

# The Struggle for Precise Rate Constants in Gas Phase Reaction Kinetics: The Reaction $\text{H} + \text{O}_2 \rightleftharpoons \text{HO} + \text{O}$

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## *Reaction Kinetics / Thermochemistry*

A short sketch of the history over the last 100 years of the  $\text{H}_2\text{-O}_2$ -system in general and of the  $\text{H} + \text{O}_2 \rightleftharpoons \text{HO} + \text{O}$  reaction in particular is given. Only after revision of the enthalpy of formation of OH in the year 2000, experimental and theoretical rate constant determinations approach an agreement within about 10 percent. Further improvements of the modeling depend on more precise thermochemical data for the reaction and on a detailed analysis of the contributions from all electronic states arising from the four open electronic shell species involved. Vibrational zeropoint energy problems of OH in classical trajectory calculations and detailed angular momentum couplings in adiabatic channel treatments have also to be mastered.

## 1. Introduction

When Wilhelm Ostwald was born 150 years ago, reaction kinetics was in its infancy. L. Wilhelmy [1] had just provided one of the first quantitative measurements of the time dependence of a second order reaction, the acid-catalyzed inversion of sucrose. 50 years later, when Ostwald wrote his textbook “Lehrbuch der Allgemeinen Chemie” [2], the situation had only started to change. The simplest rate laws were formulated, integrated, and compared with a limited, but still not too well characterized number of laboratory studies. Reaction order and molecularity were directly linked to the stoichiometry of the reaction. The brief discussion of kinetics on only 100 pages, in comparison to the 900 pages devoted to chemical equilibria, both forming the second volume of Ostwald’s textbook entitled “Chemische Dynamik”, on the one hand illustrates the limited amount of kinetic information available, on the other hand

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documents that Ostwald apparently was not particularly attracted by kinetics. Nevertheless, his interest in catalysis became quite visible in his emphasis on catalytic accelerations and attenuations of chemical processes.

In his textbook, Ostwald just missed the beginning of a new era of kinetics which started with the careful laboratory work by Max Bodenstein [3]. In contrast to Ostwald, in his textbook "Theoretische Chemie" [4], appearing at about the same time, Walther Nernst realized the importance of Bodenstein's work and referred to several of his studies. Bodenstein's identification of catalytic influences, *e.g.* on the rate of the reaction



should have caught Ostwald's attention but only Nernst was quick enough to include this seminal work in his treatise. Also, in contrast to Ostwald, Nernst for most systems did not attempt to provide a naïve relationship between rate law, detailed mechanism, and overall stoichiometry of the reaction. Although under some conditions Bodenstein found a third order rate law for reaction (1), Nernst's formulations suggest that he did not believe that reaction (1) really was a termolecular process, such as this might have been suggested by equation (1).

The next 50 years brought a rapid development of phenomenological kinetics and laid the basis for modern concepts. During the 1930's, the complex character of reactions like the overall transformation (1) was realized and mechanisms of contributing elementary atom and radical reactions were formulated, see *e.g.* Wilhelm Jost's book on combustion processes [6]. With the advent of new experimental techniques in the 1950's, allowing for the study of rapid elementary reactions and providing clean reaction conditions, finally the quantitative age of experimental reaction kinetics started. At the same time, theoretical approaches, although not being quantitative as yet, at least allowed for a rationalisation of the experimental results.

Today, 150 years after Ostwald's birthday, we have become aware of the immense complexity of chemical kinetics. We struggle to measure rate coefficients of elementary reactions with high accuracy. We try to cover the widest possible range of experimental conditions, temperatures and pressures, as well as variations of reactant environments. Critical evaluations of rate coefficients form the basis for reliable modeling of large reaction systems. The quality of this modeling, however, often is still influenced by uncertainties in thermodynamic data. Finally, spectroscopy as well as *ab initio* quantum chemistry and theoretical modeling of reaction dynamics provide complementary information. Each elementary reaction step has become a unique chemical world, asking for a careful analysis of all of its specific subtleties. As reaction (1) is a prototype of gas phase oxidation processes, in the following article recent developments within this simple chemical transformation are reviewed. An exhaustive discussion of this reaction would fill a complete book. Therefore, only

few of its elementary reaction steps are being considered. Neither Ostwald, nor Nernst, and probably also not Bodenstein would have imagined the degree of complexity hidden behind a simple transformation equation such as written for reaction (1).

## 2. Mechanisms for the oxidation of hydrogen

The mechanisms of elementary reactions behind the overall transformation equation (1) in the 1930's were all speculative. It was clear that there was some initiation reaction, homogeneous or heterogeneous, which provided hydrogen atoms. There had to be a reaction chain with branching steps and, finally, a series of termination processes, again homogeneous or heterogeneous [7]:

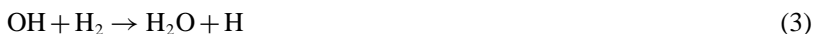
The Haber–Bonhoeffer mechanism involved the chain processes



the Hinshelwood mechanism instead proceeded via



the Lewis mechanism postulated



Some of these processes by now have been confirmed to occur, others are not taking place, new processes have been added. Current models of the H<sub>2</sub>–O<sub>2</sub> system include of the order of 30 elementary reactions [8], being of varying importance under different reaction conditions. Reactions (2), (7), (9)–(11) are

not among the considered processes. The most important chain branching and propagation processes are now well established to be

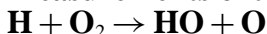


The temporarily chain-terminating formation of  $\text{HO}_2$  via reaction



is also of great importance. Often macroscopic observables such as flame velocities or explosion limits most sensitively depend on the rate coefficients  $k_4$  and  $k_6$  for reactions (4) and (6) respectively, see *e.g.* the sensitivity tests illustrated in [9]. It, therefore, appears of particular interest to look into the kinetics of these reactions and into their individual “chemical world”.

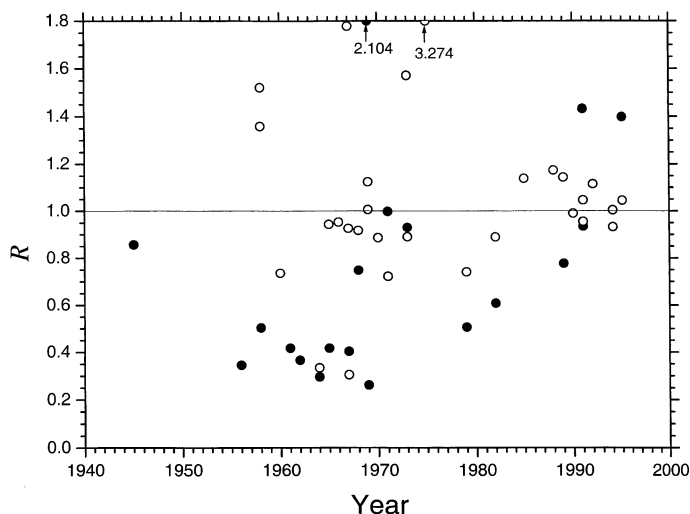
### 3. Measurements of the rate of the reaction



Quantitative experimental information on the rate of reaction (4) in the 1940's and 1950's started to become available from considerations of the first and the second explosion limits of the  $\text{H}_2$ - $\text{O}_2$  system. From the properties of the first limit, ratios of  $k_4$  and the diffusion coefficient of hydrogen atoms were derived, simple kinetic models of the second limit led to ratios  $k_4/k_6$ . Studies of the detailed properties of reaction zones in hydrogen-oxygen flames [10], the length of induction times of the  $\text{H}_2$ - $\text{O}_2$  reaction in shock waves [11] and, finally, the direct detection of concentrations of hydrogen atoms by the ESR technique [12] in flow systems paved the way to absolute values of  $k_4$ . Because of its immense practical importance in all types of oxidation processes of hydrogen-containing fuels,  $k_4$  has been measured over and over again with ever improving experimental techniques. On the one hand, it is fascinating to follow the development of new experimental techniques by their application to this reaction, on the other hand one may ask which precision in measuring  $k_4$  has been obtained today and which improvements lay ahead of us. We do not intend to discuss here the history of measurements of  $k_4$ : an excellent description of the progress until 1971 was given in [13], the evaluations [14] and [15] cover the subsequent period until about 2000. Instead, by using rate data from [13]–[15] and by comparing them with the recommended expression for  $k_4$  from the most recent data evaluation [15], *i.e.*

$$k_4 = 3.43 \times 10^{-10} T^{-0.097} \exp(-7560K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (12)$$

(with  $T$  in  $K$ ), we illustrate how measurements over the years have converged to Eq. (12) and which precision has been reached. Fig. 1 shows the ratio of



**Fig. 1.** Historical development of measurements of  $k_4$  at 800 K (●) and at 1500 K (○) (data from [13]–[15];  $R = k_{4\text{ exp}}/k_{4\text{ ref}}$ , see text).

the measured  $k_4$  (“ $k_{4\text{ exp}}$ ”) and  $k_4$  from Eq. (12) (“ $k_{4\text{ ref}}$ ”) for the two representative temperatures 800 and 1500 K. Apparently, a precision of the order of  $\pm 10$  percent now is approached although some partly unexplained deviations up to about  $\pm 50$  percent occurred still recently. There does not seem to be a trend towards smaller scatter of the data such that, for the time being,  $\pm 10$  percent may be considered the present limit of precision of a rate constant which was measured in particular detail. Does one need better data? How could they be obtained?

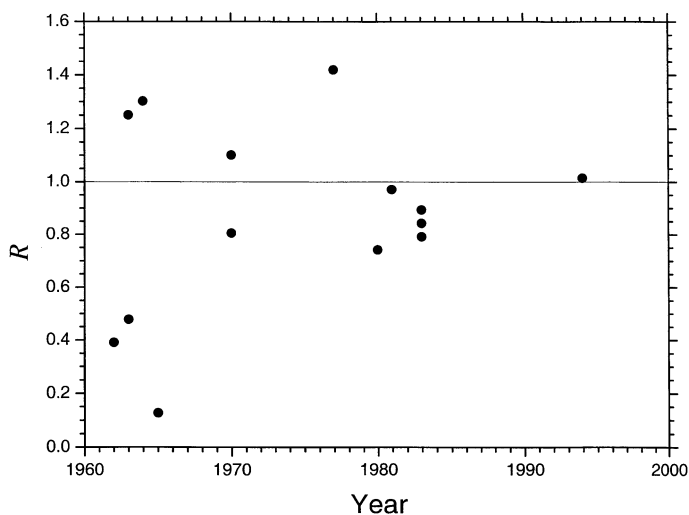
Of similar importance as reaction (4) is reaction (6). The history of the measurement of its rate again can be followed within [13]–[15]. The situation obviously is more complicated since reaction (6) is a radical recombination with a possible transition between third and second order and a dependence of  $k_6$  on the temperature, the pressure, and the chemical nature of the bath gas [M]. We do not intend to discuss  $k_6$  in this article (see *e.g.* [16]) but we mention that reactions (4) and (6) take place on the same potential energy surface with an  $\text{HO}_2$  intermediate and, hence, have to be analyzed together, see below.

Likewise, reaction (4) is linked to its reverse reaction



by the relationship

$$k_4/k_{-4} = K_{\text{eq}} \quad (13)$$



**Fig. 2.** Historical development of measurements of  $k_{-4}$  at 300 K (data from [13]–[15];  $R = k_{-4 \text{ exp}}/k_{-4 \text{ ref}}$ , see text).

where  $K_{\text{eq}}$  denotes the equilibrium constant. As reaction (-4) in contrast to reaction (4) is exothermic, it can be followed down to very low temperatures. Like reaction (6), also reaction (-4) should be analyzed together with reaction (4). It should be mentioned that reaction (-4) is of importance in atmospheric as well as in interstellar chemistry such that wide ranges of applications and conditions are linked together. Again relying on the data evaluations from [13]–[15], Fig. 2 shows the historical development of the ratio  $k_{-4 \text{ exp}}/k_{-4 \text{ ref}}$  at 300 K where  $k_{-4 \text{ ref}}$  is taken as the recommended value of  $k_{-4}$  from [15], *i.e.*

$$k_{-4} = 2.00 \times 10^{-10} T^{-0.352} \exp(113K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (14)$$

The situation obviously is less satisfactory than for  $k_4$ . It is getting even worse when temperatures of the order of 100 K are considered [17], [18] where uncertainties of a factor of 2 have not been eliminated as yet.

#### 4. Equilibrium constants for $\text{H} + \text{O}_2 \rightleftharpoons \text{HO} + \text{O}$

As shown in Sect. 3, considerable improvements in experimental measurements of  $k_4$  and  $k_{-4}$  at present do not appear to be in view. One, therefore, will ask theory to come to help. In the following we shall describe the development on this side of the problem. Theory requires the knowledge of a lot of details of the potential energy surface of  $\text{HO}_2$ . However, before anything else, the thermochemistry of reactions (4) and (-4) and the precise value of the equilibrium

constant  $K_{\text{eq}}$  from Eq. (13) needs to be known. One cannot expect to predict  $k_4$  with confidence if the endothermicity of reaction (4) is not well characterized.

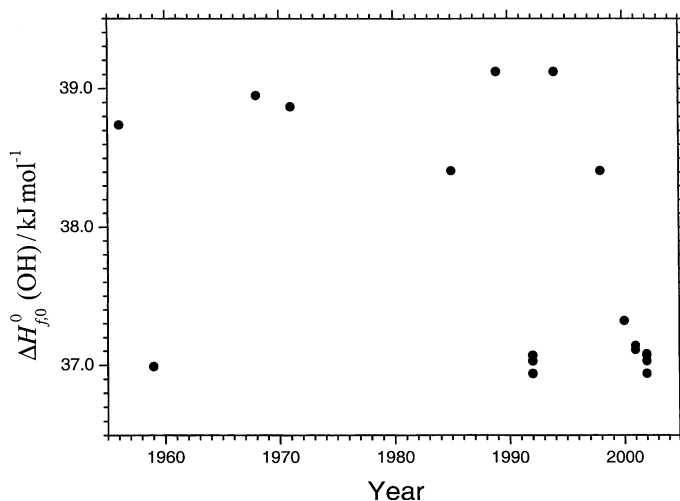
One might be surprised that it took until the year 2001 that the heat of formation of OH was firmly established [19]–[21]. The now estimated uncertainty of  $\pm 0.3 \text{ kJ mol}^{-1}$  in the exponential factor of  $k_4$  corresponds to  $\exp(\pm 36 \text{ K}/T)$  which at 800 K leads to an uncertainty of a theoretical  $k_4$  of about  $\pm 5$  percent. No matter how good a theoretical simulation of  $k_4$  may be, at present the remaining uncertainty of the heat of formation of HO, therefore, prevents theory to arrive at a considerable improvement of the precision of  $k_4$  beyond the experimental results.

One may ask why this is so and why it took so long to improve the precision of the OH-value to about  $\pm 0.3 \text{ kJ mol}^{-1}$  and why, in particular, for such a long time a value was in use which was different by about  $2 \text{ kJ mol}^{-1}$  from the now accepted number. Since this is such a crucial question, it appears useful to look as well into the historical development. Around 1960, a value for the heat of formation of OH of  $\Delta H_{f,0}^{\circ} = 36.99(\pm 2.1) \text{ kJ mol}^{-1}$  was recommended [22]. Based on a spectroscopic determination, *i.e.* an extrapolation of the B  $\rightarrow$  A system of OH [23], instead a value of  $\Delta H_{f,0}^{\circ} = 38.87(\pm 1.26) \text{ kJ mol}^{-1}$  was chosen in [24]. Over the years this value was slightly modified, misquoted, but essentially retained to be  $\Delta H_{f,0}^{\circ} = 38.41(\pm 1.21) \text{ kJ mol}^{-1}$  [25]. Other data evaluations preferred different values such that a quite unsatisfactory situation continued to last until 2001. Only then it was confirmed that the extrapolation of the spectroscopic observables was uncertain and that other determinations had to be preferred. The comparison of various experimental determinations with high level theoretical calculations now has led to a value [19]–[21] of  $\Delta H_{f,0}^{\circ} = 37.03(\pm 0.29) \text{ kJ mol}^{-1}$ . On the experimental side, more than five different techniques were employed; on the theoretical side an extrapolation of CCSD(T) calculations with aug-cc-pv (5, 6, and 7) Z basis functions was performed [19], [20]. Since the merits of the various approaches have extensively been discussed in [20], we do not consider them here. Instead, Fig. 3 again illustrates the historical development of the value of  $\Delta H_{f,298.15}^{\circ}(\text{OH})$ .

Compared to  $\Delta H_{f,0}^{\circ}(\text{OH})$ , there is much less uncertainty in the other factors entering  $K_{\text{eq}}$  such that the changes of the preferred  $K_{\text{eq}}$  with time directly reflect those of the heat of reaction. This now, for reaction (4), is equal to  $\Delta H_0^{\circ} = 67.78 \text{ kJ mol}^{-1}$  (or  $\Delta H_0^{\circ}/R = 8152 \text{ K}$ ) [20], [25]. The corresponding equilibrium constant  $K_{\text{eq}}$  between 300 and 5000 K is represented [15] by

$$K_{\text{eq}} = 2.88 \times 10^2 T^{-0.367} \exp(-8390 \text{ K}/T). \quad (15)$$

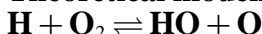
The relevance of this value for theories of  $k_4$  and  $k_{-4}$  will be demonstrated in the following. It should be noted that Eqs. (12)–(15) are not quite internally consistent. Forcing  $k_4$ ,  $k_{-4}$ , and  $K_{\text{eq}}$  on a form  $AT^{-B} \exp(-C/T)$  over



**Fig. 3.** Historical development of measurements and recommendations of  $\Delta H_{f,0}^0(\text{OH})$  (data from [19]–[25], partly reevaluated in [20]).

temperature ranges 200–5000 K is just not feasible. For this reason deviations between  $k_4/k_{-4}$  and  $K_{\text{eq}}$  within about 10 percent at temperatures, where the measurements overlap may still be encountered when data from evaluations are employed.

## 5. Theoretical modeling of the rate of the reactions



In a situation where rate constants are strongly influenced by the uncertainty of the endothermicity of the reaction, it appears most reasonable to consider the rate constant of the reverse exothermic reaction first and then to convert by the equilibrium constant. We shall do this also here, *i.e.* consider  $k_{-4}$  first. Obviously however, in a modeling, rate and equilibrium constants have to be treated in an internally consistent way.

It is now well established that reactions (4), (-4), and (6) take place on the potential energy surface of  $\text{HO}_2^*$  and, thus, involve the intermediate formation of a highly excited bound  $\text{HO}_2^*$ . Whether only the ground electronic surface is involved remains an open question, see below. The mechanism of reaction (-4), thus, can be written symbolically





The reverse reaction (4) is initiated by



and terminated by the competition of reactions (-16) and (17). The equilibrium constant  $K_{\text{eq}}$  is expressed by

$$K_{\text{eq}} = k_4/k_{-4} = k_{-16}k_{-17}/k_{16}k_{17} \quad (18)$$

while

$$k_{-4} = k_{16}k_{17}/(k_{-16} + k_{17}) \quad (19)$$

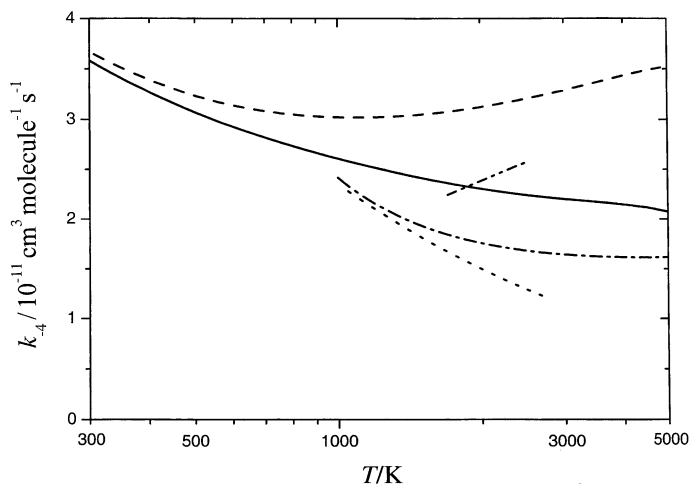
and

$$k_4 = k_{-17}k_{-16}/(k_{-16} + k_{17}) \quad (20)$$

The immediate question arises whether the exothermic reaction (-4), is capture-controlled or, in spite of its large exothermicity, involves back-dissociation of  $\text{HO}_2^*$ . In the first case one would have  $k_{-16} \ll k_{17}$  and  $k_{-4} \approx k_{16}$ , in the latter  $k_{-4}$  would be reduced by the factor  $k_{17}/(k_{-16} + k_{17})$ . One may try to answer this question by applying statistical unimolecular rate theory for the two competing dissociation channels of  $\text{HO}_2^*$ . In this approach one considers the specific rate constants  $k(E, J)$  which are given by

$$k(E, J) = W(E, J)/h\rho(E, J) \quad (21)$$

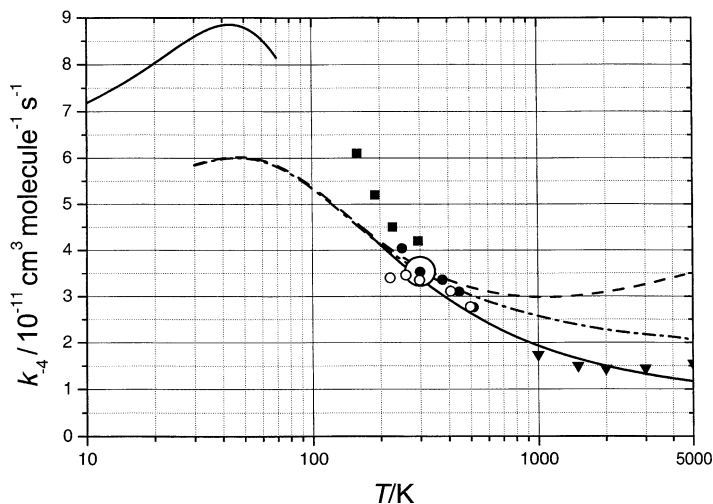
with Planck's constant  $h$ , the rovibrational density of states  $\rho(E, J)$ , and the number  $W(E, J)$  of activated complex states at the energy  $E$  and the angular momentum with the quantum number  $J$ . In order to calculate  $k_{17}/(k_{-16} + k_{17})$ , only ratios  $W_{17}(E, J)/(W_{-16}(E, J) + W_{17}(E, J))$  have to be considered and suitably averaged. On the basis of a new ab initio potential energy surface [26], [27], this modelling was done in [26], employing a combined statistical adiabatic channel/classical trajectory (SACM/CT) treatment for the separate capture (or dissociation) processes (16) and (-17) (or (-16) and (17)). The calculations indicated that reaction (-4) is practically capture-controlled at temperatures up to about 300 K whereas it is reduced through back dissociation by about 13 percent at 1000 K and by 41 percent at 5000 K. If correct, these results would indicate which part of the potential, apart from the equilibrium constant  $K_{\text{eq}}$ , is most relevant for the accuracy of a calculated  $k_4$ : it is the exit range of  $\text{HO}_2^* \rightarrow \text{HO} + \text{O}$ . Differences at the entrance  $\text{H} + \text{O}_2 \rightarrow \text{HO}_2^*$ , such as encountered between the frequently used DMBE IV potential from [28] and the more recent ab initio potential from [29] would matter for reaction (6) (see [30]) but have only little effect on reaction (4).



**Fig. 4.** Experimental and modeled values of  $k_{-4}$ : situation in 2000 from [26] (full line = statistical SACM/CT model from [26], dashed line = capture controlled CT calculations from [26], dash-dot-dot line = experiments from [31], dotted line = experiments from [35], dash-dot line = experiments from [32]–[34] such as averaged in [34]; experiments on  $k_4$  converted to  $k_{-4}$  with  $K_{\text{eq}}$  based on older high value of  $\Delta H_f^\circ(\text{OH})$ ).

The  $\text{HO}_2$  potential at the  $\text{HO} + \text{O}$ -side has a very complicated shape, because the minimum energy path at first, by dipole-quadrupole interaction, leads linearly to a weakly bound  $\text{OHO}$  intermediate which, over a small barrier below the entrance energy, then converts to the nonlinear  $\text{HOO}$  structure [26]. There is the additional complication that the electronic degeneracy of the linear structure is lifted upon bending and two bound  $\text{HO}_2$  electronic surfaces ( $^2A'$  and  $^2A''$ ) arise which both may or may not contribute to the reaction, see below. Assuming that only the lower of these surfaces contributes, the statistical SACM/CT treatment gave the result shown in Fig. 4.

The comparison of the modeled  $k_{-4}$  and the measured  $k_4/K_{\text{eq}}$  in Fig. 4 gave rise to interesting speculations [26]. At 2000 K, there was agreement between the modelling and the very careful shock wave results from [31], while the majority of the other, not less carefully done, shock wave studies [32]–[34] were about 35 percent below the modeled value. The results from [35] were even further below. The discussion in [26], from the year 2000, left two alternatives: either the experiments from [31], the assumed  $K_{\text{eq}}$ , and the statistical modeling were correct, or the experiments from [32]–[34] and the modeling were correct which would require an increase of the accepted  $\Delta H_f^\circ(\text{OH})$  by about  $2 \text{ kJ mol}^{-1}$ . Ironically, the analysis one year later, in 2001, took a different turn. First, the values of  $\Delta H_f^\circ(\text{OH})$  was not revised up but down by  $2 \text{ kJ mol}^{-1}$  [19]. Second, the system turned out not to follow a statistical competition between reac-



**Fig. 5.** Experimental and modeled values of  $k_{-4}$ : situation in 2001 from [27] ( $\blacktriangledown$ : experiments on  $k_4$  [34] converted to  $k_{-4}$  with  $K_{eq}$  based on revised low value of  $\Delta H_f^\circ(\text{OH})$ , large open circle: average of all measured  $k_4$  at 300 K [27],  $\blacksquare$ : experiments from [17],  $\circ$  and  $\bullet$ : earlier experiments, see [27], full line below 70 K: SACM modelling [27], full line above 200 K: nonstatistical CT modelling from [27], dashed line: capture controlled CT modelling from [26], dash-dot line: statistical SACM/CT modelling from [26]).

tions (-16) and (17) [27]; instead,  $k_{-16}$  was found to increase by nonstatistical effects to almost twice its statistical value [27] (even larger effects were postulated in [36], [37], see below). The latter effect at 2000 K reduced the modeled  $k_{-4}$  down to values below the experimental data for  $k_4/K_{eq}$  from [32]–[34], such as evaluated with the old  $K_{eq}$ , while the former brought the experimental data of  $k_4/K_{eq}$  with the new  $K_{eq}$  down to the modeled  $k_{-4}$ . This is illustrated in Fig. 5 from [27]. There is now agreement within  $\pm 10$  percent at 1000–3000 K between the modeled  $k_{-4}$  and the majority of the experiments [32]–[34]. It is not understood why the experiments from [31] and [35] fall above or below the consensus values such as summarized in [34]. Nevertheless, the agreement between theory [27] and experiment [34] within  $\pm 10$  percent at 1000–3000 K appears to be most satisfactory, characterizing what can be achieved today on both sides. This nice picture unfortunately is spoiled by a long list of unsolved complications which will be mentioned in the next section. It may be that these are all not relevant and that at least a 10 percent precision has been reached at this stage but this is not at all guaranteed. Further improvements on the theoretical side, which could lead beyond the experimental possibilities, however, will need a complete solution of the problems sketched in the following.

## 6. More complications

The agreement between modeled  $k_{-4}$  and measured  $k_4/K_{\text{eq}}$  in Fig. 5 between 1000 and 3000 K may suggest that theory can assist in the data evaluation, e.g. by correcting down the experimentally not so easily obtainable result at 5000 K. Likewise, the agreement between the average of the experimental results for  $k_{-4}$  at 300 K and theory looks encouraging. However, a series of unsolved problems require a solution before more progress can be made. This is the issue of the present section.

Fig. 5 includes modeling results for capture-controlled  $k_4$  at temperatures below 300 K which were obtained from classical trajectory calculations. These calculations suffer from the vibrational zero-point dilemma. Running classical trajectories from the O + OH side, some encounters lead to  $\text{HO}_2^*$  with lifetimes of the order of 0.1–1 ps during which statistical forward vs backward ratios of dissociation rates of  $\text{HO}_2^*$  are established. Other encounter pairs are so short-lived (about 1 fs) that O is practically reflected from OH without reaction. Starting with the vibrational zero-point energy in OH, at low temperatures most of these trajectories leave OH with less than its zero-point energy. What then has to be done? Starting without zero-point energy restrictions in OH, or eliminating all trajectories which, after starting at the zero-point energy, leave OH with less than the zero-point energy, gives nearly the same results [27]. It predicts nearly complete capture control at  $T \leq 300$  K, and at higher temperatures produces about twice as much back dissociation as given by the statistical SACM/CT approach. This was the basis of the comparison of Fig. 5. Retaining all trajectories starting at the zero-point energy of OH and leaving OH with gain or loss of energy instead was recommended in [36], [37]. This, however, leads to a nearly temperature independent ratio of 0.4–0.6 for the ratio  $k_{17}/(k_{-16} + k_{17})$ , such that the modeled  $k_{-4}$  would be about a factor of 2 below the measured  $k_{-4}$  near 300 K. The ultimate solution of this zero-point energy dilemma can only come from accurate quantum wave packet scattering calculations such as done – with enormous numerical effort – for H + O<sub>2</sub> scattering at higher energies [38] in comparison to the hot hydrogen atom + O<sub>2</sub>-experiments from [39]. At present such calculations are not available for O + OH encounters at lower energies. However, the agreement between experiment and theory near 300 K in Fig. 5 may suggest that the handling of the zero-point energy dilemma in [27] is more adequate than the policy proposed in [36], [37]. Fortunately, the problem becomes irrelevant for temperatures near 1000 K.

Although the situation of the heat of formation of OH has been improved by the work of [19]–[21], the remaining uncertainty still is one of the major limitations of predicting more accurate values of  $k_4$ . There is no reason why the dissociation energy of OH finally cannot be determined by some suitable spectroscopic method with spectroscopic precision. Quantum-chemical methods apparently cannot go much beyond what was achieved in [20].

It is difficult to estimate which details of the ab initio potential energy surface of HO<sub>2</sub> from [26], beyond the correct endothermicity of the reaction, need further improvement for calculating  $k_4$  under high temperature conditions. In any case it has to be clarified whether, apart from the  $^2A''$  surface, also the  $^2A'$  potential contributes which corresponds to the low-lying excited electronic state of HO<sub>2</sub>. So far this state was neglected because the electronically excited HO<sub>2</sub> does not correlate with electronic ground state H + O<sub>2</sub>. Nevertheless, this state from the HO + O-side is accessible without energy barrier (except for a small “reef” when the linear OHO adduct bends to HOO, see above).

Beyond the  $^2A''$  and  $^2A'$  potentials of the O + OH system, other electronic states have to be considered. It is quite clear that the  $9 \times 4 = 36$  electronic fine structure states of O( $^3P$ ) and OH( $^2\Pi$ ) at large distances influence each other before, at shorter distances, they separate into the two bonding doublet states  $^2A''$  and  $^2A'$  and into the remaining largely repulsive excited doublet and quartet states of HO<sub>2</sub>. At the H + O<sub>2</sub>-side of the potential, similar but less complicated interactions between the  $2 \times 3 = 6$  states need to be considered. Starting from the first calculations of the long-range potentials for the O + OH manifold in [40], a recent complete asymptotic theory of the O + OH- and H + O<sub>2</sub>-potentials with and without the effects of spin-orbit coupling has been elaborated in [41]. It will still need much work to connect all of these potential surfaces with the corresponding short range ab initio calculations. It remains unclear at present which parts out of this complicated manifold are relevant for low temperature SACM calculations of O + OH capture rates. It is known that the effects of open electronic shells shift the limit of quantum vs classical capture calculations towards higher temperatures, in the present case probably into the range 100–300 K. Simplistic SACM calculations of this kind have been included in Figs. 4 and 5. Nevertheless, it appears too early to make precise theoretical predictions of  $k_{-4}$  for the temperature range 10–20 K. Astrochemical modeling of interstellar O<sub>2</sub>-chemistry would require experimental or theoretical information on  $k_{-4}$  just in this range such that increased effort on both sides is really necessary.

## 7. Conclusions

The last hundred years have seen an enormous development of reaction kinetics, such as described here from Bodenstein’s first studies of the H<sub>2</sub>–O<sub>2</sub> reaction around 1900, through the identification of its mechanism in the 1930’s, and the quantification of its thermochemistry and rates of elementary steps starting in the 1950’s. Since this date, such as illustrated here for the H + O<sub>2</sub> ⇌ HO + O reaction system, the precision of the data – both on the experimental and theoretical side – has improved and reached about ±10 percent for the rate constants. Further improvements will primarily depend on more precise values of the reaction enthalpy which is related to the still not too well known dissoci-

ation energy of OH. Electronic structure calculations for the full manifold of fine-structure components of the open electronic shell  $O + OH$ - and  $H + O_2$ - systems finally will be required. Combined SACM/CT calculations on these potentials will provide an access to precise rate constants. A final comparison with accurate quantum scattering calculation within this complicated pattern of coupled electronic states will probably have to wait for a more distant future. Would the founding fathers of physical chemistry and reaction kinetics such as Wilhelm Ostwald, Walther Nernst, and Max Bodenstein have expected the extent of complications hidden behind a simple reaction equation like  $H + O_2 \rightarrow HO + O$ ?

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### References

1. L. Wilhelmy, *Ann. Physik. Chem. (Poggendorf)* **81** (1850) 413, 499.
2. W. Ostwald, *Lehrbuch der Allgemeinen Chemie*, 2. Auflage, Engelmann, Leipzig (1902).
3. M. Bodenstein, *Z. Phys. Chem.* **29** (1899) 147, 295, 315, 429.
4. W. Nernst, *Theoretische Chemie*, Enke, Stuttgart (1900).
5. M. Bodenstein, *Z. Phys. Chem.* **29** (1899) 665.
6. W. Jost, *Explosions- und Verbrennungsvorgänge in Gasen*, Springer, Berlin (1939).
7. H. J. Schumacher, *Chemische Gasreaktionen*, Steinkopff, Darmstadt (1938).
8. D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Frank, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, and R. W. Walker, *J. Phys. Chem. Ref. Data* **21** (1992) 411.
9. J. Warnatz, U. Maas, and R. W. Dibble, *Combustion*, Springer, Heidelberg (1996); *Verbrennung*, Springer, Heidelberg (1996).
10. C. P. Fenimore and G. W. Jones, *J. Phys. Chem.* **62** (1958) 693.
11. G. L. Schott, *J. Chem. Phys.* **32** (1960) 710.
12. K. H. Eberius, K. Hoyer, and H. Gg. Wagner, *Proc. Comb. Inst.* **13** (1971) 713.
13. D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, *Evaluated Kinetic Data for High Temperature Reactions, Vol. I: Homogeneous Gas Phase Reactions of the  $H_2$ - $O_2$  System*, Butterworths, London (1972).
14. D. L. Baulch, C. J. Cobos, R. A. Cox, P. Frank, G. Hayman, Th. Just, J. A. Kerr, T. Murrells, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, *J. Phys. Chem. Ref. Data* **23** (1994) 847.
15. D. L. Baulch, C. T. Bowman, C. J. Cobos, R. A. Cox, Th. Just, J. A. Kerr, M. J. Pilling, D. Stocker, J. Troe, W. Tsang, R. W. Walker, and J. Troe, *J. Phys. Chem. Ref. Data*, in press (2003).
16. J. Troe, *Proc. Comb. Inst.* **28** (2000) 1463.
17. I. W. M. Smith and D. W. A. Stewart, *J. Chem. Soc. Faraday Trans. 2* **77** (1981) 997.
18. S. P. K. Koehler, I. Sims, and I. W. M. Smith, private communication, 2003.

19. B. Ruscic, D. Feller, D. A. Dixon, K. A. Peterson, L. B. Harding, R. L. Asher, and A. F. Wagner, *J. Phys. Chem. A* **105** (2001) 1.
20. B. Ruscic, A. F. Wagner, L. B. Harding, R. L. Asher, D. Feller, D. A. Dixon, K. A. Peterson, Y. Song, Y. Qian, C.-Y. Ng, J. Liu, W. Chen, and D. W. Schwenke, *J. Phys. Chem. A* **106** (2002) 2727.
21. J. A. Joens, *J. Phys. Chem. A* **105** (2001) 11041.
22. P. Gray, *Trans. Far. Soc.* **55** (1959) 408.
23. R. F. Barrow, *Ark. Fys.* **11** (1956) 281.
24. D. R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd ed., NSRDS-NBS 37, US Dept. of Commerce, Washington (1971).
25. M. W. Chase, *NIST-JANAF Thermochemical Tables*, 4th ed., *J. Phys. Chem. Ref. Data*, Monograph No. 9, US Sec. of Commerce, Washington (1998).
26. L. B. Harding, A. I. Maergoiz, J. Troe, and V. G. Ushakov, *J. Chem. Phys.* **113** (2000) 11019.
27. J. Troe and V. G. Ushakov, *J. Chem. Phys.* **115** (2001) 3621.
28. M. R. Pastrana, L. A. M. Quintales, J. Brando, and A. J. C. Varandas, *J. Phys. Chem.* **94** (1990) 8073.
29. L. B. Harding, J. Troe, and V. G. Ushakov, *Phys. Chem. Chem. Phys.* **2** (2000) 631.
30. L. B. Harding, J. Troe, and V. G. Ushakov, *Phys. Chem. Chem. Phys.* **3** (2001) 2630.
31. P. Frank and Th. Just, *Ber. Bunsenges. Phys. Chem.* **89** (1985) 181.
32. A. N. Pirraglia, J. A. Michael, J. W. Sutherland, and R. B. Klemm, *J. Phys. Chem.* **93** (1989) 282.
33. D. A. Masten, R. K. Hanson, and C. T. Bowman, *J. Phys. Chem.* **94** (1990) 7719.
34. H. Du and J. P. Hessler, *J. Chem. Phys.* **96** (1992) 1077.
35. T. Yuan, C. Wang, C.-L. Yu, M. Frenklach, and M. J. Rabinowitz, *J. Phys. Chem.* **95** (1991) 1258.
36. J. A. Miller and B. C. Garrett, *Int. J. Chem. Kinet.* **29** (1997) 275.
37. J. A. Miller and S. J. Klippenstein, *Int. J. Chem. Kinet.* **31** (1999) 753.
38. E. M. Goldfield and A. J. H. M. Meijer, *J. Chem. Phys.* **113** (2000) 11055.
39. M. A. Bajeh, E. M. Goldfield, A. Hanf, C. Kappel, A. J. H. M. Meijer, H.-R. Volpp, and J. Wolfrum, *J. Phys. Chem. A* **105** (2001) 3359.
40. M. M. Graff and A. F. Wagner, *J. Chem. Phys.* **92** (1990) 2423.
41. A. I. Maergoiz, E. E. Nikitin, J. Troe, and V. G. Ushakov, In *Theory of the Dynamics of Elementary Chemical Reactions* (NATO ASI Series, ed. G. Lendvay, Kluwer, Dordrecht, 2003, in press).