Semi-Empirical Extrapolation and Estimation of Rate Constants for Abstraction of H From Methane by H, O, HO, and O_2

Robert Shaw

Chemistry Department, Lockheed Palo Alto Research Laboratory, 3251 Hanover Street, Palo Alto, California 94304

It has been concluded that for extrapolating rate constants of atom transfer reactions to and from high temperatures, a useful form of the rate constant is $k=AT^2\exp(-C/T)$, where A and C are fitted constants. For $k/[\mathrm{cm^3/(mol\ s)}]$ and T/K, on the basis of previous experimental data, the values of log A and C for the following reactions are: $H+CH_4=H_2+CH_3$, log A=7.15, C=4449; $O+CH_4=OH+CH_3$, log A=6.71, C=3240; $HO+CH_4=H_2O+CH_3$, log A=6.93, C=1485 and $O_2+CH_4=O_2H+CH_3$, log A=6.93, C=26153. At all temperatures, abstraction by HO is faster than by O. The form of the rate constant is equivalent to assuming that $\Delta C_p{}^{\circ\ddagger}$, the heat capacity at the constant pressure of activation, is zero. When $\Delta C_p{}^{\circ\ddagger}$ was estimated and assumed to be constant (in principle, a more accurate assumption than $\Delta C_p{}^{\circ\ddagger}=0$), the fit to the experimental data was slightly worse. It is confirmed that at 400 to 700 K, the kinetic and thermodynamic equilibrium constants for the reaction $H+CH_4=H_2+CH_3$ are significantly different. (At 1340 K, they are in agreement.)

Key words: Estimated rate constants; hydrogen abstraction; methane combustion.

1. Introduction

The original goal of this research was to address the problem [1][1] of extrapolating rate constants to combustion temperatures by using a previously-developed [2] technique on two sets of reactions, namely (1) to (4)

$$H+CH_4=H_2+CH_3 \tag{1}$$

$$O+CH_4=HO+CH_3 \tag{2}$$

$$HO+CH_4=H_2O+CH_3 \tag{3}$$

$$O_2+CH_4=O_2H+CH_3 \tag{4}$$

and reactions of the type

$$W+XYZ=WX+YZ \tag{5}$$

where W, X, Y, and Z are H or O atoms. The results for reaction (5) have already been published. For completeness, they are shown in table 1.

Almost at the end of the research it became clear that an approach simpler than the earlier one fitted the data even better. The simpler approach is to fit the data to the equation

$$k=AT^2\exp(-C/T), \tag{6}$$

where k is the rate constant, A and C are constants, and T is in kelvins.

The principle of both methods is outlined here.

From transition state theory,

$$\mathrm{int}\ k=(\kappa T/h)K_c{}^{\circ\ddagger} \tag{7}$$

$$=(\kappa T/h)R'\,TK_p{}^{\circ\ddagger} \tag{8}$$

$$=(\kappa T/h)R'\,T\exp(\Delta S_T^{\circ\ddagger}/R)\exp(-\Delta H_T^{\circ\ddagger}/RT) \tag{9}$$

where int k is the rate constant per transferable atom and has units of $\mathrm{cm^3/(mol\ s)}$, κ is Boltzman's constant, h is Planck's constant, $K_c{}^{\circ\ddagger}$ is the equilibrium constant of activation in units of concentration, $K_p{}^{\circ\ddagger}$ is the same in pressure units, $R'=82$ atm $\mathrm{cm^3/(mol\ K)}$, $R=1.987$ cal/(mol K)[2], and $\Delta S_T^{\circ\ddagger}$ is the entropy of activation at T in units of cal/(mol K), and $\Delta H_T^{\circ\ddagger}$ is the enthalpy of activation at T in units of cal/mol.

If the rate constant is expressed in the form

$$\mathrm{int}\ k=AT^B\exp(-C/T) \tag{10}$$

and if $\Delta C_p{}^{\circ\ddagger}$ is assumed to be constant, then

$$A/(\mathrm{cm^3/mol\ s\ K})=[(R'\kappa/h)\ 298^{-(\Delta C_p{}^{\circ\ddagger}/R)}]\ \exp[(\Delta S_{298}^{\circ\ddagger}-\Delta C_p{}^{\circ\ddagger})/R] \tag{11}$$

$$B=2+(\Delta C_p{}^{\circ\ddagger}/R) \tag{12}$$

$$\mathrm{C/(kcal/mol)}=(\Delta H_{298}^{\circ\ddagger}\ -298\ \Delta C_p{}^{\circ\ddagger})/R \tag{13}$$

If $\Delta C_p{}^{\circ\ddagger}/R=-2$, then eq (10) reduces to the Arrhenius equation. If $\Delta C_p{}^{\circ\ddagger}/R=0$, then eq (10) reduces to eq (6). The technique for estimating $\Delta C_p{}^{\circ\ddagger}=$ constant for reactions (1) to (4) is described in the next section.

---

[1] Figures in brackets indicate literature references at the end of this paper.

[2] 1 cal=4.184 J.

TABLE 1. Summary of estimated rate constants for W+XYZ=WX+YZ, where W, X, Y, and Z are H and O atoms, and for which $\Delta C_p{}^{\circ\ddagger}/R = -1.25 \pm (0.25 \text{ to } 1.75)$

Reaction	No. of transferable atoms	$\Delta S^{\circ\ddagger}_{298}$ / cal/(mol K)	ΔH°_{298} / (kcal/mol)	$k = AT^B \exp(-C/T)$ cm³/(mol s)		
				log A	B	C
$H+O_2H = HO+OH$	1	−22.0	−0.74	11.06	0.75	0
$H+O_3 = HO+O_2$	2	−22.0	−0.74	11.36	0.75	0
$O+O_2H = O_2+OH$	1	−22.0	−0.74	11.06	0.75	0
$H+HO_2 = H_2+O_2$	1	−22.0	−0.74	11.06	0.75	0
$HO+HO = H_2O+O$	2	−27.0	−0.74	10.27	0.75	0
$HO+H_2 = H_2O+H$	2	−27.0	2.39	10.27	0.75	1.58
$O+O_3 = O_2+O_2$	2	−27.0	2.39	10.27	0.75	1.58

2. Estimation of the Heat Capacity of Activation, $\Delta C_p{}^{\circ\ddagger}$

Estimation of $\Delta C_p{}^{\circ\ddagger}$ is done in the exothermic direction to avoid contributions from the overall heat capacity. From JANAF values [4] for heats of formation at 298 K, reactions (1) to (4) in the exothermic direction are:

$$H + CH_4 = H_2 + CH_3 \qquad (1)$$

$$CH_3 + HO = CH_4 + O \qquad (-2)$$

$$HO + CH_4 = H_2O + CH_3 \qquad (3)$$

$$CH_3 + HO_2 = CH_4 + O_2 \qquad (-4)$$

If electronic heat capacity is neglected then the heat capacities of the reactants and the transition state (TS) are each given by the sum of the translational, rotational, and vibrational heat capacities, plus the gas constant. The translational and rotational heat capacities are known exactly [5], so the problem is to estimate the change in vibrational heat capacity on going from the reactants to the TS. The vibrational heat capacity is composed of contributions from stretches, bends, and hindered internal rotations. The stretches of the TS are assumed equal to those of the reactants, plus the reaction coordinate. None of the reactants have hindered internal rotations and their bends are assumed to be unchanged in the TS. The TS on the other hand has some extra bends and hindered internal rotations. Bends vary from 0 to R [5], so each may be assigned an average value of $R/2 \pm R/2$. Similarly, over most of the temperature range hindered internal rotations vary from $R/2$ to R, giving an average of $3R/4 \pm R/4$.

For reaction (1), $C_p{}^{\circ}(H) = 5R/2$; $C_p{}^{\circ}(CH_4) = 8R/2 + C_p{}^{\circ}{}_{vib}(CH_4)$; and $C_p{}^{\circ}(H \ldots H \ldots CH_3) = 8R/2 + C_p{}^{\circ}{}_{vib}(H \ldots H \ldots CH_3)$. Assuming the TS to be nonlinear, it has $3n-6=12$ frequencies of which 5 are stretches and 7 are deformations. Of the 5 stretches, 4 are assumed to be those in CH_4 and 1 is the reaction coordinate. Of the 7 deformations, 6 are bends and 1 is an internal rotation. Of the bends, 5 are assumed to be those in CH_4, leaving 1 bend which contributes $R/2 \pm R/2$ and 1 internal rotation which contributes $3R/4 \pm R/4$. That is $\Delta C_p{}^{\circ\ddagger} = 8R/2 + 5R/4 \pm 3R/4 - 5R/2 - 8R/2 = -5R/4 \pm 3R/4$.

For reaction (2), $C_p{}^{\circ}(CH_3) = 8R/2 + C_p{}^{\circ}{}_{vib}(CH_3)$; $C_p{}^{\circ}(HO) = 7R/2 + C_p{}^{\circ}{}_{vib}(HO)$; and $C_p{}^{\circ}(CH_3 \ldots H \ldots O) = 8R/2 + C_p{}^{\circ}{}_{vib}(CH_3 \ldots H \ldots O)$. Assuming the TS to be nonlinear, it has $3n-6=12$ frequencies of which 5 are stretches and 7 are deformations. Of the stretches, 3 are assumed to be those in CH_3, 1 is assumed to be that in HO, and the other is the reaction coordinate. Of the 7 deformations, 3 may be assumed equal to those in CH_3 leaving 4 deformations of which 3 are bends at $R/2 \pm R/2$ each and 1 internal rotation at $3R/4 \pm R/4$. That is, $\Delta C_p{}^{\circ\ddagger} = 8R/2 + 9R/4 \pm 7R/4 - 8R/2 - 7R/2 = -5R/4 \pm 7R/4$.

For reaction (3), $C_p{}^{\circ}(HO) = 7R/2 + C_p{}^{\circ}{}_{vib}(HO)$; $C_p{}^{\circ}(CH_4) = 8R/2 + C_p{}^{\circ}{}_{vib}(CH_4)$; and $C_p{}^{\circ}(HO \ldots H \ldots CH_3) = 8R/2 + C_p{}^{\circ}{}_{vib}(HO \ldots H \ldots CH_3)$. Assuming the TS to be nonlinear, it has $3n-6=15$ frequencies of which 6 are stretches and 9 are deformations. Of the stretches, 4 are assumed to equal those in CH_4, 1 is assumed equal to that in HO, and 1 is the reaction frequency. Of the 9 deformations, 5 are assumed equal to those in CH_4, leaving 4 of which 2 are bends at $R/2 \pm R/2$ each, and 2 are internal rotations at $3R/4 \pm R/4$ each. That is $\Delta C_p{}^{\circ\ddagger} = 8R/2 + 5R/2 \pm 3R/2 - 7R/2 - 8R/2 = -R \pm 3R/2$.

For reaction (4); $C^{\circ}{}_p(CH_3) = 8R/2 + C^{\circ}{}_{p\,vib}(CH_3)$; $C_p{}^{\circ}(HO_2) = 8R/2 + C_p{}^{\circ}{}_{vib}(HO_2)$; and $C_p{}^{\circ}(CH_3 \ldots H \ldots O_2) = 8R/2 + C_p{}^{\circ}{}_{vib}(CH_3 \ldots H \ldots O_2)$. Assuming the TS to be nonlinear, it has $3n-6=15$ frequencies of which 6 are stretches and 9 are deformations. Of the 6 stretches, 3 are assumed equal to those in CH_3, 2 are assumed equal to those in HO_2, and 1 is the reaction frequency. Of the 9 deformations, 3 are assumed equal to those in CH_3, 1 is assumed equal to that in HO_2, leaving 5 of which 3 are bends at $R/2 \pm R/2$ each and 2 are internal rotations at $3R/4 \pm R/4$ each. That is, $\Delta C_p{}^{\circ\ddagger} = 8R/2 + 6R/2 \pm 4R/2 - 8R/2 - 8R/2 = -R \pm 2R$.

The results are summarized in table 2.

Insertion of the values of $\Delta C_p{}^{\circ\ddagger}$ from table 2 into eq (10) gives, for reactions (1) and (−2):

$$\text{int } k = 10^{15.87} \exp(\Delta S^{\circ\ddagger}_{298}/R)\, T^{0.75} \exp[-(\Delta H^{\circ\ddagger}_{298} + 0.74)/RT], \qquad (14)$$

and for reactions (3) and (−4):

TABLE 2.—Summary of estimated heat capacities of activation, $(\Delta C_p^{\circ\ddagger}/R)$

Reaction	Reactants tr+rot	Transition State (TS)			Difference TS—Reactants $=\Delta C_p^{\circ\ddagger}/R$
		tr+rot	extra bends	hind. int. rot	
$H+CH_4=$ $H\ldots H\ldots CH_3$	13/2	8/2	1/2±1/2	3/4±1/4	−5/4±3/4
$CH_3+HO=$ $CH_3\ldots H\ldots O$	15/2	8/2	3/2±3/2	3/4±1/4	−5/4±7/4
$HO+CH_4=$ $HO\ldots H\ldots CH_3$	15/2	8/2	1±1	3/2±1/2	−1±3/2
$CH_3+HO_2=$ $CH_3\ldots H\ldots O_2$	16/2	8/2	3/2±3/2	3/2±1/2	−1±2

int $k=10^{15.14}\exp(\Delta S^{\circ\ddagger}_{298}/R)\,T\exp$

$$[-(\Delta H^{\circ\ddagger}_{298}+0.59)/RT]. \qquad (15)$$

3. The Reaction $H+CH_4=H_2+CH_3$

Previously measured rate constants for reaction (1) are listed in table 3 and are shown in figures 1 to 3. Most of the points were plotted directly from papers [6, 7 to 13]. Nalbandyan and Gorban's results [14], reported as Arrhenius parameters by Kondratiev [15], were plotted as a single point, calculated from the Arrhenius parameters at the middle of the reciprocal temperature range. Panfilov's results [16] and those of Bush and Dyer [17] were treated the same way. Jamieson and Brown's values [18] were plotted as three points, each of which represented four or five original points. Fenimore and Jones' results [19] were corrected by more recent [20] values for their reference reaction (16):

$$H+N_2O=HO+N_2. \qquad (16)$$

Roth and Just's 16 values [21] were averaged as a single point using their own [21] result for their reference reaction (17):

$$CH_4+M=CH_3+H+M \qquad (17)$$

Klein, McNesby, Scheer, and Schoen [22] measured k_{19}/k_{18} and k_{20}/k_{18}

$$D+D_2CO=D_2+DCO \qquad (18)$$

$$D+CH_4=DH+CH_3 \qquad (19)$$

$$D+H_2=DH+H. \qquad (20)$$

From their ratio of k_{19}/k_{20}, from an assumption that $k_{19}/k_{20}=k_1/k_{21}$

$$H+H_2=H_2+H, \qquad (21)$$

and from Westenberg and de Haas' value [23] for reaction (21) k_1 was calculated.

Kurylo and Timmons' earlier work [24] has been revised [8] so the earlier results were not plotted in fig-

TABLE 3. Data points used in figures 1 to 3 for the reaction $H+CH_4=H_2+CH_3$ [a]

Authors, Year	Ref.	*a*	*b*	*c*	Authors, Year	Ref.	*a*	*b*	*c*
RJ 1975	[21] [b]	13.04	6.50	0.54	D LW 1967	[12]	10.6	4.69	1.11
BLP 1976	[10]	11.85	5.61	0.76	ANM–Y 1964	[13]	10.47	4.58	1.13
		12.30	5.92	0.65	P 1964	[16] [b]	10.27	4.44	1.22
		12.67	6.33	0.60	W 1968	[7]	10.8	5.02	1.29
		12.88	6.42	0.59	BNW 1967	[11]	10.45	4.67	1.29
PM 1973	[2]	12.51	6.09	0.62	NG 1961	[14] [b]	9.98	4.27	1.39
FJ 1962	[19] [b]	11.79	5.62	0.82	KMSS 1959	[22] [b]	10.22	4.49	1.36
		11.96	5.73	0.77			10.13	4.42	1.39
		12.15	5.82	0.68			9.95	4.27	1.45
		12.48	5.98	0.56			9.81	4.18	1.53
KHT 1970	[8]	10.36	4.63	1.37			9.45	3.86	1.61
		10.05	4.38	1.47	JB 1964	[18] [b]	8.50	3.12	2.04
		9.56	4.03	1.70			8.84	3.30	1.70
		8.77	3.37	2.00			9.68	3.89	1.28
		8.93	3.54	2.03	BL 1954	[9]	7.37	2.23	2.69
		8.13	2.86	2.32			7.64	2.41	2.43
		8.23	2.96	2.36			7.76	2.48	2.29
BD 1976	[17] [b]	11.10	5.10	1.00	CD/J 19	[25] [b]	12.0	5.76	0.75

[a] Where $a=\log\,[k/\{\mathrm{cm^3/(mol\ s)}\}]$, $b=\log\,[(k/T^2)/\{\mathrm{cm^3/mol\cdot s\cdot K^2}\}]$, and $c=10^3\mathrm{K}/T$.

[b] See text.

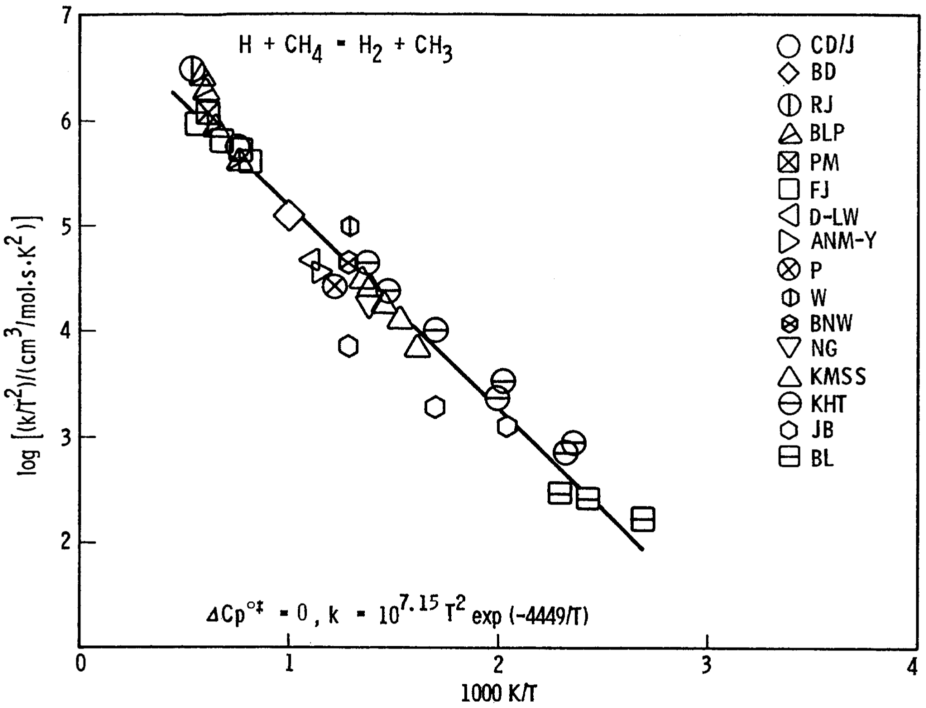

FIGURE 1. Comparison of measured rate constants for the reaction $H+CH_4=H_2+CH_3$ with the equation $k=10^{7.15}T^2\exp(-4449/T)$ $cm^3/(mol\ s)$. The data points are in table 3.

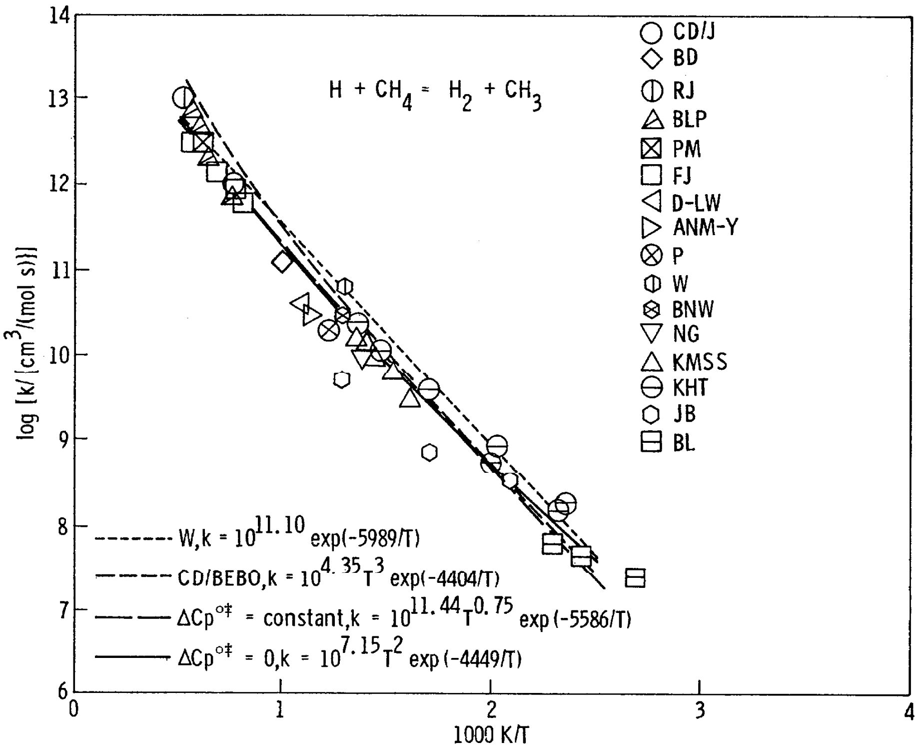

FIGURE 2. Comparison of measured rate constants for the reaction $H+CH_4=H_2+CH_3$ with several evaluations The data points are in table 3.

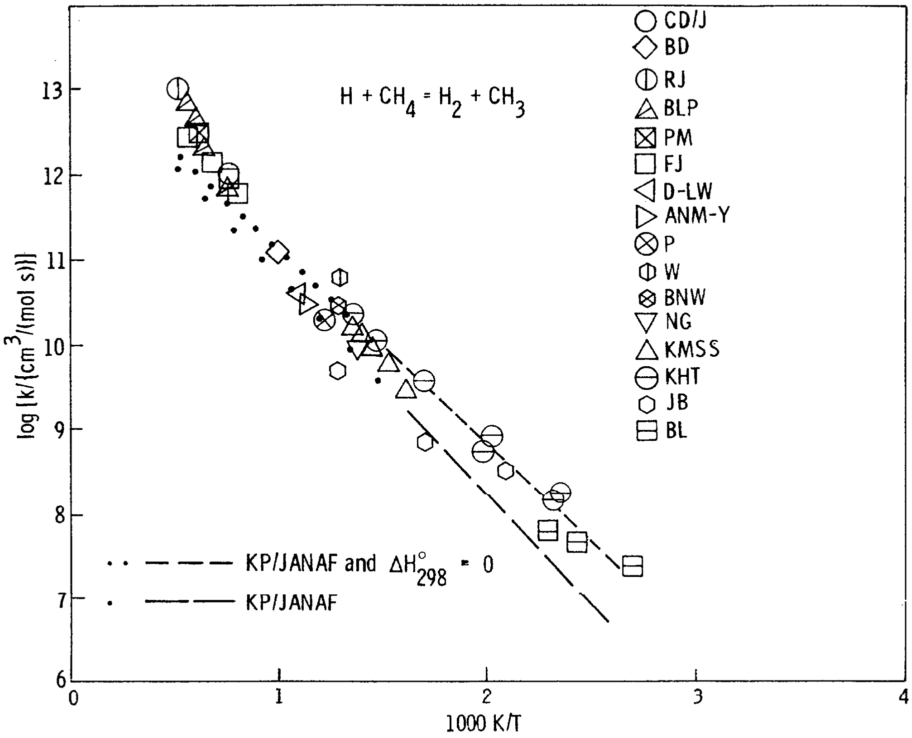

FIGURE 3. Comparison of measured rate constants for the reaction $H+CH_4=H_2+CH_3$ with an evaluation based on the reverse reaction [29], JANAF thermochemical data [4], and JANAF thermochemical data adjusted to give $\Delta H^\circ_{298}=0$. The data points are in table 3.

ure 1. Clark and Dove [25] have measured $k_{-1}=10^{10.66}$ cm^3/(mol s) at 1340 K. The JANAF [4] value for K_1 at this temperature is $10^{1.36}$, giving $k_1=10^{12.02}$cm^3/(mol s) at 1340 K.

Benson [25,26] has pointed out that in general rate constants in the middle of an Arrhenius plot are more accurate than at the extremes because experimental problems are less severe at intermediate temperatures. From the experimental data in figure 1, $k_1=10^{9.9}$ cm^3/(mol s) at 667 K has been selected as the best single rate constant for reaction (1).

3.1. $\Delta Cp^{\circ\ddagger}=0$

In figure 1, rate constants in the form log (k/T^2) are plotted against reciprocal temperature. The best straight line was drawn through the value of the best rate constant at 667 K and through the low temperature data, giving

$$k_1=10^{7.15}T^2\exp(-4449/T). \qquad (22)$$

3.2. $\Delta Cp^{\circ\ddagger}=$ constant

Previously [3] it was found for reaction (5) that $\Delta S^{\circ\ddagger}_{298}=-22$ cal/(mol K). It is reasonable to expect that $\Delta S^{\circ\ddagger}_{298}$ for reaction (1) will be similar to that for reactions like reaction (5) (see table 1 for examples) because the greatest loss of entropy in each case is the loss of the translational entropy of the atom. Substitution of int $k_1=10^{-0.6}k_1$ (methane has four abstractable hydrogen atoms) and $\Delta S^{\circ\ddagger}_{298}=-22$ cal/(mol K) into eq (14) gave

$$k_1=10^{11.66}T^{0.75}\exp(-5940/T)\ \text{cm}^3/(\text{mol s}). \qquad (23)$$

When k_1 was calculated from 400 to 2000 K using eq (23) it was found to fit the experimental data in figure 1 reasonably well, except at 400 K where the calculated value was about half a power of ten lower than the experimental results. When $\Delta S^{\circ\ddagger}_{298}=-23$ cal/(mol K) was used

$$k_1=10^{11.44}T^{0.75}\exp(-5586/T)\ \text{cm}^3/(\text{mol s}). \qquad (24)$$

3.3. Heat of Formation of Methyl

There is an interesting side issue concerning reaction (1). Kerr and Parsonage [29] have critically evaluated the data for reaction (−1)

$$CH_3+H_2=CH_4+H. \qquad (-1)$$

They recommend $k_{-1}=10^{11.93}\exp(-5486/T)$cm^3/(mol s) between 370 and 700 K. Kerr and Parsonage point out a discrepancy between k_{-1} and a value calculated from $k_{-1}=k_1/K_1$, Walker's evaluation [7] of k_1, and JANAF data [4] for the equilibrium constant K_1. The difference is shown in figure 3, where the lower line is given by $k_1=k_{-1}K_1$, where k_{-1} is Kerr and Parsonage's recommended value (which I accept between 370 and 700 K), and K_1 is from JANAF. Thus there is a difference between the kinetic and thermodynamic equilibrium constants for reaction (1) in this temperature range. At 1340 K, the discrepancy disappears as Clark and Dove's value for k_{-1} and the JANAF value for K_1 at 1340 K give a value for k_1 that is in good agreement with rate constants measured directly by others at the same temperature.

If the discrepancy exists only at low temperature, and if the rate constants for reaction (1) are accurate (as claimed by Kurylo [30] and, also, if the rate constants for reaction (−1) are accurate, then Chupka's value [31] for the heat of formation of the methyl radical is in error. However, on the other hand, Rosenstock [32] has pointed out that Stockbauer's [33] finding of nearly zero (<0.6 kcal/mol) kinetic energy release at threshold for the photoionization fragments of methane supports the validity of Chupka's value. McCulloch and Dibeler [34] have recently measured $\Delta Hf^{\circ}_{0}(\mathrm{CH_3}) = 35.7 \pm 0.1$ kcal/mol and it is in excellent agreement with Chupka's value of 35.6±0.2 kcal/mol. Furthermore, Smith's hydrocarbon pyrolyses [35] are consistent with Chupka's value.

Equation (24) is shown in figure 2 and gives a good fit to the experimental data, except at the lowest and highest temperatures. Clark and Dove's BEBO calculation [28]

$$k_1 = 10^{4.35} T^3 \exp(-4404/T) \ \mathrm{cm^3/(mol\ s)} \qquad (25)$$

shown in figure 2, gives excellent agreement with eq (24) up to about 700 K and then is significantly higher.

Figure 2 shows that eq (24) and (25) are essentially linear below 700 K, but then start to curve upward, with eq (25) curving more steeply. This is a consequence of eq (10)

$$k = AT^B \exp(-C/T)$$

because it follows that $d^2 \ln k / d(1/T)^2 = BT^2$. In other words, the curvature of plots of log k versus $1/T$ is more noticeable at high temperatures and for large values of B.

Also shown in figure 2 is Walker's evaluation [7]

$$k_1 = 10^{11.10} \exp(-5989/T) \ \mathrm{cm^3/(mol\ s)}. \qquad (26)$$

Equation (26) fits the data at high and low temperatures but overestimates most of the data at intermediate temperatures so it is not recommended.

Furthermore, although the total error limit for estimating $\Delta C_p{}^{\circ\ddagger}$ for reaction (1) is quite large ($\Delta C_p{}^{\circ\ddagger} = -5R/4 \pm 3R/4$), it turns out that the contributing errors tend to cancel. For example, at sufficiently high temperature for all the vibrations to be classical, $\Delta C_p{}^{\circ\ddagger} = -1$, a difference of only 1/4 not 3/4 from the average value.

Nevertheless, if the discrepancy between the kinetic and thermodynamic rate constants is indeed due to an error in the heat of formation of the methyl radical, then the issue may be resolved by making reaction (1) thermoneutral at 298 K, and the value of $\Delta Hf^{\circ}_{298}(\mathrm{CH_3})$ is 33.6 kcal/mol. This then is just within Golden, Walsh, and Benson's measurement [36] of 34.1±0.5 kcal/mol. The value of 33.6 kcal/mol is 1.22 kcal/mol less than the JANAF value. The upper line in figure 3 was calculated from

$$k_1 = k_{-1} K_1 \exp(614/T) \qquad (27)$$

where k_{-1} is Kerr and Parsonage's value and K_1 is from JANAF and $614 = 1220/R$.

4. The Reaction $\mathrm{O+CH_4=OH+CH_3}$

Previously measured rate constants for reaction (2) are shown in figures 4 and 5 and are listed in table 4. In 1973, Herron and Huie [37] critically evaluated the data on reaction (2) and recommended 4 sets of rate constants [38 to 41] which were plotted on figure 5 together with their recommended Arrhenius equation $k = 10^{13.32} \exp(-4550/T)$. Froben's results [42] were divided by 3.8 for stoichiometry, following Herron and Huie's practice. Brabbs and Brokaw's results [43] were averaged in figure 4 and plotted as published in figure 5. Other results [13, 44 to 47] were plotted as published. Also shown in figure 5 are two points calculated by Mayer and Schieler [48], using the BEBO technique.

4.1. $\Delta Cp^{\circ\ddagger} = 0$

In figure 4, rate constants in the form log (k/T^2) are plotted against reciprocal temperature. The best straight line drawn through Herron and Huie's 4 sets of rate constants is

$$k_2 = 10^{6.71} T^2 \exp(-3240/T) \ \mathrm{cm^3/(mol\,s)}. \qquad (28)$$

4.2. $\Delta Cp^{\circ\ddagger} = \text{constant}$

From the experimental data, the best single rate constant was selected to be $k_2 = 10^{9.30}$ cm³/(mol s) at 500 K. At 500 K, the JANAF value of K_2, multiplied by exp $(614/T)$ for the modified heat of formation of methyl, is $10^{1.10}$. That is $k_{-2} = k_2/K_2 = 10^{8.20}$ cm³/(mol s) at 500 K. $\Delta S^{\circ\ddagger}_{298}$ for reaction (−2) was estimated as −30 cal/(mol K) from an estimate of −23 cal/(mol K) for $\Delta S^{\circ\ddagger}_{298}$ of reaction (2), [based on the same value for reaction (1)], and the overall value of 7.3 cal/(mol K) for ΔS°_{298} of reaction (2) from JANAF. Substituting the values for $k_{-2} = \mathrm{int}\ k_{-2} = 10^{8.2}$ cm³/(mol s) and $\Delta S^{\circ\ddagger}_{298} = -30$ cal/(mol K) into eq (14) gives

$$k_{-2} = 10^{9.31} T^{0.75} \exp(-3602/T) \ \mathrm{cm^3/(mol\,s)}. \qquad (29)$$

From eq (29), K_2, and $k_2 = k_{-2} K_2$, values of k_2 were calculated at 400, 500, 667, 1000, and 2000 K and a line was drawn in figure 5. Herron and Huie's recommended Arrhenius plot and eq (28) are also shown.

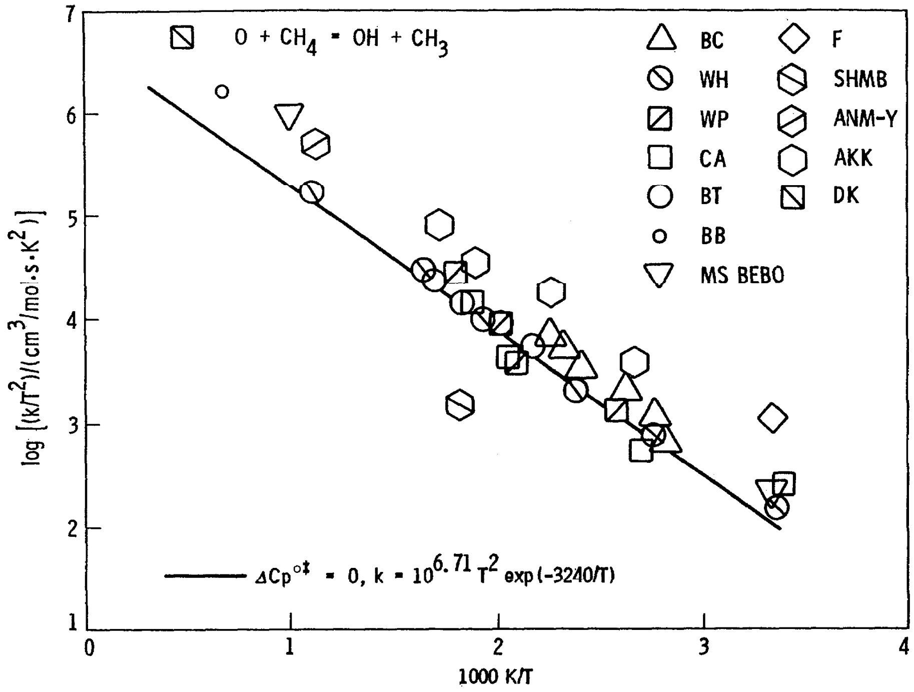

FIGURE 4. Comparison of measured rate constants for the reaction $O+CH_4=OH+CH_3$ with the equation $k=10^{6.71}T^2\exp(-3240/T)$ $cm^3/(mol\ s)$. The data points are in table 4.

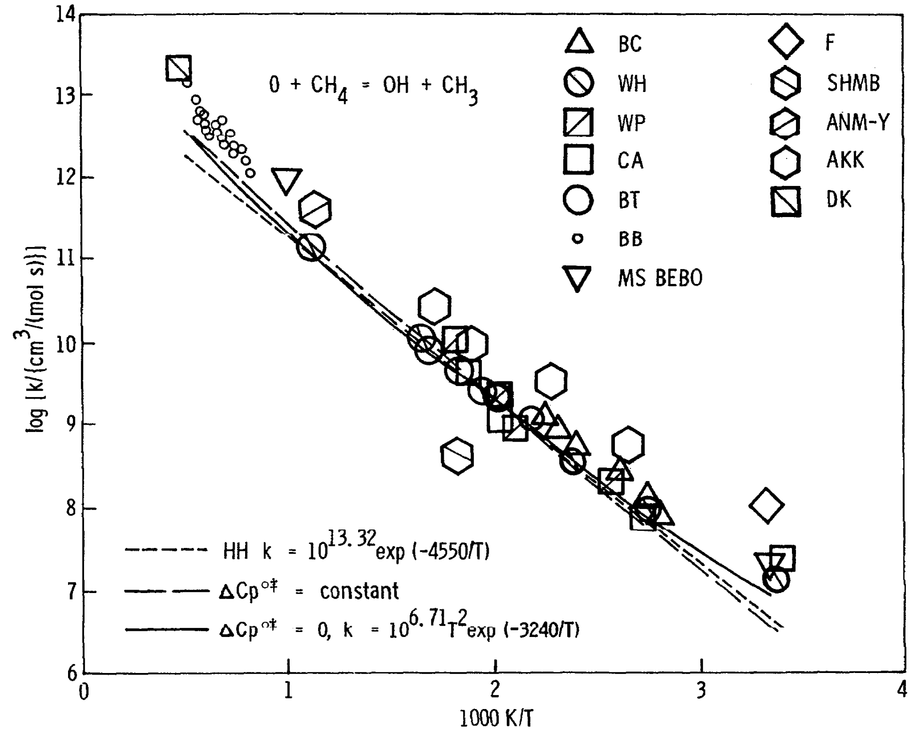

FIGURE 5. Comparison of measured rate constants for the reaction $O+CH_4=OH+CH_3$ with several evaluations. The data points are in table 4.

TABLE 4. Data points used in figures 4 and 5 for the reaction $O+CH_4=OH+CH_3$ [a]

Authors, Year	Ref.	a	b	c	Authors, Year	Ref.	a	b	c
WH 1969		7.12	2.18	3.37	BB 1974	[43]	12.33		0.78
		7.99	2.87	2.76			12.37		0.74
		8.56	3.32	2.39			12.27		0.74
		9.42	4.0	1.94			12.41		0.71
		10.06	4.49	1.65			12.38		0.70
		11.14	5.23	1.11			12.46		0.69
WP 1967	[41]	8.30	3.12	2.58			12.74		0.68
		8.95	3.59	2.10			12.66		0.66
		9.36	3.97	2.02			12.33		0.83
		10.04	4.55	1.80			12.61		0.66
CA 1965	[38]	7.34	2.4	3.39			12.56		0.65
		7.83	2.7	2.72			12.50		0.63
		9.04	3.67	2.06			12.55		0.62
		9.62	4.17	1.88			12.68		0.60
BT 1967	[40]	9.08	3.76	2.18			12.72		0.57
		9.34	3.95	2.01	MS 1968	[48]	7.3	2.34	3.33
		9.65	4.17	1.83			12.0	6.0	1.0
		9.92	4.38	1.69	BC 1974	[44]	7.38	2.84	2.82
BB 1974	[43]						7.62	3.06	2.76
(Average Value)		12.54	6.21	0.68			7.93	3.33	2.63
BB 1974	[43]	12.32		0.79			8.24	3.56	2.41
		12.53		0.73			8.43	3.72	2.32
		12.55		0.67			8.48	3.85	2.26
		12.57		0.66	F 1968 [b]	[42]	8.02	3.06	3.33
		12.58		0.65	SHMB 1971	[45]	8.68	3.2	1.82
		12.77		0.60	ANM–Y 1964	[13]	11.60	5.71	1.13
		12.79		0.58	AKK 1963	[47]	8.76	3.61	2.67
		12.95		0.55			9.56	4.28	2.28
		13.19		0.50			10.00	4.56	1.90
		12.06		0.82			10.45	4.92	1.72
		12.21		0.80	DK 1971	[46]	13.37	6.73	0.48

[a] Where $a=\log [k/\{cm^3/(mol\ s)\}]$, $b=\log [(k/T^2)/\{cm^3/mol\cdot s\cdot K^2\}]$, and $c=10^3 K/T$.

[b] See text.

5. The Reaction $HO+CH_4=H_2O+CH_3$

The problem of plotting individual rate constants on a single graph from 24 references [6, 11, 12, 19, 49 to 68] was avoided by assigning one point per reference. Log k's and reciprocal temperatures were averaged from tables, graphs, and Arrhenius equations in all cases except Bradley, Capey, Fair, and Pritchard's result [52], when I used the Leeds-recommended value [69] for the reference reaction $HO+H_2=H_2O+H$. The results are listed in table 5 and are shown in figures 6 and 7.

5.1. $\Delta Cp°^{\ddagger}=0$

Zellner and Steinert [58] recommended $k_3=10^{9.71}$ cm^3/(mol s) at 298 K as a reliable value. In figure 6, rate constants in the form log (k/T^2) are plotted against reciprocal temperature. The best straight line drawn through the best rate constant at 298 K gives

$$k_3=10^{6.93}T^2\exp(-1485/T) \qquad (30)$$

The fit to the experimental data is good.

5.2. $\Delta Cp°^{\ddagger}=$constant

From Zellner and Steinert's [58] value of k_3 at 298 K, eq (15), int $k_3=10^{-0.6}k_3$, and a value of $\Delta S^{\circ\ddagger}_{298}=-27$ cal/(mol K) (the same as for $HO+H_2$ [3]),

$$k_3=10^{9.34}T\cdot\exp(-1787/T)\ cm^3/(mol\ s). \qquad (31)$$

Equation (31) is drawn in figure 7.

Comparison of measured and estimated rate constants shows that equation (31) fits the experimental data reasonably well except at the highest temperatures. Also shown in figure 7 are Zellner and Steinert's statistical fit,

$$k_3=10^{3.54}T^{3.08}\exp(-1010/T)\ cm^3/(mol\ s), \qquad (32)$$

which gives a good fit to the measured data, except perhaps being too high at the highest temperatures, and the Arrhenius lines of Wilson [70] and of Davis, Fischer, and Schiff [68]. Wilson's line is a good fit at high temperatures, but is slightly high at intermediate and low temperatures. Davis, Fischer, and Schiff's line is a good fit at low temperatures but is significantly low at high temperatures.

TABLE 5. Data points used in figures 4 and 5 for the reaction $HO+CH_4=H_2O+CH_3$[a]

Authors, Year	Ref.	*a*	*b*	*c*	*d*	*e*
WOF 1969	[49]	13.00	6.36	0.48	—	1750 to 2000
WF 1961	[50]	13.30	6.81	0.57	—	1650 to 1840
FJ 1961	[19]	13.29	6.92	0.65	—	1225 to 1800
F 1963	[51]	13.29	6.92	0.65	3271	1360 to 1810
PM 1973	[6]	12.54	6.25	0.72	3030	1100 to 1900
BCFP[b] 1976	[52]	12.70	6.47	0.77	—	1300
DW 1967	[12]	12.50	6.28	0.78	2670	1285
P 1967	[53]	12.00	5.84	0.83	—	1200
EHW 1976	[54]	12.61	6.68	1.08	—	780 to 1200
H 1966	[55]	11.68	5.92	1.32	—	798
BNW 1967	[11]	11.88	6.12	1.32	—	773
BCHM 1965	[56]	11.68	5.92	1.32	—	773 to 623
BEHW 1968	[57]	11.92	6.16	1.32	—	773
ZS[b] 1976	[58]	10.65	5.33	2.20	—	300 to 900
GM 1975	[59]	10.36	5.16	2.51	—	381 to 416
AK 1964	[60]	9.78	4.59	2.53	—	323 to 513
G 1970	[61]	10.32	5.17	2.66	—	378
HN 1967	[62]	10.60	5.49	2.80	2520	300 to 425
MKA 1974	[63]	10.07	4.98	2.86	1850	290 to 440
WW 1967	[65]	9.81	4.85	3.33	2516	300
CDH 1976	[66]	9.66	4.71	3.36	—	298
HE 1976	[67]	9.76	4.81	3.36	—	298
OPC 1975	[64]	9.59	4.65	3.39	—	295
DFS 1974	[68]	9.61	4.68	3.42	1710	240 to 373

[a] Where $a=\log [k/\{cm^3/(mol\ s)\}]$, $b=\log [(k/T^2)/\{cm^3/mol\cdot s\cdot K^2\}]$, $c=10^3K/T$, $d=$(activation energy/R)/K, and $e=$(temperature range of study/K)

[b] See text.

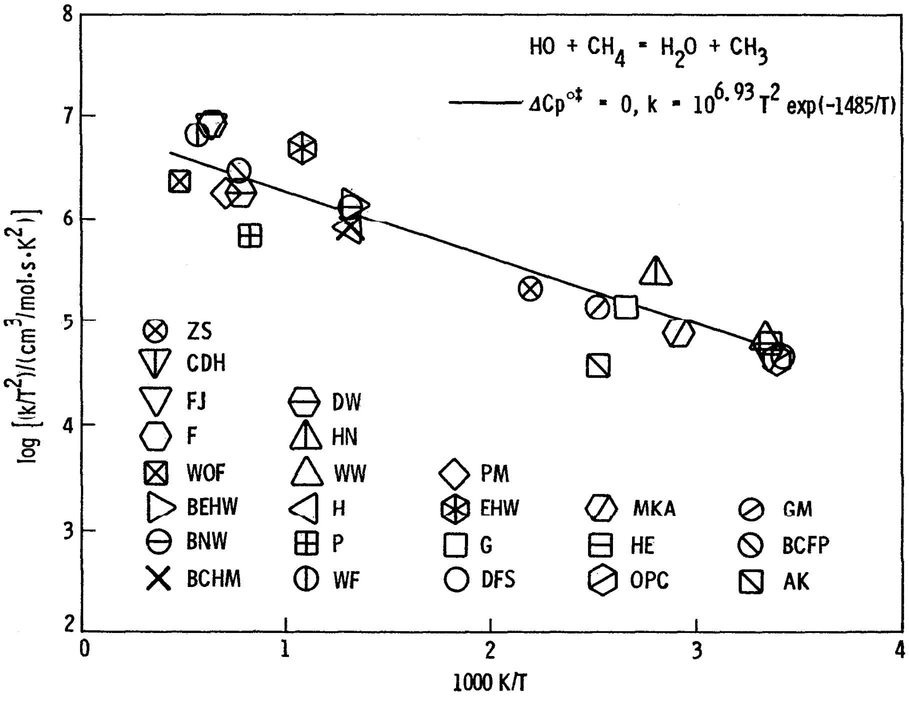

FIGURE 6. Comparison of measured rate constants for the reaction $HO+CH_4=H_2O+CH_3$ with the equation $k=10^{6.93}T^2\exp(-1485/T)$ cm³/(mol s). The data points are in table 5.

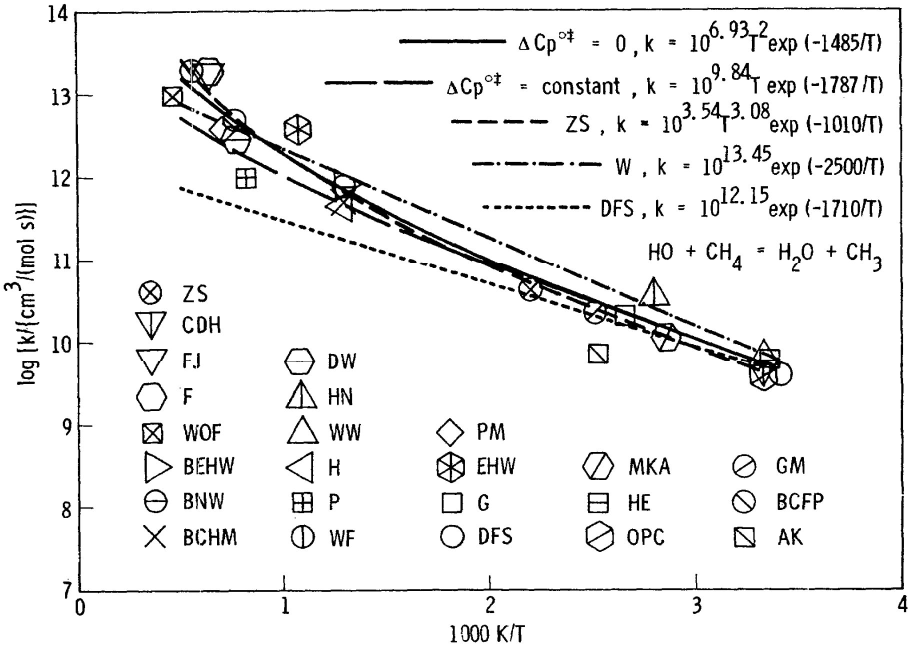

FIGURE 7. Comparison of measured rate constants for the reaction $HO+CH_4=H_2O+CH_3$ with several evaluations. The data points are in table 5.

6. The Reaction $O_2+CH_4=O_2H+CH_3$

Baldwin and Walker [71] have highlighted the problem of measuring the rate constants of hydrocarbon initiations such as eq (4). They have shown that secondary initiation (degenerative branching, $H_2O_2+M\rightarrow 2HO+M$) is faster than reaction (4) when $10^{-4}\%$ of CH_4 has been converted to H_2O_2 in the temperature range 772 to 1273 K.

I was unable to find any experimental measurements of k_4 or k_{-4}, and so have used estimates by Skinner, Lifshitz, Scheller, and Burcat [72], of k_4 and k_{-4} in the region 1500 to 2000 K:

$$k_4=10^{13.90}\exp(-28183/T)\ \mathrm{cm^3/(mol\ s)} \qquad (33)$$

$$k_{-4}=10^{12.00}\exp(-201/T)\ \mathrm{cm^3/(mol\ s)}. \qquad (34)$$

6.1. $\Delta Cp^{\circ\ddagger}=0$

At 1670 K, $k_4=10^{6.57}$ cm³/(mol s). Assuming that A for reaction (4) is the same as that for reaction (3) then

$$k_4=10^{6.93}T^2\exp(-26153/T). \qquad (35)$$

6.2. $\Delta Cp^{\circ\ddagger}$ = constant

At 1670 K, $k_{-4}=10^{11.95}$cm³/(mol s). It was assumed that $\Delta S^{\circ\ddagger}_{298}=-30$ cal/(mol K) for reaction (−4), the same value as for reaction (−2), $CH_3+HO=CH_4+O$. Insertion of these values into eq (15) gave

$$k_{-4}=10^{8.58}T\ \exp(-579/\mathrm{T})\ \mathrm{cm^3/(mol\ s)}. \qquad (36)$$

At 1000 K, from eq (35), $k_{-4}=10^{11.83}$cm³/(mol s), not significantly different from $k_{-4}=10^{11.91}$cm³/(mol s) from eq (34). Similarly at 2000 K, $k_{-4}=10^{12.01}$ from eq (35) and $10^{11.96}$cm³/(mol s) from eq (34). Using the JANAF equilibrium constant, modified by the change of heat of formation of methyl, together with eq (36), gave $k_4=10^{1.27}$ at 1000 K and $10^{7.68}$cm³/(mol s) at 2000 K. The value at 2000 K may be compared with some other estimates, all in cm³/(mol s), $10^{7.8}$ [72], and $10^{7.99}$ [73]. Seery and Bowman's [74], value of E/R of 22,700 should be 27,700 [75].

Denisov [76] calculated from transition state theory an Arrhenius A factor of $10^{11.6}$cm³/(mol s) at 400 K, and an Arrhenius activation energy of 56.6 kcal/mol (assuming D (CH_3–H) = 103.6 kcal/mol), for reaction (4). At 400 K Denisov's value of k_4 is $10^{-19.3}$ compared with $10^{-17.4}$ cm³/(mol s) calculated from eq (35), and the JANAF equilibrium constant, and $\Delta Hf^\circ(CH_3)=33.6$ kcal/mol. The difference in pre-exponential factors is about a power of 10. Fristrom and Westenberg's Arrhenius A factor of 10^{14} cm³/(mol s) is probably a little high.

7. Discussion

Comparison of the previously measured results with those estimated here shows that the data are fitted better by the assumption $\Delta C_p{}^{\circ\ddagger}/R=0$ than by $\Delta C_p{}^{\circ\ddagger}$ = constant. It is not clear why this is so because, in principle, the latter assumption is a higher order approximation. Nevertheless the fit between the experimental data and those calculated from the equation

$$k=AT^2\exp(-C/T) \qquad (6)$$

especially for reaction (3)

$$HO+CH_4=H_2O+CH_3 \qquad (3)$$

shown in figure 6 strongly suggests that eq (6) may be more widely applied for extrapolating rate constants for atom-transfer reactions to and from high temperatures.

As regards the controversy [1] over whether reaction (3) or (2)

$$0+CH_4=OH+CH_3 \qquad (2)$$

is faster at combustion temperatures, rate constants calculated from eq (6) and fitted values of A and C for the two reactions show that abstraction by HO is faster than by 0 at all temperatures.

More experimental data are needed for reaction (2) at both high [75] and low [78] temperatures, and for reaction (4) at all temperatures. More work is also needed to resolve the discrepancy between the thermochemical and kinetic equilibrium constants for reaction (1) at low temperatures.

In placing this work in perspective with earlier efforts, it may be concluded that extrapolation of room temperature data to higher temperatures is possible, at least, in the examples cited. The use of $\Delta C_p{}^{\circ\ddagger}=0$ seems to provide a better fit than does $\Delta C_p{}^{\circ\ddagger}=\text{constant}$. The method for estimation has been extended to a larger number of reacting species, and at the same time the size of B has been increased so that for X +YZ, B is 0.5; for W+XYZ, B is 0.75; and for $HO+CH_4$, B is 1.0. This seems to indicate an increase in non-Arrhenius behavior as the reacting species get larger.

A number of problems remain unresolved. Further tests of the method with other reacting species are needed. The difference between theory and experiment needs resolution. Similarly the differences between the kinetic and photoionization methods for determining the heat of formation of the methyl radical remain a problem. Correlation of estimates of $\Delta C_p{}^{\circ\ddagger}$ with $\Delta S^{\circ\ddagger}_{298}$ needs further effort. Perhaps these can be considered as the body of experimental data grows to the point where a more detailed examination of theory and experiment becomes possible.

8. Literature Searched

The following sources were valuable keys to the literature: Chemical Kinetics Information Center, National Bureau of Standards, U. S. Department of Commerce, Washington, D.C., 20234; reviews by Westley [79] Hampson and Garvin [80], Drysdale and Lloyd [81], Herron and Huie [37], Kerr and Parsonage [29], Engleman [82], Kondratiev [15], Wilson [70], and Baulch, Drysdale, Horne, and Lloyd [20] and [69]; Citation Abstracts; and Chemical Reviews.

9. Acknowledgements

For support and helpful discussion, I thank L. H. Gevantman, D. Garvin, R. F. Hampson, F. Gornick, J. T. Herron, R. E. Huie, W. Tsang, H. M. Rosenstock, and R. Stockbauer of the U. S. National Bureau of Standards; D. M. Golden, T. Mill, and G. Smith of SRI International; C. T. Bowman of Stanford University; D. L. Baulch of Leeds University; J. A. Kerr of Birmingham University; W. Whalley and and N. Bruno of Whalley, Tomkin, and Williams, Inc.; G. A. Lo, F. G. Borgardt, E. L. Littauer, D. Duran, N. Kusnezov, G. Kull, C. Yasukawa, and M. Furio of Lockheed Palo Alto Research Laboratory, and Isabel Shaw.

This work was supported by the Office of Standard Reference Data of the National Bureau of Standards under Contract 6-35786 and by Lockheed Missiles & Space Company, Inc.

10. References

[1] Rosenstock, H. M., Garvin, D., Herron, J. T., and Tsang, W., *The Role of Chemical Kinetics in Energy Conservation*, NBSIR 75–910, Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, October 1975, 112 p.

[2] Benson, S. W., Golden, D. M., Lawrence, R. W., Shaw, R., and Woolfolk, R. W., Int. J. Chem. Kin. Symp. No. 1, 399 (1975)

[3] Shaw, R, Int. J. Chem. Kin., **9**, 929 (1977).

[4] *JANAF Thermochemical Tables*, Dow Chemical Company, Midland, Michigan.

[5] Benson, S. W., *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, John Wiley and Sons, Inc., New York, 1968.

[6] Peeters, J., and Mahnen, G., *14th International Symposium on Combustion*, p. 133, The Combustion Institute, Pittsburgh, Pa., (1973)

[7] Walker, R. W., J. Chem. Soc. (A), 2391, (1968).

[8] Kurylo, M. J., Hollinden, G. A., and Timmons, R. B., J. Chem. Phys. **52**, 1773 (1970).

[9] Berlie, M. R., and Le Roy, D. J., Can. J. Chem. **32**, 650 (1954).

[10] Biordi, J. C., Lazzara, C. P., and Papp, J. F., Comb. and Flame, **26**, 57 (1976).

[11] Baldwin, R. R., Morris, A. C., and Walker, R. W., *11th International Symposium on Combustion*, p. 889, Combustion Institute, Pittsburgh, Pa., (1967).

[12] Dixon-Lewis, G., and Williams, A., *11th International Symposium on Combustion*, p. 951, Combustion Institute, Pittsburgh, Pa., (1967).

[13] Azatyan, V. V., Nalbandyan, A. B., and Meng-Yuan, T., Kin. and Cat. **5**, 177 (1964).

[14] Nalbandyan, A. B., and Gorban, N. I., Akad. Nauk Arm. SSR Doklady **33**, 49 (1961) Trans. Spec. Lib. Assoc. 63–15456.

[15] Kondratiev, V. N., *Rate Constants of Gas Phase Reactions*, translated by Holtschlog, L. J., edited by Fristrom, R. M., U. S. Dept. of Commerce, NBS, COM–72–10014.

[16] Panfilov, V. N., Author's summary of Dissertation, Siberian Section, Acad. Sci USSR Novosibirsk, 1964.

[17] Bush, S. F., and Dyer, P., Proc. Roy. Soc. (London) **A351**, 33 (1976).

[18] Jamieson, J. W. S., and Brown, G. R., Can. J. Chem. **42**, 1638 (1964)

[19] Fenimore, C. P., and Jones, G. W., J. Phys. Chem. **65**, 2200 (19617).

[20] Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., *Evaluated Kinetic Data for High Temperature Reactions*, Vol 2. Butterworths, London 1973.

[21] Roth, P., and Just, Th., Ber. Bun. Ges. **79**, 682 (1975).

[22] Klein, R., McNesby, J. R., Scheer, M. D., and Schoen, L. J., J. Chem. Phys. **30**, 58 (1959).

[23] Westenberg, A. A., and de Haas, N., J. Chem. Phys. **47**, 1393 (1967).

[24] Kurylo, M. J., and Timmons, R. B., J. Chem. Phys. **50**, 5076 (1969).

[25] Clark, T. C., and Dove, J. E., Can. J. Chem. **51**, 2155 (1973).

[26] Benson, S W., University of Southern California private communication to Golden, D. M., SRI International.

[27] Golden, D. M., SRI International private communication to Shaw, R.

[28] Clark, T. C., and Dove, J. E., Can. J. Chem. **51**, 2147 (1973).

[29] Kerr, J A., and Parsonage, M. J., *Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals*, Butterworths, London, 1976.

[30] Kurylo, M. J., National Bureau of Standards, private communication.

[31] Chupka, W. A., J. Chem. Phys. **48**, 2337 (1968).

[32] Rosenstock, H. M., National Bureau of Standards, private communication.

[33] Stockbauer, R., to be published.

[34] McCulloh and Dibeler, V. H., J. Chem. Phys. **64**, 4445 (1976).

[35] Smith, G., SRI International, private communication.

[36] Golden, D. M., Walsh, R., and Benson, S. W. J. Amer. Chem. Soc. **87**, 4053 (1965).

[37] Herron, J. T., and Huie, R. E., J. Phys. Chem. Ref. Data, **2**, 467 (1973).

[38] Cadle, R. D., and Allen, E. R., J. Phys. Chem. **69**, 1611 (1965).

[39] Westenberg, A. A., and de Haas, N., J. Chem. Phys. **50**, 2512 (1969).

[40] Brown, J. M., and Thrush, B. A., Trans. Faraday Soc. **63**, 630 (1967).

[41] Wong, E. L., and Potter, A., Can. J. Chem. **45**, 367 (1967).

[42] Froben, F. W., Ber. Bunsen Ges. Phys. Chem. **72**, 996 (1968).

[43] Brabbs, T. A., and Brokaw, R. S., *15th International Symposium on Combustion*, p. 893, Combustion Institute, Pittsburgh, Pa., 1975.

[44] Barassin, J., and Combourieu, J., Bull. Soc. Chim. Fr. **1974**, 1.

[45] Simonaitis, R., Heicklen, J., McGuire, M. M., and Bernheim, R. A., J. Phys. Chem. **75**, 3205 (1971).

[46] Dean, A. M., and Kistiakowsky, G. B., J. Chem. Phys. **54**, 1718 (1971).

[47] Avramenko, L. I. Kolesnikova, R. V., and Kuznetsova, N. L., Izvest. Akad. Nauk SSSR, Ofdel, Khim. Nauk 620 (1963).

[48] Mayer, S. W., and Schieler, L., J. Phys. Chem. **72**, 2628 (1968).

[49] Wilson, W. E., O'Donovan, J. T., and Fristrom, R. M., *12th Combustion Symposium*, p. 929, The Combustion Institute, Pittsburgh, Pa., 1969.

[50] Westenberg, A. A., and Fristrom, R. M., J. Phys. Chem. **65**, 591 (1961).

[51] Fristrom, R. M., *9th Combustion Symposium*, p. 560, The Combustion Institute, Pittsburgh, Pa., 1963.

[52] Bradley, J. N., Capey, W. D., Fair, R. W., and Pritchard, D. K., Int. J. Chem. Kin. **8**, 549 (1976).

[53] Pratt, N. H., *11th Combustion Symposium*, p. 1150, The Combustion Institute, Pittsburgh, Pa., (1976).

[54] Eberius, K. H., Hoyermann, K., and Wagner, H. G., private communication in ref. 36.

[55] Hoare, D. E., Proc. Roy. Soc. (London), **A291**, 73 (1966).

[56] Blundell, R. V., Cook, W. G. A., Hoare, D. E., and Milne, G. S., *10th Combustion Symposium*, p. 445, The Combustion Institute, Pittsburgh, Pa. (1965).

[57] Baldwin, R. R., Everett, C. J., Hopkins, D. E., and Walker, R. W. Adv. Chem. Ser., **76**, 124 (1968).

[58] Zellner, R., and Steinert, W., Int. J. Chem. Kin. **8**, 397 (1976).

[59] Gordon, S., and Mulac, W. A., Int. J. Chem. Kin. Symp. **1**, 289 (1975)

[60] Avramenko, L. I., and Kolesnikova, R. V., *Advances in Photochemistry*, p. 25, Wiley, New York, 1964.

[61] Greiner, N. R., J. Chem. Phys. **53**, 1070 (1970).

[62] Horne, D. G., and Norrish, R. G. W., Nature (London) **215**, 1373 (1967).

[63] Margitan, J. J., Kaufmann, F., and Anderson, J. G., Geophys. Res. Lett. **1**, 80 (1974).

[64] Overend, R., Paraskevopoulos, G. and Cvetanovic, R. J., Can. J. Chem. **53**, 3374 (1975).

[65] Wilson, W. E., and Westenberg, A. A., *11th Combustion Symposium*, p. 143, The Combustion Institute, Pittsburgh, Pa., (1967).

[66] Cox, R. A. Derwent, R. G., and Holt, P. M., J. Chem. Soc. Faraday I, 2031 (1976).

[67] Howard, C. J., and Evenson, K. M., J. Chem. Phys. **64**, 197 (1976).

[68] Davis, D. D., Fischer, S., and Schiff, R., J. Chem. Phys. **61**, 2213 (1974).

[69] Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., *Evaluated Kinetic Data for High Temperature Reaction*, Vol 1., Butterworths, London, 1973.

[70] Wilson, W. E., J. Phys. Chem. Ref. Data **1**, 535 (1972).

[71] Baldwin, R R., and Walker, R. W., *14th International Symposium on Combustion*, p. 241, The Combustion Institute, Pittsburgh, Pa. (1973).

[72] Skinner, G. B., Lifshitz, A., Scheller, K., and Burcat, A., J. Chem. Phys. **56**, 3853 (1972)

[73] Fristrom, R. M., and Westenberg, A. A., *Flame Structure*, McGraw-Hill, New York (1965), p. 341.

[74] Seery, D. J., and Bowman, C. T., Comb. and Flame **14**, 37 (1970).

[75] Bowman, C. T., Stanford University, private communication

[76] Denisov, E. T., Russ. J. Phys. Chem. **38**, 1 (1964).

[77] Benson, S W., *Thermochemical Kinetics*, 2nd Edition, Wiley, New York 1976.

[78] Huie, R. E., National Bureau of Standards, private communication.

[79] Westley, F., *Chemical Kinetics of the Gas Phase Combustion of Fuels*, NBS SP499, U.S. Department of Commerce, Washington, D.C., 20234 (1977).

[80] Hampson, R. F., Jr., and Garvin, D., *Chemical Kinetic and Photochemical Data for Modelling Atmosphere Chemistry*, NBS Tech Note 866, U. S. Department of Commerce, Washington, D.C., 20234.

[81] Drysdale, D. D., and Lloyd, A. C., *Gas Phase Reactions OH Radical*, Oxid. and Comb. Rev. **4**, 157 (1970)

[82] Engleman, V. S., *Survey and Evaluation of Kinetic Data on Reactions in Methane/Air Combustion*, EPA-600/2-76-003, U. S. Environmental Protection Agency, Office of R. & D., Washington, D. C., 20460.