A Simple Method for Calculating Quantum Effects on the Temperature Dependence of Bimolecular Reaction Rates: An Application to CH$_4$ + H → CH$_3$ + H$_2$

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Abstract

The temperature dependence of the rate of the reaction CH$_4$ + H → CH$_3$ + H$_2$ is studied using classical collision theory with a temperature-dependent effective potential derived from a path integral analysis. Analytical expressions are obtained for the effective potential and for the rate constant. The rate constant expressions use a temperature-dependent activation energy. They give better agreement with the available experimental results than do previous empirical fits. Since all but one of the parameters in the present expressions are obtained from theory, rather than by fitting to experimental reaction rates, the expressions can be expected to be more dependable than purely empirical expressions at temperatures above 2000 K or below 350 K, where experimental results are not available.
I. INTRODUCTION

The validity of the Arrhenius expression for the rate constant of a bimolecular reaction, 
\[ k = A \exp(-E_a/RT), \]
where \( E_a \) is the activation energy and \( R \) is the gas constant, has long been the subject of controversy [1]. \( E_a \) is generally assumed to be independent of temperature, and any deviation from linear behavior in the plot of \( \log k \) vs. \( 1/T \) is attributed to temperature dependence in \( A \). Classical collision theory [2] suggests only a weak temperature dependence of the preexponential factor, of the form \( A \propto T^{1/2} \), while theoretical arguments based on transition-state theory (TST) with corrections for quantum mechanical tunneling [1,3] can predict a significantly different dependence.

We consider here the reaction
\[ \text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2. \]  
There exists an extensive literature of theoretical and experimental studies [4–14] for this reaction on account of its importance as an elementary reaction in hydrocarbon pyrolysis. The experimental results span the temperature range from 372 K up to almost 2000 K. TST studies [4–10] have predicted a distinct upward curvature in the Arrhenius plot, and an analysis by Shaw [5] of experimental results through the year 1978 generally supported this prediction. Subsequently, Sepehrad et al. [12] concluded that in fact a linear Arrhenius plot was more consistent with the data, after omitting some apparently unreliable earlier results and adding new results of their own. More recent analyses by Baulch et al. [13] and by Rabinowitz et al. [14] discerned curvature with \( A \propto T^3 \) and \( A \propto T^{2.11} \), respectively.

We propose an alternative theoretical approach to this problem, based not on transition-state theory but on classical collision theory with a temperature-dependent effective potential energy function. This approach is based on a path-integral analysis developed by Feynman [15,16] for problems in quantum statistical mechanics. He noted that the equation for the statistical density matrix is formally identical to that for the kernel that expresses the time dependence of the wavefunction of a quantum mechanical particle over a time interval that is taken to be negative and imaginary. Thus, calculations in statistical mechanics can be carried out using the path integral techniques of quantum dynamics. This idea can be used to derive an effective potential \( V_{\text{eff}} \) for the chemical reaction such that a classical mechanical calculation of the reaction rate with the effective potential is approximately equivalent to a quantum mechanical treatment using the actual potential \( V \) [17]. This simple approach was used previously to describe the diffusion of H on a Cu surface [18], and the results were later found to agree with those from an elaborate reaction-path variational TST calculation with semiclassical adiabatic tunneling corrections [19].

The path integral analysis transforms \( V \) into a temperature-dependent function \( V_{\text{eff}}(T) \), from which we obtain a temperature-dependent activation energy. Thus, our model for the chemical reaction is classical collision theory but with a temperature-dependent \( E_a \). We will include no temperature dependence in \( A \) other than the classical \( T^{1/2} \) factor. We will introduce a slight modification into the analysis so that the path-integral result, which is derived as a perturbation theory about the high-\( T \) limit, can be smoothly interpolated to the correct low-\( T \) result. For \( V \) we will use the empirical hydrocarbon potential of Brenner [20], which is constructed from Morse-type functions with modifications to take into account non-local effects.
II. METHOD

To calculate the partition function from the statistical density matrix it is sufficient to consider only paths that return to their starting point. The path integrals that need to be evaluated are very difficult on account of the large number of degrees of freedom needed to describe the many possible paths. However, if $\hbar/k_B T$ is small, where $k_B$ is the Boltzmann constant, then one can derive a simple approximate expression for the partition function,\[15,16]\]

$$Z = \left( \frac{mk_B T}{2\pi \hbar^2} \right)^{1/2} \int e^{-\beta V_{\text{eff}}(x)} dx, \quad (2)$$

where $\beta = 1/k_B T$ and

$$V_{\text{eff}}(x) = \frac{1}{\sqrt{2\pi \sigma}} \int_{-\infty}^{\infty} V(x + y) e^{-y^2/2\sigma^2} dy, \quad (3)$$

$$\sigma^2 = \hbar^2/12mk_B T. \quad (4)$$

The significance of this result is the fact that Eq. (2) has exactly the form of the classical partition function except that $V$ is replaced by the effective potential $V_{\text{eff}}$, which is just a Gaussian average of $V$ with a temperature-dependent standard deviation $\sigma$. Equation (2) is for a system with only one degree of freedom, but the extension to an arbitrary number of degrees of freedom is straightforward.

It has been suggested $^{[17]}$ that classical dynamics on the potential $V_{\text{eff}}$ could be used to simulate quantum dynamics on the true potential $V$. This would not be valid for the dynamics of a single particle, but it is a reasonable hypothesis for a statistical ensemble of particles as in a molecular dynamics simulation of a chemical reaction. In fact, it can be shown $^{[17]}$ that when $V_{\text{eff}}$ is used in place of $V$ in TST one obtains the standard Wigner tunneling correction.

This approach provides an appealing qualitative model for quantum effects. At a minimum of $V$, averaging over neighboring points according to Eq. (3) will increase the potential. This accounts for the fact that the minimum of $V$ is in practice inaccessible to the system on account of the impossibility of localizing a quantum mechanical particle. In effect, the averaging provides a zero-point energy correction. At a maximum, the averaging reduces $V$. In effect, this is a tunneling correction. At a saddle point of $V$, averaging over a given coordinate will reduce the potential if $V''$ is negative and increase it if $V''$ is positive. Elsewhere, $V$ can be approximated as a linear function, in which case the averaging in Eq. (3) will have little effect. At high $T$ the quantum effects will be small, because if the average kinetic energy is large then it is only rarely that a particle will be close enough to the potential surface to sense the difference between $V$ and $V_{\text{eff}}$. Accordingly, the standard deviation given by Eq. (4) goes to zero in the limit of infinite $T$.

At low $T$ the approximations used to derive Eq. (3) can be expected to lead to a significant error, since the system will spend much of its time in the quantum regions of $V$. However, a minor modification of the theory will ensure that it give the correct low-temperature limit.
At $T = 0$ K the system will be at rest at the nearest local minimum of $V$. The energy of the system will be the value of $V$ plus a zero-point energy correction. A minimum of $V$ in principle corresponds to a stable chemical species, for which the zero-point energy can be determined empirically from analysis of the vibrational spectrum. Thus, we can replace $T$ in Eq. (4) with

$$T_{\text{eff}} = T + T_0,$$

(5)

where $T_0$ is a constant chosen such that Eq. (3) reproduces the empirical zero-point energy of a known species.

Now consider the application of this theory to the hydrogen abstraction reaction, Eq. (1). We will treat this as a problem in two degrees of freedom $(x, y)$, where $x$ is the C—H distance for the reacting hydrogen and $y$ is the H—H distance for the reacting hydrogen. We will assume that the C—H—H configuration is linear along the reaction path. The angle $\theta$ between the reactive and nonreactive C—H bonds will be treated as a quadratic polynomial in $x$ that interpolates between $109.5^\circ$ for CH$_4$, $120^\circ$ for CH$_3$, and the transition-state geometry of $102.4^\circ$ at $x = 1.08 \, \text{Å}$ [7]. Then,

$$V_{\text{eff}}(x, y) = \frac{1}{2\pi \sigma_x \sigma_y} \int dz_y e^{-z_y^2/2\sigma_y^2} \int dz_x e^{-z_x^2/2\sigma_x^2} V(x + z_x, y + z_y),$$

(6)

where

$$\sigma_x^2 = \frac{\hbar^2}{12\mu_x k_B (T_{0,x} + T)}, \quad \sigma_y^2 = \frac{\hbar^2}{12\mu_y k_B (T_{0,y} + T)}.$$ 

(7)

Note that the mass in Eq. (3) has been replaced by the reduced mass $\mu_x = m_H(1+m_H/m_C)^{-1}$ or $\mu_y = m_H/2$.

For $V(x, y)$ we use Brenner’s potential I [20], which is a sum of two-body interactions

$$V(x, y) = V_{\text{CH}}(x, y) + V_{\text{HH}}(y, x).$$

(8)

The $V_{\text{CH}}$ and $V_{\text{HH}}$ each have the form

$$V_i(r, q) = f_i(r) \left\{ D_i^{(R)} \exp \left[ -\beta_i^{(R)} (r - r_i^{(e)}) \right] - B_i(r, q) D_i^{(A)} \exp \left[ -\beta_i^{(A)} (r - r_i^{(e)}) \right] \right\},$$

(9)

where $r$ is the coordinate of the primary, two-body, interaction while $q$ is the coordinate of the “environment.” Equation (9) has the general form of a Morse potential but is modified by the functions $f_i$ and $B_i$. $f_i(r)$ is a cutoff function that smoothly interpolates to zero in the limit of large $r$. $B_i(r, q)$ is a rather complicated function that models the effects of nearby atoms on the primary interaction. For given $(x, y)$ Eq. (3) can be evaluated by numerical quadrature. The values

$$T_{0,x} = 92K, \quad T_{0,y} = 582K$$

(10)

for the temperature shift parameters give agreement with the spectroscopically determined zero-point energies for CH$_4$ [21] and H$_2$ [22], respectively.
There is a minor inconsistency in using this procedure with the Brenner potential. For the C—H well depth Brenner simply used the bond energy of the CH molecule without subtracting the zero-point energy. Thus, we are in a sense adding zero-point energy to a potential that already includes it. This will make the calculated activation energy smaller than it ought to be. We will assume that any errors from this procedure will be insignificant, since the quantum effects for C—H interactions are much smaller than those for H—H interactions. However, in principle, one ought to refit the potential using the correct well depth. For the H—H potential, which causes most of the quantum effects, Brenner did use the correct well depth for H₂.

We find that it is possible to accurately approximate $V_{\text{eff}}$ with an analytic expression. Let $V_{\text{eff}} = \tilde{V}_{\text{CH}} + \tilde{V}_{\text{HH}}$, where

$$\tilde{V}_i(r, q) = \frac{1}{2\pi \sigma_r \sigma_q} \int dz_r e^{-z_i^2/2\sigma_r^2} \int dz_q e^{-z_q^2/2\sigma_q^2} V_i(q + z_q, r + z_r). \quad (11)$$

Note that Eq. (11) can be written as

$$\tilde{V}_i = \tilde{V}_i^{(0)} + \tilde{V}_i^{(1)} + \tilde{V}_i^{(2)} + \tilde{V}_i^{(3)},$$

where

$$\tilde{V}_i^{(0)}(r, q) = \frac{1}{\sqrt{2\pi \sigma_r}} \int dz_r e^{-z_i^2/2\sigma_r^2} \left[ D_i^{(R)} \int dz e^{-\beta(R)(r+z_i^{(e)})-z^2/2\sigma_r^2} - D_i^{(A)} B_i(r, q) \int dz e^{-\beta(A)(r+z_i^{(e)})-z^2/2\sigma_r^2} \right], \quad (13)$$

$$\tilde{V}_i^{(1)}(r, q) = \frac{1}{\sqrt{2\pi \sigma_r}} \int dz e^{-z_i^2/2\sigma_r^2} [f_i(r + z) - f_i(r)] \times \left[ D_i^{(R)} e^{-\beta(R)(r+z_i^{(e)})-z^2/2\sigma_r^2} - D_i^{(A)} B_i(r, q) e^{-\beta(A)(r+z_i^{(e)})-z^2/2\sigma_r^2} \right],$$

$$\tilde{V}_i^{(2)}(r, q) = -\frac{1}{2\pi \sigma_q \sigma_r} D_i^{(A)} \int dz_r e^{-z_i^2/2\sigma_r^2} \int dz_q e^{-z_q^2/2\sigma_q^2} \times \left[ B_i(r, q + z_q) - B_i(r, q) \right] f_i(r + z_r) e^{-\beta(A)(r+z_r^{(e)})}, \quad (15)$$

$$\tilde{V}_i^{(3)}(r, q) = -\frac{1}{2\pi \sigma_q \sigma_r} D_i^{(A)} \int dz_r e^{-z_i^2/2\sigma_r^2} \int dz_q e^{-z_q^2/2\sigma_q^2} \times \left[ B_i(r + z_r, q + z_q) - B_i(r, q + z_q) \right] f_i(r + z_r) e^{-\beta(A)(r+z_r^{(e)})}. \quad (16)$$

The term $\tilde{V}_i^{(0)}$ simply ignores the coordinate dependence of $f_i$ and $B_i$ for purposes of evaluating the integral. The integrals in Eq. (13) can be evaluated exactly, giving an expression identical to that for $V_i$ in Eq. (11) except with the prefactors $D_i$ replaced by the temperature-dependent parameters

$$\bar{D}_i^{(R)} = D_i^{(R)} \exp \left( \beta(R) \sigma_r \right)^2 / 2 \right], \quad \bar{D}_i^{(A)} = D_i^{(A)} \exp \left( \beta(A) \sigma_r \right)^2 / 2 \right]. \quad (17)$$

For the C—H interaction, we will use $\tilde{V}_{\text{CH}} \approx \tilde{V}_{\text{CH}}^{(0)}$ and ignore the three correction terms. For the H—H interaction, since $\sigma_r^2$ is over twice as large as $\sigma_q^2$, we will include all of the correction terms but replace them with approximate analytical expressions. Let
\[ V_{\text{HH}}^{(1)} = \phi_R^{(1)}(y) + B_{\text{HH}}(y, x)\phi_A^{(1)}(y), \]  

where
\[ \phi_R^{(1)}(y) = D_{\text{HH}}^{(R)} \int dz \left[ f_{\text{HH}}(y + z) - f_{\text{HH}}(y) \right] \exp \left[ -\beta^{(R)}(y - r^{(c)}_{\text{HH}} + z) - z^2/2\sigma_y \right], \]  

\[ \phi_A^{(1)}(y) = -D_{\text{HH}}^{(A)} \int dz \left[ f_{\text{HH}}(y + z) - f_{\text{HH}}(y) \right] \exp \left[ -\beta^{(A)}(y - r^{(c)}_{\text{HH}} + z) - z^2/2\sigma_y \right]. \]

We find in practice that the functions \( \phi_R^{(1)} \) and \( \phi_A^{(1)} \) can be fit quite accurately as sums of Gaussians,
\[ \phi^{(1)}_\alpha \approx h^{(1,1)}_\alpha e^{-\left(y-c^{(1,1)}_\alpha\right)^2/w^{(1,1)}_\alpha^2} + h^{(1,2)}_\alpha e^{-\left(y-c^{(1,2)}_\alpha\right)^2/w^{(1,2)}_\alpha^2}, \]

with the parameters \( h, c \) and \( w \) given by constants or by polynomials in \((T + T_{0,y})^{-1}\). The coefficients of these polynomials can be obtained by fitting to a set of exact values of the \( \phi^{(1)}_\alpha \) from numerical quadrature of Eqs. (19) and (20).

Another function that can be fit in terms of a sum of Gaussians is
\[ \phi^{(2)}(y, x) = -D_{\text{HH}}^{(A)} e^{-\beta^{(A)}(y-r^{(c)}_{\text{HH}})} \int dz \left[ B_{\text{HH}}(y, x + z) - B_{\text{HH}}(y, x) \right] e^{-z^2/2\sigma_x}. \]  

\[ \approx f_{HH}(y) \left[ h^{(2,1)} e^{-\left(y-c^{(2,1)}\right)^2/w^{(2,1)}^2} + h^{(2,2)} e^{-\left(y-c^{(2,2)}\right)^2/w^{(2,2)}^2} \right]. \]

In this case the parameters are polynomials in \((T + T_{0,y})^{-1}\) and \( y \). The second correction term is given by
\[ V_{\text{HH}}^{(2)}(y, x) = \phi^{(2)}(y, x) \left[ f_{HH}(y)e^{\beta^{(A)}2\sigma^2/2} - \phi^{(1)}/D_{\text{HH}}^{(A)} \right]. \]

Finally, we express the third correction term as
\[ V^{(3)}(y, x) = f_{CH}(x)f_{HH}(y)\phi^{(3)}(x, y)/(T + T_{0,y}), \]

with \( \phi^{(3)} \) fit as a polynomial in \( x \) and \( y \).

Using polynomials of at most degree 2 for the parameters we can fit the exact Gaussian averaged potential with an accuracy of \( \pm 0.005 \) kcal/mol in the vicinity of the transition state for \( T \) as low as 300 K. A table of fitting parameters and a full error analysis for the \( \phi^{(j)} \) will be presented elsewhere.

III. RESULTS

We obtain a temperature-dependent activation energy as the difference between \( V_{\text{eff}} \) evaluated at the \( \text{CH}_5 \) saddle point and at the reactants well. In Fig. 1 the solid curve shows our quantum mechanical result for \( E_a \), calculated from the Gaussian average with standard deviations \( \sigma_i \) in terms of effective temperatures according to Eqs. (7). This result is in effect an interpolation between the high-temperature path integral analysis and the empirical low-temperature limit. For \( T > 300 \) K we find that \( E_a \) can be accurately fit with a quadratic polynomial in \( T^{-1} \),

\[ \text{III. RESULTS} \]
\[ E_a(T) \approx 12.07 \text{ kcal mol}^{-1} - (741.2 \text{ kcal mol}^{-1} \text{ K}) T^{-1} + (7.47 \times 10^4 \text{ kcal mol}^{-1} \text{ K}^2) T^{-2}. \] 

(25)

The dashed curve shows the result of a purely high-temperature analysis, with the \( \sigma_i \) in terms of the actual temperature. The two results are in general agreement down to approximately 600 K. (The unsteadiness in the curves at low \( T \) is due to uncertainty in the determination of the geometry of the activated complex.)

The corresponding Arrhenius curves are shown in Fig. 2, where they are compared with classical collision theory (the dotted curve, corresponding to a temperature-independent activation energy equal to \( \lim_{T \to \infty} E_a(T) \)), with a recent multidimensional semiclassical variational TST analysis \[ \text{(24)} \] (the dash-dot curve), and with experimentally determined reaction rates \[ \text{(23)} \]. Our theoretical treatment yields the activation energy, but not the Arrhenius prefactor, which must be fit to the experimental results. The theory for the \( T \) dependence of \( E_a \) is exact in the high-temperature limit. Therefore, it is best to consider only high-temperature rate constants for the purpose of determining the prefactor. We will assume that the measurements by Rabinowitz et al. \[ \text{(14)} \], from the recent Brookhaven flash photolysis-shock tube study, are the most reliable of the high temperature results. Fitting the classical collision theory expression

\[ k = A_0 T^{1/2} e^{-E_a/RT} \]

(26)

to the Brookhaven results, with our theoretical formula for the function \( E_a(T) \), gives \( \log_{10}(A_0 / \text{cm}^3\text{s}^{-1}) = -11.536 \). It is clear from Fig. 2 that the Gaussian average with \( T_{\text{eff}} \) is in better agreement with the low temperature measurements than are the Gaussian average with the actual \( T \) or the classical theory with \( E_a \) independent of temperature.

IV. DISCUSSION

A. Comparison with transition-state theory

It can be seen in Fig. 2 that our theory (the Gaussian average with \( T_{\text{eff}} \)) and Truong’s TST \[ \text{(10)} \] both predict a distinct upward curvature in the Arrhenius plot at low temperature. They disagree at high temperature, with our analysis predicting a slower reaction rate than that predicted by the TST study.

Our theoretical approach differs from TST in the way in which we describe the classical dynamics and in the way we include quantum effects. In TST the expression for the rate constant can be expressed approximately in the form \( k = a_0 T^x \Gamma e^{-E_a/RT} \), where \( a_0 \) and \( x \) are temperature-independent constants and \( \Gamma(T) \) is a quantum correction \[ \text{(24)} \]. The reactants and the transition state are assumed to be in equilibrium, and the factor \( T^x \) comes from the resulting equilibrium constant, expressed as a ratio of partition functions. For \( \text{CH}_4 + \text{H} \rightleftharpoons \text{CH}_5 \) the value of \( x \) is 3/2. Thus, we can express the TST result in the form

\[ k = a_0 T^{3/2} e^{-E_a/RT}, \]

(27)

with \( E_a \) equal to a constant for classical TST and \( E_a(T) = E_a^{(cl)} \ln (\Gamma(T)) \) for quantum TST. Our approach is to use collision theory for the classical dynamics, which gives \( x = 1/2 \),
and to determine $E_a(T)$ directly from the temperature-dependent effective potential instead using one of the standard semiclassical expressions for $\Gamma(T)$. However, we could just as well have used the effective-potential values for $E_a$ in Eq. (27) instead of using the collision-theory expression Eq. (26).

A clearer comparison of theory and experiment is given by Fig. 3, which shows the difference between $\log_{10} k$ and $\log_{10} k_{cl}$, where $k_{cl}$ is the rate constant predicted by classical theory. We obtain $k_{cl}$ from Eq. (26) by setting $E_a = 12.07$ kcal/mol, which is the value given by the Brenner potential. We use the same value of $A_0$ as with the $T$-dependent $E_a$, since the quantum and classical theories have the same high-$T$ limit. The solid curve in Fig. 3 corresponds to our quantum collision theory, using Eq. (26) with the effective-potential $E_a(T)$ and with $T_{eff}$ in the standard deviations for the Gaussian averaging. The dotted curve results from using this same $E_a(T)$ in the TST expression Eq. (27). The solid curve is clearly in better agreement with the experimental points.

Figure 3 also shows Truong’s variational TST results [10] (the dash-dot curve), which were based on $ab\ initio$ calculations of the potential, and it shows results from a variational TST study by Joseph et al. [8] (the dash-dot-dot curve), which used an analytical semiempirical potential energy function. The prefactor $a_0$ used for our effective-potential TST was chosen to give agreement with the high-temperature experimental results. Note, however, that different values of $a_0$ would lead to qualitative agreement between the effective-potential TST and the variational TST studies. Although there is a fair amount of scatter in the experimental results, our quantum collision theory and the TST studies appear to agree equally well with the low-temperature experimental points, where quantum effects are expected to be most important. This is consistent with previous studies for other systems [7, 17], which showed agreement between quantum effects calculated from semiclassical TST quantum corrections and those calculated from effective potentials.

At high temperatures the results from Truong’s TST results lie above most of the experimental points. The results from semiempirical TST are in better agreement with experiment, but extrapolation of them to higher $T$ would give a larger rate constant than does our collision theory. Since barrier recrossing becomes more likely at higher $T$, one can expect that TST will increasingly overestimate the reaction rate as $T$ increases. Truong used an $ab\ initio$ result for the barrier height (16.3 kcal/mol) that was higher than the value used by Joseph et al. (12.9 kcal/mol) or the value used by us (12.07 kcal/mol). However, as $T$ increases, the value used for $E_a$ becomes less significant than the value used for the exponent $x$. At high $T$ the assumption on which collision theory is based, that only the translational degrees of freedom of the colliding molecules need to be taken into account, is reasonable since the lifetime of the activated complex will typically be too short for there to be significant conversion of translational energy into vibrational or rotational energy before it breaks apart. At lower temperature TST will be more accurate than collision theory, but the error introduced by using $x = 1/2$ will become relatively less important than errors in the value of $E_a$. The excellent agreement with experiment from our quantum collision theory would seem to indicate that this is what happens for the particular reaction considered here. In any case, the approach we have presented for calculating quantum effects can be used with TST as well as with collision theory, and it is conceivable that for other reactions, at intermediate temperatures, TST might be the more appropriate choice.
B. Comparison of analytical expressions for the rate constant

In Fig. 4 we compare our calculated results with various “best fits” of the experimental points [5,12–14]. The fitting functions are given in Table 1. For Fig. 4 we computed our rate constants using analytic expressions for $E_a(T)$. The solid curve was computed using the quadratic fitting function in Eq. (25). This curve is almost indistinguishable from the corresponding curve in Fig. 3, which was computed from our actual values for the $E_a$. The dashed curve results from a linear fit for $E_a(T)$, which yields an expression for $k$ that has only 3 parameters. Most of the empirical fits in Fig. 4 are also 3-parameter expressions.

Our results in Fig. 4 are in better agreement with the experimental points than are any of the empirical expressions. The expressions of Shaw [5] and of Baulch et al. [13] (the dash-dot and dash-dot-dot curves, respectively) seem to be too low in the low-$T$ region. Both of these fits were carried out before the data from the high-$T$ measurements by Rabinowitz et al. [14] were available. Shaw’s fit agrees with these new data while the fit by Baulch et al. appears to be too high in the high-$T$ region. Not surprisingly, the fit by Rabinowitz et al. (the dash-dot-dot-dot curve) seems accurate at high-$T$. However, it appears to be too high at low $T$. Note that only one of our parameters (the prefactor $A_0$) is fit to the experimental results. The remaining parameters are calculated theoretically. (Of course, other experimental results, such as the bond dissociation energies of CH$_4$ and H$_2$, enter our theory indirectly since we based our calculations on an empirical potential function [20].)

The most significant difference between our expressions for $k$ and the various fits is the behavior that is predicted at very high $T$, above 2000 K. Our expressions predict a significantly lower reaction rate in this region than do any of the others. Unfortunately, there are no available experimental results above 2000 K with which to compare. The quantum effects at very high $T$ are insignificant. Therefore, the accuracy of our results in that region depends only on the accuracy of the activation energy given by the Brenner potential and on the accuracy of the Arrhenius expression from classical collision theory.

C. Conclusions

We have shown that the Arrhenius expression from classical collision theory with $E_a$ expressed as a polynomial in $1/T$ gives agreement with the experimental measurements for the rate constant for CH$_4$+H that is at least as good as that from fits that include $T$ dependence in the prefactor. This is especially striking since only one of the parameters in our expressions is determined by fitting to the experimental points. The fact that the other parameters are determined theoretically suggests that our expressions are more likely to be dependable at temperatures above 2000 K or below 350 K, where experimental results are unavailable.

These calculations require that the potential energy surface be known. Otherwise, there is no choice but to choose a functional form for $k(T)$ containing parameters that are all determined by fitting to measured reaction rates. Traditionally, an Arrhenius expression is used with the temperature dependence in the prefactor. However, the theory developed here provides a justification for choosing a functional form with temperature dependence in the activation energy.
The success of our theory at describing this reaction rate over a wide temperature range has two important implications for molecular dynamics simulations of chemical reactions. First, it supports the use [23] of the Brenner hydrocarbon potential in those studies. This is an empirical potential, parameterized to a data set consisting of properties of stable chemical species, yet it seems to be able to accurately model the unstable CH$_5$ transition state, since the curvature of the Arrhenius plot depends sensitively on the topography of the potential in the vicinity of the saddle point.

The second implication is that it is possible to use a classical molecular dynamics computation, with a Gaussian-averaged effective potential, to model processes in which quantum effects are important. The evaluation of the potential function is the most time-consuming step in these computations. Therefore, the use of numerical quadrature to perform the Gaussian averaging would be impractical. However, the use of our analytic approximation, given by Eqs. (12) through (24), will have only a minor effect on the computational cost.

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TABLE I. Expressions for the rate constant for CH\textsubscript{4}+H → CH\textsubscript{3}+H\textsubscript{2}.

| Rate constant, cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} | Method | Reference |
|---------------------------------|--------|-----------|
| $k = 3.02 \times 10^{-10} \exp(-6631/T)$ | empirical fit | Sepehrad et al.$^a$ |
| $k = 2.35 \times 10^{-17} T^2 \exp(-4449/T)$ | empirical fit | Shaw$^b$ |
| $k = 2.18 \times 10^{-20} T^3 \exp(-4045/T)$ | empirical fit | Baulch et al.$^c$ |
| $k = 6.4 \times 10^{-18} T^{2.11} \exp(-3900/T)$ | empirical fit | Rabinowitz et al.$^d$ |
| $k = 2.63 \times 10^{-12} T^{1/2} \exp \left(-6076/T + 3.730 \times 10^5/T^2 - 3.76 \times 10^7/T^3 \right)$ | collision theory with effective potential; quadratic expression for $E_a$ | this study$^e$ |
| $k = 2.63 \times 10^{-12} T^{1/2} \exp \left(-6076/T + 2.759 \times 10^5/T^2 \right)$ | collision theory with effective potential; linear expression for $E_a$ | this study$^d$ |

$^a$Ref. [12].
$^b$Ref. [5].
$^c$Ref. [13].
$^d$Ref. [14].
$^e$From Gaussian average of potential with $T_{\text{eff}}$ in the standard deviations.
FIGURES

FIG. 1. Temperature dependence of the activation energy. The dotted line shows the classical, temperature-independent, result. The dashed curve was calculated from the Gaussian-averaged potential using the standard deviations given by Eq. (4). The solid curve was calculated from the Gaussian-averaged potential with $T$ in Eq. (4) replaced by $T_{\text{eff}}$ according to Eqs. (7) and (10).

FIG. 2. Arrhenius plot of rate constant vs. 1000 K/$T$ for the reaction CH$_4$+H $\rightarrow$ CH$_3$+H$_2$, with $k$ in units of cm$^3$ molecule$^{-1}$ s$^{-1}$. Experimental measurements, from Refs. [5], [12], and [14], are indicated by dots. The dotted line corresponds to classical collision theory, while the dashed and solid curves correspond to our quantum theory using $T$ and $T_{\text{eff}}$, respectively, in the standard deviations. The dash-dot curve shows results from Truong’s variational TST [10].

FIG. 3. Difference between log$_{10}$ $k$ and log$_{10}$ $k_{\text{cl}}$ vs. 1000 K/$T$, where $k_{\text{cl}}$ is the rate constant from classical collision theory with temperature-independent $E_a$. The units of $k$ are cm$^3$ molecule$^{-1}$ s$^{-1}$. The symbols indicate experimental points from the following references: Rabinowitz et al. [14] (+); Sepehrad et al. [12] (◇); and the various studies reviewed by Shaw [5] (◇). The dashed and solid curve shows results from the present study, using $T_{\text{eff}}$ in the standard deviations of the Gaussian average. The dotted curve corresponds to classical TST, according to Eq. (27), with $E_a(T)$ from the Gaussian average. The dash-dot curve corresponds to Truong’s variational TST [10], which uses ab initio calculations for the potential energy. The dash-dot-dot curve corresponds to the variational TST of Joseph et al. [8], which uses a semiempirical potential function (“J3”).

FIG. 4. Difference between log$_{10}$ $k$ and log$_{10}$ $k_{\text{cl}}$ vs. 1000 K/$T$, using the analytical expressions for $k(T)$ in Table 1. $k_{\text{cl}}$ is the rate constant from classical collision theory with temperature-independent $E_a$. The units of $k$ are cm$^3$ molecule$^{-1}$ s$^{-1}$. The symbols indicate experimental points, labeled as in Fig. 3. The dotted, dash-dot, dash-dot-dot, and dash-dot-dot-dot curves are the empirical fits from Sepehrad et al. [12], Shaw [5], Baulch et al. [13], and Rabinowitz et al. [14], respectively. The solid and dashed curves are from the present study with a quadratic and a linear fit, respectively, for $E_a$. 

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