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AN EQUILIBRIUM ANALYSIS OF COMBUSTION OF INDUSTRIAL WASTE MATERIALS

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ABSTRACT

STANJAN, computer program based on the "Element Potential Method" [1] was used to predict the species involved in combustion of industrial waste materials.

INTRODUCTION

Combustion/Incineration is an effective treatment process for the disposal of toxic organic chemical waste.
Organic waste, frequently contains hydrocarbons bearing heteroatoms such as halogens, nitrogen, oxygen and sulfur.
The presence of these heteroatoms complicate the chemistry of combustion substantially by the formation of an increased spectrum of compounds as intermediates as well as the ultimate oxidation products.
Consequently, it is of great practical interest to be able to predict the identities of species involved in combustion so that the nature of pollutant emissions from combustors can be better assessed and controled. The practical utility of such equilibium analysis is also crucial for optimization of fuels burning.

A powerful "Menu-driven" personal computer implementation [2] of code for solving chemical equilibrium problems STANJAN V.3.6 was employed in this research. The standard P.C. version of STANJAN permits the inclusion of up to 20 compounds in an equilibrium computation. By justicious selection many more than 20 species can be studied under the same specification of temperature and pressure by repeatedly solving the equilibrium problem, with new "minor species".
As an input to the program one have to know the quantity and the atomic population of the waste materials.
As an output of the program we get the mole concentration of the 20 compounds.

Using the results enable us to minimize pollution emission from incinerators.

MATHEMATICAL MODEL OF THE BASIC THEORY OF ELEMENT POTENTIAL

The Gibbs function of a system is

$$1)\quad G = \sum_{j=1}^{s} \bar{g}_j N_j$$

Where $\bar{g}_i$ is the partial molal Gibbs function and Nj is the number of moles of species in the system.
The partial molal Gibbs function are given by:

$$2)\quad \bar{g}_j = g_j(T,P) + RT \ln x_j,$$

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Where $g_j(T,P)$ is the Gibbs function of pure j evoluated at the system. The atomic population constraints are

$$3)\quad \sum_{j=1}^{s} n_{ij}N_j = p_i \quad , \quad i = 1, \ldots, a$$

Where n_{ij} is the number of i atoms in a j molecule, Pi is the population (moles) of i atoms in the system and "a" is the number of different elements (atoms types) present in the system.

The equilibrium solution at the given T, and P, is the distribution of Nj that minimizes G, subject to the atomic constraints (3), for non-negative Nj.
Minimization problems with constraints are best handled by the method of "Lagrange Multipliers".
For convenience, we denote $\tilde{g}_j = g_j(T,P)/RT$, and seek the minimum of G/RT.
Using (2) we find that for arbitrary variations in the mole number.

$$4)\quad d\left(\frac{G}{RT}\right) = \sum_{j=1}^{s} \left(\tilde{g}_j + \ln x_j\right) dN_j + \sum_{j=1}^{s} N_j \frac{1}{x_j} dx_j$$

Now the dNj are not all independent because of the atomic constraints. Relationships among the dNj are obtained by differentiating (3).

$$5)\quad \sum_{j=1}^{s} n_{ij}dN_j = 0 \quad , \quad i = 1, \ldots, a$$

We must solve for the "a" restricted dNj in terms of the "s-a" free dNj and then substitute these relation into (4) in order to express the G variation in terms of freely variable Nj. This process is equivalent to subtracting multiples of (5) from (4).

$$6.\quad d\left(\frac{G}{RT}\right) = \sum_{j=1}^{s} \left(\tilde{g}_j + \ln x_j\right) dN_j - \sum_{i=1}^{a} \lambda_i \sum_{j=1}^{s} n_{ij}dN_j$$

The λ_i are the "Lagrange Multiplier" that are required to drop out the set of restricted dNj from this equation. Thus setting the coefficients of these dNj to zero, one has;

$$7)\quad \tilde{g}_j + \ln x_j - \sum_{i=1}^{a} \lambda_i n_{ij} = 0$$

for the restricted j.
For every species we get

8) $$x_j = \exp(-\tilde{g}_j + \sum_{i=1}^{a} \lambda_i n_{ij})$$

equation (8) is the main result of element potential for mixtures of ideal gases or for ideal solutions. The multiplier λ_i is called the "Element Potential" for i atoms. Using (8) we see that

9) $$\bar{g}_j/RT = \sum_{i=1}^{a} \lambda_i n_{ij}$$

and hence λ_i represents the Gibbs function /RT per mole of i atoms. What is even more amazing is that each atom of an element contributes the same amount to the Gibbs function of the system irrespective of which molecule or phase it is in. The λ_i are properties of the system, however, and cannot be tabulated as a function of atom or molecule.
The values of the element potential are determined by the atomic constraints (3) which we rewrite as

10) $$\sum_{j=1}^{s} n_{ij} \bar{N}_{(j)} x_j = p_i \quad , \qquad i = 1, \ldots, a$$

Where $\bar{N}_{(j)}$ is the number of moles in phase containing species j.
This becomes a set of equations for the unknown i and the P unknown phases.
To this we add the P equations

11) $$\sum_{\substack{j=1 \\ \text{in } m}}^{s} x_j = 1 \quad , \qquad m = 1, \ldots, P$$

equation 10, 11 must be solved simultaneously to determine the element potentials and phase moles.

RESULT AND DISCUSSION

As an example of combustion of an industrial waste we tested methanethiol. The oxidizing reaction of methanethiol is shown in Fig.1 and Fig.2 A qualitative comparison between the the traditinal oxidizing reaction of methanthiol and its combustion is done. The comparison shows that:

-Less liquid and solid waste are produced in the combustion process.

-In the chemical process the oxidizing reagents produce additinal pollutants (MnO_2 , S)

-In the combustion process air is used as oxidizing ageant and there fore it does not couse any further pollution.

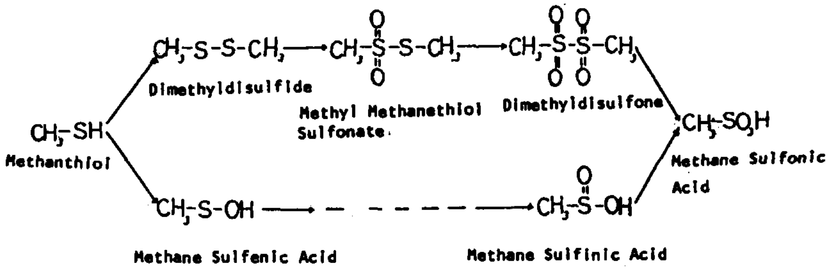

Fig.1 OXIDATION OF METHANETHIOL chemical reaction

$$CH_3\text{-}SH + O_2 \longrightarrow \overset{\text{I}}{\text{MAIN PRODUCTS}}\ CO_2 + SO_3 + H_2O + \overset{\text{II}}{\text{BY PRODUCTS}}\ [CO + H_2S + SO_2 + COS + CH_4S + C_2H_6S + C_2H_6S_2]$$

Fig.2 combustion of methanethiol

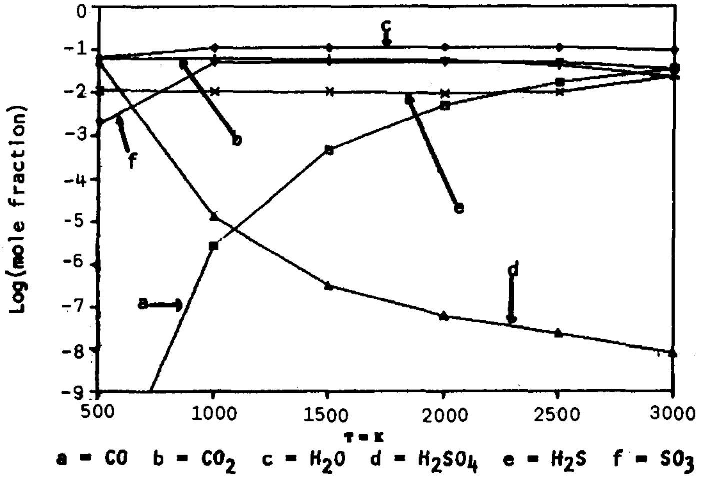

Fig. 3.a combustion of methanethiol molar ratio Air/Methanethiol = 0.9

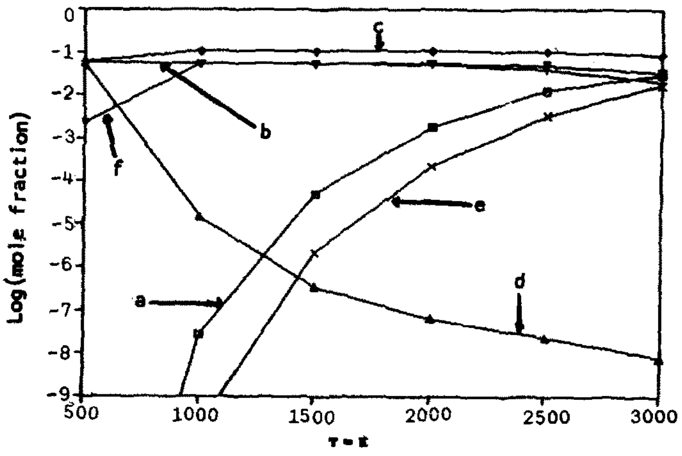

Fig. 3.b combustion of methanethiol molar ratio Air/Methanethiol = 1.0

CONCLUSIONS

The analysis of combustion of methanethiol by the " Element Potential" method shows that the optimal condition for the destruction of methanethiol are:

-Temperature: 1000° K
-Molar ratio Air/Methanethiol>1
-The overall mole fraction of sulfides as shown in Fig. 3.b is less than 10^{-9}

The main sulfur by product obtaines SO_3 .

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