

Metals vapour oxidation in diffusion flames

Oleg E. Kashireninov

Institute of Structural Macrokinetics, USSR Academy of Sciences
142432 Chernogolovka, Moscow Region, USSR

Abstract - The structure of metal combustion zone in oxidizing atmosphere is greatly determined by mechanism and kinetic parameters of gas-phase reactions which generate the condensing oxide vapours. The role of the heterogeneous reactions and condensation in the flame structure formation is considered for diffusion flames of magnesium.

INTRODUCTION

Until recently, combustion of metals in oxidizing atmospheres was of interest in connection with the elaboration of powerful, relatively compact chemical sources of thermal energy. In this field dozens of theoretical and experimental investigations were carried out and many complicated technical problems were solved.

Currently, the interest to combustion of metals has noticeably decreased. However, a number of questions which are vital for understanding of these complex processes remain unclarified. First of all, it concerns the mechanism and kinetics of the chemical reactions in the combustion zone and aggravated by the processes of the condensed products formation which are coincident with reactions in time and space. The present paper attempts to analyse some processes occur in the flames of metal vapour in oxygen.

PROBLEM CHARACTERISTICS

Thermochemistry In terms of thermodynamics, the most advantageous is the solid metal oxidation to solid oxide (see Table 1). However, seeing that during the metal combustion the temperature reaches 3000K and higher this process may be of significance only for the initial stages of ignition.

Thermal effects of liquid metals reactions bring about the liquid oxides formation are also sufficiently high but because of action of kinetic factors they do not seem able to play a leading role in combustion processes.

It is natural to assume that during the combustion of metals the both, small particles and bulk samples, the limiting chemical reactions take place in the gas phase. The existence of the diffusion zone close to the metal surface is proved by a number of investigations (e.g. Refs. 3-6) not only for easily evaporated magnesium but also for beryllium, titanium and zirconium.

At the same time, the data of Table 1 show, for metals the initial gas-phase reactions with molecular oxygen do not compile the heat source providing their gasification as observed for combustion of other fuels. Reactions of dimers also are not able to play this role, due either to the absence of dimers in the metals vapour at combustion temperatures (Mg, Ti, Zr) or to their very low concentrations Al) (Refs. 1,7). Thus, the key heat sources in the flames of metals are the condensation of the

forming oxide vapours and the termolecular recombination reactions of oxygen and metal atoms and oxide radicals in various combinations. Thermal effects of these processes for the metals under consideration as a rule range from 400 to 800 kJ/mole (Ref. 1).

TABLE 1. Thermal Effects of Some Metals Oxidation by Molecular Oxygen, calculated on the data of Ref. 1 (at 0 K, in kJ/mole)

Reaction	Be	Mg	Al ^a	Ti ^a	Zr ^a	Fe ^b
M(s) + O ₂ → MO _x (s)	606	597	1664	939	1095	272?
M(l) + O ₂ → MO _x (l)	533	529	1564	886	1019	264
M(g) + O ₂ → MO(g) + O	- 59	- 39 ^c	13	174	266	- 84
MO(g) + O ₂ → MO ₂ (g) + O	- 76 ^b		- 101	123	153	
M ₂ O(g) + O ₂ → M ₂ O ₂ (g) + O	178		11			
M ₂ (g) + O ₂ → MO(g) + MO(g)	-131 ^b	413 ^b	327	716		
MO(g) → MO _x (s)	738	535	1119	619	780	523
MO(l) → MO _x (s)	86	77	111	68	90	21
T _m (MO), K	2851	3100	2327	2030		1650
M(g) → M(s)	320	146	327	471	598	414
M(l) → M(s)	13	9	11	15	14	13
T _m (M), K	1560	923	934	1944	2133	1809

^a x in MO_x fits the highest oxide

^b Calculated on JANAF Tables

^c Evaluated using D(MgO)=455 kJ/mole (Ref. 2)

Kinetics and Mechanism At combustion temperatures the supersaturation of the metal oxides vapour may be high enough and the final size of the oxide particles forming in diffusion flame by homogeneous condensation measures about 40-100 Å (Refs. 8-11). The developed surface of the condensed phase, distributed through the combustion zone, makes it possible to assume the prevalence of the heterogeneous reactions of metal atoms with adsorbed oxygen (Refs. 12-13). In spite of the criticism expressed on this matter (Refs. 14-16) the question concerning the type of the process dominating in the metal flames still remains open.

Since the gas-phase reactions of the metal atoms with oxygen are sufficiently fast (see Table 2) the question arises concerning the ratio of

TABLE 2. Rate Constants for Gas-Phase Reactions of Some Metals

Reaction	T, K	k, cm ³ /mole·s	Refs.
Be + O ₂ → BeO(g) + O	1000	4 × 10 ⁹	17
Mg + O ₂ → MgO(g) + O	1000	(9.1±7.2) × 10 ¹⁰	18
Al + O ₂ → AlO(g) + O	300-1700	(2.0±1.3) × 10 ¹³	19
AlO + O ₂ → AlO ₂ (g) + O	1400	(1.9±1.0) × 10 ¹¹	19
Fe + O ₂ → FeO(g) + O	1600	(2.1±0.8) × 10 ¹¹	20

the MO(g) formation and its condensation rate. These ratios determine the possibility of the equilibrium existence in the combustion zone but they are still unknown.

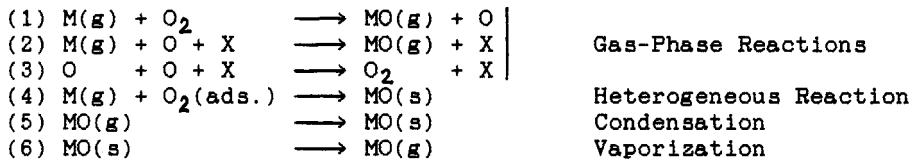
MACROKINETICS

The description of the metal vapour combustion zone can be obtained using the macrokinetic approach jointly taking into consideration the equations of chemical kinetics, diffusion and heat conductivity.

Formulation of problem The construction of the complete and rigorous model of combustion which make allowance, in particular, for the change in the metal vapour flow due to the heterogeneous oxide condensation on the surface of droplet, currently is hardly possible. The absence of the necessary data on the state and behaviour of condensed oxides in contact with the liquid metals is responsible for this. Besides taking into account these factors can not change a qualitative picture of the flame.

Hence, analysis of the processes in the diffusion flames can be conducted on a simplified model in which a spherical source of fixed metal vapour flow (\dot{m}) with the small typical dimension R_0 and the same temperature (T_0) as the oxidizing atmosphere outside the combustion zone is considered. Such a model corresponds to conditions of the kinetic experiments with diluted diffusion flames (see e.g. Ref. 21) and resembles the metal droplet combustion.

Kinetic scheme Gas-phase metal oxidation scheme with the following steps can be used as a kinetic model of process:



Such a scheme is sufficiently closely realized, for example, during the oxidation of magnesium and other alkaline-earth metals vapour (Refs. 22, 23). For aluminium the process substantially complicated through the formation and cross reactions of a number of suboxides (AlO , AlO_2 , Al_2O and Al_2O_2). For titanium, zirconium and iron the oxide MO also is not the final product and its oxidation to MO_2 follows primary gas-phase reactions (1) and (2).

Mathematical model The whole complex of the processes in the studied spherical diffusion flame zone is described by the system of dimensionless equations

$$\frac{\partial}{\partial \tau} (p_c + p_g) + \nabla [(p_c + p_g) \vec{v}] = 0 \quad (1)$$

$$\frac{\partial p_i}{\partial \tau} + \nabla (p_i \vec{v}) = \Delta p_i + \sum_j W_j \quad (i=1,2,3,4; j=1,2,\dots,6) \quad (2)$$

$$\frac{\partial N_n}{\partial \tau} + \nabla (N_n \vec{v}) = \nabla \left(\frac{D_n}{D_1} \vec{v} N_n \right) - M_c \sum_j W_j \quad (j=4,5,6) \quad (3)$$

$$\frac{\partial \theta}{\partial \tau} + \vec{v} \cdot \nabla \theta = \frac{\Delta \theta}{Le} + \sum_j \frac{1}{\gamma_j} W_j + \frac{M_c}{3B} \int_{n=2}^{\infty} \Phi(\theta_n - \theta) dn \quad (4)$$

$$\frac{\partial \theta_n}{\partial \tau} + \vec{v} \cdot \nabla \theta_n = \frac{M_c}{\beta n \sqrt{3}} [(\theta - \theta_n) + (p_3 - \hat{p}_3 F)(Q_5 - \beta n \frac{\partial \theta_n}{\partial n}) + \frac{M_3}{M_1} p_1 p_2 G(Q_4 - \beta n \frac{\partial \theta_n}{\partial n})] \quad (5)$$

The following nomenclature was used in this system: p_1 - metal vapour density, p_2 - molecular oxygen density, p_3 - oxide vapour density, \hat{p}_3 - density of saturated oxide vapour at $\theta=0$, p_4 - atomic oxygen density, M_i - corresponding molecular masses.

In the continuity equation (1): the condensed phase density $p_c = \int_{n=2}^{\infty} N_n dn$, where N_n - number of condensed particles contained n molecules of MO ; gas density $p_g = \sum_{i=1}^4 p_i$ ($i=1,2,3,4$). In the balance equation for gaseous components (2): the gas-phase reaction rate

$$W_j = n_j D_{aj} \Pi p_i \exp\left(\frac{\theta}{1 + \beta \theta}\right) \quad (j=1,2,3) \quad (6)$$

where

$$Da_j = \frac{k_j^0 \exp(-E_j/RT_0) R_0^2 \rho_0}{D_1} \quad (7)$$

and $\rho_0 = \frac{\dot{m}}{\pi R_0 D_1}$ - scale density of a gas;

the heterogeneous reaction rate

$$W_4 = M_c P_1 P_2 \int_{n=2}^{\infty} \Phi G dn \quad (8)$$

where

$$M_c = \frac{4\pi\alpha\bar{u}R_0^2 N \rho_0}{M_3 D_3} \left(\frac{3m_3}{4\pi\rho_c}\right)^{2/3} \quad (9)$$

$$\Phi = N_n \cdot n^{2/3} \quad (10)$$

$$G = \frac{k_4}{k_4 + \alpha\bar{u}}; \quad (11)$$

the homogeneous condensation rate

$$W_5 = M_c \int_{n=2}^{\infty} \Phi dn; \quad (12)$$

the evaporation rate

$$W_6 = M_c \hat{P}_3 \int_{n=2}^{\infty} \Phi F(n, \theta_n) dn, \quad (13)$$

where

$$F(n, \theta_n) = \exp\left[\frac{\omega}{n^{1/3}(1+\beta\theta_n)}\right] \quad (14)$$

In expression (14) $\omega = \frac{2\sigma M_3}{\rho_c R T_0} \left(\frac{4\pi\rho_c}{3m_3}\right)^{1/3}$, where σ - surface tension of condensed phase.

In the distribution function equation (3):

D_n - the Brown diffusion coefficient of the condensed particles.

In the heat balance equation for gas (4):

$$\gamma_j = \frac{c_g P_g}{q_j} \cdot \frac{RT_0^2}{E_j}, \text{ where } c_g - \text{heat capacity of gas atmosphere, } q_j -$$

thermal effect of the corresponding reaction; B - constant in Sherman's equation.

In the heat balance equation for particles (5):

$$Q_4 = \frac{q_4}{c_c T_0} \text{ and } Q_5 = \frac{q_5}{c_c T_0}, \text{ where } c_c - \text{heat capacity of condensed phase.}$$

Other parameters in Eqs.(1)-(5) have the meaning generally accepted in the theories of combustion and homogeneous condensation.

The calculations according to aforementioned model under the edge conditions

$$\begin{array}{llll} \tau = 0 & P_{1,3,4} = 0 & P_2 = P_2^0 & N_n = 0 \\ & \theta = 0 & \theta_n = 0 & V = \text{const} \end{array}$$

and the terminal conditions

$$\begin{array}{llll} x = 1 & -\frac{\partial P_1}{\partial x} - Vp_1 = 1 & x = \infty & \frac{\partial P_1}{\partial x} = 0 \\ & -\frac{\partial P_i}{\partial x} + Vp_i = 0 \quad (i=2,3,4) & & \frac{\partial P_i}{\partial x} = 0 \\ & V = V_0 & & P_2 = \text{const} \\ & N_n = 0 & & \frac{\partial N_n}{\partial x} = 0 \\ & \theta = 0 & & \theta = 0 \\ & \theta_n = 0 & & \theta_n = \theta \end{array}$$

are being currently conducted and their results to be published.

QUANTITATIVE EVALUATIONS

The model formulated makes it possible to do some limiting estimations of the rates of processes in the flame zone. Cited below are the results of the approximate calculations for the diffusion flame of magnesium at temperatures $T=1000-3000\text{K}$ and pressures $P=1-10000\text{ kPa}$ ($\text{Ar}+10\%\text{O}_2$). For rough estimations the kinetic scheme can be simplified and termolecular reactions (2) and (3) as well as the condensed oxide vaporization (6) excluded from consideration.

Gas-phase reaction and condensation It is easy to see, the parameter Da in expression (6) for the rate of gas-phase reaction is determined by the ratio of the characteristic times of diffusion and reaction:

$$Da_1 \sim t_d/t_1.$$

Parameter M_c assigned by formula (9) depends on the ratio of characteristic times of diffusion and condensation:

$$M_c \sim t_d/t_5.$$

Thus, the ratio of these parameters characterizes the ratio of the gas-phase reaction and the homogeneous condensation rates:

$$W_5/W_1 \sim M_c/Da_1 = 4.8 \times 10^7 \frac{\bar{u}}{k_1} \cdot \frac{D_1}{D_3}$$

It must be noted, this relation is independent of the metal flow \dot{m} .

The evaluation of W_5/W_1 was carried out for $R_0=0.05\text{ cm}$ and $\rho_c=3.58\text{ g/cm}^3$ using the effective rate constants for reaction (1) (Ref. 23) and diffusion coefficients D_1 and D_3 , calculated with collision integral values taken from Ref. 24. The obtained results show (Fig. 1 and 2), the ratio W_5/W_1 significantly depends on P and T . The dependence W_5/W_1 vs. P is defined by the variations of the effective rate constant considered in Ref. 23. Curves W_5/W_1 vs. T linearize in coordinates $\log(W_5/W_1) \sim 1/T$ (Fig. 2) and the slope weakly increase with pressure increasing:

$$\begin{aligned} \log(W_5/W_1) &= 0.76 + 3500/T & (1\text{ kPa}) \\ &= 1.71 + 4140/T & (100\text{ kPa}) \\ &= 3.75 + 4460/T & (10000\text{ kPa}) \end{aligned}$$

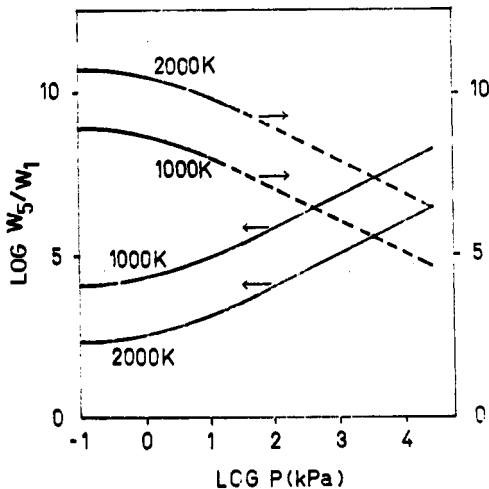


Fig. 1. Relation of condensation and gas-phase reaction rates depending on pressure at 1000 and 2000 K.

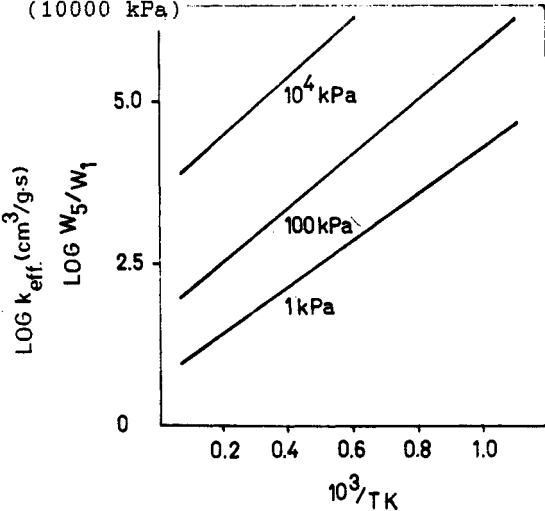


Fig. 2. Dependence of W_5/W_1 vs. $1/T$ at 1, 100 and 10000 kPa.

It follows from Fig. 1 and 2, the condensation rate of $\text{MgO}(g)$ always considerably exceeds the rate of gas-phase reaction (1). This conclusion

is rather significant since from it follows that in magnesium diffusion flames the gas-phase reaction is unable to generate the oxide vapour concentrations over the equilibrium ones. Hence, in this case the concept of equilibrium homogeneous condensation theory is valid for description of nucleation and growth of MgO particles.

Heterogeneous and gas-phase reactions As seen from the analysis of Eqs. (6) and (8) at the limit of low Θ

$$W_4/W_1 \longrightarrow \frac{M_c}{Da_1} \cdot \Phi \quad (15)$$

where Φ determined by formula (10) has the meaning of the condensed particles surface. It is obvious that at minor particles surface ($\Phi \ll Da_1/M_c$) gas-phase reaction (1) is prevailed in the diffusion flame zone. At $\Phi \approx Da_1/M_c$ the rates of reactions (1) and (4) equalize ($W_4 \approx W_1$) and rather large surface ($\Phi \gg Da_1/M_c$) heterogeneous reaction (4) can dominate.

Strict determination of Φ values requires the knowledge of condensed particles distribution with size taking into account diffusion as well as concentration and temperature gradients in the reaction zone. Such calculation is rather a complicated independent problem and for purposes pursued in the present work simple formulas of homogeneous condensation theory (Ref. 25) can be used.

To estimate the upper limit for W_4/W_1 , it can be suggested that condensation occurs in the medium where concentration of MgO(g) is gradientless and corresponds scale density of gas, i.e. is equal to Mg(g) concentration on the R_0 boundary:

$$N_{3\max} = [Mg(g)]_{\max} \sim \frac{\dot{m}}{\pi R_0 D_1 m_1} \quad (\text{cm}^{-3}) \quad (16)$$

Regardless of the conclusions of the previous part it can be assumed that gas-phase reaction supplies the MgO vapour with a velocity providing $N_{3\max}$ constancy in time. It is clear that such conditions are limiting and maximal concentration of condensed particles and the highest rate of heterogeneous reaction (4) fit to them.

The number of MgO molecules in the nucleus (\hat{n}) of the condensed phase is determined by vapour supersaturation S :

$$\hat{n} = \frac{32\pi\sigma^3 v_3^2}{3(kT \ln S)^3} \quad (17)$$

where v_3 is molecular volume of MgO, $\sigma = 1090 \text{ erg/cm}^2$ (Ref. 26). For calculation of Φ the following values were used:

$$N_{n\max} = \frac{N_{\max}^* m_3}{\rho_0} \quad (18)$$

where N_{\max}^* is the concentration of nuclei and

$$N_{\max}^* = N_{3\max} \exp\left(-\frac{\hat{n} \ln S}{2}\right) \quad (19)$$

It was assumed that n in formula (10) corresponds to typical (Refs. 8-11) size of condensed particles ($r=20 \text{ \AA}$) formed in magnesium diluted diffusion flames, i.e. $n \approx 2 \times 10^3$. Dependences of Φ and \hat{n} from S at temperatures of 1000, 2000 and 3000K depicted in logarithmic coordinates in Fig. 3.

The estimation shows, the ultimate supersaturation of vapour over the growing nucleus of condensed phase at $T > 1000\text{K}$ can not exceed the value of $S \sim 10^7$ and it decreases with temperature increasing. Thus, supersaturation at which any MgO(g) molecule is formally a nucleus, i.e. every dual collision results in the growth of $(MgO)_n$ complexes, equals $\sim 10^7$ for 1000K. At 3000K such supersaturation is lower by the order of 4. Line a-a in Fig. 3 responds to the ultimate supersaturation of vapour which involves the maximum rate of nucleation. Cross-sections of lines b-b, c-c and d-d with curves $\log \Phi (\log S)$ for temperatures of 1000, 2000 and

3000K corresponds to the values of $\phi' = Da_1/M_c$ at which $W_4 \approx W_1$ for pressures 1, 100 and 10000 kPa, respectively.

ϕ' values decrease with increasing of pressure. $\phi'(P)$ dependences in the logarithmic coordinates at 2000 and 3000K are linear in the pressure range of 1-10000 kPa (Fig. 4):

$$\begin{aligned} \log \phi' &= -2.36 - 0.86 \log P \text{ (2000K)} \\ &= -1.62 - 0.86 \log P \text{ (3000K)}. \end{aligned}$$

However, a slight deviation from linearity is observed for 1000K.

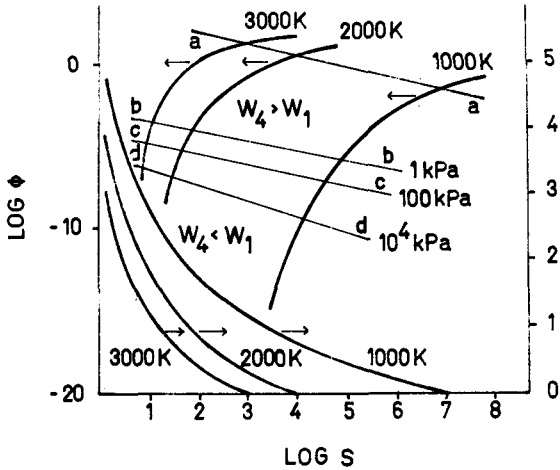


Fig. 3. Number of MgO molecules in condensed phase nucleus (\hat{n}) and parameter ϕ dependence on MgO vapour supersaturation (S) at 1000, 2000 and 3000 K.

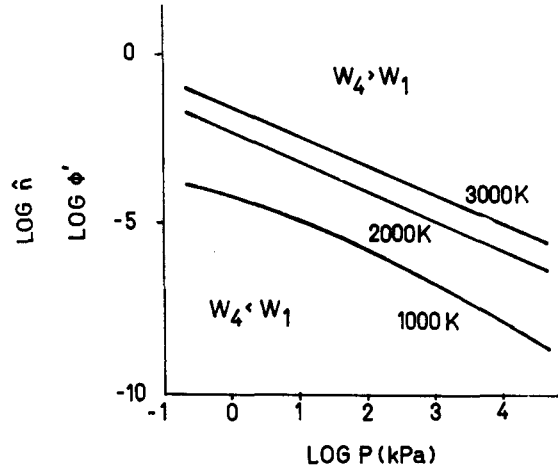


Fig. 4. Dependence of parameter ϕ' at which $W_4=W_1$ on pressure at 1000, 2000 and 3000 K.

Dependences of $\log \phi'$ vs. $1/T$ (Fig. 5) are also linear, while decrease with temperature decreasing:

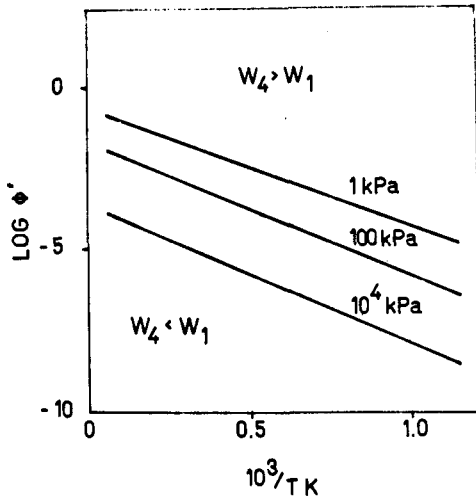


Fig. 5. Dependence of parameter ϕ' on the reverse temperature at 1, 100 and 10000 kPa.

$$\begin{aligned} \log \phi' &= -0.69 - 3542/T \text{ (1 kPa)} \\ &= -1.71 - 4194/T \text{ (100 kPa)} \\ &= -3.70 - 4194/T \text{ (10000 kPa)} \end{aligned}$$

Analysis of the data obtained shows that under otherwise equal conditions, the dispersed condensed phase surface area, sufficient for the progress of reactions (1) and (4) with comparable rates, decreases at increasing of pressure and decreasing of temperature.

Of special interest is the evaluation of W_4/W_1 value dependence on the oxide vapour supersaturation, which unequivocally determines the nucleus size at given temperature. Figure 6 shows dependences of W_4/W_1 on S at studied temperatures and pressures in logarithmic coordinates.

As it follows from these data, supersaturation at which $W_4 \approx W_1$, fall inside the limits of $2 \times 10^4 - 2 \times 10^5$ for 1000K, 40-160 for 2000K and 10-20 for 3000K, depending on pressure. According to calculations, the results of which are shown in Fig. 3, at such supersaturations the number of MgO molecules in nucleus \hat{n} must fall inside the limits of 5-2', 11-4 and 14-6, respectively.

Evaluated dependence W_4/W_1 vs. T at different pressures for threshold values $\hat{n} = 2$ and $\hat{n} = 14$ (Fig. 7) shows that heterogeneous reaction (4)

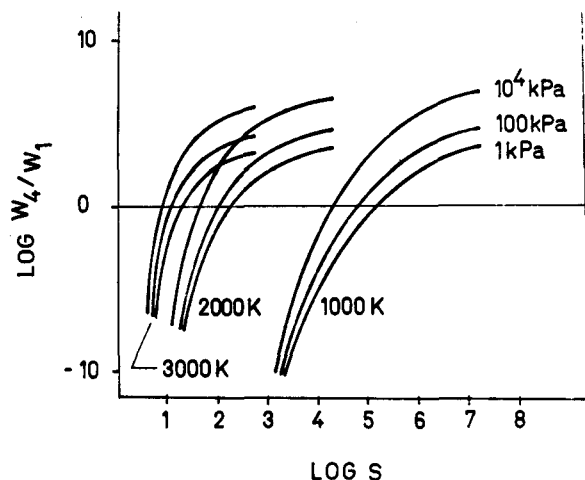


Fig.6. Relation of the heterogeneous (W_4) and gas-phase (W_1) reaction velocities dependent on the MgO vapour supersaturation (S) at 1000, 2000 and 3000K and 1,100 and 10000 kPa.

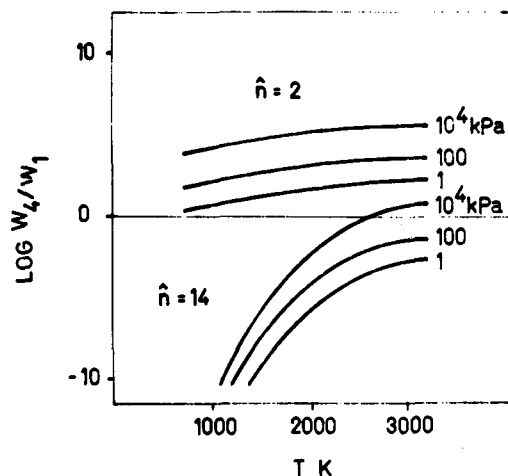


Fig.7. Dependence of $\log W_4/W_1$ on temperature for $\hat{n}=2$ and $\hat{n}=14$ at 1,100 and 10000 kPa.

may be faster than gas-phase reaction (1) only at smaller sizes of nuclei ($\hat{n} < 10$), sufficiently high pressures ($P \approx 10000$ kPa) and high temperatures ($T \approx 3000$ K). Taking into account the directivity of the limiting assumptions did in the beginning of this section, it must be concluded that for magnesium diffusion flames the possibility of the heterogeneous reaction predominance over the gas-phase reaction is minute.

Besides these evaluations, one more fact exists calling in question the very possibility of the heterogeneous reaction occurrence in the oxygen flames of metals. Indeed, the collision of metal atom with condensed particle can bring about the reaction only when oxygen molecules are adsorbed on the particle surface. In the opposite case, the reaction will be termolecular and, taking into account low mobility of condensed particles; its velocity can not be high. At the same time it is known (Ref. 27) that adsorption of molecular oxygen can take place only on the reduced surface of oxides. Such surface can not be formed in oxidizing atmosphere.

REFERENCES

1. Thermodynamic Properties of Individual Substances, L.Gurvich et al., Eds., Science, Moscow, Vol. 3 (1981), Vol. 4 (1982).
2. L.Galan and J.D.Winefordner, J.Quant.Spectry **7**, 251 (1967).
3. T.A.Brzustowski and I.Glassman, Progress in Astronautics and Aeronautics, Vol. 15, Heterogeneous Combustion, H.G.Wolfhard et al., Eds., p.75, Academic Press, N.Y. (1964).
4. D.K.Kuehl, AIAA Journal, **3**, 2239 (1965).
5. P.L.Harrison, 7th Symposium (International) on Combustion, p. 913, Butterworths, London (1959).
6. L.S.Nelson, D.E.Rosner et al., 12th Symposium (International) on Combustion, p.59, The Combustion Institute, Pittsburgh (1969).
7. An.N.Nesmeyanov, Vapour Pressure of Chemical Elements, USSR Academy of Sciences, Moscow (1961).
8. G.H.Markstein, See Ref. 3, p.177.
9. W.G.Courtney, See Ref. 6, p. 677.
10. W.G.Courtney, 11th Symposium (International) on Combustion, p.237, The Combustion Institute, Pittsburgh (1967).

11. O.E.Kashireninov, V.A.Kuznetsov and G.B.Manelis, J.Phys.Chem.(USSR), 50, 1474 (1976).
12. G.H.Markstein, See Ref. 10, p.219.
13. G.H.Markstein, See Ref. 6, p.49.
14. H.P.Sullivan and I.Glassman, Combust.Sci.Technol., 4, 241 (1972).
15. C.K.Law and F.A.Williams, Combustion and Flame, 22, 383 (1974).
16. O.E.Kashireninov, V.A.Kuznetsov and G.B.Manelis, AIAA Paper 74-145, January (1974).
17. O.E.Kashireninov, V.A.Kuznetsov and G.B.Manelis, AIAA Journal, 15, 1035 (1977).
18. O.E.Kashireninov, G.B.Manelis and L.F.Repka, J.Phys.Chem.(USSR), 56, 1030 (1982).
19. A.Fontijn, W.Felder and J.J.Houghton, 16th Symposium (International) on Combustion, p.871, The Combustion Institute, Pittsburgh (1977).
20. A.Fontijn, S.C.Kurzus and J.J.Houghton, 14th Symposium (International) on Combustion, p.167, The Combustion Institute, Pittsburgh, (1973).
21. O.E.Kashireninov, V.A.Kuznetsov and G.B.Manelis, Proc. USSR Acad. Sci., 215, 908 (1974).
22. A.Hodgson and J.C.Mackie, Combustion and Flame, 35, 323 (1979).
23. O.E.Kashireninov and B.L.Psikha, Chem.Phys.(USSR), 8, 510 (1989).
24. J.O.Hirschfelder, C.F.Curtiss and R.B.Bird, Molecular Theory of Gases and Liquids, N.Y., 1954.
25. J.Frenkel, Kinetic Theory of Liquids, Oxford University Press, London, 1946.
26. J.W.Taylor, Progress in Nuclear Energy, Ser.V, Vol.2, p.398, Pergamon Press, London-New York-Paris-Los Angeles (1959).
27. B.M.W.Trappnell, Chemisorption, Butterworths (1955).