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Rate Constants for the Reactions of F Atoms with H_2 and D_2 over the Temperature Range 220–960 K

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Abstract

The kinetics of the reactions of F atoms with hydrogen and deuterium has been studied in a discharge flow reactor combined with an electron impact ionization quadrupole mass spectrometer at nearly 2 Torr total pressure of helium and in the temperature range 220 – 960 K. The rate constant of the reaction F + $H_2 \rightarrow$ HF + H (1) was determined using both relative rate method (using reaction F + Br_2 as a reference) and absolute measurements, monitoring the kinetics of F atom consumption in excess of H_2: $k_1 = (1.24 \pm 0.09)\times10^{-10}$ exp(-(507 ± 23)/T) $cm^3 molecule^{-1} s^{-1}$. The rate constant of the reaction F + $D_2 \rightarrow$ DF + D (2) was measured under pseudo-first order conditions in excess of D_2 over F atoms: $k_2 = (8.47\pm 0.42)\times10^{-11}$ exp(-(670 ± 16)/T) $cm^3 molecule^{-1} s^{-1}$ (the uncertainties on both k_1 and k_2 represent precision at the 2σ level, the estimated total uncertainty on the rate constants being 15% at all temperatures). The kinetic isotope effect measured independently, k_1/k_2 = (1.58 ± 0.05)×exp((131 ± 2)/T), was found to be in excellent agreement (within 7% in the temperature range of the work, T = 220-960 K) with the ratio of k_1 to k_2 calculated with the Arrhenius expressions for k_1 and k_2 determined in the study. The kinetic data from the present work are discussed in comparison with previous measurements and theoretical calculations.

Keywords: F, hydrogen, rate coefficient, temperature dependence, KIE.

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Supporting Information is available in the online issue at www.wileyonlinelibrary.com.

1 INTRODUCTION

Reaction of F atoms with H_2

$$F + H_2 \rightarrow HF + H \quad (1)$$

is of practical and theoretical interest and was extensively studied over the past few decades. The kinetics of this reaction was explored in multiple studies, at high temperatures (up to 765 K),[1] in relation with problematic of chemical lasers based on the vibrationally excited HF formed in the reaction, and at very low temperatures (down to 10 K), in relation to the chemistry in interstellar environments where reaction (1) is considered as the only source of HF.[2] In parallel, the F + H_2 reaction has been the subject of numerous dynamic and theoretical investigations (e.g. review 3 and refs therein). Indeed, since 1972, when the first *ab initio* potential energy surface (PES) was created,[4] about two dozen new or modified PES have appeared.[3] Theoretical research of the F + H_2 reaction has made a progress, and at present the theory seems to reproduce the experimental kinetic and dynamic observations quite well.[3]

Accurate experimental determination of the Arrhenius parameters for the rate constants of the reactions of F atom with H_2 and its isotope D_2

$$F + D_2 \rightarrow DF + D \quad (2)$$

in an extended temperature range is of importance for theory, since they carry information on the energetics of the reaction and the extent of the tunneling effect, which are important for further refinement of PES. However, despite the interest to the reactions of F atoms with H_2 and D_2, and a large number of dedicated studies, kinetic database for these reactions seems incomplete and unsatisfactory compared to the current high level of the theoretical calculations. For the F + H_2 reaction, only two[5,6] of the four most extended temperature-dependent studies[5-8] were carried out at temperatures above 376 K, and, in addition, the data on the rate constant from one of them[6] are widely scattered. For reaction F+ D_2, only one study[5] was realized at temperatures above 373 K and the results of three available relatively extended temperature-dependent studies differ by a factor of 1.3-1.5 at temperatures between 230 and 360 K.[5,7,8] As a result of the uncertainties in the values of the rate constants for reactions (1) and (2) (k_1 and k_2, respectively), the kinetic isotope effect (KIE) calculated as k_1/k_2 varies by a factor of up to 1.7 depending on temperature. Above

analysis is in line with the conclusion of the most recent critical review of the kinetic data for reactions (1) and (2) by Persky and Kornweitz[1] that "additional careful experimental studies of the kinetics of the F + H_2 system would be very useful in order to support our evaluations or to update them."

This paper presents the results of an experimental study of the reactions of F atom with H_2 and D_2, including measurements of the rate constants and an independent determination of the kinetic isotope effect (k_1/k_2 ratio) as a function of temperature in an extended temperature range, T = 220 - 960 K.

2 EXPERIMENTAL

Kinetic measurements have been conducted at nearly 2 Torr total pressure of Helium using a conventional fast-flow reactor combined with a molecular beam sampling electron-impact ionization mass spectrometer operated at 25–30 eV energy.[9-11] Depending on the temperature range two different flow reactors were used. High temperature reactor, used at T = 299 – 960 K, consisted of a Quartz tube (45 cm length and 2.5 cm i.d.) with an electrical heater and water-cooled attachments (Figure S1a, Supporting Information (SI)).[12] Low temperature reactor (Figure S1b, SI), used at T = 220 – 325 K, consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) surrounded by a jacket through which a thermostated ethanol was circulated. To reduce the heterogeneous loss of F atoms, the inner surface of the low temperature reactor was coated with Halocarbon wax.

Fluorine atoms were generated from the microwave discharge in F_2/He mixtures in a ceramic (Al_2O_3) tube (Figures S1a – S1c), which was used to avoid potential reactions of F atoms with glass surface inside the microwave cavity. Monitoring of molecular fluorine by mass spectrometry showed that more than 95% of F_2 was dissociated in the microwave discharge. Prior to their sampling to the mass spectrometer, fluorine atoms were converted to FBr by reaction with Br_2 ($[Br_2]$ = (4 - 6)×10^{13} molecule cm^{-3}, added at the end of the reactor 6 cm upstream of the sampling cone as shown in Figure S1a),

$$F + Br_2 \rightarrow Br + FBr \qquad (3)$$

$k_3 = (1.28 \pm 0.20) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} (T = 299 – 940 K),[13]

and were finally detected at m/z = 98/100 (FBr^+). Reaction (3) in excess of Br_2 was also used for the determination of the absolute concentrations of F atoms by linking the concentration of F atoms to the consumed fraction of $[Br_2]$: $[F] = [FBr] = \Delta[Br_2]$. The absolute concentrations of all stable species (H_2, D_2, Br_2, F_2) in the reactor were calculated from their flow rates obtained from the measurements of the pressure drop of their mixtures in He stored in calibrated volume flasks. All species were detected by mass spectrometry at their parent peaks: *m/z*= 160 (Br_2^+), 98/100 (BrF^+), 38 (F_2^+), 21 (DF^+).

The purities of the gases used were as follows: He >99.9995% (Alphagaz), passed through liquid nitrogen trap; D_2 >99.7% (Alphagaz); H_2 >99.998% (Alphagaz); Br_2 >99.99% (Aldrich); F_2, 5% in helium (Alphagaz).

3 RESULTS AND DISCUSSION

3.1 Rate Constant of Reaction (1): Absolute Measurements

The absolute measurements of k_1 were carried out under pseudo-first order conditions monitoring consumption of F atoms ($[F]_0 = (2 - 4)\times10^{11}$ molecule cm^{-3}) in excess of H_2 (the ranges of the initial concentrations of H_2 used are shown in Table 1). The flow velocity in the reactor was in the range (1750-2920) cm s^{-1}. The F atom decays were treated with an exponential function, $[F] = [F]_0\times\exp(-k_1'\times t)$, where $k_1' = k_1\times[H_2]+k_w$ is the pseudo-first-order rate constant and k_w corresponds to F atom loss rate in the absence of H_2 in the reactor. Examples of the kinetic runs observed at T = 400 K are shown in Figure S2 (SI). To take into account the consumption of the excess reactant, H_2, the average concentration of H_2 in the reaction zone, calculated as $[H_2]=[H_2]_0-\Delta[F]\times(k_1'-k_w)/k_1'$, was used in the treatment of the experimental data. As one could expect, the corrections on $[H_2]_0$ were insignificant (within a few percent) in the most kinetic runs, however reached up to 20% in a few experiments with the lowest concentrations of H_2. Examples of the dependencies of the pseudo-first order rate constant, $k_1' = k_1\times[H_2]+k_w$, on concentration of H_2 at different temperatures are shown in Figures 1 and S3(SI). All measured values of k_1' were corrected for the effects of axial and radial diffusion of fluorine atoms.[14] Corrections were <10 % in the vast majority of the experiments and up to 18% in a few kinetic runs. The slopes of the straight lines in Figures 1 and S3 provide the values of k_1 at respective temperatures. All the results of the absolute

measurements of k_1 at different temperatures are shown in Table 1. The combined uncertainty on the measurements of the rate constants was estimated to be ≤ 15 %, including (in quadrature) statistical error (within a few percent, Table 1) and those on the measurements of the flows (5%), pressure (3%), temperature (1%) and absolute concentration of H_2 (< 10%).

3.2. Rate Constant of Reaction (1): Relative Measurements

In this series of experiments, the rate constant of the reaction of F atoms with H_2 was measured relative to that of F atoms with Br_2. The experiments consisted in a fast titration of F atoms in reaction with a mixture of H_2 and Br_2 and the measurements of FBr yield as a function of the $[H_2]/[Br_2]$ ratio:

$$F + H_2 \rightarrow HF + H \qquad (1)$$

$$F + Br_2 \rightarrow FBr + Br \qquad (3)$$

The fraction of the initial concentration of F atoms, $[F]_0$, transformed to FBr in reaction 3, is:

$$[\mathrm{FBr}] = \frac{k_3[\mathrm{Br_2}]}{k_3[\mathrm{Br_2}]+k_1[\mathrm{H_2}]+k_w} \times [\mathrm{F}]_0$$

Rearrangement of this expression provides:

$$\frac{[\mathrm{F}]_0}{[\mathrm{FBr}]} - 1 = \frac{k_1[\mathrm{H_2}]}{k_3[\mathrm{Br_2}]} + \frac{k_w}{k_3[\mathrm{Br_2}]} \qquad (\mathrm{I})$$

At a constant concentration of Br_2, the second term in equation (I) is constant and k_1/k_3 can be determined as a slope of the linear dependence of $([F]_0/[FBr] - 1)$ on the $[H_2]/[Br_2]$ ratio. In the experiments, FBr was monitored in the presence of Br_2 in both H_2 -free system, corresponding to $[F]_0$, and in the presence of H_2 in the reactor, corresponding to the fraction of $[F]_0$ reacted with Br_2. Reaction time was around 0.02 s, $[F]_0 = (0.5\text{-}1.0)\times10^{11}$, $[Br_2] \approx 9\times10^{12}$ molecule cm^{-3}, the ranges of concentrations of H_2 are presented in Table 2.

The relative measurements of k_1 were carried out in an uncoated quartz reactor at three temperatures: T = 320, 370 and 575 K. The observed experimental data are shown in Figure 2. In accordance with Equation I, the slopes of the straight lines in Figure 2 provide the values of k_1/k_3 at respective temperatures. Final values of k_1 (Table 2) were calculated with $k_3 = (1.28 \pm 0.20) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} (T = 299 – 940 K), determined in a recent study from this group.[13]

3.3. Rate Constant of Reaction (1): Comparison with Previous Data

Figure 3 summarizes the results of the current measurements of the rate constant of reaction (1) in comparison with those from previous temperature dependence studies. The multiple experimental data for k_1 at room temperature (293-300 K)[15-24] were analyzed in previous evaluations.[1,25] Persky and Kornweitz[1] considered that the most accurate results for k_1 available at that moment were those of Clyne and Hodgson,[22] Wurzberg and Houston,[8] and Stevens et al.,[7] and recommended $k_1 = (2.43 \pm 0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at T = 298 K, the mean value from the three studies. Concerning the results from this study, one can note an excellent agreement between absolute and relative measurements of the rate constant. Least-squares analysis of the present temperature dependent data for k_1 yields the following Arrhenius expression in the temperature range T = 220-960 K:

$$k_1 = (1.24 \pm 0.09)\times10^{-10} \exp(-(507 \pm 23)/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with 2σ uncertainties representing the precision of the fit. Our data are in very good agreement with the previous studies of Wurzberg and Houston,[8] and Stevens et al.,[7] reporting $k_1 = 1.0\times10^{-10} \exp(-(433 \pm 50)/T)$ at T = 190-373 K and $(1.2 \pm 0.1)\times10^{-10} \exp(-(470 \pm 30)/T)$ cm^{3}molecule^{-1}s^{-1} at T = 221-376 K, respectively. In the work of Stevens et al.,[7] the rate constant of reaction (1) was measured in a discharge flow system under experimental conditions close to those of the present work. F atoms were detected through their chemical conversion to D atoms in reaction with D_2, followed by D-atom detection by atomic resonance scattering. In the study of Wurzberg and Houston,[8] the reaction rate constant was derived by monitoring the chemiluminescence of the reaction product, HF, formed upon dissociation of SF_6 in the presence of H_2. Similar method was applied in the study of Heidner et al.[5] who reported $k_1 = (2.16 \pm 0.42)\times10^{-10} \exp(-(595 \pm 50)/T)$ cm^{3}molecule^{-1}s^{-1} at T = 295-765 K. The absolute values of k_1 measured by Heidner et al.[5] are by a factor of 1.4-1.7 higher than the current data, and the difference increases with temperature. The values of k_1 measured by Igoshin et al.[26] at two temperatures (195 and 296 K), although considered in previous reviews as rather uncertain,[1,25] and those reported by Homann et al.[27] (in a rather narrow temperature range 300-400 K) are also in a reasonable agreement with the present measurements. Ioffe et al.[6] determined k_1 at T = 293-700 K in a discharge flow system with direct detection of fluorine atom decays in excess of H_2 by Electron Spin Resonance (ESR)

method. As one can see in Figure 3, their rather scattered data differ significantly from other studies, especially at T < 500 K. The present measurements are in good agreement (within <20%) with the recommendation from the critical review of Persky and Kornweitz,[1] k_1 = (1.1 ± 0.1)×10^{-10} exp(-(450 ± 50)/T) $cm^3molecule^{-1}s^{-1}$ for T = 190-376 K (dashed blue line in Figure 3), and with that from the most recent NASA/JPL evaluation,[28] k_1 = 1.4×10^{-10} exp(-500/T) $cm^3molecule^{-1}s^{-1}$ (uncertainty factor of 1.2) for T = 190-765 K (dotted blue line in Figure 3).

In Figure 4, the experimental data for k_1 are shown in comparison with some theoretical calculations[29-31] of the rate constant in the relevant temperature range. Looking at Figure 4, one can state that the current level of theoretical understanding of the F + H_2 system makes it possible to reproduce the kinetic data with very good accuracy. It is interesting to note the almost perfect agreement (most likely, accidental) between experimental data from the present work and those calculated by Wang et al.[31] and Chen et al. with CSZ (Chen, Sun and Zhang) PES.[30]

3.4. Rate Constant of Reaction (2)

The rate constant of the reaction of F atoms with D_2 was determined in an absolute way, similar to the measurements of k_1, from the kinetics of F atom consumption ($[F]_0$ = (2.0 – 4.0)×10^{11} molecule cm^{-3}) monitored in excess of D_2 (see Table 3 for the range of D_2 concentrations). Examples of F atom decays observed at different concentrations of D_2 at T = 440 K are shown in Figure S4 (SI). Typical plots of the pseudo-first-order rate constant, $k_2' = k_2 \times [D_2] + k_w$, versus concentration of D_2 are shown in Figures 5 and S5 (SI). Diffusion corrections on k_2' were usually less than 10% being up to 15% in a few kinetic runs at highest temperatures of the study. All the results obtained for k_2 in the current work are shown in Table 3.

The available for k_2 experimental data are summarized in Figure 6. The solid line in Figure 6 results from a least-squares analysis of the present experimental data and provides the following Arrhenius expression for k_2:

k_2 = (8.47± 0.42)×10^{-11} exp(-(670 ± 16)/T) $cm^3molecule^{-1}s^{-1}$,

where the uncertainties are 2σ statistical ones. The total uncertainty on the rate constant of 15% is estimated for the whole temperature range of the study. The present data for k_2 are

practically identical to those reported by Stevens et al.[7] at T = 228-358 K: k_2 = (9.3± 1.1) × 10^{-11} exp(-680± 50/T) cm^3 $molecule^{-1}$ s^{-1}. The absolute values of k_2 reported by Heidner et al.[5] (T = 295-678 K) and Wurzberg and Houston[8] (T = 190-373 K) are up to a factor of 1.5 higher than the present data, although the reaction activation factors reported in those studies, 604±71 and 554±50 K, respectively, are close to those determined by Stevens et al.[7] and in the present work. The parallel shift between the two sets of kinetic data seems to support the assumption of Stevens et al.[7] on the possible systematic error between their data and those of both Heidner et al.[5] and Wurzberg and Houston.[8] The values of k_2 reported by Igoshin et al.[26] at two temperatures, 195 and 295 K, which are significantly higher than all other data, were analyzed in the reviews of Anderson[25] and Persky and Kornweitz[1] and estimated to be highly uncertain. The Arrhenius expression k_2 = (1.06± 0.12) × 10^{-10} exp(-635± 55/T) $cm^3molecule^{-1}s^{-1}$ (dashed line in Figure 6), recommended by Persky and Kornweitz[1] in a critical evaluation of the available kinetic data for reaction of fluorine atoms with D_2 for T = 190-376 K, provides the values of k_2 by a factor of 1.4-1.5 higher than those measured in the present work. The above recommendation was based on the expression for k_1 = 1.1×10^{-10} exp(-450/T) $cm^3molecule^{-1}s^{-1}$ [1] and that for the kinetic isotope effect, k_1/k_2 = 1.04×10^{-10} exp(186/T).[34] It can be noted that k_1/k_2 = 1.46 × 10^{-10} exp(163/T), based on the Arrhenius expressions for k_1 and k_2 determined in the present work, provides the values of KIE by nearly 30% higher (at T = 220-376 K) compared with those used in the critical evaluation. To determine the kinetic isotope effect more accurately, we have carried out independent relative measurements of the k_1 to k_2 ratio described in the next section.

3.5. Kinetic Isotope Effect

In addition to the direct measurements of the rate constants k_1 and k_2, their ratio was measured using a relative rate method. The applied procedure was similar to that employed in the relative measurements of the rate constant of the F + H_2 reaction. F atoms were titrated with a mixture of H_2 and D_2 (Figure S1c, SI) and the yield of DF was measured as a function of the $[H_2]/[D_2]$ ratio:

$$F + H_2 \rightarrow HF + H \quad (1)$$

$$F + D_2 \rightarrow DF + D \quad (2)$$

The fraction of the initial concentration of F atoms, $[F]_0$, transformed to DF, is:

$$[\mathrm{DF}] = \frac{k_2[\mathrm{D_2}]}{k_2[\mathrm{D_2}]+k_1[\mathrm{H_2}]+k_w} \times [\mathrm{F}]_0,$$

or after rearrangement:

$$\frac{[\mathrm{F}]_0}{[\mathrm{DF}]} - 1 = \frac{k_1[\mathrm{H_2}]}{k_2[\mathrm{D_2}]} + \frac{k_w}{k_2[\mathrm{D_2}]} \qquad \text{(II)}$$

Examples of the observed experimental data are shown in Figures 7 and S6 (SI). The final values of k_1/k_2 at different temperatures, determined, in accordance with equation II, from the slopes of the linear dependencies in Figures 7 and S6, are given in Table 4.

Figure 8 summarizes the results of the previous and current temperature dependent measurements of the kinetic isotope effect for the F atom reactions with H_2 and D_2. One can note that the experimental data from the present study obtained with two different methods, direct measurements of k_1 and k_2 (dashed black line, k_1/k_2 = 1.46×exp(163/T) with estimated total uncertainty of 20% at all temperatures) and relative measurements of KIE (filled circles, fitted with a solid black line, k_1/k_2 = (1.58±0.05)×exp((131±2)/T) (with 2σ statistical uncertainties, total estimated uncertainty being of nearly 10%), are in excellent agreement (within 7%) in the temperature range used, T = 220 – 960 K. Although KIE derived from the rate constant data of Heidner et al. (k_1/k_2 = 2.1×exp(9/T))[5] and Stevens et al. (k_1/k_2 = 1.29×exp(210/T))[7] exhibit different temperature dependence, the absolute values of k_1/k_2 from these studies deviate by less than 15% from the present results. KIE reported in the relative measurements of Grant and Root, k_1/k_2 = (1.04±0.06)×exp((192±18)/T),[35] and Persky (k_1/k_2 = (1.04±0.02)×exp((186±5)/T),[34] are very close to each other and are by approximately 20% lower compared to the current data. Grant and Root[35] used a reactive competition between $H_2(D_2)$ and C_3F_6 for F atoms, measuring HF(DF) yield as a function of the composition of the $H_2(D_2)$ + C_3F_6 mixtures. In the study of Persky,[34] carried out in a discharge flow system, KIE was determined through mass spectrometric detection of [HF] to [DF] ratio upon consumption of F atoms in competitive reactions with H_2 and D_2. Similar approach, except for a few details, was used in the present relative measurements of KIE. Firstly, in the current work only DF was monitored and, as a result, there was no need to apply the corrections on HF signal due to formation of this compound in the microwave discharge and on the walls of the reactor and movable injector, and due to contribution of D_2O at m/z = 20.[34] Secondly, there was no need to measure the absolute concentrations of HF and DF (in ref. 34 the sensitivities for the detection of these species by mass spectrometry were

assumed to be identical): in the current experiments, initial concentration of F atom in the reactor could be related to DF signal intensity in the H_2 -free system, when F atoms are consumed exclusively in reaction with D_2.

Considering the self-consistence of the independent measurements of the rate constants, k_1 and k_2, and their ratio, the following Arrhenius expressions are recommended from this study at T = 220 – 960 K:

$k_1 = (1.24 \pm 0.09)\times10^{-10} \exp(-(507 \pm 23)/T)$ cm^{3}molecule^{-1}s^{-1},

$k_2 = (8.47\pm 0.42)\times10^{-11} \exp(-(670 \pm 16)/T)$ cm^{3}molecule^{-1}s^{-1},

with conservative independent of temperature uncertainty of 15%. For the kinetic isotope effect both expression resulting from the ratio of the recommended k_1 and k_2,

$k_1/k_2 = 1.46\times\exp(163/T)$,

and that directly measured (leading to similar within 7% results),

$k_1/k_2 = 1.58\times\exp(131/T)$,

can be used with conservative uncertainty of 10% at all temperatures of the study.

The self-consistent kinetic data set for the reaction of F atom with H_2 and its isotope analog F + D_2, reported in this paper, seems to represent a good experimental basis for further refinement of the theoretical models.

4 CONCLUSIONS

The rate constants of the reactions of F atoms with H_2 and D_2 have been measured using a discharge flow reactor combined with an electron impact ionization mass spectrometer at T = 220 – 960 K: $k_1 = (1.24 \pm 0.09)\times10^{-10} \exp(-(507 \pm 23)/T)$ cm^{3}molecule^{-1}s^{-1} and $k_2 = (8.47\pm 0.42)\times10^{-11} \exp(-(670 \pm 16)/T)$ cm^{3}molecule^{-1}s^{-1}. The Arrhenius expressions for k_1 and k_2 and independently measured kinetic isotope effect, $k_1/k_2= (1.58\pm0.05)\times\exp((131\pm2)/T)$, provide a self-consistent data set for the F + H_2 reaction and its isotope analog F + D_2 over an extended temperature range and represent a good experimental basis to further refine the theoretical calculations.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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TABLES LEGENDS

TABLE 1 Reaction F + H_2: summary of the absolute measurements of the rate constant

TABLE 2 Experimental conditions and results of the relative measurements of k_1

TABLE 3 Reaction F + D_2: summary of the measurements of the rate constant

TABLE 4 Experimental conditions and results of the relative measurements of k_1/k_2

TABLES

TABLE 1 Reaction F + H_2: summary of the absolute measurements of the rate constant

T (K) [a]	$[H_2]$ (10^{13} molecule cm^{-3})	k_1 (± 2σ) (10^{-11} cm^3 $molecule^{-1}$ s^{-1})	Reactor surface [b]
220	0.18-2.98	1.39±0.03	HW
235	0.22-3.31	1.47±0.02	HW
250	0.17-3.09	1.66±0.02	HW
265	0.18-2.98	1.84±0.03	HW
285	0.12-2.44	1.97±0.03	HW
298	0.13-2.97	2.26±0.04	HW
299	0.16-2.26	2.24±0.04	Q
320	0.15-2.51	2.40±0.03	HW
340	0.20-1.85	2.59±0.05	Q
400	0.17-1.87	3.51±0.07	Q
445	0.21-1.82	3.83±0.04	Q
540	0.12-1.51	4.92±0.07	Q
660	0.12-1.14	5.77±0.03	Q
780	0.11-1.14	6.44±0.11	Q
960	0.08-0.97	7.90±0.11	Q

[a] 8-13 kinetic runs at each temperature.
[b] HW: halocarbon wax; Q: quartz.

TABLE 2 Experimental conditions and results of the relative measurements of k_1

T (K)	$[H_2]$ [a]	$[H_2]/[Br_2]$	k_1/k_3 (± 2σ)	k_1 [b]
320	0.64-26.5	0.58-25.9	0.187±0.002	2.39
370	0.49-16.3	0.51-17.2	0.238±0.002	3.05
575	0.45-14.0	0.54-16.7	0.414±0.004	5.30

[a] Units of 10^{13} molecule cm^{-3}.
[b] Units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, estimated total uncertainty on k_1 is nearly 20% and includes the uncertainty on the rate constant of the reference reaction.

TABLE 3 Reaction F + D_2: summary of the measurements of the rate constant

T (K) [a]	$[D_2]$ (10^{13} molecule cm^{-3})	k_2 (± 2σ) [b] (10^{-11} cm^3 $molecule^{-1}$ s^{-1})	Reactor surface [c]
220	0.64-7.77	0.416±0.034	HW
235	0.57-7.06	0.494±0.007	HW

250	0.64-6.04	0.580±0.009	HW
265	0.36-6.21	0.666±0.008	HW
285	0.31-4.70	0.835±0.007	HW
299	0.46-4.95	0.861±0.012	Q
305	0.30-6.21	0.930±0.017	HW
325	0.30-5.69	1.04±0.09	HW
365	0.31-3.30	1.39±0.02	Q
440	0.25-3.11	1.72±0.02	Q
535	0.12-2.09	2.45±0.03	Q
650	0.15-1.84	3.00±0.04	Q
790	0.20-2.18	3.65±0.04	Q
960	0.13-1.59	4.39±0.08	Q

[a] 9-11 kinetic runs at each temperature.
[b] estimated total uncertainty on k_2 is ≤ 15%.
[c] HW: halocarbon wax; Q: quartz.

TABLE 4 Experimental conditions and results of the relative measurements of k_1/k_2

T (K) [a]	$[H_2]$ [b]	$[D_2]$ [b]	k_1/k_2 (± 2σ)	Reactor surface [c]
220	0.21-6.0	8.2	2.98±0.04	HW
235	0.32-6.4	6.6	2.74±0.03	HW
250	0.19-7.2	5.9	2.62±0.02	HW
265	0.21-6.7	5.4	2.54±0.04	HW
285	0.27-6.1	4.9	2.44±0.02	HW
298	0.17-6.7	5.8	2.38±0.03	HW
301	0.19-5.5	4.2	2.45±0.02	Q
320	0.30-6.0	5.2	2.36±0.04	HW
365	0.11-4.7	4.6	2.31±0.02	Q
440	0.18-4.6	3.9	2.12±0.01	Q
535	0.12-4.9	4.0	2.08±0.02	Q
650	0.18-4.7	3.2	1.90±0.02	Q
790	0.08-3.6	2.5	1.85±0.04	Q
960	0.06-3.1	2.0	1.81±0.02	Q

[a] 10-13 runs at each temperature.
[b] Units of 10^{13} molecule cm^{-3}.
[c] HW: halocarbon wax; Q: quartz.

FIGURE LEGENDS

FIGURE 1 Reaction F + H_2: plots of pseudo-first-order rate constant k_1' versus concentration of H_2 at different temperatures. Partially shown error bars represent typical uncertainties (≤5%) on the determination of k_1'.

FIGURE 2 Yield of FBr from F atom titration by the reaction with Br_2 + H_2 mixtures at different temperatures. Partially shown error bars represent typical uncertainties of the measurements (~ 5%).

FIGURE 3 Reaction F + H_2: summary of the data on the temperature dependence of the reaction rate constant.

FIGURE 4 Reaction F + H_2: comparison of the experimental data with theoretical calculations of the reaction rate constant. Potential energy surface (PES) used in calculations: SW (Stark and Werner),[32] FXZ (Fu, Xu and Zhang),[33] CSZ (Chen, Sun and Zhang).[30]

FIGURE 5 Reaction F + D_2: plots of pseudo-first-order rate constant k_2' versus concentration of D_2 at different temperatures.

FIGURE 6 Reaction F + D_2: summary of the available data on the temperature dependence of the reaction rate constant.

FIGURE 7 Yield of DF from F atom titration with D_2 + H_2 mixtures at different temperatures. Partially shown error bars represent typical uncertainties of the measurements (~ 5%).

FIGURE 8 Temperature dependence of the kinetic isotope effect k_1/k_2. AM: k_1/k_2 calculated from the reported values of k_1 and k_2; RM: relative measurements of the k_1 to k_2 ratio. Partially shown error bars represent estimated total uncertainty of 10% on the present measurements.

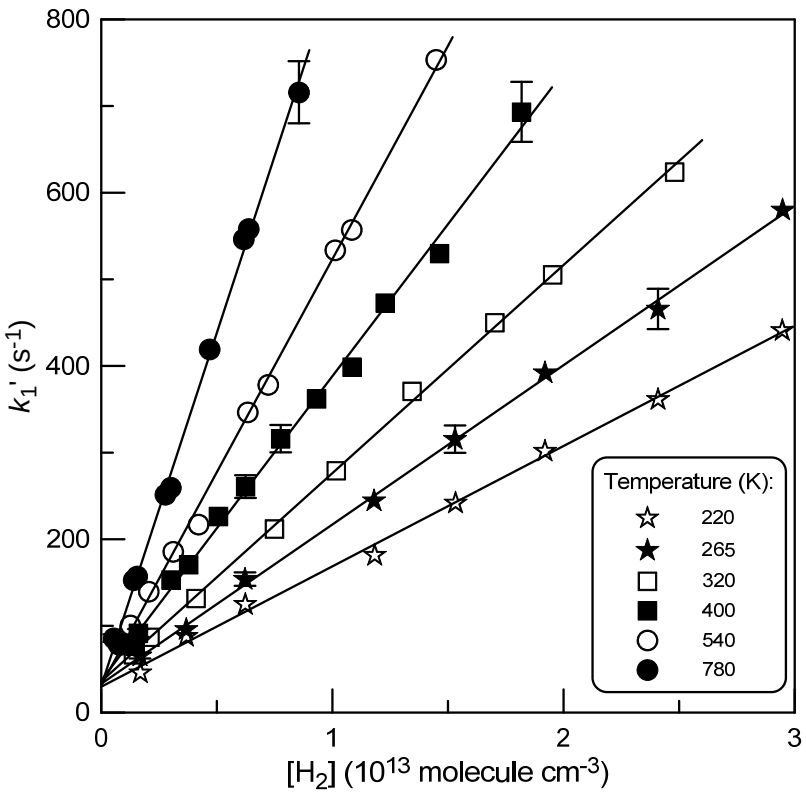
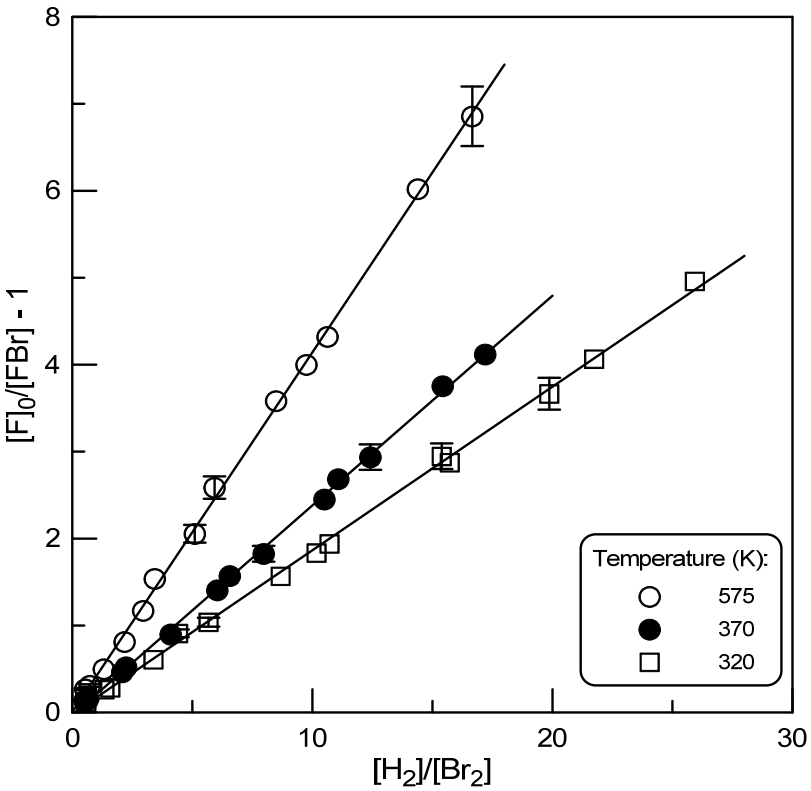


Figure 1.



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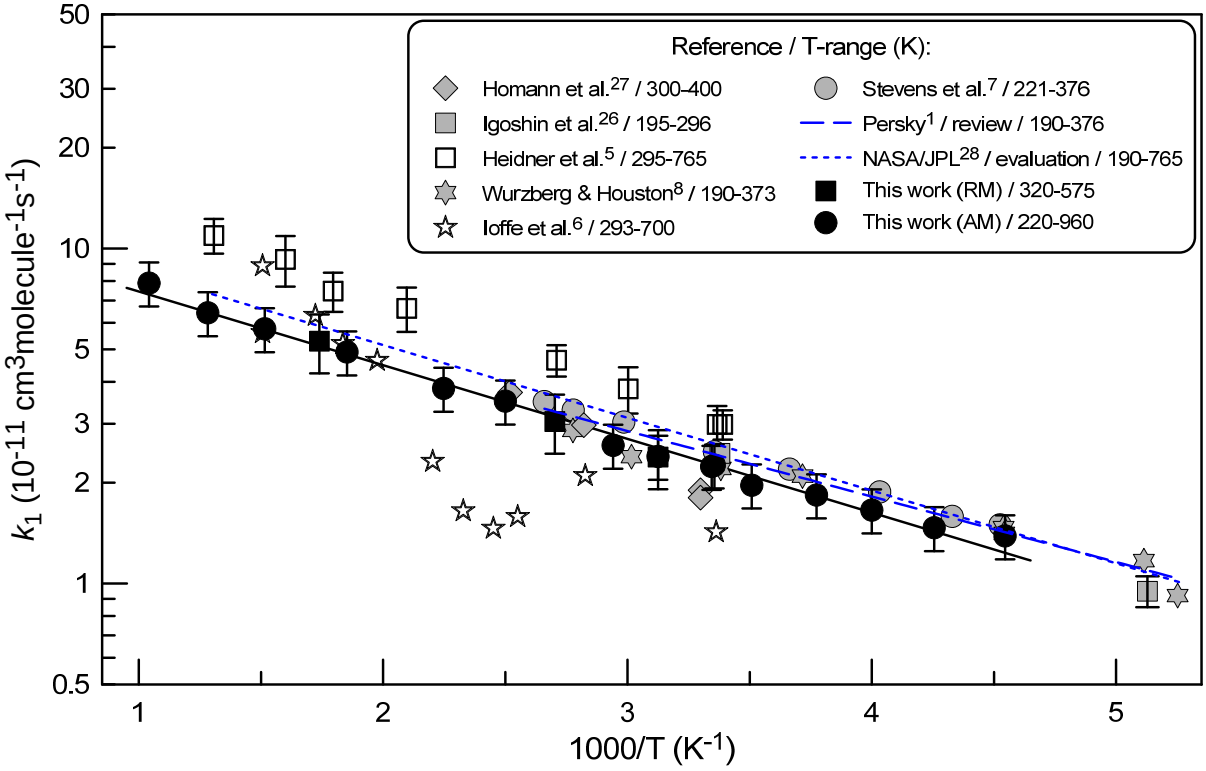

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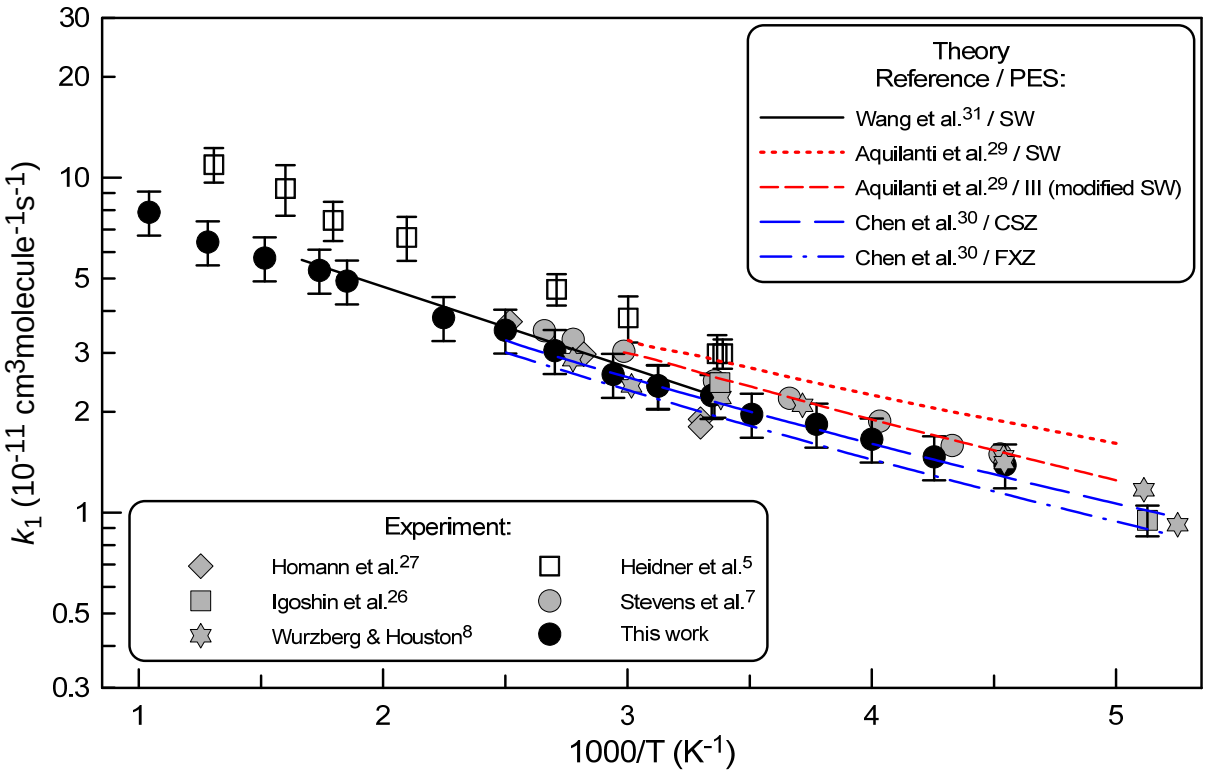

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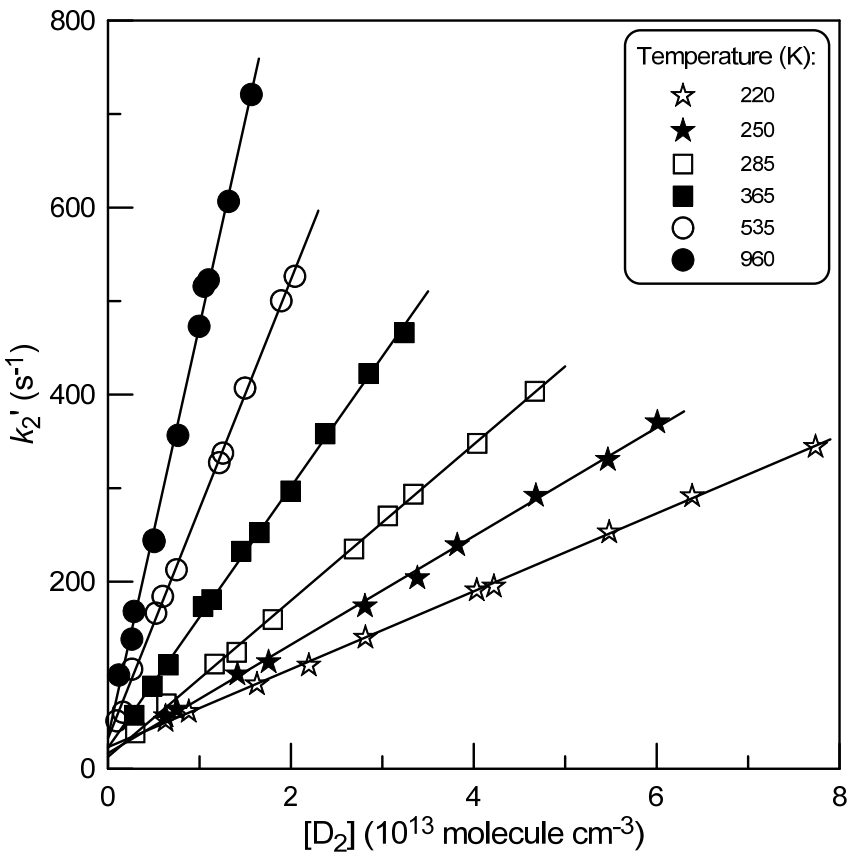

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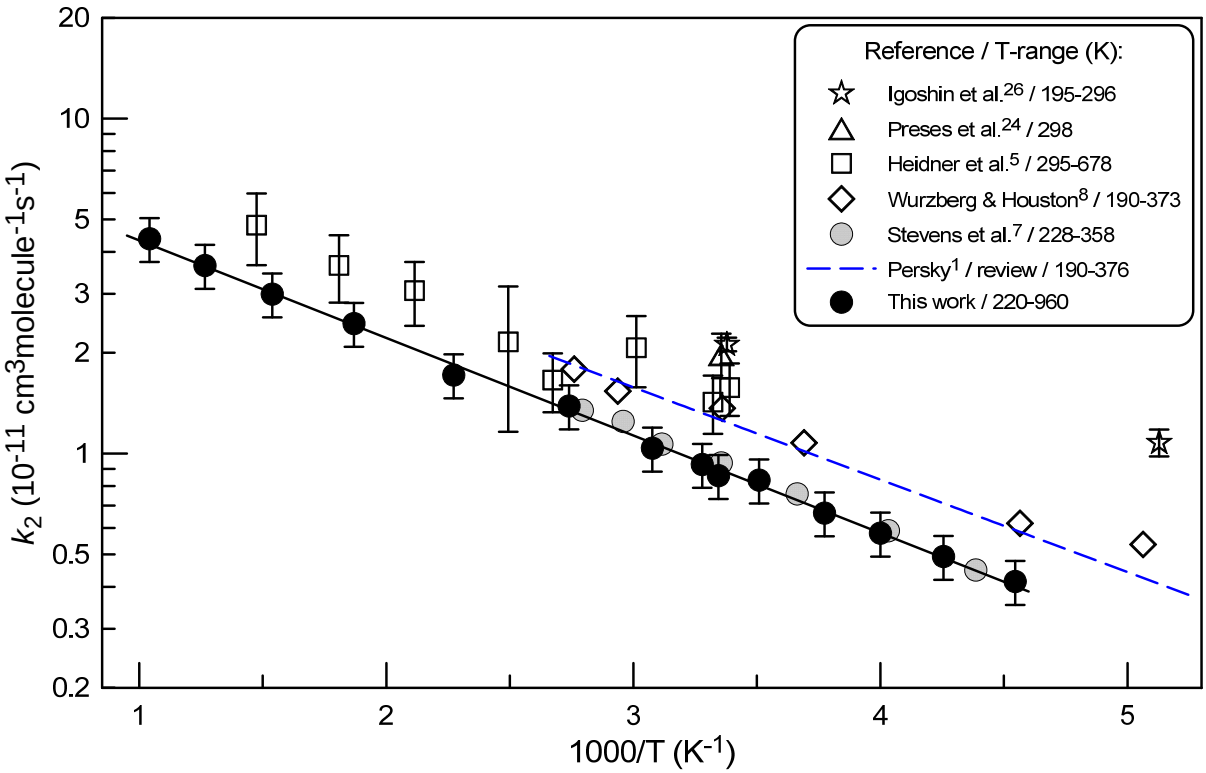

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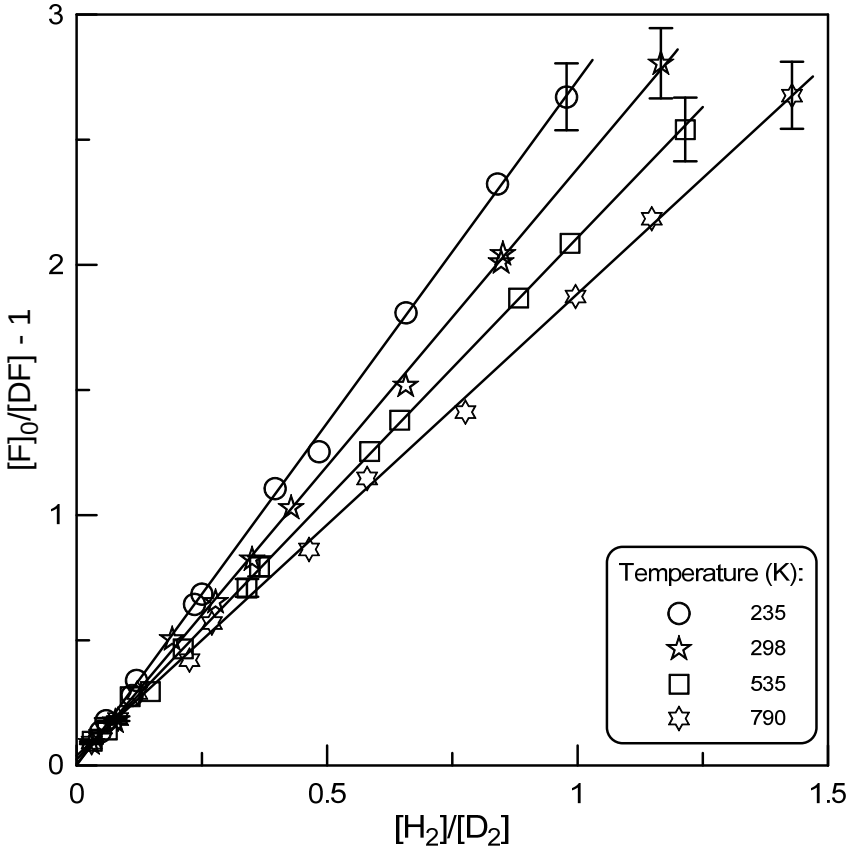

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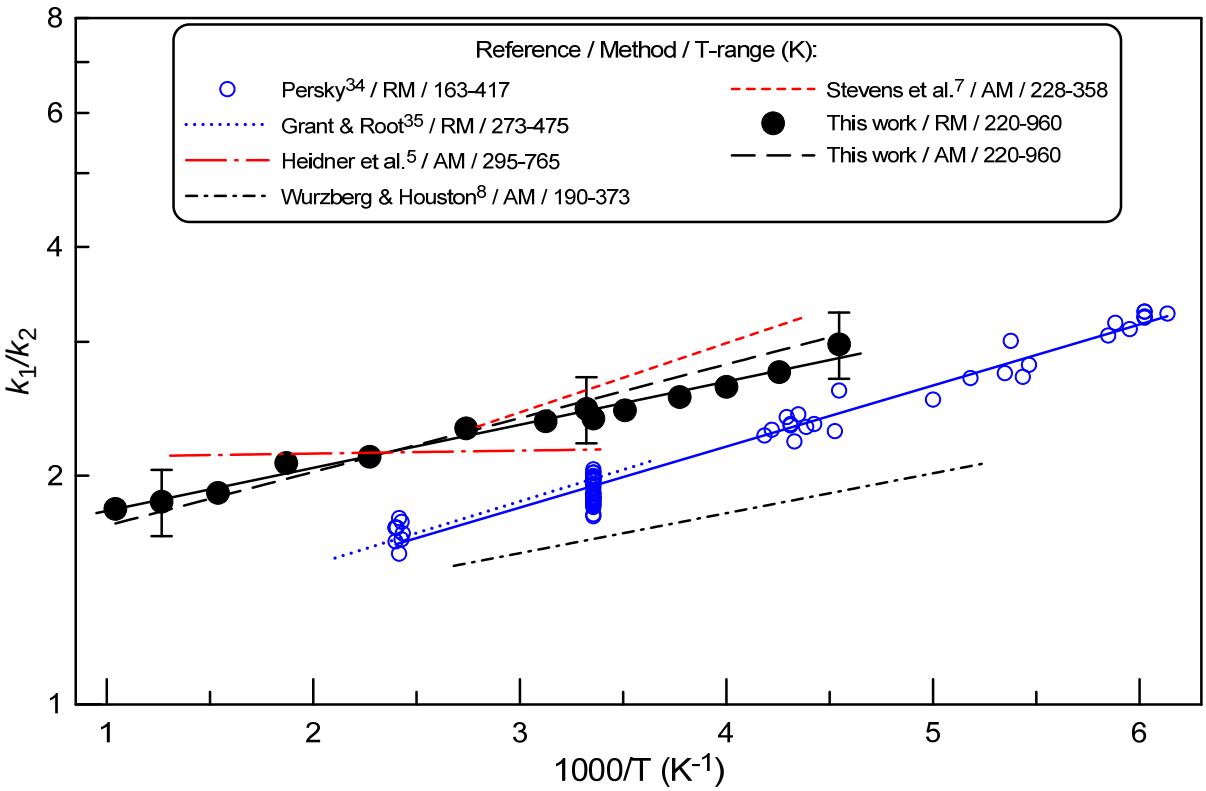

Figure 8.