

# Kinetics of the Cl-H<sub>2</sub> system. I. Detailed balance in the Cl+H<sub>2</sub> reaction

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A well-known problem in chemical kinetics is the observation that the ratio of the measured rate constants for the reactions Cl + H<sub>2</sub> and H + HCl apparently does not equal the known equilibrium constant. Previous work has indicated that the difficulty exists in the H + HCl measurements, which were complicated by wall effects and secondary reactions of H. We have measured both rate constants over the temperature range 200–500 K, using a resonance fluorescence–flash photolysis apparatus in which wall effects were insignificant. The ratio of our measured rate constants is in excellent agreement with detailed balance.

## INTRODUCTION

The reactions of halogen atoms with hydrogen molecules have been studied for nearly a century and have played a central role in the history of chemical kinetics.<sup>1</sup> Despite the intense effort to understand these elementary systems, there remain outstanding a number of significant problems. One of these deals with the forward and reverse reactions



It is commonly assumed that, in general, the ratio of  $k_f$  and  $k_r$  equals the equilibrium constant:

$$k_f/k_r = K_{\text{eq}} \quad (2)$$

even though  $k_f$  and  $k_r$  are usually measured far from equilibrium. Surprisingly, this was not found to be the case for Reaction (1). Westenberg and de Haas<sup>2</sup> measured  $k_f$  and  $k_r$  independently in a flow apparatus. Over the temperature range 200–500 K they observed that  $k_f/k_r$  was two to three times smaller than  $K_{\text{eq}}$ . Various explanations have been offered to resolve this paradox. While it is always true that microscopic reversibility holds for individual state-to-state transitions, Eq. (2) need not be valid for macroscopic rate constants unless the reactants and products are in thermal equilibrium. For example, Snider<sup>3</sup> and Clyne<sup>4</sup> suggested that the observed  $k_f$  could be smaller than anticipated if Cl(<sup>2</sup>P<sub>1/2</sub>) is much more reactive than Cl(<sup>2</sup>P<sub>3/2</sub>), so that its relative concentration were significantly depleted by the reaction. Alternatively, Westenberg and de Haas<sup>2</sup> suggested that  $k_r$  could be larger than expected if HCl formed in the forward reaction has sufficient excess rotational energy to enhance the reverse reaction rate.

Because of the usefulness of Eq. (2) in many areas of chemical kinetics, the possibility that it might not be valid in this test case would have profound significance. Galante and Gislason<sup>5</sup> pointed out, however, that the postulated enhanced reactivities of electronically excited Cl and rotationally excited HCl could not compete with quenching processes under actual experimental conditions. Consequently, an alternate viewpoint which has been offered by various authors is that the measurements of  $k_f$  and/or  $k_r$  were erroneous. Since a recent measurement<sup>6</sup> of  $k_f$  using different methods confirmed the earlier results, it appears that the error lies in  $k_r$ . Every recent study<sup>2, 7–9</sup> of the H + HCl reaction has been accom-

plished using flow reactors in which wall reactions of Cl were present. To account for the secondary reactions of H, various mechanisms were postulated which introduced stoichiometric corrections. These mechanisms invoked collisions of product Cl atoms with the flow tube wall resulting in the formation of species such as Cl<sub>2</sub>,<sup>8</sup> HCl<sub>2</sub>,<sup>9</sup> and vibrationally excited HCl,<sup>9, 10</sup> and desorption of these species into the reaction mixture. An unambiguous measurement of the H + HCl rate constant has not been reported to date.

Because of the experimental difficulties present in the flow studies, we decided to re-examine the Cl-H<sub>2</sub> system with a method that virtually eliminates wall effects. The flash photolysis–resonance fluorescence (FP–RF) technique is ideal for this purpose because the reaction

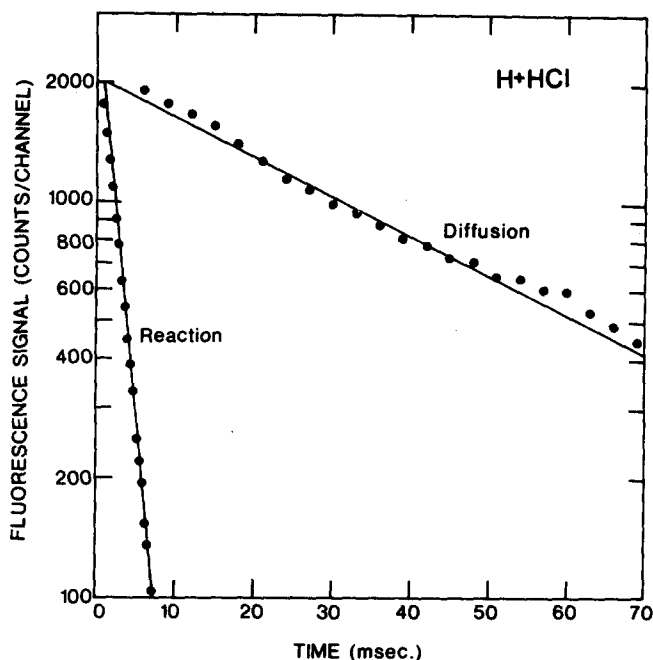


FIG. 1. Comparison of the diffusion and reaction rates for a typical H+HCl run. The experimental parameters for the diffusion data were: CH<sub>4</sub> pressure=0.227 Torr, total pressure=40 Torr, T=294.7 K, flash energy=162 J. For the reaction data the parameters were: HCl pressure=0.217 Torr, total pressure=40 Torr, T=296.3 K, flash energy=162 J. Data were accumulated for 80 flashes for both diffusion and reaction, with a channel width of 3 ms/channel for diffusion and 0.4 ms/channel for reaction.

TABLE I. Summary of experiments for Cl + H<sub>2</sub>.

Temperature (K)	Cl source pressure (mTorr)	H <sub>2</sub> pressure (Torr)	Total pressure <sup>a</sup> (Torr)	Flash energy (J)	No. of experiments	$k_f$ (cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> × 10 <sup>-9</sup> )
199.2 ± 0.7	49 <sup>b</sup>	1.57	20	180	8	0.234 ± 0.009 <sup>c</sup>
201.2 ± 0.4	73 <sup>b</sup>	2.35	30	180	8	0.242 ± 0.007
201.3 ± 0.3	97 <sup>b</sup>	3.14	40	180	8	0.238 ± 0.004
203.0 ± 0.2	122 <sup>b</sup>	3.92	50	180	8	0.245 ± 0.005
203.6 ± 0.1	146 <sup>b</sup>	4.70	60	180	8	0.252 ± 0.004
204.2 ± 0.1	170 <sup>b</sup>	5.49	70	180	8	0.237 ± 0.007
202.2 ± 1.7					48	0.242 ± 0.008
231.9 ± 0.2	58 <sup>d</sup>	1.20	30	128	12	1.13 ± 0.04
231.6 ± 0.1	97 <sup>d</sup>	2.01	50	128	12	1.05 ± 0.06
231.8 ± 0.2					24	1.09 ± 0.07
257.9 ± 0.1	39 <sup>d</sup>	0.802	20	128	12	3.29 ± 0.13
258.1 ± 0.5	78 <sup>d</sup>	1.60	40	128	12	3.03 ± 0.12
258.0 ± 0.4					24	3.16 ± 0.18
298.7 ± 0.2	39 <sup>d</sup>	0.802	20	128	7	9.33 ± 0.56
298.8 ± 0.1	78 <sup>d</sup>	1.60	40	128	6	8.87 ± 0.57
298.7 ± 0.2					13	9.08 ± 0.61
298.2 ± 0.2	40 <sup>b</sup>	0.783	20	128	12	9.13 ± 0.52
298.1 ± 0.7	80 <sup>b</sup>	1.57	40	128	12	8.83 ± 0.43
298.1 ± 0.5					24	8.98 ± 0.40
375.1 ± 0.3	42 <sup>d</sup>	0.087	20	144	5	41.1 ± 1.8
375.7 ± 0.1	62 <sup>d</sup>	0.131	30	144	5	36.2 ± 2.1
375.9 ± 0.1	83 <sup>d</sup>	0.174	40	144	5	38.5 ± 2.4
375.9 ± 0.1	104 <sup>d</sup>	0.218	50	180	5	47.0 ± 1.7
375.7 ± 0.2					20	40.7 ± 4.5
422.3 ± 0.1	61 <sup>b</sup>	0.184	20	180	11	105 ± 3
422.5 ± 0.9	91 <sup>b</sup>	0.276	30	180	11	101 ± 5
421.1 ± 0.6	121 <sup>b</sup>	0.368	40	200	11	103 ± 3
422.0 ± 0.9					33	103 ± 4
498.7 ± 0.2	42 <sup>d</sup>	0.087	20	144	8	214 ± 24
498.9 ± 1.0	62 <sup>d</sup>	0.131	30	144	9	197 ± 25
497.8 ± 0.9	83 <sup>d</sup>	0.174	40	144	7	228 ± 13
498.4 ± 0.9	104 <sup>d</sup>	0.218	50	144	7	229 ± 24
498.0 ± 1.3					31	216 ± 25

<sup>a</sup>Ar used as diluent.<sup>b</sup>CF<sub>3</sub>Cl used as Cl atom source.<sup>c</sup>Errors are one standard deviation.<sup>d</sup>CCl<sub>4</sub> used as Cl atom source.

takes place in the center of the cell at a rate which is typically two orders of magnitude faster than the rate of diffusion to the walls.

## EXPERIMENTAL

The FP-RF apparatus employed in this study is similar to the one described by Stief and co-workers.<sup>11</sup> Basically, the equipment consists of a variable temperature (200–500 K) reaction cell housed in a vacuum chamber with three mutually perpendicular optical ports to accommodate a flash lamp, resonance lamp, and photomultiplier tube. The reaction cell was fabricated from a 7.6 × 7.6 × 10.2 cm brass block with 5.7 cm ID hole bored through the center. To eliminate wall corrosion and minimize light scattering, the inner surface of the reaction vessel was coated with a flat black, high temperature Teflon coating that was thoroughly degassed at 525 K to remove possible contaminants.

Temperature was measured with a 0.025 cm chromel–alumel thermocouple equipped with a digital indicator

(Omega-410A, 0.1 °C resolution). The thermocouple was in direct contact with the reaction gas to insure measurement of the actual gas temperature. Gas pressure in the cell was measured with a capacitance manometer equipped with a 100 Torr head (MKS 310BH).

Atomic reactants were generated with a tungsten flash lamp operating at approximately atmospheric pressure of flowing N<sub>2</sub>. The lamp was equipped with a MgF<sub>2</sub> window (115 nm outoff). The lamp was placed 20.3 cm from the center of the cell, and was collimated with four 0.95 cm apertures for H atom production and 1.3 cm apertures for Cl. The nominal lamp energy was 100–200 J/pulse, at a pulse rate of 0.3 to 0.5 Hz. The reaction mixture was flowed at a rate sufficient to be replenished at least once between flashes. The resonance radiation used to monitor hydrogen (121.6 nm) and chlorine (six lines between 135 and 140 nm)<sup>12</sup> atoms was generated by passage of an appropriate molecular species through a Pyrex lamp fitted with a MgF<sub>2</sub> window. The lamp was coupled to an Evenson–Broida microwave cavity powered at 2450 MHz. The window was located

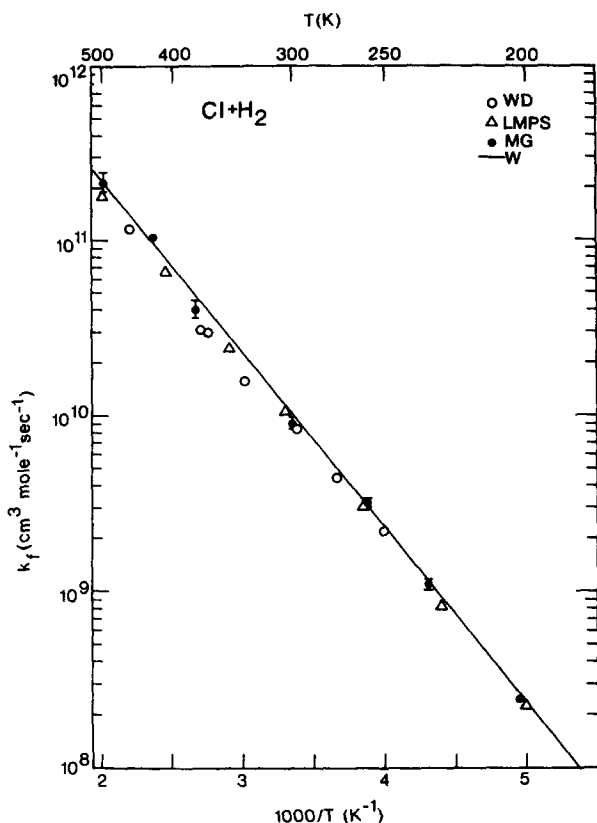


FIG. 2. Rate constants for the reaction Cl + H<sub>2</sub>. The data points are from the studies of Westenberg and de Haas (WD), Lee *et al.* (LMPS), and the present work (MG). The line is the recommendation of Watson. Error bars are one standard deviation.

35.6 cm from the cell center and collimated with the same apertures that were used for the flash lamp. For the Lyman alpha radiation the impurities in ultra pure helium were sufficient to provide an adequate signal, while a 0.1% mixture of Cl<sub>2</sub> in helium was required to produce the Cl atomic lines. Selectivity of these atomic lines was enhanced by the choice of an appropriate filter.<sup>12</sup> An oxygen gas filter was employed for the H atomic line and a BaF<sub>2</sub> window for the Cl atom lines.

Detection of the fluorescent signal was accomplished by means of a solar blind photomultiplier tube (EMR 542 G-08-18) mounted perpendicular to the flash and resonance lamps. The tube was positioned 14.0 cm from the center of the cell and collimated with two 1.59 cm apertures followed by a 1.3 cm length of a "honeycomb" collimator. Individual photon pulses produced by the capacitively coupled tube were amplified, discriminated, counted, (Ortec 9302 amplifier-discriminator, Ortec 770 Counter) and stored in an LSI-11 computer. After accumulation of multiple flashes this signal was analyzed by a PDP-11/45 computer.

Experimental conditions were chosen to guarantee that pseudo-first order kinetic behavior was obtained (i.e., [H<sub>2</sub>] ≫ [Cl] or [HCl] ≫ [H]). Consequently, a linear exponential decay of the resonant signal was always observed, after correction for background due to light scattering. A further correction must be applied to ac-

count for the diffusion of the atomic species from the reaction zone. This correction is accomplished by producing the same atomic species in a "nonreactive" environment. The signal decay in this case is a measure of the diffusion rate. Figure 1 exhibits a typical pseudo-first-order decay for reaction and diffusion. Since the diffusion rate is a function of experimental parameters such as temperature, pressure, pumping speed, and diluent, the actual value varies between 1%–10% of the reaction rate.<sup>13</sup> The correction to the pseudo-first-order reaction rate for Cl + H<sub>2</sub> is given by

$$k_{\text{obs}} = k_f [\text{H}_2] + k_D, \quad (3)$$

where  $k_{\text{obs}}$  is the observed decay rate, and  $k_D$  is the observed Cl diffusion rate. An equivalent expression applies to H + HCl.

All gas mixtures were prepared and stored in 22 or 50 liter Pyrex bulbs at slightly greater than atmospheric pressure and allowed to equilibrate for at least 24 h to insure thorough mixing. Diffusion gas mixtures consisted of CH<sub>4</sub> in Ar for H atoms and CF<sub>3</sub>Cl or CCl<sub>4</sub> in Ar for Cl atoms. Reactive mixtures consisted of CH<sub>4</sub> and/or HCl in Ar for the H + HCl study, and H<sub>2</sub> with either CF<sub>3</sub>Cl or CCl<sub>4</sub> in Ar for Cl + H<sub>2</sub>. He (Matheson-99.9999%), Ar (Matheson-99.9995%), and H<sub>2</sub> (Matheson-99.9999%) were used without purification, while CCl<sub>3</sub>F (Matheson-99.9%), CCl<sub>4</sub> (Fisher-certified A.C.S. grade), Cl<sub>2</sub> (Matheson-99.5%), and HCl (Matheson-99.99%) were subjected to several freeze thaw cycles for degassing and two bulb to bulb fractionations, with the middle fraction being retained.

## RESULTS AND DISCUSSION

In order to test the accuracy of our apparatus, we decided first to study the forward reaction Cl + H<sub>2</sub> for which reliable data are available in the literature.<sup>14</sup> The rate constant  $k_f$  was measured at seven temperatures. For a constant temperature,  $k_f$  was found to be independent of pressure, flash energy, and chlorine atom source.<sup>15</sup> These experiments are summarized in Table I. The measured rate constants can be described accurately by an Arrhenius function  $A \exp(-E/RT)$  as shown in Fig. 2. The fitted Arrhenius parameters are listed in Table II. Our data are in good agreement with previous measurements, and in particular with the FP-RF data of Lee *et al.*<sup>6</sup> Although our pre-exponential factor is somewhat larger than theirs, our Arrhenius parameters are in excellent agreement with Watson's recommended value.

The reverse reaction H + HCl was studied under nearly identical conditions. Again there was no noticeable variation of the rate constant with pressure or flash energy. In every instance the H atom decay was exponential. These experiments are summarized in Table III. The rate constants are plotted in Fig. 3, and the fitted Arrhenius parameters are listed in Table II, together with the values obtained in the earlier flow studies. As indicated in the table, our results are in disagreement with each of the previous studies. Our activation energy is larger than the values of Clyne and Stedman<sup>7</sup> and Ambidge *et al.*,<sup>8</sup> while our pre-exponential factor is half that of Westenberg and de Haas.<sup>2</sup>

The quantity of immediate interest is the ratio  $k_f/k_r$ ,

TABLE II. Comparison of Arrhenius parameters.<sup>a</sup>

Temperature range (K)	A		E		Reference
	(cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> × 10 <sup>-13</sup> )	(kcal mol <sup>-1</sup> )	(kcal mol <sup>-1</sup> )	<i>k</i> at 298 K (cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> × 10 <sup>-10</sup> )	
Cl + H <sub>2</sub>					
251-546	1.2 ± 0.3	4.3 ± 0.2		0.84 ± 0.04	Westenberg and de Haas
200-500	1.60 ± 0.23	4.42 ± 0.12		0.90 ± 0.18	Lee <i>et al.</i> <sup>g</sup>
200-300	2.1	4.55		0.97	Watson <sup>f</sup>
199-499	2.20 ± 0.17	4.59 ± 0.04		0.96 ± 0.18	Present study
H + HCl					
195-373	0.9 <sup>c</sup>	3.1 <sup>c</sup>		4.9	Clyne and Stedman <sup>e</sup>
195-497	2.3 ± 0.7	3.5 ± 0.2		6.2 ± 0.4	Westenberg and de Haas <sup>h</sup>
298-521	0.93 ± 0.71	3.17 ± 0.47		4.6 ± 3.0	Ambidge <i>et al.</i> <sup>d,1</sup>
199-502	1.09 ± 0.02	3.50 ± 0.03		3.0 ± 0.3	Present study

<sup>a</sup>Errors are three standard deviations except for Ref. 6, where they are the errors stated by the authors.

<sup>b</sup>Recommended values.

<sup>c</sup>Data show considerable curvature on an Arrhenius plot.

<sup>d</sup>Parameters were fitted to the data taken in the presence of added SF<sub>6</sub>.

<sup>e</sup>Reference 6.

<sup>f</sup>Reference 15.

<sup>g</sup>Reference 7.

<sup>h</sup>Reference 2.

<sup>1</sup>Reference 8.

TABLE III. Summary of experiments for H + HCl.

Temperature (K)	HCl pressure (Torr)	H source pressure (mTorr)	Total pressure <sup>a</sup> (Torr)	Flash energy (J)	No. of experiments	<i>k<sub>r</sub></i> (cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> × 10 <sup>-8</sup> )
199.2 ± 0.2	1.63		20	112-200	15	1.65 ± 0.07 <sup>b</sup>
199.8 ± 0.2	2.47		30	112-200	14	1.62 ± 0.05
199.1 ± 0.5	3.29		40	112-200	14	1.51 ± 0.06
199.4 ± 0.5					43	1.59 ± 0.09
226.8 ± 0.2	0.862		20	112-200	15	4.61 ± 0.25
227.2 ± 0.1	1.29		30	112-200	14	4.51 ± 0.19
227.0 ± 0.3					29	4.56 ± 0.23
258.2 ± 0.1	0.362		20	112-200	14	12.9 ± 0.5
258.4 ± 0.1	0.544		30	112-200	13	12.4 ± 0.4
258.4 ± 0.1	0.725		40	112-200	13	12.0 ± 0.5
258.6 ± 0.2	0.906		50	112-200	9	11.5 ± 0.2
258.4 ± 0.2					49	12.3 ± 0.7
295.8 ± 0.3	0.109		20	112-200	13	29.3 ± 2.9
296.6 ± 0.2	0.163		30	112-200	13	27.9 ± 2.9
296.5 ± 0.1	0.217		40	112-200	13	27.9 ± 2.2
296.8 ± 0.1	0.272		50	112-200	6	28.1 ± 1.4
296.3 ± 0.4					45	28.4 ± 2.6
350.5 ± 1.2	0.090	117 <sup>c</sup>	20	112-200	15	76.7 ± 3.4
350.3 ± 0.9	0.120	176 <sup>c</sup>	30	162	10	71.5 ± 4.5
350.3 ± 1.1					25	74.6 ± 4.6
427.1 ± 0.4	0.065		20	162	10	171 ± 7
427.8 ± 0.3	0.098		30	162	15	170 ± 11
427.5 ± 0.5					25	171 ± 10
502.4 ± 0.6	0.054		20	162	10	334 ± 19

<sup>a</sup>Ar used as diluent.

<sup>b</sup>Errors are one standard deviation.

<sup>c</sup>CH<sub>4</sub> used as H atom source.

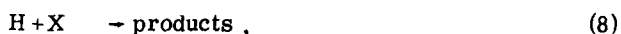
which is plotted in Fig. 4 for all of the studies, omitting stoichiometric corrections. Also shown is the exact value of the equilibrium constant,<sup>16</sup> which is accurately represented by the expression

$$K_{eq} = 1.94 \exp(-1110/RT). \quad (4)$$

In comparison, our data are fitted by the expression

$$k_f/k_r = 2.00 \exp(-1082/RT). \quad (5)$$

It is clear from the figure that the data of Westenberg and de Haas<sup>2</sup> could be brought into good agreement by dividing their  $k_r$  by a factor of 2. As has been pointed out previously,<sup>5</sup> such a factor results from a general mechanism of the type



where X is some product formed on the wall. If we assume that Cl and X are in steady state concentrations, then the loss rate of H is just  $2k_r[Cl]$ . Ambidge *et al.*<sup>8</sup> invoked a similar mechanism to explain the fact that their observed rate constants varied with the initial H atom concentration and the pressure of added SF<sub>6</sub>. Since their observed rate constants should be divided by a stoichiometric factor of 2, their apparent agreement with our data above room temperature is fortuitous. The data of Clyne and Stedman<sup>7</sup> exhibit considerable curvature, and it is difficult to draw any firm conclusions from

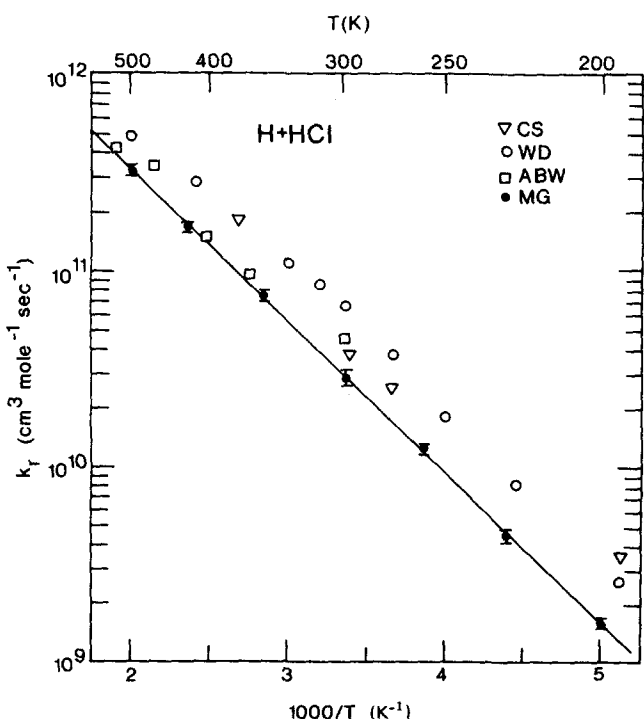


FIG. 3. Rate constants for the reaction H+HCl. The data points are from Clyne and Stedman (CS), Westenberg and de Haas (WD), Ambidge *et al.* (ABW), and the present study (MG). Stoichiometric corrections suggested by the various authors have not been included. Error bars are one standard deviation.

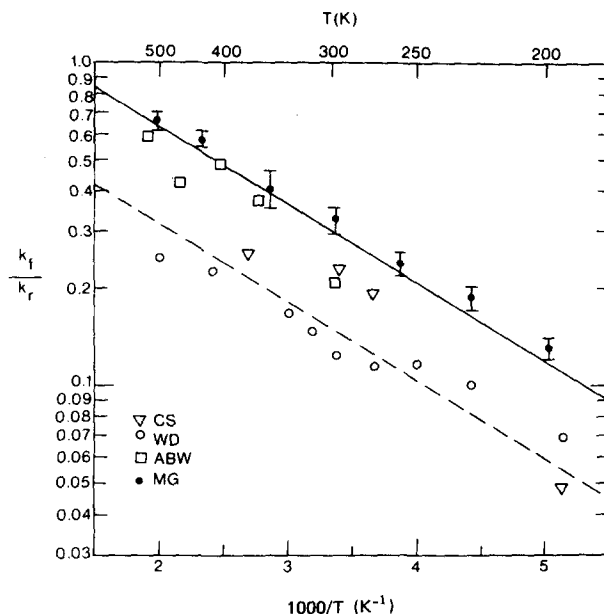


FIG. 4. Ratio of forward to reverse rate constants. Symbols are the same as in Figs. 2 and 3. The solid line is the exact  $K_{eq}$ , while the dashed line is  $0.5 K_{eq}$ . For the data of Clyne and Stedman and Ambidge *et al.* the recommended values of Watson were used for  $k_r$ . Stoichiometric corrections suggested by the various authors have not been included. Error bars are one standard deviation.

from their results. Spencer and Glass<sup>9</sup> showed that the measured value of  $k_r$  is sensitive to the surface conditions of the reactor wall. Extrapolating their measurements to the limit of unit stoichiometry, they obtain the proper value of  $k_r$ . Unfortunately, their study was limited to room temperature. From the present study, where wall reactions were not a problem, we conclude that the ratio of the forward to the reverse rate constant is indeed equal to the equilibrium constant.

#### ACKNOWLEDGMENTS

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- <sup>13</sup>This corresponds to diffusion out of the field of view. Diffusion to the cell walls is considerably slower.
- <sup>14</sup>In preliminary studies not included in Table I, many runs were carried out to assure that  $k_f$  is independent of flash energy.
- <sup>15</sup>R. T. Watson, *J. Phys. Chem. Ref. Data* 6, 871 (1977).
- <sup>16</sup> $K_{eq}$  was calculated from the tables in K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).