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MATHEMATICAL EQUATIONS FOR DETERMINING THE THERMODYNAMIC PROBABILITY OF THE CHEMICAL INTERACTION OF AMMONIA AND CARBON DIOXIDE

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Abstract : Technical solutions have been developed to create a technology for obtaining calcium cyanamide from lime, carbonate anhydride and industrial ammonia. A technological scheme for producing nitrogen fertilizer and an effective defoliant - calcium cyanamide - has been developed and optimal technological parameters of the process on an experimental installation a pilot batch of calcium cyanamide was produced.

Key words: Carbon dioxide, ammonia, expansion gas, calcium cyanamide, waste gases.

The basis for thermodynamic calculations of the thermal decomposition of ammonia was the following, which we derived mathematically by multiplying by the given coefficient of 4.184; the results of thermodynamic calculations were converted from the metric system of measures to the international SI system.

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

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

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

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

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

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

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

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

5. Using the Kirchhoff equation, the dependence of the true molar isobaric heat capacity of the reactants on temperature is determined:

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

Where: Δa, Δb, Δc^1- the constant coefficients of the equation are defined as the algebraic difference between the corresponding parameters of the reaction products and starting substances, taking into account their stoichiometric coefficients;

where: T is the temperature in degrees Kelvin.

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

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

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

6. The integration constant of the equation for the dependence of the change in enthalpy of a 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 enthalpy of the components is calculated using the following formula

$\Delta H^o_T = \Delta H^o_0 + \int_{298}^{T} \Delta C^o_P dT = \Delta H^o_0 + \int\downarrow 298\uparrow T \equiv [(\Delta a] + \Delta b\cdot T + \Delta C^1/T^2)dT$

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 defined as follows:

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

9. Using the Vant Hoff isobar equation, the dependence of the equilibrium constant of a chemical reaction on temperature is determined:

$d\ln K_{PT}/dT = \Delta H^o_T/R*T^2$

where:

$d\ln K_{PT} = (\Delta H^o_T/R*T^2)dT$

or:

$d\ln K_{PT} = \Delta H^o_T/(R*T)$

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

$\lg K_{P298} = -\Delta G^o_{298}/R\cdot 298$

11. The integration constant of the equation for the dependence of the decimal logarithm is found by the equation:

$K_0 = \lg K_{P298} + \Delta H^o_0/(4{,}576*\lg 298) - (\Delta a*\lg 298)/1{,}987) - (\Delta b*\lg 298)/9{,}150) - \Delta c^/ /(9{,}150*\lg 298^2) - (\Delta c^/ *\lg 298^2)/27{,}45$

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

$\lg K_{PT} = -\Delta H^o_0/(4{,}576*T) + (\Delta a*\lg T)/1{,}987) +$
$+(\Delta b*\lg T)/9{,}150)*\Delta c^1/(9{,}150*T^2) + (\Delta c^/ *298^2)/27{,}45 + K^o_0$

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

$\Delta G^o_T = -R*T*\lg K^o_{PT} = -4{,}576*T*\lg K^o_{PT}$, cal/mol

When synthesizing calcium cyanamide, it is possible to propose the following chemical reaction, which can result in additional consumption of expensive ammonia:

$CO_{2(г)} + 2NH_{3(г)} = CH_{4(г)} + H_2O_{(п)} + N_{2(г)} + 0{,}5O_{2(г)}$

In order to carry out thermodynamic calculations of the probability of this reaction occurring, the following equations were compiled:

1. Under standard conditions, the change in enthalpy of the reaction under consideration is calculated according to Hess's law:

$\Delta H^o_{298} = \sum \Delta H^o_{298пр} - \sum \Delta H^o_{298и.в.} = ((\Delta H^o_{CH4} + \Delta H^o_{H2O(П)} + \Delta H^o_{N2} + 0{,}5\Delta H^o_{O2}) -$
$-(\Delta H^o_{CO2} + 2\Delta H^o_{NH3})*10^3$, cal/mol

2. At a temperature of 298K, the thermal effect of a chemical reaction is determined from the following expression:

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

3. For a temperature of 298K, an equation is drawn up to calculate the change in entropy of the system:

$\Delta S^o_{298} = \sum \Delta S^o_{пр} - \sum \Delta S^o_{и.в.} = (\Delta S^o_{CH4} + \Delta S^o_{H2O(П)} + \Delta S^o_{N2} + 0{,}5\Delta S^o_{O2}) - (\Delta S^o_{CO2} + 2\Delta S^o_{NH3})$, cal/mol

4. For a temperature of 298K, the value of the change in Gibbs energy is determined:

$\Delta^{o}_{298} = \Delta H^{o}_{298}-T\_\Delta S^{o}_{298}$, cal/mol

5. The heat capacity of the system at different temperatures is calculated using the Kirchhoff equation:

$\Delta C^{o}_{p} = \Delta A+\Delta B*T1+\Delta C1/T^{2}+\Delta C*T1^{2}$,

where: ΔC^{o}_{p} – true molar heat capacity of the substances of the system at P=const cal/mol·deg,

ΔA, ΔB, ΔC_1, ΔC – constant coefficients of each substance (p=const) of the equation for determining the heat capacity of the system;

T_1- temperature for which heat capacity is determined, in K.

6. The equation for the algebraic difference of the constant coefficient ΔA has been compiled:

$\Delta A = \sum\Delta A_{\text{пр}} -\sum\Delta A_{\text{и.в.}}= (\Delta A_{CH4}+ \Delta A_{H2O(\Pi)}+ \Delta A_{N2}+0{,}5\Delta A_{O2}) - (\Delta A_{CO2}+2\Delta A_{NH3})$, cal/mol•degree

7. Next, the algebraic difference of the constant coefficient of the system is determined by the equation:

$\Delta B = \sum\Delta B_{\text{пр}}-\sum\Delta B_{\text{ив}}= (\Delta B_{CH4}+\Delta B_{H2O(\Pi)}+\Delta B_{N2}+0{,}5B_{O2}) - (\Delta B_{CO2}+2\Delta B_{NH3})$, cal/mol•degree

8. To determine the algebraic difference of the constant coefficient ΔC^{1} of the system, the following equation is compiled:

$\Delta C1=\sum\Delta C1_{\text{пр}}-\sum\Delta C1_{\text{и.в.}}=(\Delta C1_{CH4}+\Delta C1_{H2O(\Pi)}+\Delta C1_{N2}+0{,}5\Delta C1_{O2})-(\Delta C1_{CO2}+2\Delta C1_{NH3})$, cal/mol•degree

9. Next, an equation will be drawn up for determining the algebraic difference of the constant coefficient ΔC of the system:

$\Delta C=\sum\Delta C_{\text{пр}}-\sum\Delta C_{\text{и.в.}}=(\Delta C_{CH4}+0+0+0{,}5*0)-(0+2*0)=C_{CH4}$

10. For a temperature of 298K, an equation is drawn up to determine the integration constant for the change in enthalpy of the system:

$\Delta HO=\Delta H298-\Delta A*T-\Delta B*T1^{2}/2+\Delta C1/T-\Delta C*T1^{3}/3$

11. For temperatures T1, an equation is drawn up to determine the change in enthalpy of the system:

$\Delta HT1=\Delta HO+\Delta A*T1+\Delta B*T^{2}/2-\Delta C*T^{3}/3$, кал/моль

12. The thermal effect of a chemical reaction for temperatures T1 is determined by equality:

QPT1=-ΔHT1, cal/mol

13. For a temperature of 298K, the logarithm of the equilibrium constant of the chemical reaction is calculated:

$\lg KP298=-\Delta GO298/(4{,}576*T)$

14. For a temperature of 298K, an equation is drawn up to calculate the integration constant of the equation, the logarithm of the system:

$KO=\lg KP298+\Delta HO/(4{,}576*T)-(\Delta A*\lg T)/1{,}987-(\Delta B*\lg T)/9{,}150-(\Delta C1*T^{2})/9{,}150-(\Delta C*T^{2})/27{,}45$

15. For temperature T1, an equation is drawn up for calculating the equilibrium constant of the reaction:

$\lg KPT1 = -\Delta HO/(4{,}576*T1)+(\Delta A*\lg T1)/1{,}987+(\Delta B*\lg T1)/9{,}150+\Delta C1/(9{,}150*T1^{2})+$
$+(\Delta C*T1^{2})/27{,}45+KP$

16. The Gibbs energy value for temperature T1 is calculated using the equation:

$\Delta GT = -4{,}576*T1*\lg KPT1$, cal/mol

To carry out thermodynamic calculations, the C++Builder 6 computer program was used, into which the initial physicochemical constants from Table 1 of this dissertation were entered.

The program 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);
}
    //---------------------------------------------------------------------------
```

Using the compiled program, we calculated the values of the thermodynamic quantities: DHO298, DS298, GO298, QPT1, DHOT1, LOGKPT1, DGOT1, etc. for temperatures from 873 to 1473 K with a step of 100 K. To do this, each time in operand 138 the value of T1 was changed to the corresponding temperature in degrees Kelvin.

The obtained results of thermodynamic calculations on the probability of occurrence of the reaction under study are presented in Figures 1, 2 and 3.

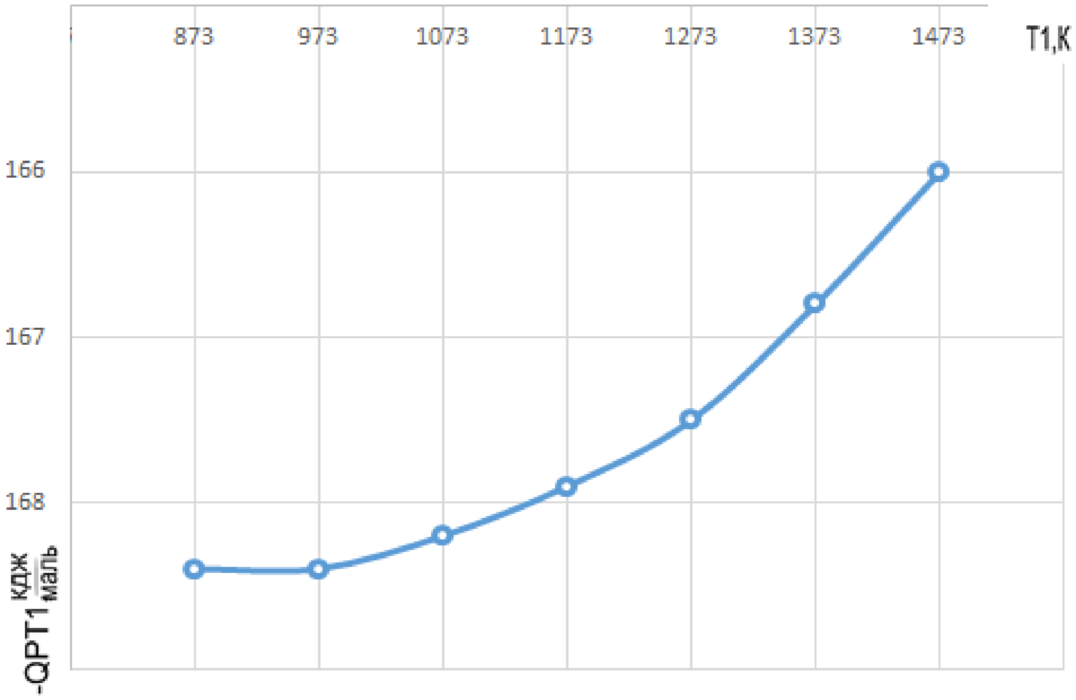

Figure 1. Dependence of the thermal effect on the reaction temperature

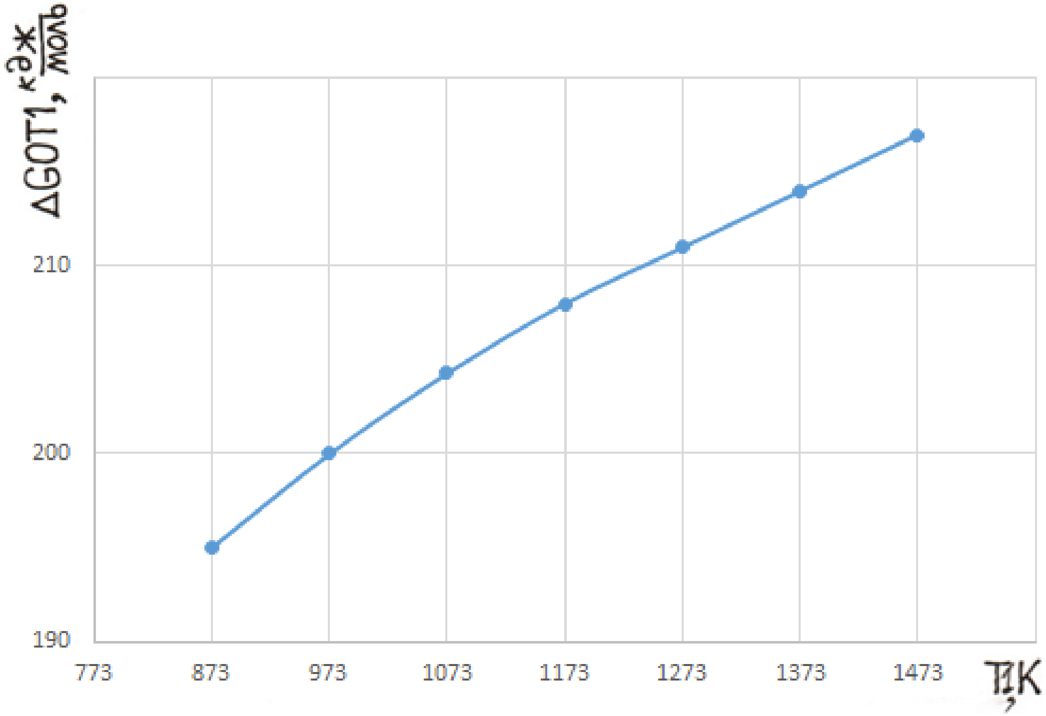

Figure 2. Dependence of the change in Gibbs energy on the reaction temperature $CO_2 + 2NH_{3(r)} = CH_{4(r)} + H_2O_{(n)} + N_{2(r)} + 0{,}5O_{2(r)}$

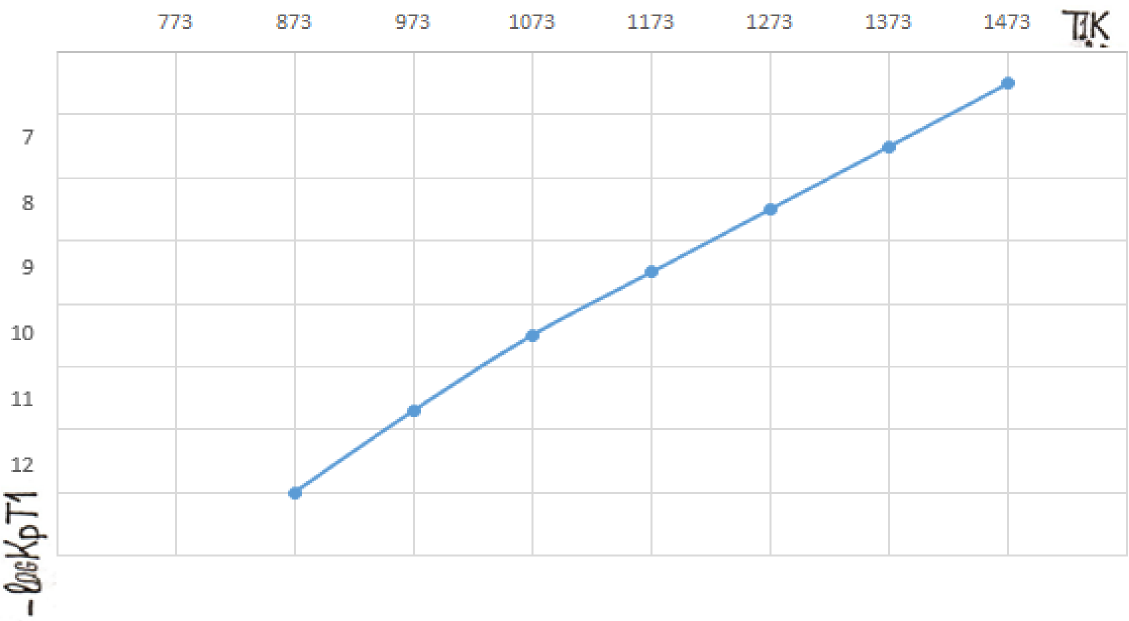

Figure 3. Dependence of the logarithm of the equilibrium constant on the reaction temperature

The results of the above thermodynamic calculations using a computer indicate that under standard conditions the reaction under study is endothermic, does not proceed spontaneously and is thermodynamically impracticable.

The thermal effect of the reaction in the temperature range 873-1473 K is endothermic, i.e. the reaction occurs with the absorption of heat from the outside.

- Thermodynamic calculations of the chemical interaction between ammonia and carbon dioxide with the formation of methane, water vapor, nitrogen and oxygen in the temperature range 873-1473 K established the thermal effect of the reaction - 168395 J/mol, and the change in the Gibbs energy at 1073 K - (+20238394 J/mol).
- Thermodynamically calculated values of the change in the Gibbs energy showed that their absolute values decrease with increasing temperature.
- Experimental data have proven that during the synthesis of calcium cyanamide from calcium oxide, ammonia and carbon dioxide in the temperature range 873-1373K, no free carbon is formed.

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