

## Wide-temperature range observations on reactions of metal atoms and small radicals

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The role of metal species in combustion processes, whether as fuels, additives, or, (often toxic) impurities is described. Optimization and control of these, and other, high-temperature processes requires understanding and knowledge of the kinetics of the individual gas-phase reactions involved, leading to meaningful models. Our experimental techniques to study the reactions in isolation from each other are discussed. The equipment used allows measurements in the approximately 300-1800 K temperature range, at pressures from 10-1000 mbar. Semi-empirical techniques have been developed to predict the temperature dependence of the rate coefficients for further reactions. Recent findings show that association and insertion reactions can play an important role in cases where abstraction was thought to be the operative mechanism.

### I. INTRODUCTION

The desire to understand the dependence of chemical reaction rate coefficients and mechanisms on temperature, is to a major degree due to the necessity to control combustion processes. Metals as impurities, additives, or fuel components are present in most combustion systems, and are involved in many other high-temperature gas-phase processes. Their role can be both beneficial and detrimental. In waste incineration, power generation, and some other large scale industrial processes, they give rise to toxic emissions, whether as fine particulates or as gases.<sup>1</sup> The low ionization potentials of alkali metals used as additives enhances the ionization of flames, which can be used to change flame shape to prevent or enhance surface interaction, increase flame temperature, and for electrohydrodynamic and magnetohydrodynamic power generation.<sup>2,3</sup> On the other hand the electron cloud resulting from the presence of alkali metals as impurities in rocket propellants hinders communication with the vehicle, but helps locating enemy missiles.<sup>4</sup> However, aluminum is a major constituent of many solid rocket propellants.<sup>5</sup> Hot corrosion by metal compounds formed in turbine engines is a severe problem.<sup>6</sup> Combustion synthesis is increasingly being used for production of nanoscale refractory solids of controlled narrow size distribution and high purity.<sup>7</sup> For fire retardation metallic nanoparticles, formed in situ in flames, are among the most promising replacements for the environmentally unacceptable halons in current use.<sup>8a</sup> A preferred way for analyzing the metal content of flammable materials is analytical flame spectrometry.<sup>9</sup> (Reference 9 also gives an excellent overview of the underlying physics and thermochemistry of metallic species in flames.)

With so many applications, it might be assumed that the chemistry of metals in flames is well known. However, many practical flames are diffusion flames, which do not lend themselves to fundamental physico-chemical observations because of continuous concentration gradients of fuels, oxidants, and intermediates. Many are turbulent and most are not observable from outside the devices that are powered by them, or in which they are contained. In special research burners, which are typically of the premixed flat flame type,<sup>10</sup> a fair amount of thermochemical information on individual species and their equilibria has been obtained, particularly for charged metallic species.<sup>9, 11</sup> Important as this is, flames are inherently non-equilibrium systems and their chemical characterization requires knowledge of individual reaction rate coefficients,  $k$ , as functions of temperature,  $T$ , and sometimes pressure,  $P$ . As a multitude of reactions are taking place simultaneously, reliable data on individual reactions can rarely be obtained from flames. Kinetic models with sensitivity analysis are increasingly being prepared for specific situations. In these, most rate coefficients are estimated by theoretical chemical methods. To improve the models  $k(T,P)$  measurements are needed for individual reactions.

In our laboratory we have developed several reactor types for measurements on isolated combustion reactions at temperatures from 300-1800 K and pressures from about 0.01 to 1 bar. In this chapter their application to homogeneous gas-phase reactions of neutral metal atoms, metal oxides, and metal halides are discussed. In other work, one of these techniques (HTP) has also been used for reactions of O, N, H, and Cl atoms, but these are outside the scope of this presentation. The use of the reactors for study of gas-particle interactions also appears feasible, but has not yet been attempted.

The work is not restricted to metals, but includes their nearest neighbors in their periodic table groups. The reactions studied thus far include those of: Al, AlCl, AlO, BCl, BO, and BO<sub>2</sub> in the context of rocket propellants and advanced explosives, Cr and Cd as important toxic components from waste incinerators, Cu and CuCl because of the catalytic role of copper in forming toxic dioxins from combustion, Na which is present in most combustion systems. Earlier studies of Sn, Ge, and Ba were largely inspired by the interest in purely chemical lasers, where the high bond energies of metal oxides could be utilized. This latter work has previously been reviewed,<sup>12</sup> and will not be further considered here. A more recent review of some of the metal oxidation reactions has also appeared.<sup>13a</sup> Most of the reactions studied have been oxidation reactions with O<sub>2</sub>, CO<sub>2</sub>, SO<sub>2</sub>, N<sub>2</sub>O, Cl<sub>2</sub>, or HCl. However, the reaction of CH<sub>4</sub> with AlO has also been investigated because of the importance of such reactions for understanding the surface phenomena of metal oxide catalysts for hydrocarbon up-conversion into the petrochemical industry. The BO<sub>2</sub> investigations have been reduction studies.<sup>8b</sup>

While a considerable data base is thus beginning to emerge, reliable models would require significantly larger input. Practical applications can not wait until the quite time-consuming experimental work provides these. We have therefore also started to use our data base for the development of predictive techniques. The status of these semi-empirical approaches followed is also discussed in the following.

## II. EXPERIMENTAL TECHNIQUES

We have developed two basic techniques for kinetic measurements over the about 300-1800 K temperature regime. These have in common that metal, or other refractory, -atoms, -oxides, or -halides are produced in small concentrations, typically 10<sup>10</sup> to 10<sup>11</sup> cm<sup>-3</sup>, and are reacted with sufficient excess of the second, molecular, reactant to allow the measurements of the consumption of the metallic reactant to be made under pseudo first-order conditions. The concentrations of both reactants are small compared to that of the bath gas, normally Ar. This allows the pressure and temperature to be set at the desired values independently of the heat of reaction. As the concentration of the limiting reactant is small, so is that of the products. The result is that the rate of any reactant disappearance by interaction with the products is necessarily very small and usually negligible. For the rate coefficient measurements the relative concentration of the metallic species is monitored by pulsed laser-induced fluorescence, or by cw atomic absorption or fluorescence using a hollow cathode lamp. The measurable rate coefficient range is typically in the 10<sup>-10</sup> - 10<sup>-15</sup> cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>, i.e. from reaction upon every hard-sphere collision to one in every 10<sup>5</sup> collisions. While the temperature range that can be covered is very wide, small reaction rates at lower temperatures, and thermal stabilities of the reactants at high temperatures, can limit the observation range for given reactions.

The reactors consist of a refractory reaction tube (alumina, mullite, or industrial grade quartz), surrounded by, in sequence, SiC resistance heating elements, Zircar insulation, and a water cooled vacuum housing. Openings in the reaction tube and insulation face the window in the housing for the spectrometric measurements. In one reactor type, the HTFFR (high-temperature fast-flow reactor), Fig. 1, the metallic reactant is produced by evaporative methods, similar to those used in thin film production techniques.<sup>14</sup> Alternatively, we use microwave discharge flow methods through a precursor compound in bath gas Ar, e.g. BCl<sub>3</sub> for BCl,<sup>13a</sup> or trimethyl-aluminum<sup>15</sup> for Al at low temperatures. In either case the reactant can be converted to a larger reactant by a fast reaction (e.g. Al + O<sub>2</sub> → AlO + O),<sup>15</sup> immediately beyond the source, upstream from the 20 cm observed reaction zone. This zone begins at the second reactant inlet and terminates at the level of the observation windows. Flow velocities of 10 to 150 m s<sup>-1</sup> at pressures of 5 to 100 mbar are used in the 2.0-2.5 cm i.d. reaction tubes, leading to observation times in the 10<sup>-2</sup> to 10<sup>-3</sup> s range.

The other basic type, the MHTP (metals high-temperature photochemistry) reactor, Fig. 2, operates in a pseudo-static mode. A mixture of photolyte, second reactant, and bath gas flows slowly, 5-50 cm s<sup>-1</sup>, to the window plane of the wide, 5.0 cm i.d., reaction tube. A flash lamp or pulsed excimer laser is used to produce the metallic species of interest, which reacts in essentially the same volume element in which it is formed. The photolyte is typically a metal halide or

carbonyl. Time scales for the measurements vary in the  $10^{-5}$  to  $10^{-3}$  s or  $10^{-3}$  to  $10^{-1}$  s range depending on the generation and relative concentration measurement method used. Photolytic pulse rates are set at 1-5 Hz to provide a fresh mixture for each pulse. Total pressures are in the range of 50 to 600 mbar, but higher pressures would be accessible. As diffusion times to the walls are long compared to the observation times, MHTP operation is free of wall interference, which is an advantage over HTFFR experiments. This has, for example, allowed measurements on Na atoms,<sup>16</sup> which were found to be reversibly absorbed by HTFFR alumina walls. When a cooled inlet<sup>17</sup> is used in an MHTP reactor, thermally less stable second reactants can be used to higher temperatures than in an HTFFR, e.g.  $\text{N}_2\text{O}$  to about 1250 instead of 950 K, again due to the absence of wall interactions. On the other hand, a potential drawback of MHTP is that the second reactants are also in the photolysis beam and care is needed to select photolysis conditions where these are not affected. The HTFFR metal species production techniques are also more versatile.

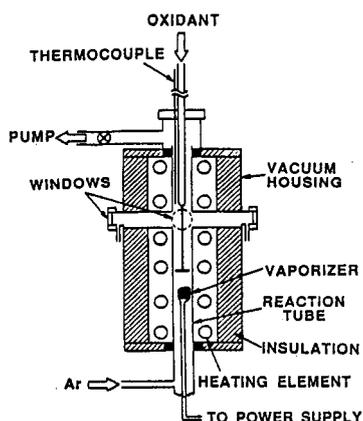


Figure 1. Schematic of an HTFFR

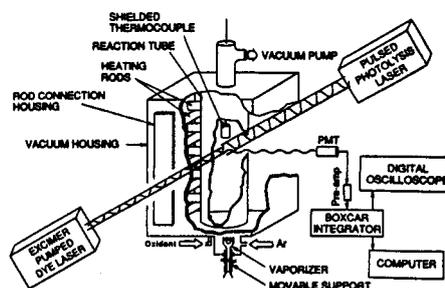


Figure 2. Schematic of an MHTP Reactor

In practice then, the two techniques well complement each other. They have several times been checked against each other and to other techniques.<sup>18</sup> The earlier reviews,<sup>12,13</sup> together with the referenced papers,<sup>15-18</sup> give a more extensive description of the techniques and operational procedures than is possible here. Recently, an HTFFR has been coupled to a molecular beam mass spectrometer. This has considerably enhanced the ability to identify products and hence reaction mechanisms. The first results are discussed in Section III C.<sup>19</sup>

### III. CURRENT KNOWLEDGE AND OPEN QUESTIONS

The measured rate coefficients of elementary reactions, when considered over wide temperature ranges, most frequently follow the equation

$$k(T) = AT^n \exp(-E/RT) \quad [1].$$

Here,  $A$ ,  $n$  and  $E$  are constants for given reactions and  $R$  is the gas constant. In the following section, III A, we are particularly concerned with predicting the factors that determine the temperature dependence of rate coefficients. The  $A$  coefficients can readily be estimated from classical collision theory, taking into account statistical and steric factors.<sup>20</sup> Equation (1) is an expression of the fact that Arrhenius plots,  $\ln k$  vs  $T^{-1}$ , are curved, though this can frequently not be seen within the accuracy of experiments. The fundamental reasons for this behavior have been discussed in several places, e.g. Ref. 21. It should be noted that  $E$  is not identical to the traditional Arrhenius activation energy  $E_A$ , which merely gives the local slope of these plots. Physically,  $E$  is the difference in the potential energy of the activated complex (transition state) and the sum of the potential energies of the reactants, i.e. it is the activation barrier.

Measured  $k(T)$  values do not necessarily contain information on the products. For simple abstraction reactions these values correspond to the  $k(T)$  for product formation. However, increasingly examples of other mechanisms are being encountered. These include simple pressure-dependent association reactions (Section III B), insertion reactions (Section III C), and a few<sup>22</sup> four center reactions.

### A. Comparison of Experimental Temperature Dependences to those from Semi-Empirical Theories

Figure 3 shows measurements of metallic species consumption rate coefficients in four reactions and the curves corresponding to the best fit expressions. The steeper rise of the CO<sub>2</sub> reactions would suggest a larger E factor than for the O<sub>2</sub> reactions, but since eq. (1) has two T-dependence factors such a comparison is not straightforward. It can however be achieved if it is assumed that all these reactions have, in first approximation, the same n-factor. This is reasonable as these are similar (i.e. homologous) reactions, which should have similar transition state structures. Classical transition-state theory, TST, gives

$$k(T) = \frac{k_B T}{h} \frac{q^\ddagger}{q_A q_B} \exp(-\Delta E^\ddagger/RT) \quad [2],$$

where  $k_B$  is the Boltzmann and  $h$  the Planck constant, and the  $q$  are the partition functions of the transition state ( $^\ddagger$ ) and of the reactants A and B, respectively.  $n$  is the multiplied temperature dependence of the pre-exponential terms and can in principle be found by ab initio calculations, though these can not yet be made with good reliability for most metallic species. Approximate values for  $n$  can be taken from the experimental best fit expressions. By using such values for a number of homologous reactions, plots like those of Fig. 4 are obtained, which show that the respective E values correlate with the sums of the ionization potentials IP of the metal species MeX, plus their promotion energies PE for the first allowed  $\Sigma$ - $\Pi$  electronic transitions minus the electron affinities EA of the oxidant OY. A wide range of  $n$  values give such correlations, and allow good  $k(T)$  predictions, but neither such arbitrary  $n$  nor the corresponding E are physically meaningful. Values approximating the physically meaningful are found by taking the average difference, for the reactions of Fig. 4, between the experimental and SECI theory E values (see below) for each of a number of  $n$  values. The desired  $n$ , 1.9 in this case, is the one for which this difference is at a minimum, cf. Ref. 23. Different series of similar reactions will have different transition state structures in common and require other values of  $n$ . This is shown in Fig. 5 for  $s^1$ ,  $s^2$ , and  $s^2p^1$  atom reactions with N<sub>2</sub>O, for which  $n = 0.5$ .<sup>24</sup>

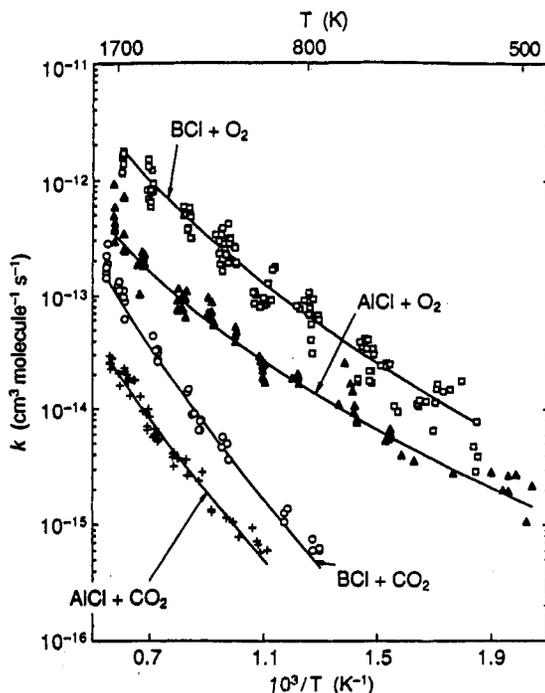


Figure 3. Rate coefficients for four homologous reactions

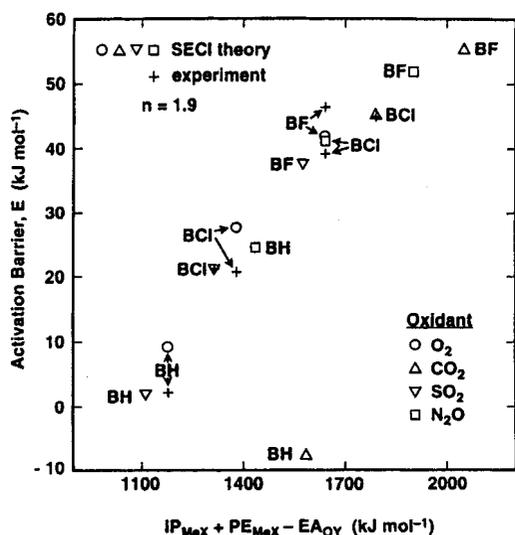


Figure 4. Comparison of theoretical to experimental activation barriers for some diatomic boron species reactions

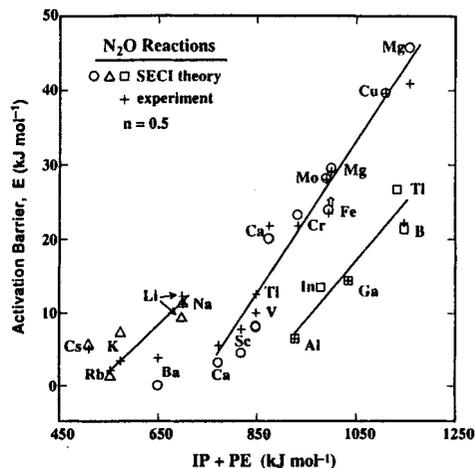


Figure 5. Comparison of theoretical to experimental activation barriers for reactions of metal atoms with  $N_2O$

SECI (Semi-Empirical Configuration Interaction Theory), is based on simple Pauling-type resonance theory and provides the physical justification for the correlation of  $E$  with  $IP$ ,  $PE$ , and  $EA$ .  $E$  is found from the properties of three hypothetical resonating activated complexes, i.e. those resulting from (i) purely ground state interaction for which the barrier is  $q$ , (ii) the interaction involving the lowest excited state from an allowed  $s-p$  or  $\Sigma-\Pi$  transition of the metallic reaction partner, and (iii) ionic interaction. The wave function of the actual complex resulting from these structures is given by

$$\Psi = c_1\Psi_1 + c_2\Psi_2 + c_3\Psi_3 \quad [3],$$

where the  $c$  factors give the contributions of each structure. The actual  $\Psi$  will be that for which  $E = \int \Psi^*H\Psi d\tau$  is at a minimum. This condition can be expressed as a set of simultaneous linear equations, ultimately resulting in

$$aq + bq^2 + cqE + dq^2E + eE + fE^2 + gE^3 = 0 \quad [4],$$

where  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ ,  $f$ , and  $g$ , are constants derived from tabulated physical properties of the individual reaction partners. These properties are  $IP$ ,  $PE$ ,  $EA$  and the attractive Coulomb and repulsive Born potential, and univalent radii for the hypothetical ionic species.

$E$  and  $q$  can not simultaneously be found from first principles. For each series, e.g. the  $s^1$  atoms, an experimental  $E$  is used for one metallic reactant, which allows finding  $q$  for that series. This  $q$  then allows finding the  $E$  for the other reactants. As already shown in Figs. 4 and 5, good agreement is obtained between these theoretical  $E$  values and those obtained experimentally. We are currently extending the calculations to  $s^2p^2$  atoms. Others have attempted to apply SECI to transition metal atoms and found sometimes less good agreement<sup>26-28</sup> than for the main group atoms. This will be investigated further. There is no a priori reason to consider only three resonating states. Quite likely, interactions involving  $d$  electrons have to be considered for transition elements.

In other semi-empirical theoretical work, for which the present format leaves no room, we have shown that, for abstraction reactions, a modified form of TST allows predicting the shape of an Arrhenius plot from a measurement at one temperature.<sup>29,30</sup>

## B. Association Reactions

Association reactions of metallic species have frequently been observed, e.g. oxidation reactions of alkali and alkaline earth atoms.<sup>13b,16</sup> Most of these have negative temperature dependences and their potential contribution at high temperatures has tended to be neglected. An example of this is the Cr/O<sub>2</sub>/M system (M ≡ third body), which is important for the formation of highly carcinogenic hexavalent chromium in incinerators. There were reports in the literature that near room temperature the reaction proceeded by association



whereas above about 800 K the mechanism would be abstraction



Below that temperature in an MHTP study, we only found evidence for reaction (5) and above it, reaction (6) indeed proceeded at a measurable rate, but was initially not dominant. The measurements showed that even at 1500 K and 1 bar, upper limits for incinerator conditions, reaction (6) is only some 1.4 times faster than (5).<sup>18</sup> The problem was that in the original T > 800 K study the pressure had not been varied. It has yet to be established if (5) and (6) are independent reactions or proceed through a common CrO<sub>2</sub> intermediate, the dissociation of which becomes more significant with increasing temperature.

Another example here is the AlO/O<sub>2</sub>/M system. In an early HTFFR study, with considerable data scatter, no pressure dependence had been found which led to the erroneous interpretation of a complex abstraction reaction with a negative T-dependence. Later HTFFR work, following many apparatus improvements, showed an association reaction to dominate to about 1000 K for which k(T) = -25.36-1.69log(T/K) cm<sup>6</sup>molecule<sup>-2</sup>s<sup>-1</sup>, while above that temperature a second order process was also observed with k(T) = 7.7x10<sup>-10</sup>exp(-10008 K/T) cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>.<sup>15</sup> The likely reaction mechanism is, like for the preceding example, a competition between collisionally stabilized association and dissociation



There have not been any direct gas-phase observations of AlO<sub>3</sub>, but the species has been observed in matrix work.<sup>31</sup> By contrast, the O<sub>2</sub> reaction of the "iso-electronic" species BO has been found to be pressure independent over the 300-960 K range, where it shows a negative T-dependence: k(T) = 7.9x10<sup>-12</sup>exp(161 K/T) cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>.<sup>8b</sup> The mechanism proposed here is<sup>32</sup>



where the smaller pre-exponential of k(T), as compared to that for AlO<sub>2</sub> + O formation, indicates a preferential dissociation of the intermediate to the reactants. Ab initio calculations have suggested a branched ring OBO<sub>2</sub> structure for BO<sub>3</sub>,<sup>32</sup> similar to that indicated for AlO<sub>3</sub> in the matrix study.

## C. Insertion Reactions

There have been frequent experimental and theoretical studies of metal atoms inserting into molecular bonds.<sup>33</sup> Most of the experiments have been conducted at room temperature and below. Similar reactions involving gaseous metal oxides would also be of interest, as these would be representative of processes occurring on metal oxide catalysts. In this context, an ab initio study has predicted that AlO can directly abstract an H atom from methane in an exothermic reaction with a considerable barrier, 67 kJ mol<sup>-1</sup>.<sup>34</sup> However, an HTFFR investigation over the 590-1350 K range showed much lower activation energies except at the highest temperatures; the complex expression, required to fit the data, indicated competition between several paths.<sup>35</sup> Further calculations suggest that direct abstraction can indeed occur, but that insertion leading to CH<sub>3</sub>AlOH is the most likely initial attack step.<sup>35</sup>

A more direct example of a high temperature insertion reaction was obtained for Cu + HCl.<sup>19</sup> No pressure dependence was observed and a simple Arrhenius plot with k(680-1500 K) =

$1.2 \times 10^{-10} \exp(-7719 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was obtained, suggesting an abstraction reaction. However, mass spectrometric observations over the approximate 1150-1500 K range showed, in addition to the product CuCl, a species HCuCl, the formation of which would require a third-body collision. Ab initio calculations indicated that the initial reaction proceeds over a common rate-controlling barrier, after which the HCuCl complex can either be stabilized into a potential well, or dissociate to H + CuCl. This suggested that increasing pressure would favor the branching to HCuCl, while increasing temperature would decrease its relative importance. This was borne out by experiment.

These observations lead to the questions how common such reactions are and whether other reactions, that on the basis of rate coefficient observations have been assumed to proceed by abstraction, are in fact more complex. In our further work we hope to start providing answers. Hranisvljevic has suggested the use of some orbital symmetry rules and electron configuration arguments to help predict when to expect insertion.<sup>36,37</sup> We plan to start testing these shortly.

#### IV. CONCLUDING REMARKS

In this brief review the emphasis has been placed on the temperature dependence of metallic species reactions, particularly with a view toward high-temperature observations. The study of gas-phase metallic species reactions per se had not been of major interest to kineticists. A 1992 edited volume<sup>13</sup> had already shown that this is changing, with most work being done well below 1000 K. Since then several other investigators have joined and we may, as a result, expect rapid advances. However, a disturbing trend, fortunately restricted to few investigators, must be noted. That is, work done only at one pressure or one [M]. The discussion of Section III B shows that this can readily lead to erroneous interpretations. Likewise, I urge my colleagues to use as wide a temperature range as their experiments allow, when determining activation energies or barriers; such data from narrow  $T^{-1}$  ranges can not be very reliable.

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