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Estimation of Rate Constants for Near-diffusion-controlled Reactions in Water at High Temperatures

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Rate constants measured over the temperature range 20–200 °C are reported for the following reactions: (*a*) reaction of the hydrated electron with oxygen, the proton, hydrogen peroxide, nitrate, nitrite, nitrobenzene and methyl viologen; (*b*) reaction of the hydroxyl radical with another hydroxyl radical and ferrocyanide; (*c*) reaction of the hydrogen atom with permanganate and oxygen. To evaluate methods of estimating rate constants at high temperatures these rate constants and others in the literature have been fitted to the following equation:

$$k_{obs} = k_{diff}/(1 + k_{diff}/k_{react})$$

where k_{obs} is the measured rate constant for the bimolecular reaction in solution, k_{diff} is the encounter rate constant of the two reacting species, and k_{react} is the rate constant that would be measured if diffusion of the species was not rate influencing. With the exception of reactions of the hydrated electron with nitrate and nitrite ions and nitrous oxide, good fits have been obtained to the above equation, and the results demonstrate that few, if any, of the reactions which are pertinent to water radiolysis are truly diffusion controlled at elevated temperatures.

To model the radiolysis of water in the primary heat-transport system of a nuclear power reactor, the rate constants of *ca.* 80 reactions[1] need to be known at 250–300 °C. Because of the nature of many of these reactions, it may be impossible to measure every required rate constant at elevated temperatures; instead, these rate constants will have to be estimated. To date, in modelling calculations of water radiolysis at 250–300 °C, an estimate has been made for the rate constant of a reaction at these temperatures by assuming an Arrhenius relationship.[2–5] If no value of the activation energy was available and the room temperature rate constant was near-diffusion controlled. *i.e.* $> 3 \times 10^9$ dm^3 mol^{-1} s^{-1}, an activation energy of 12.6 kJ mol^{-1} was generally assumed. This value is less than the activation energy of self-diffusion in water which ranges, for example, from 21 kJ mol^{-1} at 5 °C to 12 kJ mol^{-1} at 200 °C.[6] The value of 12.6 kJ mol^{-1} was chosen by Jenks[2] based on generalised comments on diffusion-controlled reactions by Benson,[7] who stated that the activation energy of diffusion in a liquid was approximately one third of its heat of vaporization.

Recent experimental results indicate that the above method is inappropriate since, not only are the measured Arrhenius activation energies less than 12.6 kJ mol^{-1}, but also the fits to the Arrhenius relationship are often non-linear.[8–11] Most of these experimental data were obtained over a limited temperature range (20–90 °C). In order to develop more reliable methods to estimate high-temperature rate constants, it is necessary to establish the kinetic behaviour of reactions over as wide a temperature range as possible. To this end, we report the rate constants for a number of reactions involving OH, H and e_{aq}^- over the temperature range 20–200 °C. We have taken this information, along with other data in the literature, and have evaluated the use of eqn (1),[12–16]

$$1/k_{obs} = 1/k_{diff} + 1/k_{react} \quad (1)$$

to estimate rate constants at elevated temperatures. k_{obs} is the observed rate constant for the bimolecular reaction in solution, k_{diff} is the encounter rate constant of the two reacting species and k_{react} is the rate constant that would be measured if diffusion of the species was not rate influencing.

As a result of this study it has become apparent that there are few reactions which are truly diffusion controlled over the 20–200 °C temperature range. Most reactions with rate constants at room temperature $> ca.\ 3 \times 10^9$ dm^3 mol^{-1} s^{-1} are influenced by both diffusion and chemical processes. In a number of cases where a reaction has been studied in both the solution and the gas phase, it is possible, by using eqn (1), to estimate k_{react} and compare its value to the gas-phase rate constant.

Experimental

All the new experimental data acquired for this paper were measured at the Cookridge Radiation Research Centre using the experimental procedures described in earlier publications.[11,17] The chemicals were analytical grade or better and were used as supplied. Solutions were prepared in triply distilled water and saturated with the appropriate gas using the syringe-bubbler technique.

Method of Analysis

In order to fit eqn (1) to the experimental data, it was rearranged as

$$k_{calc} = k_{diff}/(1 + k_{diff}/k_{react}) \quad (2)$$

where k_{calc} is the computed value to be compared to the measured value, k_{obs}. Here k_{diff} is given by

$$k_{diff} = 4\pi(D_A + D_B)(r_A + r_B)N \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}. \quad (3)$$

Eqn (3) is the Smoluchowski equation[13] where D_i (m^2 s^{-1}) is the diffusion coefficient, r_i (nm) is the reaction radius of species '*i*', and *N* is the Avogadro number. When the reactants are ions, eqn (3) is multiplied by the Debye factor $\delta/(e^\delta - 1)$, where δ is given by eqn (4).[18]

$$\delta = Z_A Z_B e^2/4\pi\varepsilon_0 \varepsilon(r_A + r_B)k_B T \quad (4)$$

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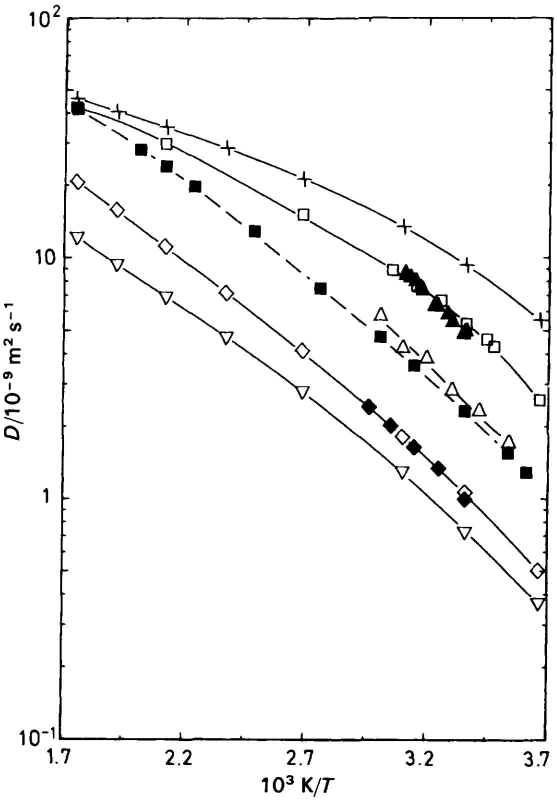

Fig. 1. Diffusion coefficients as a function of reciprocal absolute temperature: the proton (+)[19], the hydroxyl ion (□)[20], the hydrated electron (▲)[21], oxygen (△)[22], water (■) (see text), 2-propanol (◆)[23], the sulphate ion (◇)[19] and the iron(II) ion (▽)[19].

Table 1. Values for diffusion coefficients and reaction radii

reactant	D (25 °C) /10^{-9} m^2 s^{-1}	ref.	reaction radius /nm	ref.
	primary radicals			
OH	2.2	24	0.22	24
H	7.0	24	0.13	[d]
e^-_{aq}	4.82	21, 24	0.275	24
	molecules			
H_2	4.8	25	0.14	36
O_2	2.4	25	0.17	36
N_2O	2.11	26	0.19	36
H_2O_2	2.3	[a]	0.21	36
nitrobenzene	0.80	27	0.57	[e]
methanol	1.55	28	0.26	37
2-propanol	1.05	23	0.36	37
t-butyl alcohol	0.95	29, 30	0.37	37
	ions			
H^+	9.3	19	0.25	[f]
formate ion	1.45	31	0.26	[g]
NO_3^-	1.9	32, 33	0.26	[h]
NO_2^-	1.9	34	0.26	[i]
$Fe(CN)_6^{4-}$	0.735	32	0.42	42
Cu^{2+}	0.71	19	0.07	42
Fe^{2+}	0.71	19	0.07	42
$S_2O_3^{2-}$	1.06	[b]	0.38	[j]
CO_3^{2-}	0.955	34	0.27	42
HCO_3^-	1.18	34	0.27	[k]
Cd^{2+}	0.717	34	0.43	42
MV^{2+}	0.71	35	0.2	[e]
MnO_4^-	1.0	[c]	0.31	42

[a] Assumed same as water.[6] [b] Assumed same as the sulphate ion.[19] [c] Assumed similar to comparable sized anions.[34] [d] Assumed same as helium atom.[36] [e] Fitted: see text. [f] Calculated as reaction distance for ($H^+ + OH^- \rightarrow H_2O$) of 5.8 nm[38] minus reaction radius for OH^- of 0.33 nm.[39] [g] Assumed same as methanol. [h] N—O bond distance from sodium nitrate[40] plus oxygen van der Waals radius.[41] [i] Assumed same as for the nitrate ion. [j] Assumed same as the radius of hydrated sulphate ion.[42] [k] Assumed same as for the carbonate ion.

Z_i is the charge on ion 'i', ε_0 is the permittivity of free space (8.84×10^{-12} F m^{-1}) and ε is the relative permittivity (dielectric constant) of the medium. The quantity $(r_A + r_B)$ is the reaction distance.

The value of k_{react} is represented by the Arrhenius eqn (5)

$$k_{react} = A \exp(-E_{act}/RT) \qquad (5)$$

where A is the pre-exponential factor and E_{act} is the Arrhenius activation energy. Theoretical interpretations based on collision theory and activated complex theory of bimolecular reactions in the gas phase suggest that both A and E_{act} should exhibit a small temperature dependence.[13,15] However, this was not detected in this work, as will be shown later.

For reactions between ions, both k_{diff} and k_{react} must be corrected for the effect of ionic strength. The correction was made using the equation[15]

$$\ln k = \ln k^\circ + 8.38 \times 10^6 Z_A Z_B f(I)/(\varepsilon T)^{3/2} \qquad (6)$$

where I (mol dm^{-3}) is the ionic strength; the equation

$$f(I) = I^{1/2}/(1 + I^{1/2}) \qquad (7)$$

was used for $f(I)$ as I was always less than 0.1 mol dm^{-3}.

Fits of k_{calc} to k_{obs} were obtained using eqn (2) by calculating k_{diff} using the appropriate form of eqn (3) and then varying E_{act} and the 25 °C value of k_{react} until a fit of the experimental data was obtained. It was assumed that E_{act} and A in eqn (5) are not dependent on temperature.

Calculation of k_{diff} requires a knowledge of D_i and r_i. Fig. 1 shows plots of log D_i vs. T^{-1} for H^+, OH^- and H_2O over the temperature range 0–300 °C. The values of D_{H_2O} up to 225 °C were taken from the review by Weingartner[6] and were extrapolated to 300 °C by the Stokes–Einstein relationship[13] using the viscosity of water. Also in fig. 1, the diffusion coefficients for the sulphate and iron(II) ions are given along with the more limited data for e^-_{aq}, O_2 and 2-propanol. As can be seen, all have a similar temperature dependence to D_{H_2O}. As a result of this, species for which we do not know the temperature dependence for diffusion are assumed to have the temperature dependence of D_{H_2O}. The values of D_i at 25 °C used in the calculations are listed in table 1.

Estimation of reaction radii is difficult and subjective. For addition and abstraction reactions of H and OH involving molecules, the radius derived from gas viscosity data was used where possible on the basis that the reactants have to make contact before reaction occurs. For ions, the crystallographic radius was used. In a few cases the reaction radii were calculated from interatomic distances and the van der Waals radii of the external atoms.

The hydrated ion radius was used for the reaction radius of an ion when it reacted with the hydrated electron. For this paper, the choice of ionic reaction radius was often not critical because many of the ionic reactions evaluated were either not greatly influenced by diffusion or were reactions between oppositely charged ions where k_{diff} is relatively insensitive to the choice of reaction radius.

It was assumed that reaction radii for all species did not change with temperature. This assumption seems reasonable for all reactants except possibly the hydrated electron. However, evidence will be presented which suggests that even its reaction radius is temperature invariant. The radii used are listed in table 1.

Experimental Results

In most cases, the rate constants reported here extend the temperature range of previously published data.

Hydrated Electron

All solutions were deoxygenated by bubbling with argon and were irradiated at natural pH unless otherwise stated. The decay of the hydrated electron was followed within the 700–900 nm region to optimize the signal size. All rate constants were corrected for the natural decay of the hydrated electron in the absence of solute.

The decay of the hydrated electron was measured in the following aqueous solutions containing: 1×10^{-5} and 2×10^{-5} mol dm^{-3} nitrobenzene (fig. 2); 1.05×10^{-5} mol dm^{-3} 1,1'-dimethyl-4,4'-bipyridinium ion (methyl viologen, MV^{2+}; fig. 2); 5.2×10^{-5} mol dm^{-3} oxygen (fig. 3); 10^{-4} mol dm^{-3} perchloric acid (fig. 4); 4.4 and 13.8×10^{-5} mol dm^{-3} hydrogen peroxide (fig. 5); 2.1 and 8.4×10^{-5} mol dm^{-3} sodium nitrite (fig. 6); 8.4×10^{-5} mol dm^{-3} sodium nitrite plus 10^{-3} mol dm^{-3} sodium borate (fig. 6); 9.8×10^{-5} mol dm^{-3} sodium nitrate (fig. 6); and 10^{-2} mol dm^{-3} sodium thiosulphate (table 2).

In measuring the rate of reaction of the hydrated electron with hydrogen peroxide, sufficient thermal decomposition of the solute,

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad (8)$$

to form oxygen was probably occurring above 120 °C to interfere with the measurements. The heating time for the solution in the cell was *ca.* 3–5 min whereas the half-life for the thermal decomposition is *ca.* 50 min at 120 °C, 5–10 min at 150 °C and *ca.* 1 min at 200 °C.[5,52] The data recorded for solution temperatures above 120 °C are included in fig. 5 as solid triangles.

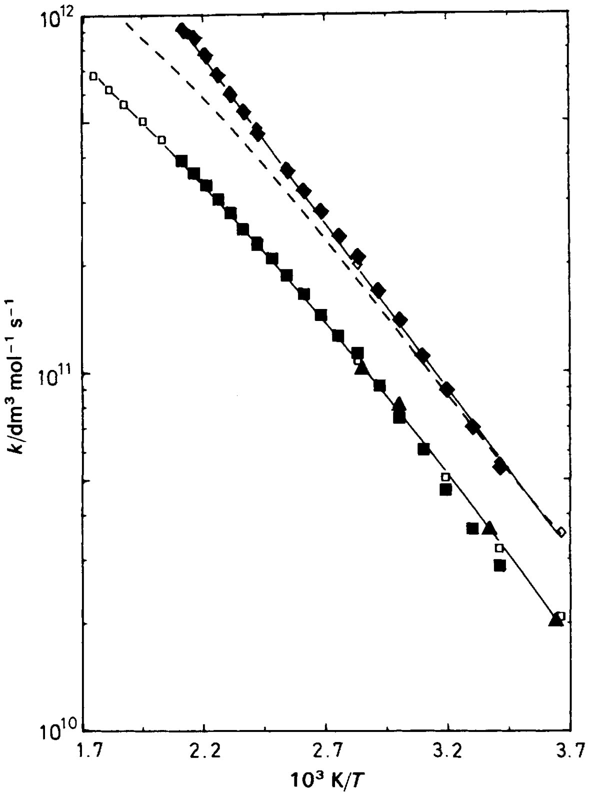

Fig. 2. Rate constants for the reaction of the hydrated electron with nitrobenzene: k_{obs} (■, ▲[43]) and k_{calc} assuming diffusion control (□); and with methyl viologen: k_{obs} (◆) and k_{calc} assuming diffusion control with charge correction (◇) and without charge correction (– – –) see text.

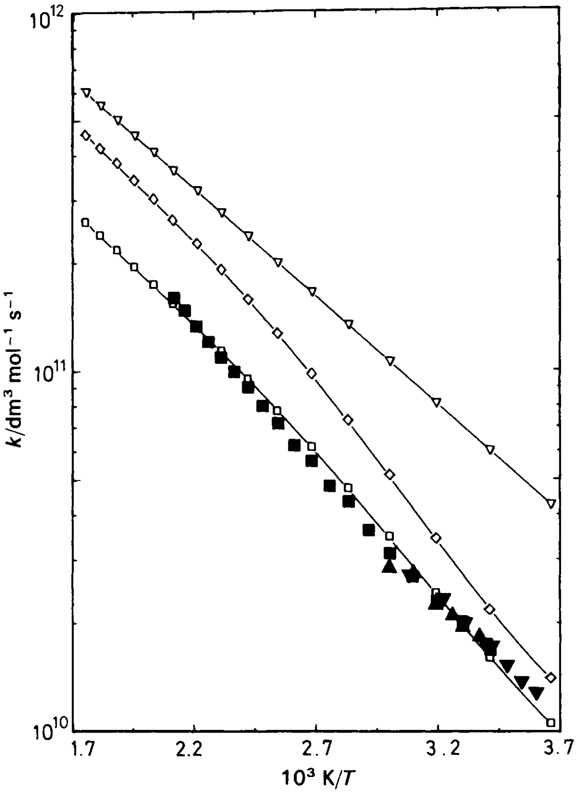

Fig. 3. Rate of reaction of the hydrated electron with oxygen: k_{obs} (■, ▲[10], ▼[44]), k_{diff} (◇), k_{react} (▽) and k_{calc} (□).

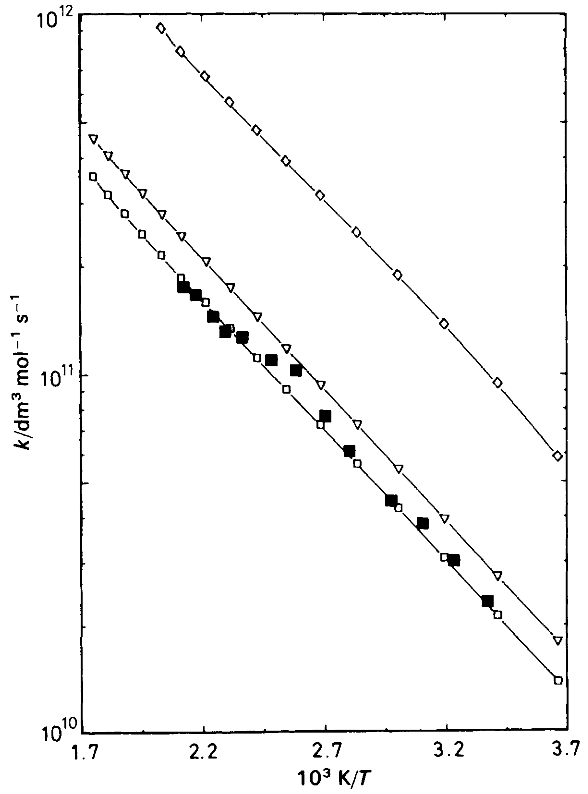

Fig. 4. Rate of reaction of the hydrated electron with the proton: k_{obs} (■), k_{diff} (◇), k_{react} (▽) and k_{calc} (□).

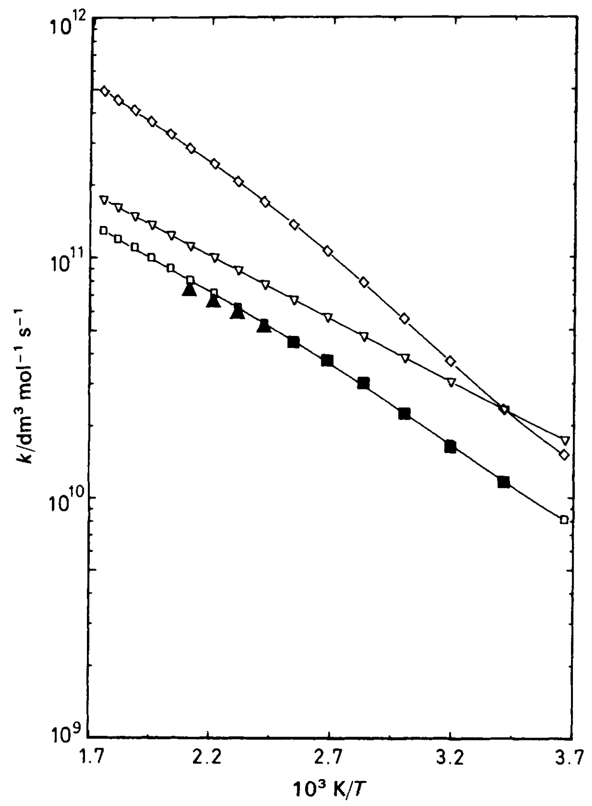

Fig. 5. Rate of reaction of the hydrated electron with hydrogen peroxide: k_{obs} (■), k_{diff} (◇), k_{react} (▽) and k_{calc} (□). Thermal decomposition of hydrogen peroxide was probably occurring for data given by (▲).

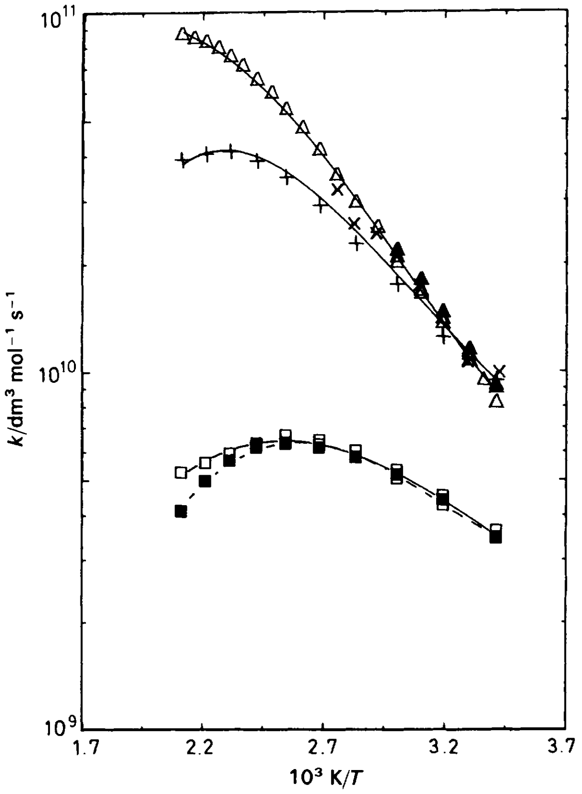

Fig. 6. Rate constants for the reaction of the hydrated electron with: nitrate ion (+, ×[45]), nitrous oxide (△[11], ▲[10]), and nitrite ion at pH 6.5 (■) and at pH 9.2 (□).

Table 2. Parameters for reactions whose rates are reactivity controlled [eqn (5)]

reaction	k_{react}^{25} /10^8 dm^3 mol^{-1} s^{-1}	E_{act} /kJ mol^{-1}	temp. range /°C	ref.
$OH + H_2$	0.4	18	15–230	46, 47
$OH + H_2O_2$	0.3	13	14–160	48
$OH + HCO_3^-$	0.085	21.2	0–200	17
$OH + CO_3^{2-}$	4.2	23.6	0–200	17
$OH + Cu^{2+}$	3.4	13.3	20–220	49
$OH + Fe^{2+}$	4.6	9.2	20–220	49
$H + H_2O_2$	0.5	16.6	20–80	10
$e_{aq}^- + S_2O_3^{2-}$ [a]	1.0	4.0	20–200	[b]
$HO_2 + HO_2$	0.008	22.8	20–300	50, 51

[a] Zero ionic strength. [b] This work.

Where the present data extend previously measured data, the earlier results are included in the figures and, as can be seen, the correspondence is generally good. The present results are also consistent with the recommended room-temperature values.[24]

Hydroxyl Radical

The bimolecular decay of the hydroxyl radical was followed at 250 nm in water saturated with nitrous oxide at room temperature. Since the shape of its absorption spectrum was the same at 20 and 200 °C, the extinction coefficient of 51 m^2 mol^{-1} at 250 nm was assumed to be temperature independent. An uncertainty of $\pm 15\%$ is estimated for the measured rate constants and, although they are 10–15% higher than those reported earlier,[10] the discrepancy is within experimental error (see fig. 7).

The reaction of hydroxyl radicals in nitrous oxide saturated 5×10^{-5} mol dm^{-3} potassium ferrocyanide solutions

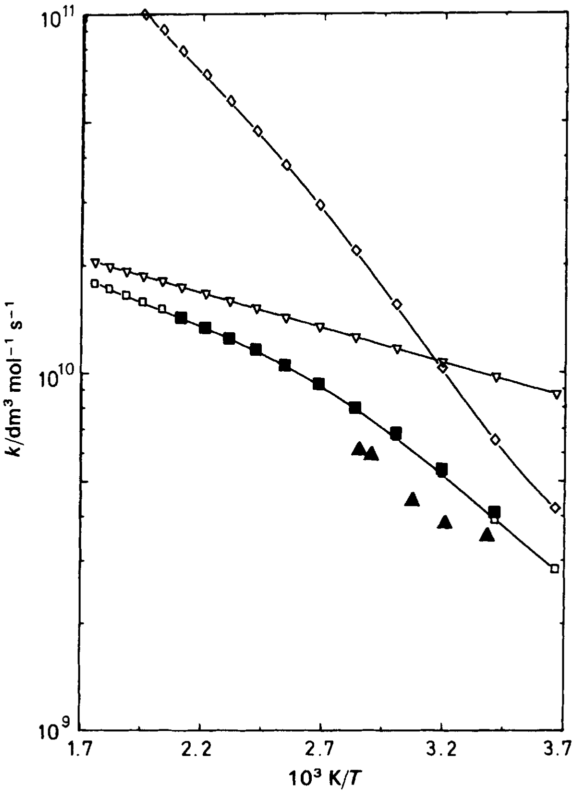

Fig. 7. Rate constants for dimerization of hydroxyl radicals: k_{obs} (■, ▲[10]), k_{diff} (◇), k_{react} (▽) and k_{calc} (□).

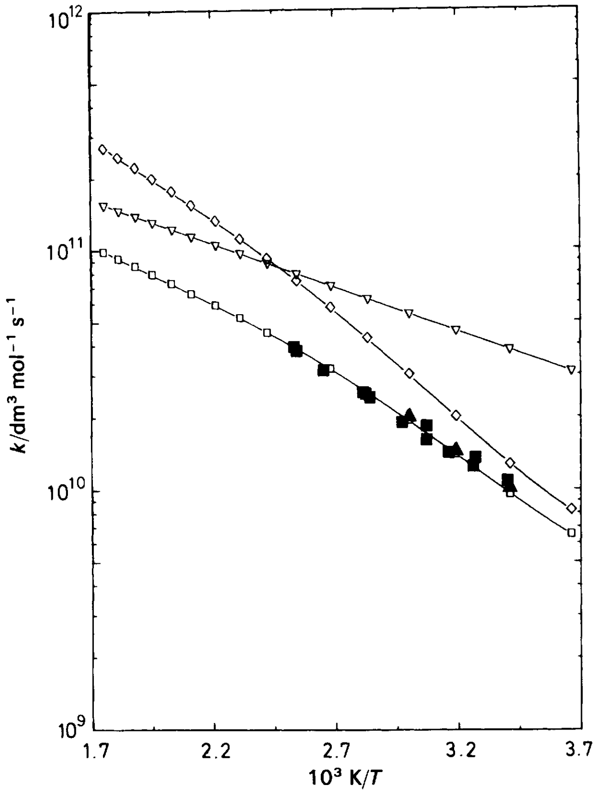

Fig. 8. Rate constants for reaction of the hydroxyl radical with ferrocyanide ion: k_{obs} (■, ▲[8]), k_{diff} (◇), k_{react} (▽) and k_{calc} (□).

was monitored by the build-up of the ferricyanide ion absorption at 420 nm. As it was evident that these solutions decompose thermally at temperatures above 140 °C, kinetic measurements were not made above 120 °C. These results are shown in fig. 8 along with less extensive data reported earlier.[8]

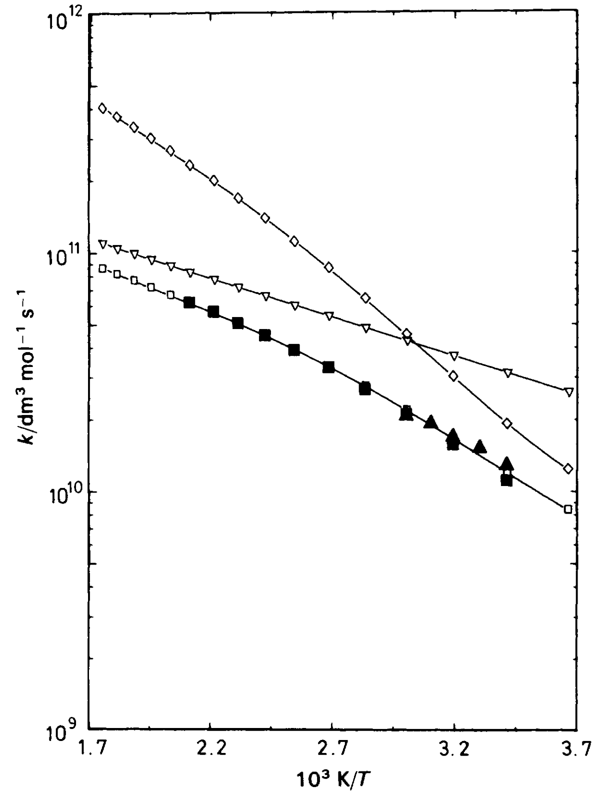

Fig. 9. Rate constants for reaction of the hydrogen atom with oxygen: k_{obs} (■, ▲[10]), k_{diff} (◇), k_{react} (▽) and k_{calc} (□).

Hydrogen Atom

In previous work, the rate constant for the reaction of the hydrogen atom with oxygen was measured using ferricyanide as the reference solute for competition studies up to 70 °C.[10] However, the ferricyanide ion is suspected to decompose at 200 °C, so in this work the permanganate ion was used as a reference solute as thermal stability tests suggested it was sufficiently stable at 200 °C. The rate of reaction of the hydrogen atom in a deoxygenated 2×10^{-5} mol dm^{-3} potassium permanganate solution containing 10^{-2} mol dm^{-3} perchloric acid was followed by the loss of the absorbance due to MnO_4^- at 525 nm. The sufficient thermal stability of MnO_4^- at 200 °C was confirmed by the fact that the bleaching rate and total loss of absorbance due to its reaction with the hydrogen atom was independent of the time (3–10 min) that the solution was held at 200 °C before a measurement was made. The rate constant was 2.5×10^{10} dm^3 mol^{-1} s^{-1} at 25 °C and is in agreement with that reported earlier.[53]

A study of the competition for the hydrogen atom between 2.8×10^{-4} mol dm^{-3} oxygen and 2×10^{-4} mol dm^{-3} permanganate ion gave a constant rate constant ratio of 0.44 ± 0.02 over the 20–200 °C temperature range studied. The oxygen results are summarized in fig. 9 along with the earlier data.[10]

Evaluation of Kinetic Data

Reactivity-controlled Reactions

Reactivity-controlled reactions are those where the diffusion processes have no influence on the rate of reaction, *i.e.* $k_{obs} = k_{react}$. The reactions which we have identified in this category are listed in table 2. All of these reactions show linear plots for the Arrhenius relationship, implying that there is no significant temperature dependence in A or E_{act}, or that any dependences tend to cancel out.

Diffusion-controlled Reactions

Diffusion-controlled reactions are those for which $k_{obs} = k_{diff}$. None of the hydrogen atom or hydroxyl radical reactions analysed were diffusion controlled over a significant temperature range. This can be seen in fig. 7–10 by noting that the calculated values of k_{diff} (diamonds) have a significantly greater temperature dependence than the experimental data.

It is often assumed that many of the hydrated electron reactions are diffusion controlled,[54] or nearly so, at room temperature, yet, in our data analysis, only the reactions

$$e_{aq}^- + C_6H_5NO_2 \rightarrow C_6H_5NO_2^- \qquad (9)$$

$$e_{aq}^- + MV^{2+} \rightarrow MV^+ \qquad (10)$$

appear to be so over the 20–200 °C range studied. Both solutes are non-spherical in shape, and this makes estimating a reaction radius difficult. Therefore, it was assumed that the reactions are diffusion controlled and the reaction radius was used as a fitting parameter. For reaction (10) this is not a problem since the reaction is between oppositely charged ions and the calculated k_{diff} is not very sensitive to the size of the reaction distance. The reaction radius of MV^{2+} required for a fit was 0.2 nm (see fig. 2). For reaction (9), a fit between k_{diff} and k_{obs} was obtained with a reaction radius of 0.57 nm for nitrobenzene, *i.e.* the reaction distance for reaction (9) is 0.82 nm (see fig. 2). While 0.57 is larger than might be expected from crystallographic data where the longest dimension is *ca.*

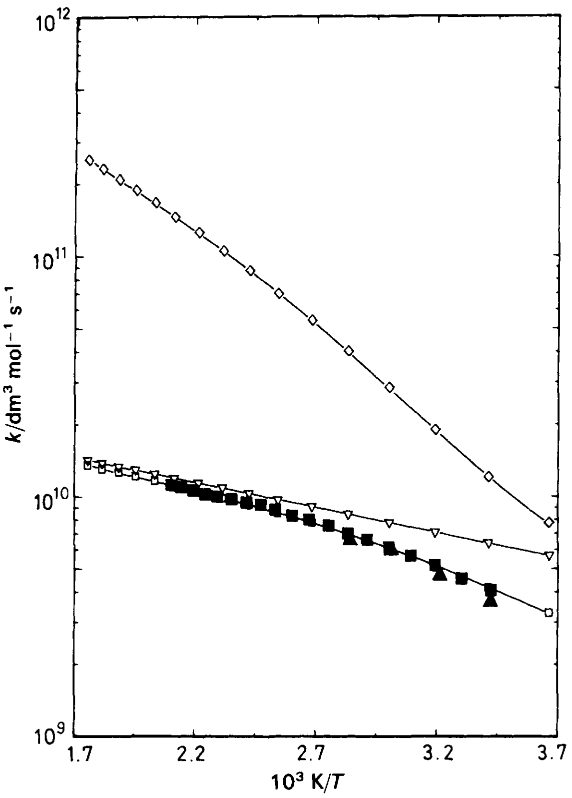

Fig. 10. Rate constants for the reaction of the hydroxyl radical with formate ion: k_{obs} (■, ▲[8]), k_{diff} (◇), k_{react} (▽) and k_{calc} (□).

0.6 nm[40] not including van der Waals radii, large reaction distances have been found before for reactions of e_{aq}^- for which quantum-mechanical tunnelling effects have been recognized.[55]

In the reaction of the hydrated electron with nitrobenzene, there is no coulombic effect and the reaction rate constant follows the self-diffusion profile of water. However, if the coulombic effects are neglected for the methyl viologen reaction, the experimental data cannot be satisfactorily fitted as shown by the dashed line in fig. 2.

A further important point to note is that both the nitrobenzene and methyl viologen data can only be fitted when the temperature dependence of the diffusion coefficient of the hydrated electron is assumed to be the same as that of the self-diffusion coefficient of water as opposed to that of the proton or hydroxyl ion. This suggests that the hydrated electron does not diffuse by a Grotthuss conduction mechanism. However, as it diffuses at over twice the rate for self-diffusion of water, a tunnelling process may be involved which depends on the reorientation of bulk water molecules to create a new trapping site.

Another assumption implicitly made was that the reaction radius of the hydrated electron does not change with temperature. The fit of the methyl viologen and nitrobenzene data support the validity of this assumption, which in turn suggests that the bathochromic shift in the spectrum of the hydrated electron with increasing temperature is due to changes in the potential-energy surface of the excited state rather than the ground state.

Reactions where k_{obs} Conforms to eqn (2)

Hydrogen-Atom and Hydroxyl-radical Reactions

Fits of eqn (2) to hydroxyl-radical reactions (11)–(13) and hydrogen-atom reactions (14) and (15) (see table 3) are shown in fig. 7–10. The data used to obtain the fits are given in table 1 and 3.

Table 3. $k_{act}{}^{25}$ and E_{act} for reactions whose rate constants are described by eqn (2)

reaction	$k_{react}{}^{25}$ /10^{10} dm^3 mol^{-1} s^{-1}	E_{act} /kJ mol^{-1}
(11) $OH + Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + OH^-$	4.0	7.0
(12)[a] $OH + OH \rightarrow H_2O_2$	1.0	3.7
(13) $OH + HCO_2^- \rightarrow CO_2^- + H_2O$	0.65	4.0
(14) $H + MnO_4^- \rightarrow MnO_4^{2} + H^+$	23.5	0
(15) $H + O_2 \rightarrow HO_2$	3.25	6.25
(16) $e_{aq}^- + O_2 \rightarrow O_2^-$	6.5	11.5
(17) $e_{aq}^- + H^+ \rightarrow H$	3.0	14.5
(18) $e_{aq}^- + H_2O_2 \rightarrow OH + OH^-$	2.5	10.0
(19) $e_{aq}^- + Cd^{2+} \rightarrow Cd^+$	50.0	12.0

[a] Fitted to eqn (20) with $\beta = 1$.

In evaluating the reaction between two radicals, the electron spin of the radical has to be taken into account and eqn (2) has to be modified to account for the fact that only those encounters that produce a singlet electronic state will contribute to the reaction rate.[56] This modification is given in eqn (20) where β is the fraction of encounters that lead to a singlet state.

$$k_{obs} = \beta k_{diff}/(1 + \beta k_{diff}/k_{act}) \tag{20}$$

For radicals whose spin–lattice relaxation time is much longer than the encounter time (*ca.* 10^{-8}–10^{-10} s)[13], β will be 0.25, whereas when the relaxation time is much shorter than the encounter time then β is unity. Most radicals have relaxation times in the range (1–10) × 10^{-6} s[57,58] so that a β of 0.25 is appropriate. However, the hydroxyl radical has a very short relaxation time ($< 10^{-9}$ s)[57] such that the spin might reorient within the encounter cage, *i.e.* β will be unity. A value for β of unity is supported by the present results where, for the self-reaction of the hydroxyl radical, if β is set at 0.25 instead of unity, it is impossible to obtain a fit because βk_{diff} is less than k_{obs} for the chosen values of diffusion coefficient and reaction radius.

Hydrated-electron Reactions

Fits of eqn (2) to measured values of k_{obs} are shown in fig. 3–5 and the fit parameters are listed in table 1 and 3. The reaction of the solvated electron with the proton (fig. 4) has an activation energy similar to that of diffusion in water, but k_{obs} is almost five times lower than k_{diff}, so that this reaction is almost entirely reactivity controlled. A possible reason for the slow reaction rate on encounter is that the electron has to be located on one water molecule (H_2O^-) before a proton transfer from H_3O^+ can occur.

The value of k_{obs} for the reaction of the hydrated electron with oxygen is less than 50% smaller than k_{diff} (fig. 3). However, if this reaction is assumed to be diffusion controlled, the reaction radius for oxygen would have to be zero to make $k_{obs} = k_{diff}$. This strongly suggests that the reaction of the hydrated electron with oxygen is not truly diffusion controlled.

The reaction of the hydrated electron with Cd^{2+} ion is another example of a reaction that is close to being diffusion controlled, but not completely so, as can be seen in fig. 11. The hydrodynamic radius for Cd^{2+} (0.46 nm) was used to calculate k_{diff} because this ion has strongly bound water of

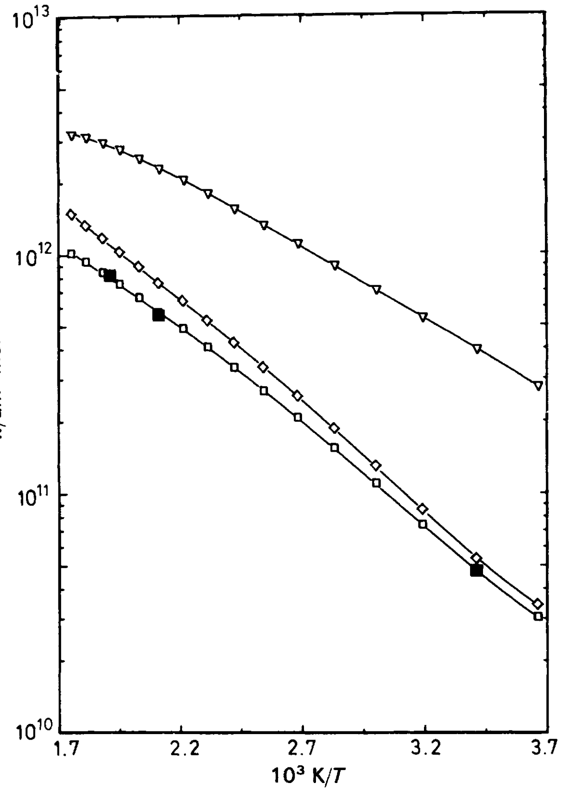

Fig. 11. Rate of reaction of the hydrated electron with Cd^{2+}: k_{obs} (■[59]), k_{diff} (◇), k_{react} (▽) and k_{calc} (□).

hydration which will prevent the closer approach of the hydrated electron. Even when a smaller reaction radius of 0.094 nm for Cd^{2+} (which is near the crystallographic radius[42]) was used, k_{diff} was still larger than k_{obs} and values of k_{react}^{25} of 4×10^{12} dm^3 mol^{-1} s^{-1} and E_{act} of 0 kJ mol^{-1} were still required to obtain a fit.

Reactions where k_{obs} does not conform to eqn (2)

Values of k_{obs} for reactions of the hydrated electron with the nitrite ion, nitrate ion and nitrous oxide (see fig. 6) cannot be fitted by eqn (2). All of these reactions appear to require a further step to stabilize the added electron before the final products are formed as shown in reactions (21)–(23):

$$NO_2^- + e_{aq}^- \rightarrow NO_2^{2-}(+H_2O) \rightarrow NO + 2OH^- \qquad (21)^{60}$$

$$NO_3^- + e_{aq}^- \rightarrow NO_3^{2-}(+H_2O) \rightarrow NO_2 + 2OH^- \qquad (22)^{61}$$

$$N_2O + e_{aq}^- \rightarrow N_2O^- \rightarrow N_2 + O^-. \qquad (23)^{62}$$

Christensen and Sehested[63] have followed the bimolecular decay of the hydrated electron in alkaline solutions and found that k_{obs} increased in accordance with the Arrhenius relationship up to 150 °C but then decreased sharply at higher temperatures. [One of us (G.V.B.) has confirmed the pattern of these results up to 200 °C at pH 11.] Their data also cannot be fitted to eqn (2). They have postulated that reaction (24) could explain their results.

$$e_{aq}^- + e_{aq}^- \rightleftarrows (e_2)aq^{2-}(+H_2O) \rightarrow H_2 + OH^- \qquad (24)$$

These multistep reactions [(21)–(24)] require more study.

Discussion

A characteristic of several of the fast reactions investigated here is that although they are largely influenced by diffusion at room temperature (*i.e.* in the high viscosity region for water), they become almost reactivity controlled at 200 °C and above (*i.e.* low viscosity region for water). The significant feature of the data in table 3 is the low values of E_{act} that are required to account for k_{obs}. The important practical consequence from the computer-modelling point of view is that k_{obs} does not increase nearly so much with temperature as had hitherto been anticipated based on the assumption that most fast reactions at room temperature are diffusion controlled. Some striking examples of this are the mutual-reaction of hydroxyl radicals (fig. 7), the reaction of the hydrogen atom with oxygen (fig. 9) and the reaction of the hydroxyl radical with the formate ion (fig. 10).

It is somewhat fortuitous that earlier computer-modelling studies of high-temperature water radiolysis used 12.6 kJ mol^{-1} as the activation energy for diffusion in water as opposed to the correct temperature dependence for diffusion in water.[6] The consequence of this can be seen in table 4, where the rate constants at 300 °C for a number of reactions have been estimated using eqn (2), the Arrhenius relationship with E_{act} equal to 12.6 kJ mol^{-1} and the temperature dependence for self-diffusion in water.[6] The error in using 12.6 kJ mol^{-1} is not as great as when the correct dependence for diffusion in water is used.

In recent years, there have been attempts to correlate rate constants for reactions of the hydroxyl radical with organic compounds in aqueous solution with those in the gas phase in order to use the extensive solution data, obtained at *ca.* 25 °C, to estimate rate constants for atmospheric modelling calculations.[64,65] In general, hydroxyl-radical reactions with organic compounds in aqueous solution are slow enough at 25 °C that they are essentially reactivity controlled. However, it should be recognized that for reactions where k_{obs} is described by eqn (2), it is k_{react} that should be correlated with the gas-phase data. Furthermore, these solution–gas phase correlations have been made with rate constants measured at *ca.* 25 °C in solution, yet it is apparent from the limited data available that the temperature dependence for a given reaction can be different in the two phases as can be seen in table 5. Take, for example, the hydroxyl radical reacting with the three different alcohol molecules. Comparing solution data with gas-phase data, the E_{act} are the same for methanol, slightly higher for 2-propanol, and very much greater for t-butyl alcohol [In solution, for methanol and t-butyl alcohol, the reactions were reactivity controlled within experimental error whereas for 2-propanol there is a slight influence of diffusion so that k_{react} and E_{act} have been derived from a fit of eqn (2) using the parameters in table 1.]

As the gas-phase reaction of atomic hydrogen with oxygen and of the dimerization of hydroxyl radicals are third-body reactions, the high-pressure-limit values of the rate constants have been used to estimate the gas-phase activation energy.

Table 4. Comparison of estimates of rate constants at 300 °C

reaction	k/dm^3 mol^{-1} s^{-1}			
	25 °C	300 °C[a]	300 °C[b]	300 °C[c]
$H + O_2$	1.3×10^{10}	8.6×10^{10}	1.5×10^{11}	2.3×10^{11}
$e_{aq}^- + O_2$	1.8×10^{10}	2.6×10^{11}	2.0×10^{11}	3.2×10^{11}
$e_{aq}^- + H^+$	2.3×10^{10}	3.5×10^{11}	2.6×10^{11}	4.1×10^{11}
$e_{aq}^- + H_2O_2$	1.2×10^{10}	1.3×10^{11}	1.5×10^{11}	2.1×10^{11}
$OH + Fe(CN)_6^{4-}$	1.0×10^{10}	9.8×10^{10}	1.2×10^{11}	1.8×10^{11}
$OH + OH$	4.2×10^{9}	1.8×10^{10}	4.8×10^{10}	7.5×10^{11}
$OH + HCO_2^-$	4.3×10^{9}	1.3×10^{10}	4.9×10^{10}	7.7×10^{11}

[a] Based on eqn (2). [b] Based on Arrhenius relationship with E_{act} = 12.6 kJ mol^{-1}. [c] Based on the self-diffusion of water.

Table 5. Comparison of solution values of k_{react} and E_{act} with gas-phase values

reaction	$k_{\text{react}}{}^{25}$/dm^3 mol^{-1} s^{-1}		E_{act}/kJ mol^{-1}		ref.	
	soln	gas	soln	gas	soln	gas
$H + H_2O_2$	5.7×10^7	2.9×10^7	16.6	16.6	10	66
$H + O_2$	3.2×10^{10}	4.5×10^{10}	6.2	~0	[a]	67
$OH + OH$	1.0×10^{10}	9.0×10^9	3.7	~0	[a]	68
$OH + H_2$	4.0×10^7	4.0×10^6	18.0	17.5	46, 47	67
$OH + H_2O_2$	3.0×10^7	1.0×10^9	13.0	1.3	48	67
OH + methanol	1.1×10^8	5.2×10^8	4.0	4.0	9	69
OH + 2-propanol	2.9×10^9	3.5×10^9	3.5	0.25	8	69
OH + t-butyl alcohol	7.0×10^8	6.4×10^8	11.0	2.6	8	70
$HO_2 + HO_2$	8.0×10^5	9.0×10^8	22.8	5.0	50, 51	67

[a] This work.

Of the reactions listed in table 5 which are relevant to the radiolysis of water at high temperatures, only the reaction of the hydrogen atom with hydrogen peroxide and possibly the dimerization of hydroxyl radicals have comparable values of $k_{\text{react}}{}^{25}$ and E_{act} in both gas and solution phases. Many of the others have quite dissimilar values which probably arise from mechanistic differences in the two phases as well as the effects of solvation in the liquid phase. This suggests that using gas-phase values of k_{react} and E_{act} in eqn (2) is an unreliable method of estimating k_{obs} for reactions in solutions at high temperatures.

Conclusions

The major conclusion to be drawn from this work is that experimental data for the rate constants of many of the reactions involved in the radiolysis of water and aqueous solutions are described by:

$$k_{\text{obs}} = k_{\text{diff}}/(1 + k_{\text{diff}}/k_{\text{react}})$$

and not by the Arrhenius equation. This means that k_{obs} must be measured over a range of temperature which is sufficient to establish the contributions of k_{diff} and k_{react} to k_{obs}. When this condition is met it is possible to extrapolate kinetic data up to 300 °C with some confidence.

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