Technical Notes

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Kinetics of Alkaline-Earth Atoms Reactions with Molecular Oxygen

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THE advancement of modern science and engineering has motivated a special interest in the study of processes occurring under conditions of high temperatures, aggressive atmospheres, etc. In most works on high-temperature oxidation of metals, either kinetics of heterogeneous reactions as a whole or ignition and combustion are analyzed. Considerable advances have been made in these areas but it is rather difficult, and sometimes impossible, to obtain reliable kinetic information on gas-phase reactions of metals oxidation from widely used experiments on ignition of bands, wires, and single particles, since in these experiments the effect of various complicating factors is not fully eliminated.

The most suitable experiment in this sense may be the method[3] where zones of metal evaporation and reaction are separated and evaporation is realized by an independent heat source rather than by reaction heat. The diffusion flame method[1] which was extensively used in the 1930's for the study of atomic and atomic-molecular reactions of alkaline metals meets these requirements. Due to difficulties associated with processes at higher temperatures, this method was practically unusable for investigation of other metals reactions. Markstein[2] used the idea to determine the reaction rate constant for magnesium with oxygen but the conditions of this experiment corresponded to the usual gas burner rather than to the diluted diffusion flame.

Thermocouple variation of the diffusion flame (TVDF) method[3] is a more convenient way for studying high-temperature metal vapor reactions. But common methods of treating experimental data obtained by the TVDF method are unusable for a majority of metals gas-phase oxidation. To obtain correct kinetic constants by this method it was necessary to develop new, more general calculation methods. These methods take into account high gradients of temperature and secondary reactions in the diffusion flame zone, condensation of products, and other complicated factors. The description of these methods is given in Refs. 4-6.

The apparatus for studying alkaline-earth metals gas-phase oxidation kinetics consisted of a stainless steel reaction chamber placed into the furnace-thermostat, evacuation system, inlet and exhaust systems, and semiautomatic control for temperature recording in the reaction zone. Argon was used as a gas dilutant and carrier gas. A detailed description of the installation and experiments is given in our previous works.[4,7,8]

It has been previously found for the case of gas-phase magnesium oxidation by molecular oxygen[4] that alkaline-earth metals reactions in the diffusion flame occur homogeneously for the most part and products condensation does not notably influence the kinetics. Analysis of other mechanisms, for instance those considered in Mellor's et al. paper,[9] has shown that in oxygen diffusion flames of alkaline-earth metals (M) the reactions are either improbable (mechanisms with participation of dimer and metal peroxide), or an atomic-molecular reaction $M(\text{gas}) + O_2 \rightarrow MO(\text{gas}) + O$ is a limiting stage (thermolecular mechanism). Based on these facts we believe that the observed kinetic parameters relate to those reactions which define the structure of diffusion flames ($M + O_2$).

The analysis of the experimental data obtained shows that the rate constants of magnesium, calcium, strontium, and barium reactions with oxygen are well described by the Arrhenius equation, $k = A\exp(-E/RT)$. Experimental conditions and parameters of this equation are listed in Table 1. This table also gives the values of thermal effects at 1000K.[10]

For the whole series the Polanyi-Semenov rule is satisfied, and is expressed in this case by the formula $E = 14.3 - 0.13Q$. Regular changes of the studied reactions parameters allow us to suppose the common character of the reaction mechanisms and to establish a quantitative correlation between their kinetic characteristics.

Investigation of the reaction of barium and strontium with oxygen in molecular beams[11-12] has shown that though the

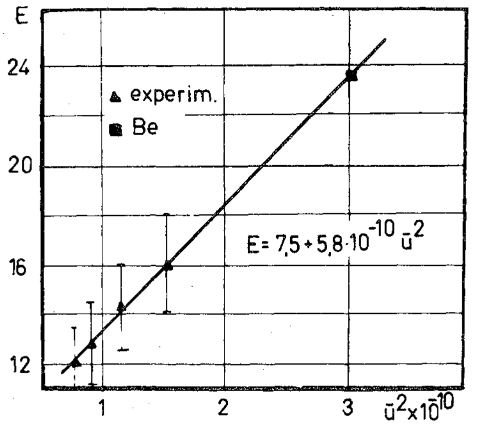

Fig. 1 Experimental (points) and calculated (straight line) activation energies of alkaline-earth metals reactions with O_2.

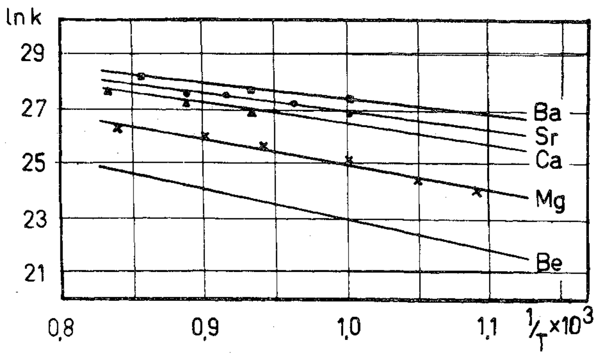

Fig. 2 Semilogarithmic anamorphosis for alkaline-earth metals reactions with O_2.

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Table 1 Experimental conditions and kinetic parameters of the reactions M(gas) + $O_2 \rightarrow M$O(gas) + O

Metal	Temperature interval, K	Total pressure, torr	Q kcal/mole	$A \cdot 10^{-14}$ cm^3/mole·sec	E kcal/mole
Mg	770 – 1024	6.0 – 10.0	– 18.9	2.1 ± 0.2	16.0 ± 2.1
Ca	1000 – 1200	2.0 – 6.0	– 3.7	2.5 ± 0.3	14.4 ± 2.1
Sr	1000 – 1200	1.0 – 3.0	– 6.7	2.4 ± 0.2	13.0 ± 1.8
Ba	970 – 1180	1.5 – 3.0	+ 18.2	1.7 ± 0.2	12.2 ± 1.4

Table 2 Calculated kinetic parameters of the reactions M(gas) + $O_2 \rightarrow M$O(gas) + O

			Pre-exponential factor cm^3/mole·sec		Activation energy kcal/mole	
Metal	σ Å^2	$\bar{u} \cdot 10^{-4}$ cm/sec	Calculated A_{gas}	Taken A_0	Calculated from $\bar{u}$	Calculated from $E = a + bQ$
Mg	23.3	12.3	1.77	2.12	16.3	17.8
Ca	26.3	10.9	1.79	2.13	14.3	14.8
Sr	30.5	9.5	1.73	2.08	12.7	13.2
Ba	31.5	9.0	1.71	2.05	12.2	12.3

reaction of strontium exhibits a weak tendency toward realization of the harpoon mechanism, the rebound mechanism is most probable for these reactions.

In the case of rebound mechanism, correlations of pre-exponential factors and activation energies with mean rate values of the colliding particles mass centers $\bar{u} = (8kT/\pi\mu)^{1/2}$ should be most accurate (μ is reduced mass). Table 2 gives the values of the gas-kinetic collision cross sections (σ) calculated from atomic radius of metals and molecular diameter of oxygen, values of $\bar{u}$ at 1000K as well as pre-exponential factors calculated by formula $A_{gas} = \sigma\bar{u}$.

Since σ values (in Å^2) in turn can be described for a given series of colliding pairs by the relationship $\sigma(\bar{u}) = 52.3 - 2.3 \cdot 10^{-4}\bar{u}$ the calculated pre-exponential factors (in cm^3 ·sec^{-1}) conform to the formula $A_{gas} = (52.3 - 2.3 \cdot 10^{-4}\bar{u})\,\bar{u}$. Function A_{gas} ($\bar{u}$) has a maximum at $\bar{u} = 11.3 \cdot 10^4$/cm/sec which is close to the $\bar{u}$ value for calcium and corresponds to a maximum of the pre-exponential factors in the investigated series. Experimental A values are in satisfactory agreement with the calculated ones A_{gas} ($\bar{u}$) and mean ratio of them is equal to 1.2 ± 0.2. The fact that experimental A values fall into the strip[13] $A = (1.2 \pm 0.2)\ (52.3 - 2.3 \cdot 10^{-4}\bar{u})\,\bar{u}$ permits the values $A_0 = 1.2 A_{gas}$ to be taken for the pre-exponential factors of the investigated reactions (see Tables 1 and 2).

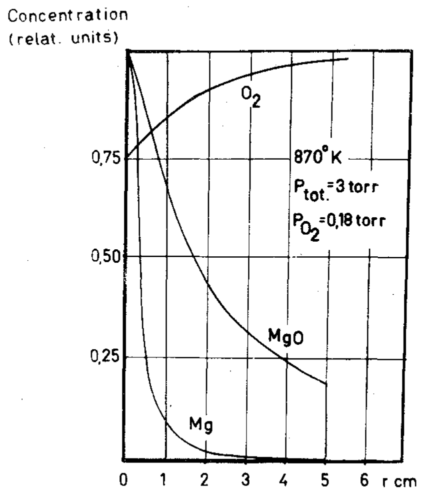

Fig. 3 Concentrations distribution in (Mg + O_2) diffusion flame zone (calculated).

Experimental values of the activation energy in reactions of alkaline-earth metals with molecular oxygen is described with good accuracy (Fig. 1) by the formula $E = 7.5 + 5.8 \cdot 10^{-10}\bar{u}^2$.

Thus, established quantitative correlations permit an evaluation of the pre-exponential factor and activation energy to be made for reaction of beryllium vapors with molecular oxygen. Such an evaluation is especially interesting as direct determination of these parameters for the reaction Be(gas) + $O_2 \rightarrow$ BeO(gas) is so far impossible.

Rate constants of the gas-phase reactions between alkaline-earth metals and molecular oxygen are equal to (in cm^3/mole·sec):

$$
\begin{array}{ll}
\mathrm{Be} + \mathrm{O}_2 & k = 1.6 \cdot 10^{14} \exp(-21100/RT) \\
\mathrm{Mg} + \mathrm{O}_2 & \,2.1 \cdot 10^{14} \exp(-16500/RT) \\
\mathrm{Ca} + \mathrm{O}_2 & \,2.1 \cdot 10^{14} \exp(-14200/RT) \\
\mathrm{Sr} + \mathrm{O}_2 & \,2.1 \cdot 10^{14} \exp(-13500/RT) \\
\mathrm{Ba} + \mathrm{O}_2 & \,2.0 \cdot 10^{14} \exp(-12100/RT)
\end{array}
$$

A comparison is shown in Fig. 2 of the experimental points and the semilogarithmic anamorphosis calculated by the taken parameters. This comparison provides further support for the accuracy of the evaluation.

The results demonstrate that the TVDF method is really one of the most convenient and productive for kinetic investigations of reactions between metal vapors and various oxidants. A great advantage of this method is the possibility for a rigorous quantitative description of the processes occuring in the diffusion flame zone, and hence, their mathematical simulation. A mathematical model of a diffusion flame (Mg + O_2) is presented in Fig. 3 based on reliable experimental data. On this basis, an experimentally substantiated model of vapor-phase combustion for metal particle can be created in the near future.

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On Optimized Prestressed Trusses

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Introduction

An earlier publication[1] has presented a basic formulation of the optimization problem for indeterminate structures that are prestressed by component mismatch as well as subjected to multiple independent-load conditions. Illustrative examples, consisting of a stress-limited 3-bar truss[1] and two-span beam,[2] have demonstrated that designs that include optimal selection of mismatch parameters can be significantly lower in weight than their nonprestressed counterparts.

It is the purpose of this Note to extend the examination of the effects of such prestressing by considering several trusses of varying size and complexity, including stress, displacement, and minimum area limits. In particular, attention will be focused on a 10-bar truss, a 25-bar truss, and a 72-bar truss, examples that are encountered most frequently in current optimization studies.[3-8] Redesign of these trusses, incorporating component mismatch, should provide some definitive insight into actual and potential consequences of this prestressing mechanism.

Synthesis

A truss optimization problem in which element mismatches are included as design parameters may be stated in the basic form[1]: find the components of a vector of design variables

$$\{\tilde{D}\}^T \equiv \{D^T \,\vdots\, D_p^T\} = \{d_1 \ldots d_n \ldots d_N \,\vdots\, d_{N+1} \ldots d_m \ldots d_M\}$$

such that

$$g_k(\tilde{D}) \geq 0 \qquad k = 1,2,\ldots,K \tag{1}$$

and such that weight $W(D)$ is minimized, i.e.,

$$W(D) \rightarrow \min \tag{2}$$

where D is a vector of basic variables (i.e., cross-sectional areas) and D_p is a vector of initial element elongations (changes in length from nominal). Since variables may be linked, integers N and $M-N$ represent the number of independent areas and independent elongations, respectively, where N and $M-N$ are less than or equal to I, I being the total number of truss components.

The inequalities in Eq. (1) represent behavioral and side constraints, which specify that 1) the initial prestress in element i of the unloaded structure, σ_{i0}, $i = 1, \ldots, I$, must be bounded by allowable tensile and compressive limits; 2) the stress in element i of the prestressed structure with load condition ℓ superposed, $\sigma_{i\ell}$, $\ell = 1, \ldots L$, must be bounded by the allowable tensile and compressive limits; 3) the magnitude of the jth system displacement coordinate in load condition ℓ, $u_{j\ell}$, $j = 1, \ldots, J$, $\ell = 0, 1, \ldots, L$, must be bounded by allowable limiting values; and 4) the cross-sectional areas must be greater than or equal to minimum allowable values. It may be noted that truss weight [see Eq. (2)], is a function of D only, whereas all constraints except those involving minimum area are functions of $\tilde{D}$.

For the examples considered herein, the design problem given by relations (1) and (2) was solved by use of CONMIN,[9] a computer program based on Zoutendijk's feasible direction algorithm.[10] This algorithm requires gradients of the objective function and constraints, and the CONMIN program has the capability of computing these gradients by finite-differences or of accepting, as part of user-supplied structural analysis subroutines, analytic expressions for these gradients.

Since W is a linear function of d_n, $n = 1,\ldots,N$, an analytic expression for the gradient of $W(D)$ is easily obtained. The use of analytic constraint gradients is also desirable in order to avoid the excessive number of structural analyses that would be required for their finite-difference computation. (Note that the total number of independent variables in this class of problem can be relatively large; e.g., $2N$ for linking based only on structural symmetry.) The development of analytic expressions for the components of constraint gradients (i.e., derivatives of stresses and displacements with respect to design variables), for the prestressed structures under consideration, is shown in the Appendix.

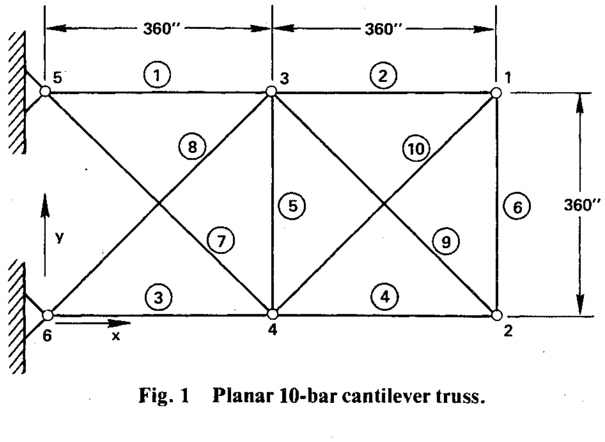

Fig. 1 Planar 10-bar cantilever truss.

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