471,445

Table 2

Values of the thermal effect of the ammonia decomposition reaction at different temperatures.

QPT1	T1, K	373	473	573	673	773
	кал/моль	-116674,204	-12046,9	-12393,931	12703,199	12972
	Дж/моль	-48815,581	-50404,229	-51856,207	53150,184	542,75

Continuation of Table 3

Values of the thermal effect of the ammonia decomposition reaction at different temperatures.

QPT1	T1, K	873	973	1073	1173	1273	1373	1473
	кал/моль	13199,737	13384,890	-13527,271	-13626,375	-13682,162	13694,412	13663
	Дж/моль	55227,699	56002,379	-56598,101	-57012,753	-57246,165	57297,419	57166

Table 4

Values of the logarithm of the equilibrium constant of the ammonia decomposition reaction at various temperatures.

T1, K	373	473	573	673	773	873
LOGKT1	-1,2411	+0,1918	+1,1587	+1,8587	+2,3913	+2,8104
T1, K	973	1073	1173	1273	1373	1473
LOGKT1	+3,1493	+3,4285	+3,7440	+3,8611	+4,0314	+4,1783

Table 5

The values of the change in the Gibbs's energy of the reaction of decomposition of ammonia at different temperatures.

ΔGOT1	T1, K	373	473	573	673	773
	кал/моль	+2118,309	-415,141	-3038,167	-5724,142	-8458,621
	Дж/моль	+8862,984	-1736,95	-2711,69	-3949,81	-35390,87

ΔGOT1	T1, K	873	973	1073	1173	1273	1373	1473
	кал/моль	1122	-14022,094	-16834,099	-20096,474	-22491,865	-25328,673	-28163,612
	Дж/моль	4697	-58668,441	-70433,87	-84083,647	-94105,963	-105975,16	-117836,55

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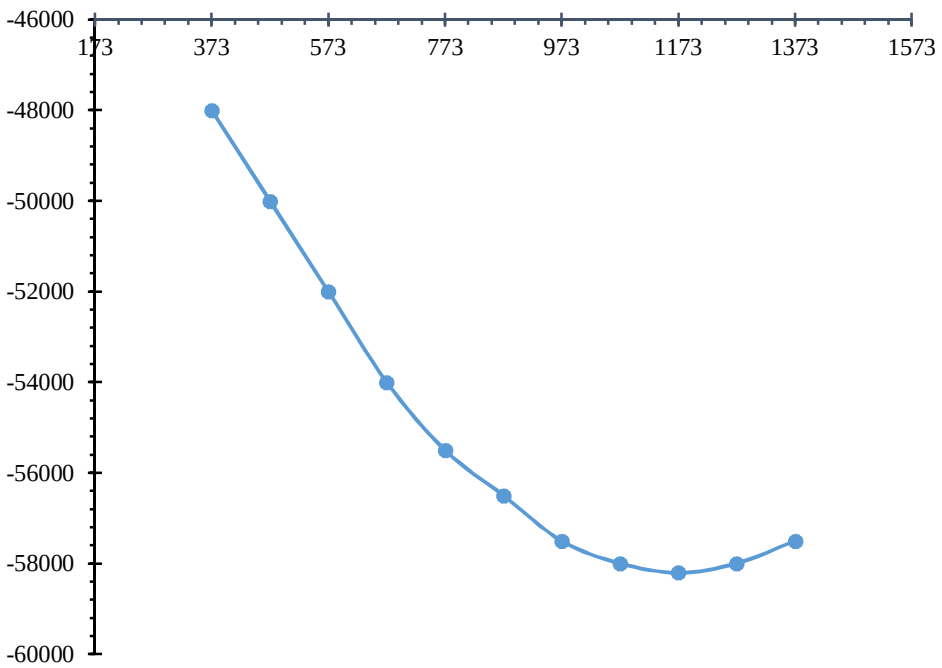


Fig.1. Dependence of the heat effect of the ammonia decomposition reaction on temperature based on new constants

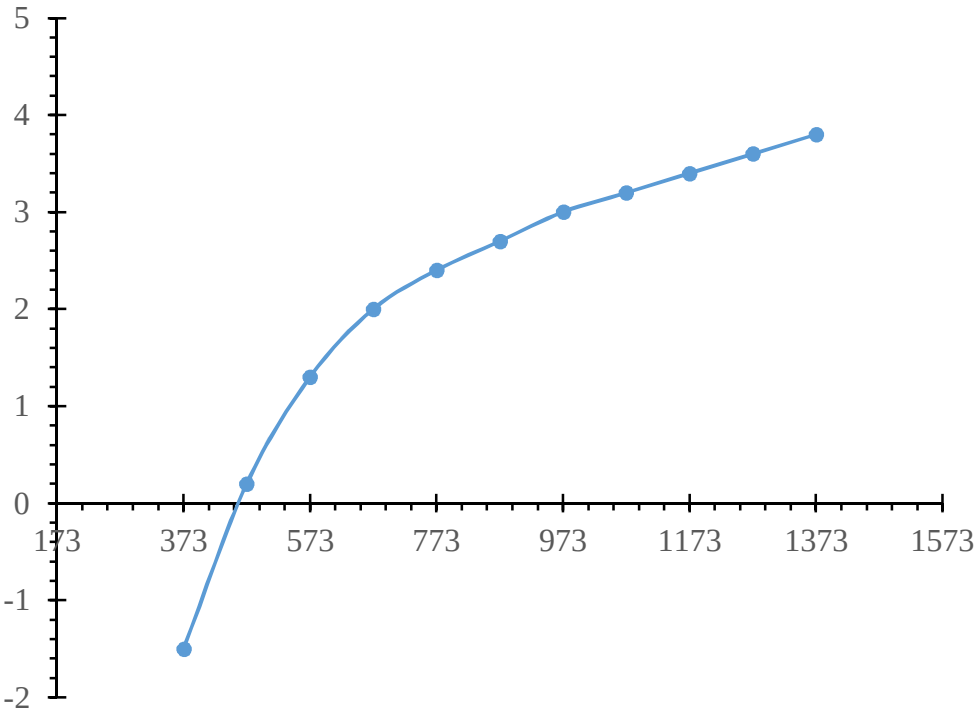


Fig.2. Dependence of the logarithm of the equilibrium constant on the decomposition temperature of ammonia

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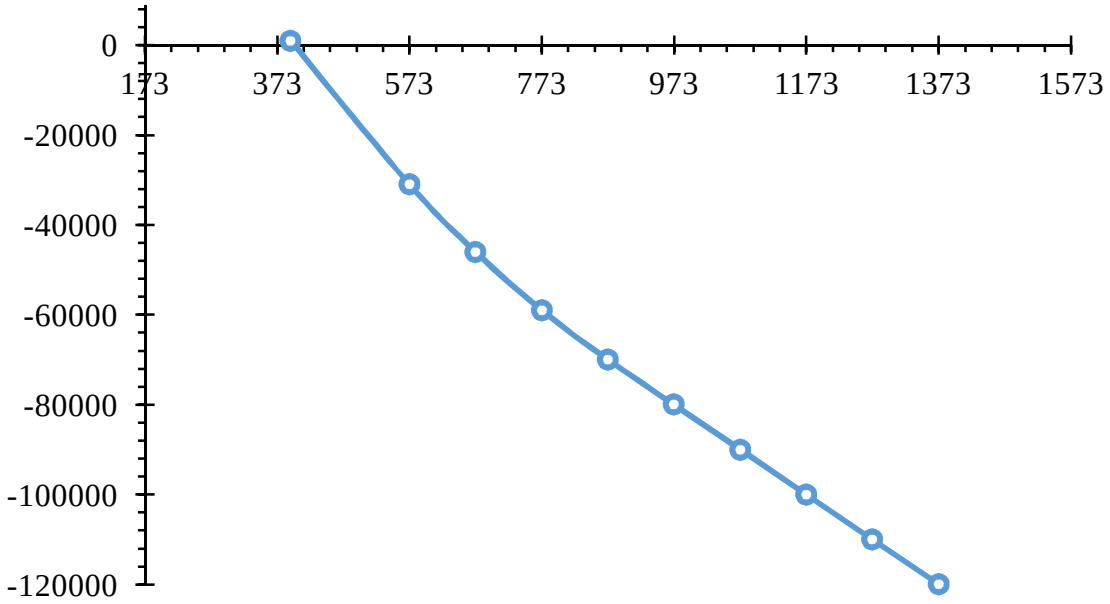


Fig. 3. Dependence of the magnitude of the change in the Gibbs's energy on the temperature of decomposition of ammonia

At 373K the value of the decimal logarithm had a negative sign (Table 3.4), and at 458K it was equal to zero. With a further increase in temperature, a slight increase was observed and at 1073K the value of the decimal logarithm was - + 3.4285. At a temperature of 1073K, which is optimal in the process of obtaining calcium cyanamide from calcium oxide, carbon dioxide and ammonia [119, p. 5], the value of the Gibbs energy change is -70433.87J/mol, which follows from Fig.3.3.

Based on the methodology used,thermodynamic calculations were carried out on the basis of the old constants. According to the old physicochemical constants, the temperature of the onset of ammonia decomposition turned out to be 456K, and according to the new ones, it was 459K [119, p. 6].

Thus, the ammonia decomposition temperature of 459K can be considered more reliable, since it was determined according to new literature data.

II. FINDINGS

1) Thermodynamic studies of the thermal decomposition of ammonia according to new physical and chemical constants have shown that the decomposition temperature of ammonia 459K can be considered more reliable, since it is determined according to new literature data.

2) Thermodynamically calculated values of the change in the Gibbs energy showed that their absolute values decrease with increasing temperature.

3) The results of computer thermodynamic calculations show that the thermal effect of the reaction in the temperature range of 873–1473 K is endothermic, the reaction proceeds with external heat absorption.

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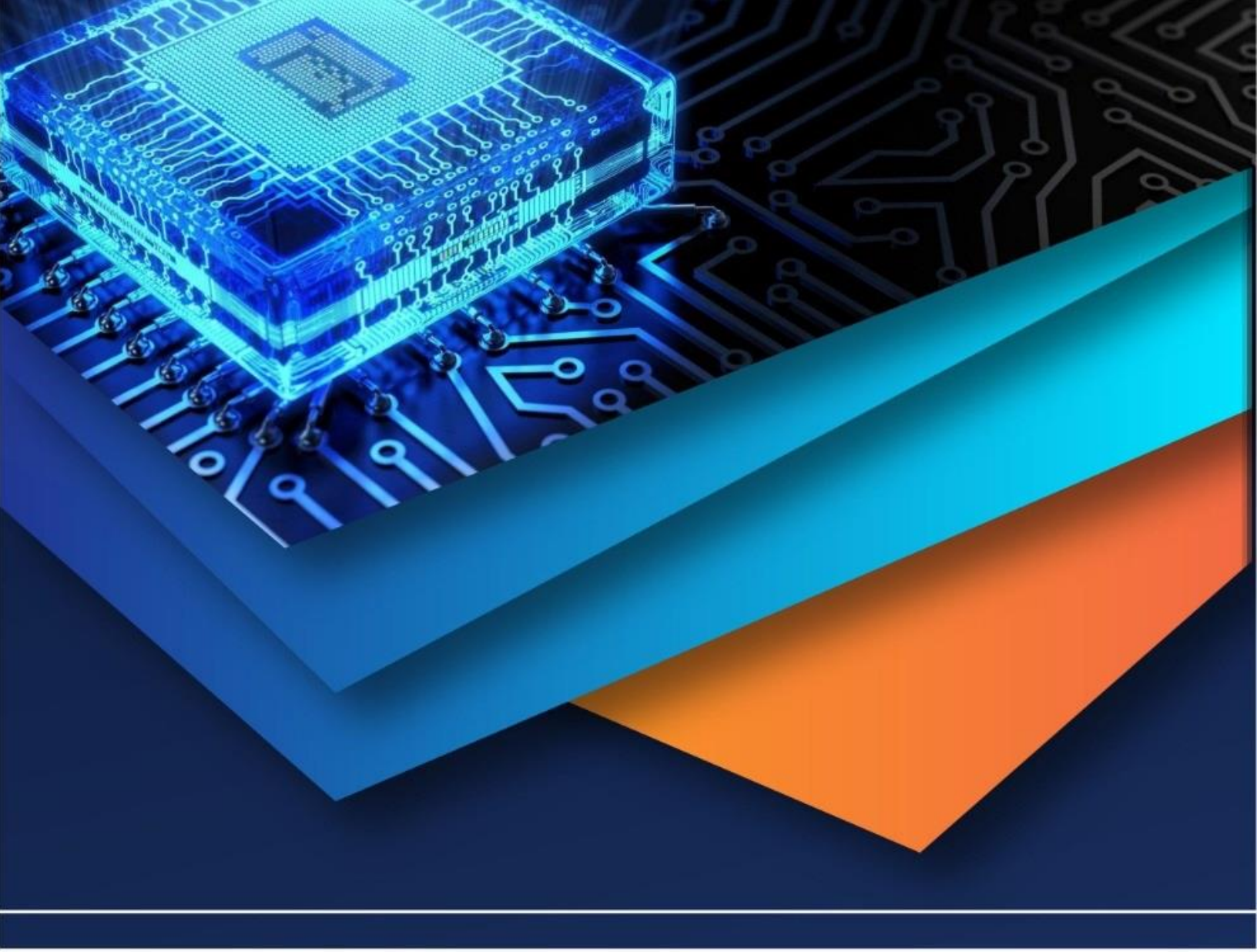
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