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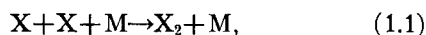
On the Mechanism of Low-Temperature Termolecular Atomic Recombination*

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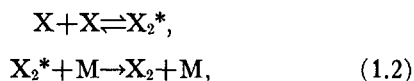
A simple theory of gas-phase termolecular atomic recombination kinetics is presented which treats the bound-complex (BC) mechanism in a fashion which parallels the Roberts, Bernstein, and Curtiss resonance theory of the energy-transfer (ET) mechanism. The ET rate constant has a low temperature maximum, but the BC rate constant does not. The contributions of the two mechanisms to the low-temperature recombination of hydrogen atoms, with He, Ar, and H₂ as third bodies, are estimated and compared. The presence (absence) of a low-temperature maximum in the observable total rate constant is determined by absence (presence) of bound vibrational levels of the hydrogen-third body van der Waals dimer. Hence, experimental studies of these reactions could yield valuable information about the interatomic potentials.

I. INTRODUCTION

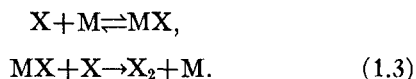
It has long been known¹ that the gas-phase termolecular recombination of X atoms in the presence of third-body atoms or molecules M,



can occur by two distinct mechanisms involving successive two-body collisions. These are the energy-transfer (ET) mechanism, summarized by



and the bound-complex (BC) or radical-molecule complex mechanism, summarized by



A number of theoretical calculations²⁻⁶ have been made to compare the importance of the two mechanisms, and it has generally been agreed²⁻⁴ that the BC mechanism is dominant if the intermolecular potential between X and M is strongly attractive. However, when M is a noble-gas atom, there has been disagreement about whether the BC⁵ or the ET⁶ mechanism is the more important. Furthermore, some authors have simply assumed that either the BC⁷ or the ET⁸⁻¹¹ mechanism was the only important one. One reason for this confusion is that the theories used for the two mechanisms have often been nonequivalent and have given unreasonable results for one or the other mechanism. In this paper we attempt to keep the methods used for the two mechanisms as alike as possible.

The most accurate and detailed calculations of the contribution of the ET mechanism are the resonance theory calculations of Roberts, Bernstein, and Curtiss¹⁰ (RBC) on the recombination of H atoms in H₂, He, and Ar. A distinguishing feature of the RBC results is a predicted maximum in the rate constant at about 100°K. However, Ham, Trainor, and Kaufman¹² studied the low-temperature recombination of H in H₂ experimentally to check this feature and found no maximum. Calculations by Shui and Appleton¹³ using

Keck's^{14,15} classical phase-space theory (which includes contributions from both mechanisms) also show no maximum and agree well with the experimental data. Hence, one is led to suspect that the loss of the maximum is due to contributions by the BC mechanism.

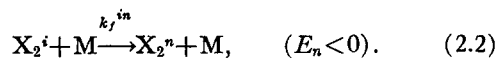
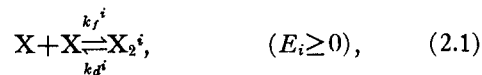
Although simple phase-space theories such as those of Keck¹³⁻¹⁵ are about as accurate as justified by presently available intermolecular potentials and experimental rate constants, they include both the BC and ET mechanisms automatically and cannot resolve the two contributions. Also, it is not clear whether the lack of a maximum in the phase-space theory rate constant is due to the BC mechanism or to the neglect of all quantum effects. Thus, in order to understand the presence or absence of a maximum in the observable rate constant one needs to know the separate contributions of the two mechanisms.

In the following section of this paper we first summarize and simplify the RBC theory in a way which still gives reasonable estimates of the ET contribution to the recombination rate. This allows development (in Sec. III) of a theory for the BC mechanism which parallels our treatment of the ET mechanism. In Sec. IV we review a simple method¹⁶ for determining the bound and quasibound rotation-vibration states of a diatomic molecule. The results of our calculations are presented in Sec. V and compared with other available results. And finally, Sec. VI contains a discussion of those results.

II. ENERGY-TRANSFER MECHANISM

We now summarize the theory of Roberts, Bernstein and Curtiss¹⁰ (RBC) for the contribution of the energy-transfer (ET) mechanism to the recombination rate. (Justification of the assumptions involved is found in RBC's work.)

For the recombination of X atoms in the presence of a third body, M, the detailed ET mechanism is



Here the complexes, i , are quasibound rotation-vibration states (orbiting resonances) of X_2 made possible by the rotational barrier in the effective potential, and the states, n , are true bound states with lower energy than the separated atoms.

In order to obtain the simple third-order kinetics observed experimentally for reactions of this type, it is necessary to assume that all the quasibound states that contribute appreciably to the recombination rate are in equilibrium with the reactants. Then, the over-all rate of formation of X_2 by the ET mechanism is

$$dn_{X_2}/dt = k_r^{\text{ET}} n_{X_2}^2 n_M, \quad (2.3)$$

where n is the number density of the subscripted molecule, and the ET recombination rate constant is given by

$$k_r^{\text{ET}} = \sum_i \sum_n k_f^{in} K_{\text{eq}}^i. \quad (2.4)$$

Here $K_{\text{eq}}^i = k_f^i/k_d^i$ is the equilibrium constant for the formation of X_2 molecules in the i th quasibound state. It can be calculated from equilibrium statistical mechanics using

$$K_{\text{eq}}^i = (g_i/g_X^2) (2J_i+1) \times \exp(-E_i/kT) (2\pi\hbar^2/\mu_{X_2}kT)^{3/2}, \quad (2.5)$$

where g_i is the electronic and nuclear degeneracy of X_2^i , g_X the degeneracy of X , J_i the rotational quantum number, E_i the energy of the i th state relative to the separated atoms, and $\mu_{X_2} = \frac{1}{2}m_X$ the reduced mass of X_2 .

The bimolecular specific rate constants, k_f^{in} in (2.4) are related to the inelastic scattering cross sections for the transition from state i to state n by the equation

$$k_f^{in} = (8kT/\pi\mu_{X_2-M})^{1/2} \bar{\sigma}_{in}, \quad (2.6)$$

where $\mu_{X_2-M} = m_M m_{X_2}/(m_M + m_{X_2})$ is the appropriate reduced mass, and $\bar{\sigma}_{in}$ is the Boltzmann average of the cross section $\sigma_{in}(E)$,

$$\bar{\sigma}_{in} = (kT)^{-2} \int_0^\infty \sigma_{in}(E) E e^{-E/kT} dE, \quad (2.7)$$

E being the relative energy of the X_2^i - M collision. Letting $\bar{\sigma}_i$ be the total inelastic cross section for a transition from state i to any bound state,

$$\bar{\sigma}_i = \sum_n \bar{\sigma}_{in}, \quad (2.8)$$

and using (2.6) in (2.4), one obtains

$$k_r^{\text{ET}} = (8kT/\pi\mu_{X_2-M})^{1/2} \sum_i K_{\text{eq}}^i \bar{\sigma}_i. \quad (2.9)$$

RBC calculated k_r^{ET} using the quasibound H_2 spectrum of Waech and Bernstein¹⁷ to get K_{eq}^i and a restricted distorted-wave approximation with dumbbell model potentials to get $\bar{\sigma}_i$. From the results they noted that $\sigma_{in}(E)$ varied slowly with E , so that, to a good approximation, (2.7) becomes

$$\bar{\sigma}_{in} = \sigma_{in}(kT). \quad (2.10)$$

In addition, RBC found that a useful upper bound to $\bar{\sigma}_i$ was given by the simple hard-sphere gas-kinetic cross section,

$$\sigma_i^{\text{GK}}(kT) = \pi(r_{\text{MX}} + \frac{1}{2}\langle r^2 \rangle_i^{1/2})^2, \quad (2.11)$$

where r_{MX} is the classical turning point (obtained from a model potential) for an M - X collision with energy kT , and $\langle r^2 \rangle_i^{1/2}$ is the root-mean-square internuclear distance of complex X_2^i .

Let us now modify these last two equations to obtain a simple but reasonable estimate for $\bar{\sigma}_i$. If we let $\bar{\sigma}_{in}$ be given by

$$\bar{\sigma}_{in} = \sigma_{in}(kT) = P_{in} \sigma_i^{\text{GK}}(kT), \quad (2.12)$$

where P_{in} is the probability of a transition from state i to state n , then from (2.8) we have

$$\bar{\sigma}_i = P_i \sigma_i^{\text{GK}}(kT), \quad (2.13)$$

where P_i is the probability of a transition to any bound state,

$$P_i = \sum_n P_{in} \leq 1. \quad (2.14)$$

In X_2^i - M collisions, we expect that the sum of the probabilities of elastic collisions, of transitions to unbound states, and of transitions to other quasibound states is at least as large as P_i ; hence, we require that $P_i \leq \frac{1}{2}$. In fact, we take

$$P_i = \frac{1}{2}(\delta_i/\sinh\delta_i)^2. \quad (2.15)$$

Here P_i is further decreased by a factor which arises from the theory of inelastic collisions between systems interacting by means of a repulsive exponential potential,^{10,18,19}

$$V(r) = \epsilon \exp(-r/a). \quad (2.16)$$

In terms of the steepness parameter, a , of this potential, δ_i is given by^{10,18,19}

$$\delta_i(kT) = \pi(2\mu_{X_2-M}a^2/\hbar^2)^{1/2} [(kT+E_i)^{1/2} - (kT)^{1/2}]. \quad (2.17)$$

The factor involving δ_i in (2.15) ensures that P_i becomes small if E_i is large; in other words, the probability of a transition from state i to the bound region is small if i lies far from that region.

With these approximations, (2.9) becomes

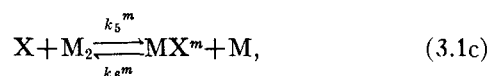
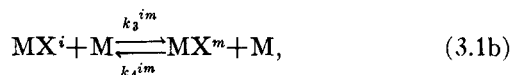
$$k_r^{\text{ET}} = (8kT/\pi\mu_{X_2-M})^{1/2} \sum_i P_i(kT) \sigma_i^{\text{GK}}(kT) K_{\text{eq}}^i. \quad (2.18)$$

In order to actually calculate k_r^{ET} , one needs to know the energies, E_i , and the internuclear distances, $\langle r^2 \rangle_i^{1/2}$, of those quasibound states that contribute appreciably to the rate; that is, those states which form and dissociate rapidly enough to maintain equilibrium with the reactant atoms yet have lifetimes much longer than those of nonresonant X - X collisions. (Specific criteria have been given by RBC.) Then, one needs an M - X potential of the form (2.16) to calculate δ_i and r_{MX} .

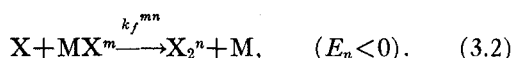
Substitution into (2.18) and summation gives the desired estimate of k_r^{ET} .

III. BOUND-COMPLEX MECHANISM

We now consider the bound-complex (BC) mechanism and develop a treatment of it which parallels the RBC theory for the ET mechanism. In detail the BC mechanism is



and



Equations (3.1) describe some possible processes for the formation and equilibration of MX dimers. Here m may be a bound ($E_m < 0$) or a quasibound ($E_m \geq 0$) rotation-vibration state of MX. In order to obtain third-order kinetics, we assume that all those dimer states MX^m that contribute appreciably to (3.2) are in equilibrium with X and M. Then the rate of formation of bound X_2 molecules via this mechanism is

$$dn_{X_2}/dt = k_r^{BC} n_X^2 n_M, \quad (3.3)$$

where

$$k_r^{BC} = \sum_m \sum_n k_f^{mn} K_{eq}^m. \quad (3.4)$$

Although this expression has the same appearance as (2.4), m now runs over bound states as well as quasibound, and k_f^{mn} is the specific rate constant for the exchange reaction (3.2) rather than the inelastic collision (2.2).

If an MX interatomic potential is known from which the properties of the rotation-vibration states of XM^m can be calculated, then K_{eq}^m can be obtained from equilibrium statistical mechanics,

$$K_{eq}^m = (g_m/g_X g_M) (2J_m + 1) \times \exp(-E_m/kT) (2\pi\hbar^2/\mu_{MX} kT)^{3/2}, \quad (3.5)$$

where $\mu_{MX} = m_X m_M / (m_X + m_M)$, and the other terms are as defined at (2.6).

Before discussing the determination of k_f^{mn} in (3.4), let us consider just which states m contribute appreciably. If M were chemically reactive, so that MX had many bound levels, one might expect the lowest levels of MX to be populated so slowly that they would contribute negligibly to the recombination rate. However, here we restrict M to be a chemically inert molecule or noble-gas atom, so that the few existing van der Waals dimers MX^m are all weakly bound. These should all be readily populated, and we expect MX to be

a "relaxed" complex⁴ (one in which all the states are in equilibrium with M and X). Shui, Appleton, and Keck¹⁴ give the condition for a relaxed complex formed via (3.1a) and (3.1b) as

$$\exp(-\epsilon_{MX}/kT) > n_X/n_M, \quad (3.6)$$

where ϵ_{MX} is the depth of the MX potential well. For the specific problems considered in this paper, this condition holds for all $T > 20^\circ\text{K}$. Furthermore, Reaction (3.1c) also produces MX dimers from M_2 dimers (provided they exist). This reaction is expected to have zero²⁰ activation energy thus keeping the complexes relaxed at even lower temperatures. Therefore, a relaxed complex was assumed at all temperatures of interest.

The specific bimolecular rate constants k_f^{mn} are related to the cross sections for the reactive collision (3.2) by equations similar to (2.6) and (2.7). To calculate k_r^{BC} accurately one must calculate accurate reactive cross sections. At present, the theory of reactive scattering is not well developed, and the calculation of accurate reactive cross sections requires heavy computations hardly justified by the crude intermolecular potential surfaces available. Hence, we seek a simpler way to estimate the needed cross sections. Reaction (3.2) has a negligible activation energy,²⁰ so that $\sigma_{mn}(E)$ is expected to be of gas-kinetic order and to vary slowly with E . Then, Eq. (2.10) holds and (3.4) reduces to

$$k_r^{BC} = (8kT/\pi\mu_{MX-X})^{1/2} \sum_m K_{eq}^m \bar{\sigma}_m, \quad (3.7)$$

where $\mu_{MX-X} = m_{MX} m_X / (m_{MX} + m_X)$.

Once again, we take

$$\bar{\sigma}_m = P_m(kT) \sigma_m^{\text{GK}}(kT), \quad (3.8)$$

where $P_m = \sum_n P_{mn}$ is the total probability of a reaction producing a bound X_2 molecule. For σ_m^{GK} we use the expression

$$\sigma_m^{\text{GK}} = \pi [(r_{XX} r_{MX})^{1/2} + \frac{1}{2} \langle r^2 \rangle_m^{1/2}]^2, \quad (3.9)$$

where r_{XX} is the classical turning point for a collision of energy kT between two X atoms. For the reaction probability, P_m , in the case that $E_m < 0$, we take

$$P_m = \frac{1}{3} G, \quad (3.10)$$

where $\frac{1}{3}$ is chosen as a reasonable steric factor, and G is the probability that the MX-X collision occurs on a potential-energy surface that can lead to bound X_2 molecules. For $E_m \geq 0$, we use²¹

$$P_m = \frac{1}{3} G (\delta_m / \sinh \delta_m)^2. \quad (3.11)$$

Here, P_m is smaller than for $E_m < 0$ because the successful reactive collisions must be vibrationally non-adiabatic and because the probability that the MX-X collision produces dissociation of MX is greater. In (3.11) we put²¹

$$\delta_m(kT) = \pi (2\mu_{MX-X} b^2 / \hbar^2)^{1/2} [(kT + E_m)^{1/2} - (kT)^{1/2}], \quad (3.12)$$

where b is the steepness parameter of the repulsive part of the MX-X potential.

With these approximations, the BC rate constant is

$$k_r^{\text{BC}} = (8kT/\pi\mu_{\text{MX-X}})^{1/2} \sum_m P_m(kT) \sigma_m^{\text{GK}}(kT) K_{\text{eq}}^m. \quad (3.13)$$

Using available interatomic potentials the rotation-vibration states of MX can be calculated as described in the next section, and with them k_r^{BC} is easily determined.

IV. ROTATION-VIBRATION STATES OF MX

To determine the rotation-vibration states of MX, we apply Connor's¹⁶ quasiclassical WKB methods. We now outline the procedures followed.

For bound states ($E_m < 0$) of MX, the energy levels were calculated by Gaussian integration of the potential-well phase integral (see Fig. 1),

$$\phi = \pi^{-1} \left(\frac{2\mu_{\text{MX}}}{\hbar^2} \right)^{1/2} \int_{r_1}^{r_2} (E - V_J)^{1/2} dr, \quad (4.1)$$

where V_J is the effective potential

$$V_J = V(r) + \hbar^2 J(J+1)/2\mu_{\text{MX}} r^2. \quad (4.2)$$

The energies, $E_m < 0$, were determined by the usual Bohr-Sommerfeld quantization condition

$$\phi = (\nu_m + \frac{1}{2})\pi, \quad \nu_m = 0, 1, 2, \dots \quad (4.3)$$

The root-mean-square internuclear distance was obtained from the WKB expectation value formula

$$\langle r^2 \rangle_m^{1/2} = \left[\int_{r_1}^{r_2} (E_m - V_J)^{-1/2} r^2 dr \right]^{1/2} \times \left[\int_{r_1}^{r_2} (E_m - V_J)^{-1/2} dr \right]^{-1/2}. \quad (4.4)$$

The energies of the quasibound states ($E_m \geq 0$) were determined using Connor's correction¹⁶

$$\phi + (2\pi)^{-1} \chi = (\nu_m + \frac{1}{2})\pi, \quad (4.5)$$

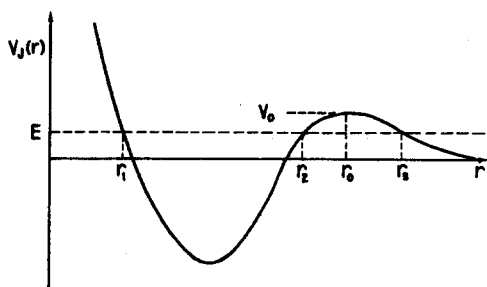


FIG. 1. Sketch of an effective interatomic potential, $V_J(r)$, for angular momentum $J \neq 0$. r_1 , r_2 , and r_3 are the classical turning points at energy E . $V_0 = V_J(r_0)$ is the height of the potential maximum, and r_0 is the position of the maximum.

TABLE I. Properties of the important quasibound states of H_2 . Here ν is the vibrational quantum number, J the rotational quantum number, E_i the energy in cm^{-1} relative to the separated atoms, $\langle r^2 \rangle_i^{1/2}$ is the root-mean-square internuclear distance in atomic units, and Γ_i is the energy width of the resonance in cm^{-1} . The E_i and Γ_i are from Ref. 29; the $\langle r^2 \rangle_i^{1/2}$ are from Refs. 10 and 24.

State i	ν_i	J_i	E_i (cm^{-1})	$\langle r^2 \rangle_i^{1/2}$ a.u.	Γ_i (cm^{-1})
1	14	5	44.1	6.55	17.4
2	14	6	81.5	6.95	104.
3	13	8	86.3	5.4657	1.48
4	13	9	191.4	5.95	52.3
5	12	11	211.4	5.0189	2.32
6	12	12	380.3	5.42	71.3
7	11	13	195.5	4.4386	0.004
8	11	14	475.7	4.8755	17.3
9	10	16	582.0	4.4536	2.84
10	9	18	722.4	4.1365	0.51

where the (small) correction term, χ , is given by

$$\chi = \theta - \theta \ln |\theta| + \arg \Gamma(\frac{1}{2} + i\theta). \quad (4.6)$$

Here Γ is the gamma function and θ is the barrier phase integral (see Fig. 1)

$$\theta = \pi^{-1} \left(\frac{2\mu_{\text{MX}}}{\hbar^2} \right)^{1/2} \int_{r_2}^{r_3} (V_J - E)^{1/2} dr. \quad (4.7)$$

The energy widths, Γ_m , of the quasibound states were obtained from¹⁶

$$\Gamma_m = [2\pi(\partial\phi/\partial E)_{E_m}]^{-1} \ln \{ 1 + \exp[-2\pi\theta(E_m)] \}. \quad (4.8)$$

The lifetime of the state, τ_m , is related to the width by

$$\tau_m = \hbar/\Gamma_m. \quad (4.9)$$

For energies below the top of the barrier, the numerical integrations to determine ϕ and θ are well defined. Above the barrier top it can be shown²² that the upper limit of the ϕ integral is r_0 , the position of the barrier maximum; hence, the ϕ integral is still easily calculated. However, the turning points r_2 and r_3 become complex²³ above the barrier top, so that determination of θ by numerical integration becomes difficult. To avoid this problem, it was noted from exact solutions for simple potential barriers (parabola, inverted Morse, etc.) that θ is an analytic function of E near $V_0 = V_J(r_0)$. Hence, an analytic form was fit to $\theta(E)$ for $E < V_0$ and used to extrapolate to energies above but near V_0 . The function,

$$\theta = (V_0/\hbar\omega_B) \ln(V_0/E), \quad (4.10)$$

where $\omega_B = (-V_0''/\mu_{\text{MX}})^{1/2}$ is the barrier frequency, was found to agree well with numerical values of θ calculated from realistic potentials. [For E very near V_0 , this reduces to the known result for a parabolic barrier,^{16,23} $\theta = (V_0 - E)/\hbar\omega_B$.]

Use of this approximate θ affects the calculated

TABLE II. Parameters used in the repulsive exponential potentials of the ET calculations. Values are from Ref. 10 and are in Hartree atomic units.

System	ϵ (a.u.)	a (a.u.)
He-H	2.832	0.5
Ar-H	20.93	0.5
H ₂ -H	7.696	0.5

energies of quasibound levels above the barrier negligibly since $\chi(\theta)$ in (4.5) is a small correction anyway, but its use does reduce the accuracy of the energy widths and lifetimes of levels above the barrier; they are probably good only to within a factor of 2.

V. CALCULATIONS AND RESULTS

The specific reactions considered were the recombination of H atoms in He, Ar, and H₂. The separate contributions of the BC and ET mechanisms were estimated for each of the three reactions.

A. Energy-Transfer Mechanism

The energies, E_i , and the internuclear distances, $\langle r^2 \rangle_i^{1/2}$, of the 10 contributing quasibound states of H₂, originally determined by Waech and Bernstein,¹⁷ have recently been redetermined accurately by LeRoy,²⁴ and we used his values (see Table I). The degeneracies needed in (2.5) are $g_H=4$, $g_i=3$ if J_i is odd, and $g_i=1$ if J_i is even. The parameters in the MH potential (2.16) were those of RBC (see Table II). The calculations using (2.18) were easily done, and the results are plotted in Figs. 2-4 together with those of RBC. Since RBC's distorted-wave approximation is known to give an upper bound, it is seen (in Fig. 2, for example) that our

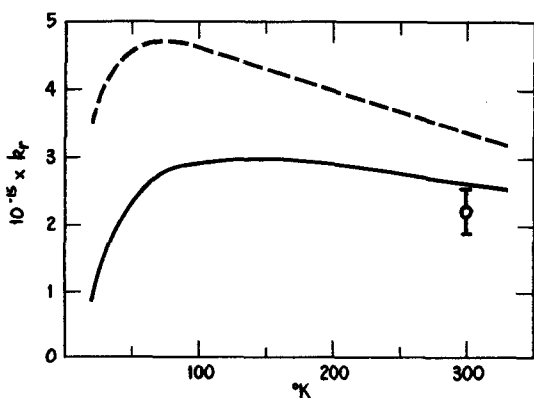


FIG. 2. Recombination rate constants for $H+H+He \rightarrow H_2+He$ in units of $\text{cm}^6/\text{mole}^2\text{-second}$. In this case $k_r = k_r^{\text{ET}}$. The dashed line is the RBC results; the solid line is the estimate of the present paper. The experimental point is from J. E. Bennett and D. R. Blackmore, Symp. Combust. 13th, Salt Lake City, 1971, 51 (1971).

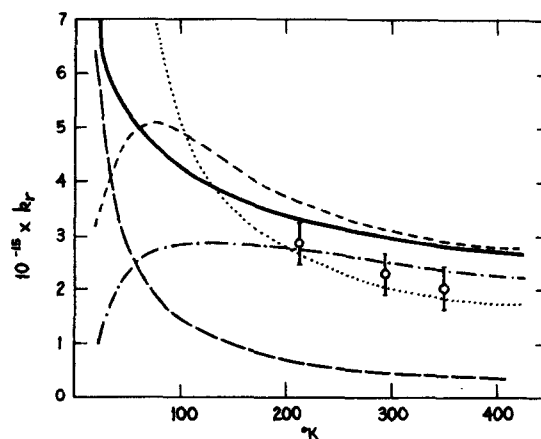


FIG. 3. Recombination rate constants for $H+H+Ar \rightarrow H_2+Ar$ in units of $\text{cm}^6/\text{mole}^2\text{-second}$. Solid line, present estimate of $k_r = k_r^{\text{BC}} + k_r^{\text{ET}}$; long dashes, present estimate of k_r^{BC} ; dot-dash, present estimate of k_r^{ET} ; short dashes, RBC's k_r^{ET} ; dotted line, results of Ref. 13; experimental points are from F. S. Larkin, Can. J. Chem. 46, 1005 (1968).

simple modifications still give reasonable estimates of k_r^{ET} .

B. Bound-Complex Mechanism: $H+H+He \rightarrow H_2+He$

The best available HeH interatomic potential is the MC SCF potential of Das and Wahl.²⁵ It is only 5.35°K deep at its equilibrium distance (6.9 a.u.) and is found to support no bound vibrational levels and no long-lived quasibound rotation-vibration states. Hence, k_r^{BC} calculated from (3.17) is zero at all temperatures, and the observable rate constant $k_r = k_r^{\text{BC}} + k_r^{\text{ET}}$ reduces to k_r^{ET} shown in Fig. 2.

C. Bound-Complex Mechanism: $H+H+Ar \rightarrow H_2+Ar$

No accurate ArH potential is available. The potential used was an empirical Lennard-Jones 12-6 potential determined from the molecular-beam value²⁶ of the strength parameter, $\epsilon r_e = 9.60 \times 10^{-4}$ a.u., and the known

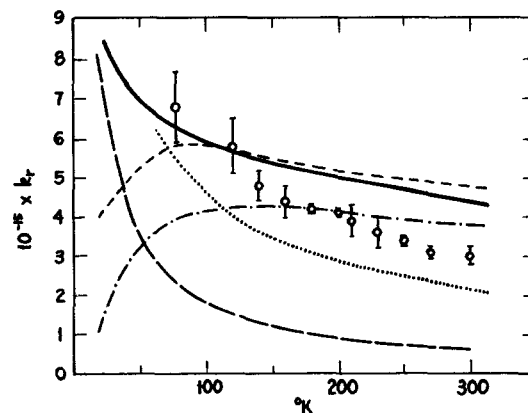


FIG. 4. Recombination rate constants for $H+H+H_2 \rightarrow 2H_2$. Units and notation are that of Fig. 3. The experimental points are from Ref. 12.

TABLE III. Rotation-vibration states of ArH calculated from a 12-6 potential with $\epsilon = 1.510 \times 10^{-4}$ a.u. and $r_e = 6.357$ a.u. V_0 is the height of the potential maximum in cm^{-1} ; r_0 its position in atomic units. The notation on the other quantities is that of Table I.

State m	ν	J	E_m (cm^{-1})	Γ_m (cm^{-1})	$\langle r^2 \rangle_m^{1/2}$ a.u.	V_0 (cm^{-1})	r_0 a.u.
1	0	0	-5.90	...	8.36	0.0	...
2	0	1	-4.02	...	8.51	0.25	18.08
3	0	2	-0.467	...	8.92	1.30	13.71
4	0	3	4.28	2.65	9.67	3.69	11.48

van der Waals coefficient,^{27,28} $C_6 = 2\epsilon r_e^6 = 19.93$ a.u. These give $\epsilon = 1.510 \times 10^{-4}$ a.u. (47.7°K) and $r_e = 6.357$ a.u. The ArH rotation-vibration states and their properties calculated from this potential are presented in Table III. Quasibound states whose widths were greater than half the vibrational level spacing were omitted.²⁹

Using the data in Table III and $g_m/g_{\text{HGAr}} = 1$, the K_{eq}^m were calculated from (3.5). In (3.9), r_{ArH} was obtained from the ArH 12-6 potential and r_{HH} from the known H_2 Morse potential. In this case $G = \frac{1}{2}$, and b in (3.12) was taken to be 0.2 Å as recommended by Herzfeld and Litovitz.³⁰

The resulting k_r^{BC} is plotted in Fig. 3 along with k_r^{ET} and the total rate constant $k_r = k_r^{\text{ET}} + k_r^{\text{BC}}$. Also plotted in Fig. 3 are the available experimental values and the phase-space results of Shui and Appleton.¹³

D. Bound-Complex Mechanism: $\text{H} + \text{H} + \text{H}_2 \rightarrow 2\text{H}_2$

The model used for $\text{H}_2\text{-H}$ was very crude. As in the works of RBC¹⁰ and Shui and Appleton,¹³ H_2 was treated as a structureless sphere, and the $\text{H}_2\text{-H}$ interaction was taken to be a 12-6 potential with parameters¹³ $\epsilon = 1.203 \times 10^{-4}$ a.u. (38°K) and $r_e = 6.42$ a.u. The rotation-vibration levels of this model are listed in Table IV. The turning point $r_{\text{H}_2\text{-H}}$ was obtained from this potential; the other parameters were those used in the previous (ArH) reaction. The results are plotted in Fig. 4 along with those of Shui and Appleton¹³ and the experimental results of Ham, Trainor, and Kaufman.¹²

VI. DISCUSSION AND CONCLUSIONS

While neither the k_r^{ET} nor the k_r^{BC} obtained in this work can be expected to be an accurate estimate, the two contributions were calculated in a consistent fashion, and one should be able to make a reasonable assessment of their relative importance.

The reason k_r^{ET} has a low-temperature maximum while k_r^{BC} has none, is that the ET mechanism involves only quasibound levels ($E_i \geq 0$) of X_2 whose equilibrium populations become small at low temperatures, while the BC mechanism involves shallow but truly bound ($E_m < 0$) states of MX whose populations become large at low temperatures. In addition, the probability of a transition from a quasibound state i to the bound region [see Eq. (2.17)] becomes small when E_i is greater than the average collisional energy.

For the recombination of H atoms in Ar or H_2 , one sees from the figures that the ET mechanism dominates at high temperatures, but the BC mechanism dominates at low temperatures, so that *no maximum in the total rate constant is predicted*. Agreement with experiment is good for such a simple theory.

For the recombination of H in Ar we also recalculated k_r^{BC} using the two ArH potentials used by Shui and Appleton.¹³ Both potentials lead to a k_r^{BC} as large or larger than the one shown, so that the resulting k_r has the same behavior (no maximum) as the one shown.

For H recombination in He, the Das-Wahl²⁶ potential implies that $k_r^{\text{BC}} = 0$, and we thus *predict that a maximum will be observed* in k_r . We note, however, that if the true HeH potential were as deep (38.4°K) as the CI potential of Miller and Schaefer,³¹ which has bound states, the BC mechanism would dominate at low temperatures, and k_r would have no maximum. To see how sensitive the existence of the maximum in k_r is to the existence of bound HeH vibrational levels, k_r^{BC} was recalculated using a 12-6 potential ($\epsilon = 12.2^\circ\text{K}$ and $r_e = 6.93$ a.u.) chosen to have only one rotationless vibrational level (bound by only 0.004°K) and no long-lived quasibound levels. The resulting k_r^{BC} was almost large enough to destroy the maximum in k_r , i.e., k_r was very flat at low temperatures. Thus, we con-

TABLE IV. Rotation-vibration states of $\text{H}_2\text{-H}$ calculated from a spherical model 12-6 potential with $\epsilon = 1.203 \times 10^{-4}$ a.u. and $r_e = 6.42$ a.u. The notation is that of Tables I and III.

State m	ν	J	E_m (cm^{-1})	Γ_m (cm^{-1})	$\langle r^2 \rangle_m^{1/2}$ a.u.	V_0 (cm^{-1})	r_0 a.u.
1	0	0	-1.81	...	9.94	0.0	...
2	0	1	+0.09	0.20	10.91	0.48	15.78
3	0	2	4.92	6.31	9.57	2.50	11.93

clude that the maximum in k_r is sensitive to the nature of the HeH potential and that experimental measurement of the rate of H recombination in He at low temperatures would give valuable information about the HeH potential. Observance of a clear maximum would mean that HeH has no bound vibrational levels. Absence of a maximum would be good evidence³² that the HeH potential is deep enough to support bound vibrational levels.

Shui and Appleton¹³ noted that the classical phase-space theory predicted no maximum in k_r even when the MH potential was taken to be purely repulsive. This is probably because their classical theory gives contributions from orbiting resonances (quasibound states) of all energies whereas the true spectrum (see Table I) is highly quantized and the lowest-lying quasibound state lies 63.5°K above the energy of the separated atoms.

Suppose we now consider the recombination of H atoms in the presence of third bodies M other than He, Ar, or H₂. It is expected that the MH potential for all such M (except possibly Ne) will be attractive enough to have bound vibrational states. Thus, k_r^{BC} should dominate at low temperatures and k_r should have no maximum.

For the recombination of atoms X which are heavier than hydrogen (or deuterium³⁴), the larger reduced mass results in more bound MX levels and a larger BC contribution. Furthermore, X₂ has lower-lying and more closely spaced quasibound levels than H₂, and the maximum in k_r^{ET} occurs at much lower temperatures where the BC mechanism is relatively even more important. Hence, we believe it unlikely that a low-temperature maximum will be observed in the rate of recombination of heavy atoms.

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