

Detailed Chemical Kinetic Models for Nanothermites Combustion

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Abstract: The development of nanothermites and the understanding of their behaviors need several improvements in many domains including thermochemistry and chemical

kinetics. In this paper a brief state of the art is presented in these fields and possible approaches are presented.

Keywords: nanothermites · combustion · kinetics · thermochemistry · modeling

1 Introduction

Nanoenergetic materials are of interest due to the applications in defense and civilian technologies [1,2]. Nanocomposite thermites (nanoparticles based energetic materials) display higher reaction rates and energy release rates than micro-scaled composites due to large reactant surface area to volume ratio of nanoparticles or small diffusion distance between nanoparticles [3]. As underlined by Dreizin [4] the final phase compositions, morphology, of a reactive nano-scaled composite material may be different from micro-scaled composite material. Reactions playing a role in ignition of micro-scaled materials may be the same or not in the ignition of nano-scaled materials. As underlined by Jian et al., another unresolved question is the way they react depending on the heating rates [5]. Issues concerning reaction mechanisms are also related to the propagation regimes because such materials support deflagration at high flame propagation velocity [6,7]. However, the occurrence of detonation in nanothermites is not nowadays assessed but because lots of different nanothermites are feasible this issue remains to be worked out, numerically and/or experimentally. Chemical kinetics or dynamics would be, or is, expected to play a significant role [8]. A review of metal-based reactive nanomaterials is reported in Dreizin [4]. All solid state reactions must be activated by external stimuli: laser, shock, isothermal or nonisothermal (low or fast, linear or nonlinear) heating. Various techniques can yield much insight into the phenomena occurring within the composites to understand the ignition or combustion mechanisms so as to improve the performances of nanoenergetic materials [9]. It is here beyond the scope of this work to describe them all and exhaustively. As in gas-phase or liquid phase systems, reaction in solids submitted to thermal activation is not simple one-step process and in fact many reactions, called elementary reactions, are occurring at the same time. Furthermore some of these reactions occurring at a given

time do not exist later whereas some “new” reactions occur. The aim of this paper is to describe the needs in terms of thermodynamic and kinetic data for modeling the combustion of nanothermites.

2 Results and Discussion

2.1 Types of Elementary Reactions at Surface

Reactions involved are, among others: formation of gases, reactions (called adsorptions) of these gases (or other gases) at surfaces leading to the formation of adsorbed species, reactions between adsorbed species (also called Langmuir-Hinshelwood mechanism), reactions between adsorbed species and gas phase species (also called Rideal-Eley mechanism), desorption of species from the surface to the gas-phase, reactions in the gaseous phase and also reactions in condensed phases. Types of elementary reactions at a surface are reported in Table 1.

2.2 Adsorption Sites at Metallic Surfaces and Preferred Adsorption Site. Implications for Pre-Ignition and Ignition Behaviors of Nanothermites

As underlined by Dreizin [4], the behavior of nano-scaled components during combustion is poorly understood. So it is during pre-ignition (See Figure 1) as well during combustion strictly speaking.

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Table 1. Types of elementary reactions at a surface. * indicates an adsorption site, A* indicates species A adsorbed on a site, B* indicates species B adsorbed on a site. Details on adsorption sites are provided in section 3.

Reaction type	Reaction
Adsorption	$A(g) + * \rightarrow A^*$
Dissociative adsorption	$A_2(g) + 2* \rightarrow 2 A^*$
Desorption	$A^* \rightarrow A(g) + *$
Associative desorption	$2 A^* \rightarrow A_2(g) + 2*$
Langmuir-Hinshelwood	$A^* + B^* \rightarrow \text{products}$
Eley-Rideal	$A^* + B(g) \rightarrow \text{products}$

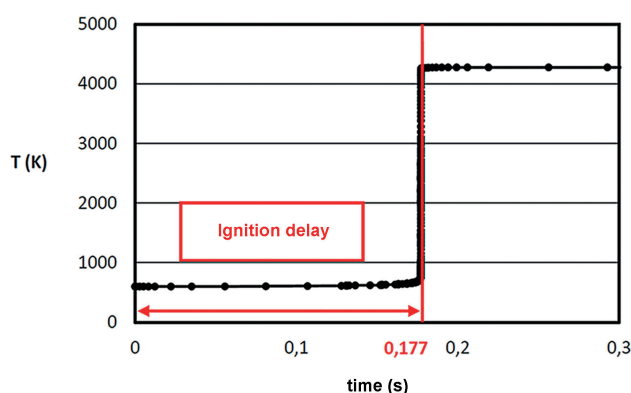


Figure 1. Ignition delay time (general case) is the pre-ignition time. All the phenomena happening during this pre-ignition time are very important and need to be worked out to understand why a nanothermite ignites or not and why, once ignited, it may detonate or deflagrate.

If one considers that some vapors or gases are emitted during pre-ignition by the metal and/or by the metallic oxide, at least for some nanothermites, then adsorption (dissociative or not) may be very important to explain ignition because chemical adsorption is exothermic and therefore these adsorption reactions are able to increase the temperature at and near the surface (Figures 2, 3, 4).

For a given surface, there are different adsorption sites which are energetically different. For instance, (111) aluminum surface has 4 adsorption site types: top, bridge and two hollow sites (fcc and hcp). Depending on the species, preferred adsorption site may be identified either experimentally or theoretically. This does not mean that a species may adsorb on only one adsorption site type but that it adsorbs preferentially on one of them. For (111) aluminum surface, theoretical calculations done by using the VASP code [10] are consistent with experimental observations [11]. Therefore, it can be expected that the VASP code [10] is able to predict correctly the preferred adsorption site for any species on any metallic surface. This is important because experimental data in that field are scarce. Issues related to the types of sites on surfaces are not further discussed here. In the case of metal/metal oxide systems, if no

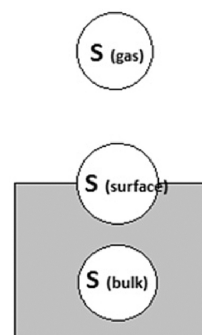


Figure 2. A gas-phase molecule, here noted S(gas), is able to adsorb at the surface on an adsorption site becoming a surface species, noted S(surface). If S(gas) adsorbs on S(surface) then S(surface) becomes S(bulk). $S(gas) + S(surface) \rightarrow S(surface) + S(bulk)$. Note that both S(surface) may be different. For instance, the adsorption reaction of an oxygen atom on an aluminum surface may be written $O(gas) + Al(surface) \rightarrow O(surface) + Al(bulk)$. Depending on the surface, the adsorption site may be an atom at the surface, for instance, as it is the case here.

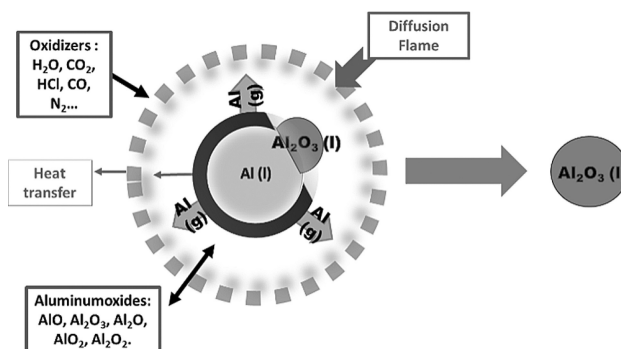


Figure 3. Phenomena observed during aluminum particle combustion in propellant atmosphere. For nanothermites the same phenomena may be observed except that surface reactions may be even more important in the processes leading to ignition.

vapors or gases are emitted, other phenomena are also likely such as the formation(s) of solid solutions, eutectics, etc. Phase changes (melting, boiling, allotropy, etc.) may also be of importance.

2.3 Detailed Chemical Kinetic Models

A global kinetic approach (through one or a very limited number of reversible steps), generally used today, is convenient for some purposes but because the chemistry is somehow frozen and therefore such models are not predictive, or with limited predictive ability, and it remains in fact of little interest.

Gas-phase systems are worked out today by using detailed chemical kinetic models which are more and more predictive for lots of applications and processes: hydro-

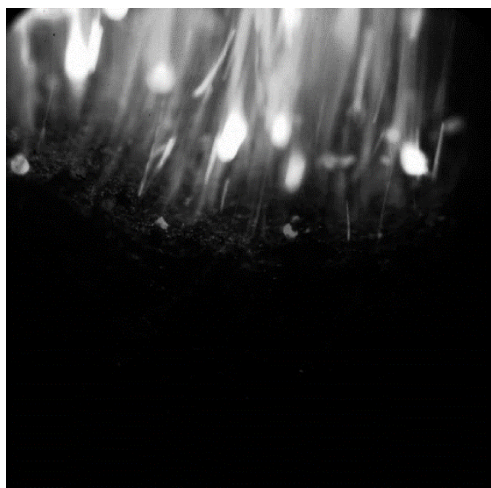


Figure 4. Frame describing the combustion of aluminum particles as it is observed in propellant atmosphere (burning of aluminum in a mixture of CO_2 , H_2O , CO , HCl , etc...). Courtesy Luigi T. DeLuca, Politecnico di Milano.

carbon combustion, hydrogen combustion, metals combustion, pyrolysis of various materials, chemical vapor deposition (thermal CVD and plasma CVD), waste incineration, etc. Despite recent progress [11] in the field of aluminum reactivity, ignition and combustion, it is still nowadays not possible to propose a predictive chemical kinetic model for nanothermites not only because of all the difficulties described above but also because of the lack of experimental data for metals or metal-containing compounds. The aim of this work is to present the interest of a detailed chemical kinetic approach for nanothermites reactivity during pre-ignition, ignition and combustion and therefore this work deals with chemical kinetics and thermodynamics. These data are needed to build and run detailed chemical kinetic models. They are experimental, estimated or calculated by using various means when experimental data are lacking or when existing experimental data are contradictory or known with large uncertainties.

For nanothermites, this approach remains almost unexplored, except in a few laser ignition experiments at extremely high heating rates for which gas-phase detailed kinetics is considered. This kinetic approach is complementary to the thermodynamic approach because, on one hand, it also needs thermodynamic data of species and, on the other hand, it is devoted to the calculation of equilibrium composition, temperature and pressure. However, the kinetic approach requires thermodynamic data of species, the ones present at equilibrium but also the ones not present at equilibrium that are all the species formed and known as intermediates. Lots of these intermediates are formed at quite low level and are generally more or less stable. These species are radicals, atoms, in their ground or excited states, and also molecules, with usually short lifetimes.

2.4 Thermodynamic Data

A large number of thermodynamic data is needed for all the systems of interest for nanothermites if one considers all the fuels and oxidants of interest. Aluminum is the most interesting fuel for high performance nanothermites. Other fuels are boron, zinc, magnesium, titane, red phosphorous and silicium. Oxidants are Sb_2O_3 , Ag_2O , Bi_2O_3 , Co_3O_4 , Cr_2O_3 , CuO , Fe_2O_3 , I_2O_5 , MnO_2 , MoO_3 , NiO , SnO_2 , TiO_2 , WO_3 and ZnO [8]. Data needed are standard enthalpy of formation, heat capacities at constant pressure (or at constant volume) against temperature and entropy against temperature. As explained just above, not only gas phase thermodynamic data are needed [11] but the consideration of gas phase thermodynamic data only is still a big amount of work. For systems supporting deflagration, gaseous products may be considered [5]. For systems supporting high speed combustion, gas phase reactions are even more important because pressures of 10–40 GPa, temperatures of 2000–4000 K and enormous power output are common [12]. It is recognized that less than 1 % of the species needed to develop C/H/O/N detailed chemical kinetic models have been experimentally measured. It is clear that the situation is worse for “exotic” species formed from metals such as copper, bismuth or titanium, among other transition metals. For instance for the Al/CuO system data are needed for Al/O, Cu/O, Al/Cu, Al/Cu/O species such as Cu_2 , CuO , Al_xO_y , among numerous others. Experimental gas phase data are available for some of these species but lots of them were only identified and the existence of some others is even not assessed as well as the spin state of the ground state. In Table 2 available experimental data for Cu/O system are reported.

Table 2. Experimental standard enthalpy of formation for gas phase copper and copper compounds. Relatively high absolute uncertainties are expected for such species other than the elements themselves (here Cu).

Species	Standard enthalpy of formation at 298.15 K (kJ mol^{-1})
Cu	337.4 ± 1.2
Cu_2	485.34
CuO	306.27

However, no experimental data are available for Cu_2O , CuO_2 (OCuO or CuOO) and Cu_xO_y (y comprised between 2 and 4) species able to form at high temperature during the combustion of Al/CuO. Therefore some of these data need to be estimated or calculated by using various means such as empirical methods (group additivity methods for instance) and also methods based on molecular modeling. Quantum chemistry composite methods are devoted to the predictions of accurate thermodynamic data such as standard enthalpy of formation within 1 kcal mol^{-1} of the experimental value. This chemical accuracy remains somehow hypothetical especially for metallic or metalloid compounds

for which experimental data are scarce and often unique and for which accurate bond enthalpies and standard enthalpies of formation are still elusive for transition metal-containing molecules in the gas phase.

Among all these methods, empirical or theoretical, the ones established for C/H/O systems are numerous and generally accurate [13,14]. For systems containing metals, things are not so worked out except for metals with low atomic number such as sodium, magnesium or aluminum for instance. For Al/O system, experimental data are available for lots of species and theoretical calculations have been performed [15,16]. G_n methods (with $n=1-4$) are of interest for Al/O compounds. However, some progress is still possible for some Al_xO_y species potentially present especially at high temperature [17].

For higher Z numbers (transition metal) specific methods have to be used to get as reliable results as possible. For compounds containing transition metals, ccCA-TM (correlation consistent Composite Approach for Transition Metals) method is recommended [18].

The newest, and more challenging, work to be done for Al/CuO may concern Al_xCu_y and $Al_xCu_yO_z$ species for which no data, neither experimental nor theoretical, are available. Some of these species may be formed at very low level but this remains to be demonstrated. The *a priori* neglect of some species may be "hazardous" because, even formed at low level, some species can play a role during the formation of a combustion wave in nanothermites, especially for flames propagating at high speed. Depending on how the nanothermites are ignited, depending on the propagation regime (low speed or high speed deflagration), gas-phase reactions may be more or less important. C/H/O systems have been exhaustively studied. Experimental gas-phase rate constants available for metals are scarce, except for aluminum for Al/H/O systems for which estimated or calculated rate constants are also available. For other metals, rate constants are usually measured at room temperature or determined in so limited temperature ranges that extrapolations at higher or lower temperatures may be doubtful. The modeling of nanothermites combustion requires data in a wide temperature range for all reactions and wide pressure range for pressure-dependent reactions.

2.5 Kinetic Data

The Al/CuO nanothermite is one of the most studied. However, few data are available at room temperature (300 K) for $Cu + O_2 \rightarrow CuO_2$. These data are almost of no interest for nanothermites ignition and combustion. It may be therefore difficult to explain the role played by O_2 formed from CuO during Al/CuO combustion in argon atmosphere.

Rate constants for $Cu + N_2O \rightarrow CuO + N_2$ data are available from ambient up to 1340 K. This reaction is potentially of interest in air or in pure nitrogen except that amounts of N_2O are initially zero in air. It is of no use in vacuum or in Ar

Table 3. Gas-phase kinetics for nanothermites: experimental elementary kinetics data for selected metal + O_2 reactions.

$Sb + O_2 \rightarrow \text{products}$	data at 300 K [19]
$W + O_2 \rightarrow \text{products}$	data in the 298–573 K range [20]
$Ti + O_2 \rightarrow TiO + O$	data at 300 K [21]
$Ti + O_2 \rightarrow \text{products}$	data in the 300–600 K range [22]
$Bi + O_2 \rightarrow \text{products}$	data at 300 K [23]
$Cu + O_2 \rightarrow CuO_2$	data in the 300–485 K [24]
$Ag + O_2 \rightarrow \text{products}$	no data
$Zn + O_2 \rightarrow ZnO + O$	data in the 820–920 K range [25]
$Sn + O_2 \rightarrow SnO + O$	data in the 300–2600 K range [26]
$Ni + O_2 \rightarrow \text{products}$	data at 296 K [27]
$Mn + O_2 \rightarrow MnO + O$	data in the 2000–2500 K [28]
$Mn + O_2 \rightarrow \text{Products}$	data at 296 K [27]
$Mo + O_2 \rightarrow MoO + O$	data in the 296–2300 K range [28]
$Si + O_2 \rightarrow SiO + O$	data in the 15–295 K range [29]
$Si + O_2 \rightarrow \text{products}$	data in the 300–350 K range [30]

atmosphere. The same report may be done for other transition metals and for lots of them the situation is even worse. Other data for metal + O_2 reactions in the gas-phase are reported in Table 3.

As reported in Table 3, occasionally products are not reported and except for Ti and Sn experimental data are generally measured at room temperature. The lack of experimental data may be overcome by using the transition state theory (TST) as reported in Table 4. The data needed to derive k and k_{-1} (Figure 5) are the rotational, translational, vibrational, electronic partition functions of reactants A and B and transition state TS for k and rotational, translational, vibrational, electronic partition functions of reactants C and D and transition state TS for k_{-1} .

Table 4. Gas-phase kinetics for nanothermites: Potential energy surface (PES) available in the literature for metal/oxygen reactions and metallic oxide/oxygen reactions. Rate constants derived or not.

$Ni + O_2 \rightarrow NiO_2$	No rate constant [31]
$Ni + O_2 \rightarrow ONiO$	No rate constant [31]
$CrO + Ni + O_2 \rightarrow NiO_2$	No rate constant [31]

$$k = \frac{k_B T}{h} \left(\frac{Q^{TS}}{Q_A Q_B} \right)_{\text{vib}} \left(\frac{Q^{TS}}{Q_A Q_B} \right)_{\text{rot}} \left(\frac{Q^{TS}/V}{Q_A/V Q_B/V} \right)_{\text{trans}} \left(\frac{Q^{TS}}{Q_A Q_B} \right)_{\text{elec}} e^{\frac{-E_{0,f}}{RT}}$$

$$k_{-1} = \frac{k_B T}{h} \left(\frac{Q^{TS}}{Q_C Q_D} \right)_{\text{vib}} \left(\frac{Q^{TS}}{Q_C Q_D} \right)_{\text{rot}} \left(\frac{Q^{TS}/V}{Q_C/V Q_D/V} \right)_{\text{trans}} \left(\frac{Q^{TS}}{Q_C Q_D} \right)_{\text{elec}} e^{\frac{-E_{0,r}}{RT}}$$

Figure 5. Expression of the forward rate constant k and reverse rate constant k_{-1} in the frame of the transition state theory (TST). Q is the partition function of reactants (A and B for the forward rate constant, C and D for the reverse rate constant) and of transition state (TS). $E_{0,f}$ and $E_{0,r}$ are the forward and reverse energy barriers, respectively.



These calculations are possible once the potential energy surface (PES) for the reaction is known. As indicated in Table 4 very few PES are available and when available no rate constant are derived and if derived generally at a given temperature generally far away from combustion temperatures.

3 Conclusions

It is shown in this paper that the topic nanothermite combustion needs to be worked out in all fields, both experimentally and theoretically because we are far to understand all the details of nanothermite combustion. The combustion of an explosive solid is accurately described at equilibrium. However, calculations at equilibrium do not provide insight into the details of reactions occurring and intermediate species even formed in small amounts may play an important role to explain the combustion regime observed.

The chemical kinetics approach is certainly able to help in this task. Experimental data are scarce and it is doubtful that new experimental elementary kinetic data will be provided in the near future. Therefore, theoretical methods, once validated on experimental data, may be of the highest interest. Although approaches exist both for thermodynamic data and for kinetic data, they are not exhaustively used and for subjects generally not related to nanothermite combustion. "Conventional" combustion science is generally complex but nanothermite combustion is even more complex because of the metallic nature (transition metals) of the reactants and because of the role probably played by surface reactions. Furthermore, one important issue is related to the equation of state valid at such extreme conditions of temperature and pressure. The choice of the equation of state may impact both the calculations at equilibrium and kinetic calculations.

References

- [1] D. G. Piercy, T. M. Klapötke, Nanoscale Aluminum – Metal Oxide (Thermite) Reactions for Application in Energetic Materials, *Cent. Eur. J. Energetic Mater.* **2010**, *7*, 115–129.
- [2] E. Lafontaine, M. Comet, Les Nanothermites, ISTE Editions, **2016**.
- [3] D. D. Dlott, Thinking big (and small) about energetic materials, *Mater. Sci. Technol.* **2006**, *22*, 463–473.
- [4] E. L. Dreizin, Metal-based reactive nanomaterials, *Prog. Energy Combust. Sci.* **2009**, *35*, 141–167.
- [5] G. Jian, S. Chowdhury, K. Sullivan, M. R. Zachariah, Nanothermite reactions: Is gas phase oxygen generation from the oxygen carrier an essential prerequisite to ignition? *Combust. Flame* **2013**, *160*, 432–437.
- [6] S. Apperson, R. V. Shende, S. Subramanian, D. Tappmeyer, S. Gangopadhyay, Z. Chen, K. Gangopadhyay, P. Redner, S. Nicholich, D. Kapoor, Generation of fast propagating combustion and shock waves with copper oxide/aluminum nano thermite composites, *Appl. Phys. Lett.* **2007**, *91*, 243109–1–243109–3.
- [7] B. Khasainov, M. Comet, B. Veyssiere, D. Spitzer, Comparison of performance of fast-reacting nanothermites and primary explosives, *Propellants Explos. Pyrotech.* **2017**, *42*, 754–772.
- [8] Y. Q. Yang, Z. Y. Sun, S. F. Wang, D. D. Dlott, Fast spectroscopy of laser-initiated nanoenergetic materials, *J. Phys. Chem. B* **2003**, *107*, 4485–4493.
- [9] V. Chuzeville, G. Baudin, A. Lefrançois, M. Genetier, Y. Barbarin, L. Jacquet, J. L. Lhopitault, J. Peix, R. Boulanger, L. Catoire, Detonation initiation of heterogeneous melt-cast high explosives, *AIP Conf. Proc.* **2017**, *1793*, 030009–1–030009–5.
- [10] VASP: Vienna Ab Initio Simulation Package. www.vasp.at.
- [11] J. Glorian, L. Catoire, S. Gallier, N. Cesco, Gas-surface thermochemistry and kinetics for aluminum particle combustion, *Proc. Combust. Inst.* **2015**, *35*, 2439–2446.
- [12] J. B. Bdzil, D. S. Stewart, The dynamics of detonation in explosive systems, *Annu. Rev. Fluid Mech.* **2007**, *39*, 263–292.
- [13] A. Osmont, I. Gökalp, L. Catoire, Evaluating missile fuels, *Propellants Explos. Pyrotech.* **2006**, *31*, 343–354.
- [14] A. Osmont, L. Catoire, I. Gökalp, V. Yang, Ab initio quantum chemical predictions of enthalpies of formation, heat capacities, and entropies of gas-phase energetic compounds, *Combust. Flame* **2007**, *151*, 262–273.
- [15] A. B. C. Patzer, Ch. Chang, E. Sedlmayr, D. Sülzle, A density functional study of small Al_nO_y ($x, y = 1-4$) clusters and their thermodynamic properties, *Eur. Phys. J. D* **2005**, *32*, 329–337.
- [16] M. T. Swihart, L. Catoire, Thermochemistry of aluminum species for combustion modeling from ab initio molecular orbital calculations, *Combust. Flame* **2000**, *121*, 210–222.
- [17] J. Lam, D. Amans, C. Dujardin, G. Ledoux, A.-R. Allouche, Atomistic mechanisms for the nucleation of aluminum oxide nanoparticles *J. Phys. Chem. A* **2015**, *119*, 8944–8949.
- [18] W. Jiang, N. J. DeYonker, J. J. Detorman, A. K. Wilson, Toward accurate theoretical thermochemistry of first row transition metal complexes, *J. Phys. Chem. A* **2012**, *116*, 870–885.
- [19] D. Husain, N. K. H. Slater, Kinetic study of ground state antimony atoms $Sb(5^4S_{3/2})$ by atomic absorption spectroscopy, *J. Photochem.* **1977**, *7*, 59.
- [20] M. L. Campbell, R. E. McClean, Temperature-dependent studies of the reaction of $W(a^5D_j, a^3S_3)$ with O_2 , *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 3787–3793.
- [21] D. E. Clemmer, K. Honma, I. Koyano, Kinetics of excited-state $Ti(a^5F)$ depletion by NO, O_2 , N_2O , and N_2 , *J. Phys. Chem.* **1993**, *97*, 11480–11488.
- [22] M. L. Campbell, R. E. McClean, Kinetics of neutral transition-metal atoms in the gas phase: oxidation reactions of $Ti(a^3F)$ from 300 to 600 K, *J. Phys. Chem.* **1993**, *97*, 7942–7946.
- [23] C. F. Bell, D. Husain, Kinetic studies of $Bi(6^3S_{3/2})$ by time-resolved atomic resonance fluorescence. II: An investigation of the third-order reactions $Bi + O_2 + M$ and $Bi + NO + M$ ($M \equiv He, N_2$ and CF_4), *J. Photochem.* **1984**, *24*, 223.
- [24] C. Vinckier, P. Christiaens, M. Hendrickx, Kinetics of the molecular oxygen reactions with sodium, magnesium and copper atoms in Gas-Phase Metal reactions (Ed.: A. Fontijn), Elsevier, Amsterdam, **1992**.
- [25] O. E. Kashirenin, G. B. Manelis, L. F. Repka, Recalculation of the kinetic constants for the oxidation of alkaline-earth metal vapours, *Russ. J. Phys. Chem. (Engl. Transl.)* **1982**, *56*, 630–631.

- [26] K. Takahashi, A. Giesen, P. Roth, High Temperature Reaction of $\text{Sn}(^3\text{P}_0)$ Atoms with O_2 Based on Sn and O-Concentration Measurements, *Phys. Chem. Chem. Phys.* **2001**, 3, 4296–4300.
- [27] C. E. Brown, S. A. Mitchell, P. A. Hackett, Dioxygen complexes of 3d transition-metal atoms: formation reactions in the gas phase, *J. Phys. Chem.* **1991**, 95, 1062–1066.
- [28] U. S. Akhmadov, I. S. Zaslonko, V. N. Smirnov, Mechanism and kinetics of interaction of Fe, Cr, Mo, and Mn, *Kinet. Catal.* **1988**, 29, 251.
- [29] S. D. Le Picard, A. Canosa, D. Reignier, T. Stoecklin, A Comparative Study of the Reactivity of the Silicon Atom $\text{Si}(^3\text{P}_j)$ Towards O_2 and NO Molecules at Very Low Temperature, *Phys. Chem. Chem. Phys.* **2002**, 4, 3659–3664.
- [30] D. Husain, P. E. Norris, Kinetic study of ground state silicon atoms, $\text{Si}[3\text{p}^2(^3\text{P}_j)]$ by atomic absorption spectroscopy, *J. Chem. Soc. Faraday Trans.* **1978**, 2, 74.
- [31] F. Allouti, L. Manceron, M. E. Alikhani, The $\text{Ni} + \text{O}_2$ reaction: A combined IR matrix isolation and theoretical study of the formation and structure of NiO_2 , *Phys. Chem. Chem. Phys.* **2006**, 8, 448–455.
- [32] V. N. Smirnov, On the anomalously high rate of recombination $\text{Cr} + \text{O}_2 + \text{M} \rightarrow \text{CrO}_2 + \text{M}$, *Kinet. Catal.* **1993**, 34, 699.

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