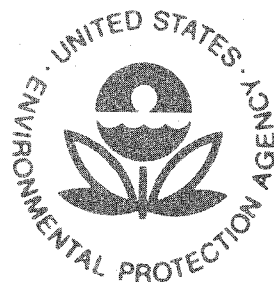EPA-600/2-75-019

August 1975

ESTIMATING
THE KINETICS OF COMBUSTION

INCLUDING REACTIONS

INVOLVING OXIDES OF NITROGEN AND SULFUR

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INVOLVING OXIDES OF NITROGEN AND SULFUR

by

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SECTION I

CONCLUSIONS

The simplest and most important conclusion from this research is that all previously measured rate constants for atom transfer reactions between atoms and diatomic molecules containing the elements carbon, hydrogen, nitrogen, oxygen, and sulfur have the same value (± a factor of three) in the exothermic direction at 2000 K. This rate constant is $10^{13.0}$ cm^3 mol^{-1} s^{-1}. The rate constants in the endothermic direction are readily obtained from the equilibrium constants, all of which can be calculated. The above conclusion is based on previously published experimental work on about a quarter of the 75 possible pairs of atom transfer reactions.

In more detail, previously measured and evaluated rate constants for the reactions X + YZ ⇌ XY + Z, X + Y + M ⇌ XY + M, and X + YZ + M ⇌ XYZ + M, where X, Y, and Z are any of the atoms C, H, N, O, and S, have been shown to fit the form:

$$k = AT^B \exp(-C/RT) \tag{1}$$

where

k = the rate constant. For a second-order rate constant, the units of k are cm^3 mol^{-1} s^{-1}. For a third-order rate constant, the units are cm^6 mol^{-2} s^{-1}.

A, B, and C = constants

T = absolute temperature in Kelvins

R = the gas constant.

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The values of the constants A, B, and C are listed in Table 1. Other symbols used in the table are defined as follows:

$$\Delta S^{o\ddagger}_{300} = \text{the entropy of activation at 300 K}$$

$$\Delta H^{o\ddagger}_{300} = \text{the heat of activation at 300 K.}$$

The entropy of activation, $\Delta S^{o\ddagger}_{300}$, is equal to -22 cal/(mol K) in the exothermic direction and $-22 + \Delta S^{o}_{300}$ cal/(mol K) in the endothermic direction; $\Delta H^{o\ddagger}_{300}$ is equal to either -1 kcal/mol for exothermic ($-1 + \Delta H^{o}_{300}$ kcal/mol for endothermic) reactions that have a transition state preceded by an intermediate that is stable with respect to the reactants or 7 kcal/mol for exothermic ($7 + \Delta H^{o}_{300}$ kcal/mol for endothermic) reactions that are concerted or that have a transition state preceded by an intermediate that is unstable with respect to the reactants. The criterion for a stable intermediate is that its heat of formation must be less than the sum of the heats of formation of the reactants.

Table 1. PARAMETERS USED IN CALCULATING RATE CONSTANTS

Elements· X, Y, and Z	Reaction	$\log_{10}A$	B	C
C, H, N, O and S	$X + YZ \rightleftharpoons XY + Z$	$16.6 + [\Delta S^{o\ddagger}_{300}/(2.3R)]$	0.5	$\Delta H^{o\ddagger}_{300} + 1$
H, N, and O	$X + Y + M \rightarrow XY + M$	18	-1	0
H, N, and O	$XY + M \rightarrow X + Y + M$	$16.1 + [\Delta S^{o}_{1500}/(2.3R)]$	-2	ΔH^{o}_{1500}
H, N, and O	$X + YZ + M \rightarrow XYZ + M$ (X and Z are both hydrogen atoms)	19	-1	0
H, N, and O	$XYZ + M \rightarrow X + YZ + M$	$17.1 + [\Delta S^{o}_{1500}/(2.3R)]$	-2	ΔH^{o}_{1500}
H, N, and O	$X + YZ + M \rightarrow XYZ + M$ (X and Z are not both hydrogen atoms)	20.2	-1.5	0
H, N, and O	$XYZ + M \rightarrow X + YZ + M$	$18.3 + [\Delta S^{o}_{1500}/(2.3R)]$	-2.5	ΔH^{o}_{1500}

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It is suggested that the rate constants listed in Table 1 may be useful in estimating rate constants for reactions that have not been studied experimentally, especially at temperatures above 1000 K.

A convenient form of the equilibrium constant, suitable for combustion reactions, is:

$$K_c / [(mol/cm^3)^{\Delta n}] = 10^{-1.9 \Delta n} [\exp(\Delta S^0_{1500}/R)] T^{-\Delta n} \exp[-\Delta H^0_{1500}/(RT)] \qquad (2)$$

where K_c = the equilibrium constant

Δn = the mole change in the reaction

ΔS^0_{1500} = the standard entropy change at 1500 Kelvin

R = the gas constant

T = the absolute temperature

ΔH^0_{1500} = the standard enthalpy change at 1500 Kelvin.

SECTION II

RECOMMENDATIONS

We recommend that the estimating techniques developed for the atom plus diatomic molecule reactions be extended to larger species, for example, diatomic plus diatomic molecule reactions such as $CH + N_2 \rightarrow HCN + N$. As the species become bigger, more reactions will be possible, so the estimating techniques will have to become more widely applicable and less detailed than for the atom plus diatomic molecule reactions. Furthermore, spin considerations will become important, as in the example above, and experimental work will be required to provide a firmer foundation for the estimates.

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SECTION III

INTRODUCTION

The aim of this research was to provide estimates of rate constants of elementary chemical reactions for use in mathematical models of combustion processes. The models are being developed by the Combustion Research Section of the Environmental Protection Agency as tools to reduce air pollution and improve the efficiency of utility boilers.

The chemical elements considered were carbon, hydrogen, nitrogen, oxygen, and sulfur. The results and ideas developed on this project are also applicable to a wide range of other problems involving chemical kinetics, such as atmospheric reactions that cause pollution. Initially, the reactions of the atomic and diatomic species of hydrogen, nitrogen, and oxygen were selected for their simplicity and because of the widely praised critical reviews by Baulch et al.[1,2] As the research progressed, the elements under consideration were extended to include carbon and sulfur. The temperature range was 200 to 3000 K.

The approach was to develop equations that would account for rate constants that have been measured and then use these equations to predict rate constants of reactions that have not been studied experimentally.

SECTION IV

ESTIMATES OF RATE CONSTANTS
FOR THE REACTIONS X + YZ $\rightleftarrows$ XY + Z

There are 75 possible pairs of reactions of the type

$$X + YZ \rightleftarrows XY + Z \qquad (3)$$

where X, Y, and Z are atoms of the elements carbon, hydrogen, nitrogen, oxygen, and sulfur. The problem of dealing with so many reactions was simplified by tackling it in three stages. The first stage was to consider only the four pairs of reactions in the H_2/O_2 and N_2/O_2 systems. The second stage was to consider only the 18 pairs of reactions in the $H_2/N_2/O_2$ systems. The details of the estimation technique and results of the first and second stages are documented in letter, quarterly, and annual reports[3-5] submitted to EPA under the first year's effort of this grant. All the methodology and results described in these reports were compiled and systematized in a paper presented at the Symposium on Chemical Kinetics Data for the Upper and Lower Atmospheres, Airlie House, Warrenton, Virginia.[6] For completeness in reporting the findings under this grant, the first year's effort is documented by the inclusion of the Airlie House paper as Appendix A. The remainder of this section documents the third stage of this study, which was to consider all 75 possible pairs of reactions.

From transition state theory[7] and from estimates of the heat capacity of activation for atom transfer reactions between atoms and diatomic molecules, it has been shown[3-5] that the form of the rate constant is:

$$k/(cm^3 \ mol^{-1} \ s^{-1}) = 10^{16.6} \ exp(\Delta S^{0\ddagger}_{300}/R) T^{0.5} \ exp[-(\Delta H^{0\ddagger}_{300} + 1)/RT] \qquad (4)$$

For all reactions such as reaction (3), $\Delta S_{300}^{0\ddagger} = 22$ cal/(mol K) in the exothermic direction. Thus, equation (4) reduces to

$$k/(\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 10^{11.8} \; T^{0.5} \; \exp\left[-(\Delta H_{300}^{0\ddagger} + 1)/RT\right] \quad (5)$$

From equation (5) it is clear that the only unknown is the value of $\Delta H_{300}^{0\ddagger}$. It has been shown[3-5] that all the previous experimental data on the H/N/O system evaluated by the Leeds group[4] can be fitted by two values of $\Delta H_{300}^{0\ddagger}$, namely, -1 or 7 kcal/mol.

If there is no way to determine which of the two possible values of $\Delta H_{300}^{0\ddagger}$ is appropriate for a given reaction, an average value of 3 ± 4 kcal/mol can be used. From equation (5), the rate constant is:

$$k/(\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 10^{11.8} \; T^{0.5} \; \exp\left[(-4 \pm 4)/RT\right] \quad (6)$$

At the high temperatures of combustion reactions, the uncertainty in the activation energy becomes less important than at lower temperatures. For example, at 2000 K, the rate constant from equation (6) becomes

$$k/(\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 10^{11.8+1.7-0.5\pm0.5} \text{ at } 2000 \text{ K}$$

$$= 10^{13.0\pm0.5} \text{ at } 2000 \text{ K} \quad (7)$$

To a first approximation ($\pm$ half a power of ten, i.e., $\pm$ a factor of three), the rate constants of all atom transfer reactions such as equation (3) have the same rate constant in the exothermic direction, namely, $10^{13.0}$ cm^3 mol^{-1} s^{-1}.

It has been suggested[3-6] that the value of $\Delta H_{300}^{0\ddagger}$ is determined by the stability of the triatomic transition state XYZ with respect to the reactants. The basic postulates are (1) that $\Delta H_{300}^{0\ddagger} = -1$ kcal/mol for reactions that have a transition state preceded by an intermediate that is stable with respect to the reactants (see Figure 1) and (2) that $\Delta H_{300}^{0\ddagger} = 7$ kcal/mol for reactions that are concerted or have a transition state preceded by an intermediate that is unstable with respect to the reactants (see Figure 2).

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REACTANTS
X + YZ

TRANSITION
STATE

$(X \cdots Y \cdots Z)^{\ddagger}$

1 kcal/mol

ΔH^0_{300}

STABLE
INTERMEDIATE
XYZ

PRODUCTS
XY + Z
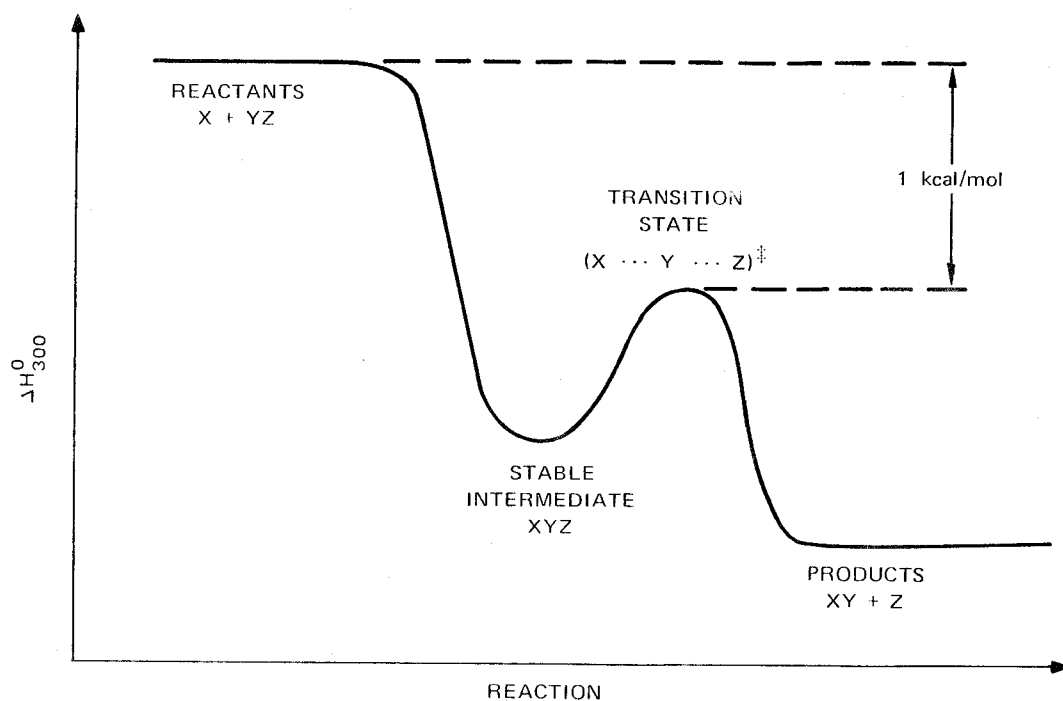
REACTION

SA-2008-3

FIGURE 1   HEAT CHANGES FOR REACTIONS HAVING TRANSITION STATES
PRECEDED BY AN INTERMEDIATE THAT IS STABLE WITH RESPECT
TO THE REACTANTS

In such cases $\Delta H^{0\ddagger}_{300} = -1$ kcal/mol.
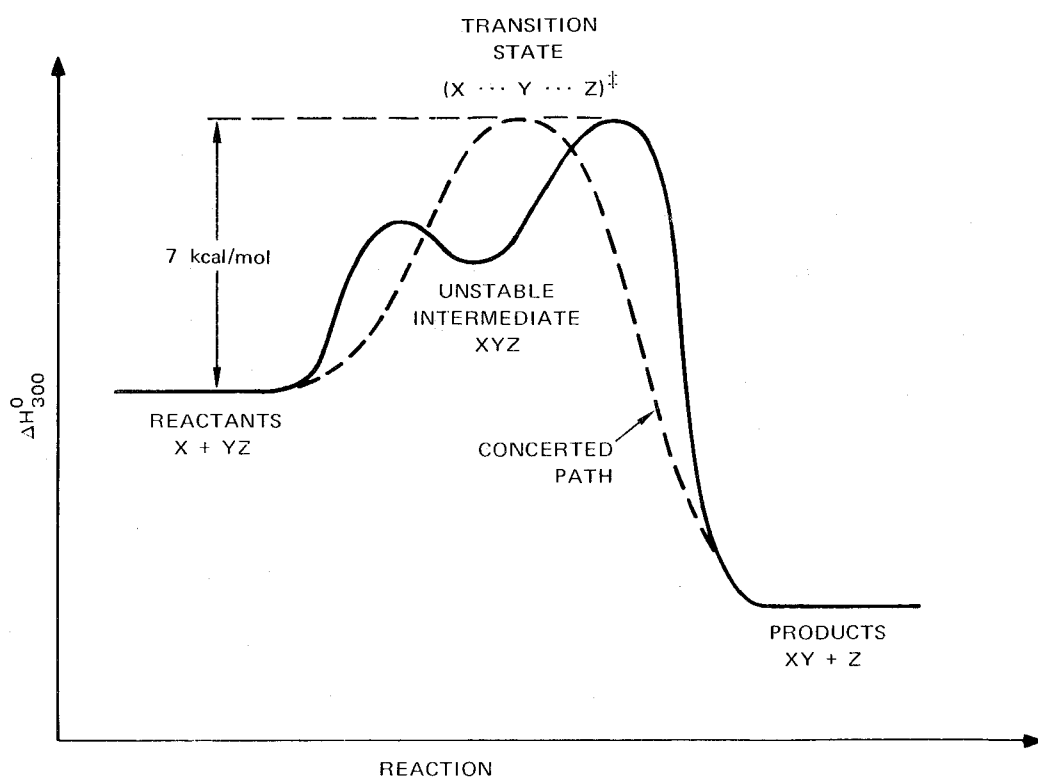
SA-2008-4

FIGURE 2   HEAT CHANGES FOR REACTIONS THAT ARE CONCERTED
OR THAT HAVE A TRANSITION STATE THAT IS PRECEDED
BY AN INTERMEDIATE THAT IS UNSTABLE WITH RESPECT
TO THE REACTANTS

In such cases $\Delta H^{0\ddagger}_{300} = 7$ kcal/mol.

The simplest case is the concerted reaction, in which a hydrogen atom is transferred. For example

$$H + HO \longrightarrow (H \cdots H \cdots O)^{\ddagger} \longrightarrow H_2 + O \qquad (8)$$
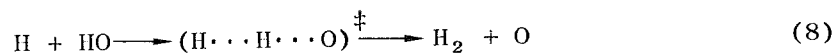
For reaction (8), $\Delta H_{300}^{o\ddagger} = 7$ kcal/mol. All reactions (involving C, H, N, O, S) of the type

$$X + YZ \longrightarrow (X \cdots Y \cdots Z)^{\ddagger} \longrightarrow XY + Z \qquad (9)$$
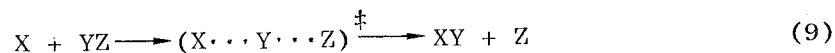
where Y is a hydrogen atom, have $\Delta H_{300}^{o\ddagger} = 7$ kcal/mol.

For all the other reactions, the triatomic intermediate XYZ was examined to determine whether it is stable or unstable with respect to the reactants. The heats of formation of the reactants and some of the intermediate are well known.[8] An example is the reaction

$$N + NO \longrightarrow (N \cdots N \cdots O)^{\ddagger} \longrightarrow N_2 + O \qquad (10)$$
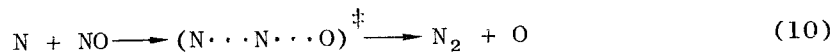
The intermediate in this case is N_2O. The sum of the heats of formation of the reactants N + NO is 134.6 kcal/mol, compared with 19.6 kcal/mol for N_2O; that is, N_2O is 115 kcal/mol more stable than N + NO. If it takes 60-80 kcal to form the triplet state N_2O, this intermediate is still 40 ± 10 kcal more stable than reactants and $\Delta H_{300}^{o\ddagger}$ (reaction 10) = -1 kcal/mol.

Another example is

$$H + O_2 \longrightarrow (H \cdots O \cdots O)^{\ddagger} \longrightarrow HO + O \qquad (11)$$

In this case, the stable molecule intermediate is HO_2. The reaction

$$H + O_2 \longrightarrow HO_2 \qquad (12)$$
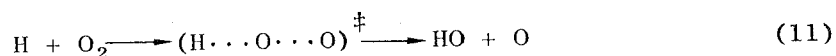
is 63.9 kcal/mol exothermic; hence, $\Delta H_{300}^{o\ddagger}$ (reaction 11) = 1 kcal/mol.

If the heat of formation of the intermediate XYZ is not known, it must be estimated. For example, consider the reaction

$$N + O_2 \longrightarrow (N\cdots O\cdots O)^{\ddagger} \longrightarrow NO + O \tag{13}$$

The intermediate is NOO produced by the reaction

$$N + O_2 \longrightarrow NOO \tag{14}$$
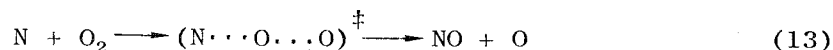
It has been estimated (see later) that $\Delta H^0_{f300}(NOO)$ is 136 ± 7 kcal/mol. Since the sum of the heats of formation of the reactants is 113 ± 1 kcal/mol, NOO is unstable with respect to $NO + O_2$, and $\Delta H^{0\ddagger}_{300}$ (reaction 13) $= 7$ kcal/mol.

In general, the estimating technique was to take the fully hydrogenated species and estimate the strengths of the bonds to the hydrogens. For example, the heat of formation of HNN was estimated from ΔH^0_{f300} (H_2NNH_2), assuming each N-H bond strength to be 95 kcal/mol. The details of the estimation are given in Appendix B, which considers the triatomic species in the complete C, H, N, O, S system.

The values assigned to $\Delta H^{0\ddagger}_{300}$ for the 75 exothermic or thermoneutral reaction are given in Tables 2 and 3. The hydrogen transfer reactions (all have 7 kcal/mol for $\Delta H^{0\ddagger}_{300}$) are in Table 2; the other reactions are in Table 3.

Equation (4) has the form

$$k/(cm^3 \ mol^{-1} \ sec^{-1}) = AT^{0.5} \exp(-C/RT) \tag{15}$$

where $A = 10^{16.6} \exp(\Delta S^{0\ddagger}_{300}/R) \ cm^3 \ mol^{-1} \ s^{-1}$

$C = -(\Delta H^{0\ddagger}_{300} + 1)$ kcal/mol

The appropriate values of $\Delta S^{0\ddagger}_{300}$ and $\Delta H^{0\ddagger}_{300}$ have been substituted in equation (15) for all reactions of the type $X + YZ \rightleftharpoons XY + Z$, where X, Y, and Z are atoms of the elements carbon, hydrogen, nitrogen, oxygen, and sulfur. The values of $\log_{10}A$, C, and $\log_{10}k$ at 1000 K for these reactions are given in Table 4.

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Table 2. HYDROGEN TRANSFER REACTIONS[a]

Formula of Triatomic Transition State XYZ		Reaction
Empirical	Structural	
CHN	CHN	$C + NH \rightarrow CH + N$
CHO	OHN	$O + HC \rightarrow OH + C$
CHS	SHC	$S + HC \rightarrow SH + C$
CH_2	HHC	$H + HC \rightarrow H_2 + C$
C_2H	CHC	$C + HC \rightarrow CH + C$
HNO	OHN	$O + HN \rightarrow OH + N$
HNS	SHN	$S + HN \rightarrow SH + N$
HN_2	NHN	$N + HN \rightarrow NH + N$
HOS	OHS	$O + HS \rightarrow OH + S$
HO_2	OHO	$O + HO \rightarrow OH + O$
HS_2	SHS	$S + HS \rightarrow SH + S$
H_2N	HHN	$H + HN \rightarrow H_2 + N$
H_2O	HHO	$H + HO \rightarrow H_2 + O$
H_2S	HHS	$H + HS \rightarrow H_2 + O$
H_3	HHH	$H + H_2 \rightarrow H_2 + H$

[a]Reactions $X + HZ \rightarrow XH + Z$ where X and Z are atoms of the elements carbon, hydrogen, nitrogen, oxygen, and sulfur. The rate constant for every reaction is: $k/(cm^3 \ mol^{-1} \ s^{-1}) = 10^{11.8}T^{0.5} \exp(-8/RT)$. Reactions are in the exothermic direction.

Table 3. ATOM TRANSFER REACTIONS[a]

Formula of Triatomic Intermediate XYZ		Reaction	$[\Delta H^o_f(X) + \Delta H^o_f(YZ)]$	$\Delta H^o_f(XYZ)$	$\Delta H^{o\ddagger}_{300}$
Empirical	Structural				
CHN	CNH	C + NH → NC + H	155 ± 5	110 ± 3[b]	-1
CHN	NCH	N + CH → NC + H	255 ± 1	32.3 ± 2[c]	-1
CHO	OCH	O + CH → OC + H	201.6 ± 0.1	{ 7.2[d] / 10.4 ± 2[c]	-1
CHO	COH	C + OH → CO + H	180 ± 1	81 ± 15[b]	-1
CHS	CSH	C + SH → CS + H	203 ± 1	123 ± 15[b]	-1
CHS	SCH	S + CH → SC + H	208.3 ± 0.1	92 ± 8[b]	-1
CH$_2$	HCH	H + CH → HC + H	194.1 ± 0.1	92.4 ± 1[c]	-1
CNO	CNO	C + NO → CN + O	192.5 ± 0.5	145 ± 17[b]	-1
CNO	CON	C + ON → CO + N	192.5 ± 0.5	220 ± 29[b]	7
CNO	OCN	O + CN → OC + N	164 ± 3	38 ± 3[c]	-1
CNS	CNS	C + NS → CN + S	234 ± 10	186 ± 25[b]	-1
CNS	CSN	C + SN → CS + N	234 ± 10	250 ± 29[b]	7
CNS	SCN	S + CN → SC + N	170 ± 3	73 ± 3[b]	-1
CN$_2$	NCN	N + CN → NC + N	217 ± 4	113 ± 5[c]	-1
CN$_2$	NNC	N + NC → N$_2$ + C	217 ± 4	140 ± 30[c]	-1

[a] Reactions X + YZ → XY + Z where Y is not a hydrogen atom and where X and Z are atoms of the elements carbon, hydrogen, nitrogen, oxygen and sulfur. If the heat of formation of the intermediate XYZ is less than the sum of the heats of formation of X and YZ, then $\Delta H^{o\ddagger}_{300}$ = -1 kcal/mol in the equation for the rate constant: $k/(cm^3 \; mol^{-1} \; s^{-1})$ = $10^{11.8}T^{0.5}$ exp $[-(\Delta H^{o\ddagger}_{300} + 1)/RT]$. If the heat of formation of the intermediate XYZ is greater than the sum of the heats of formation of X and YZ, then $\Delta H^{o\ddagger}_{300}$ = 7 kcal/mol. All units are kcal/mol. Reactions are in the exothermic direction.

[b] Estimated value for $\Delta H^o_f(XYZ)$. See Appendix B.

[c] Reference 8.

[d] Reference 7.

Table 3 (continued). ATOM TRANSFER REACTIONS

Formula of Triatomic Intermediate XYZ		Reaction	$[\Delta H^o_f(X) + \Delta H^o_f(YZ)]$	$\Delta H^o_f(XYZ)$	$\Delta H^{o\ddagger}_{300}$
Empirical	Structural				
COS	COS	C + OS → CO + S	172.1 ± 0.8	161 ± 36[b]	-1
COS	OCS	O + CS → OC + S	115 ± 5	-33.1 ± 0.3[a]	-1
COS	CSO	C + SO → CS + O	172.1 ± 0.8	164 ± 19[b]	-1
CO_2	COO	C + O_2 → CO + O	170.9 ± 0.5	135 ± 22[b]	-1
CO_2	OCO	O + CO → OC + O	33.2 ± 0.6	-94.05 ± 0.01[c]	-1
CS_2	CSS	C + S_2 → CS + S	201.7 ± 0.7	164 ± 19[b]	-1
CS_2	SCS	S + CS → SC + S	121 ± 5	28.0 ± 0.2[c]	-1
C_2H	CCH	C + CH → C_2 + H	312.9 ± 0.6	114 ± 7[c]	-1
C_2N	NCC	N + C_2 → NC + C	313 ± 2	146 ± 16[b]	-1
C_2N	CNC	C + NC → CN + C	275 ± 4	133 ± 30[c]	-1
C_2O	OCC	O + C_2 → OC + C	259.7 ± 0.9	69 ± 15[c]	-1
C_2O	COC	C + OC → CO + C	144.5 ± 1.1	213 ± 30[b]	7
C_2S	SCC	S + CC → SC + C	266.5 ± 0.9	130 ± 15[b]	-1
C_2S	CSC	C + SC → CS + C	266 ± 5	248 ± 30[b]	7
C_3	CCC	C + C_2 → C_2 + C	371 ± 1	196 ± 4[b]	-1
HNO	ONH	O + NH → ON + H	150 ± 4	23.8[b]	-1
HNO	NOH	N + OH → NO + H	122 ± 1	77 ± 11[b]	-1
HNS	SNH	S + NH → SN + H	156 ± 4	65 ± 11[b]	-1
HNS	NSH	N + SH → NS + H	146 ± 2	112 ± 11[b]	-1
HN_2	HHH	N + NH → N_2 + H	203 ± 5	152 ± 16[b]	-1
HOS	SOH	S + OH → SO + H	75.6 ± 0.3	11 ± 13[b]	-1

Table 3 (concluded). ATOM TRANSFER REACTIONS

Formula of Triatomic Intermediate XYZ		Reaction	$[\Delta H^o_f(X) + \Delta H^o_f(YZ)]$	$\Delta H^o_f(XYZ)$	$\Delta H^{o\ddagger}_{300}$
Empirical	Structural				
HOS	OSH	$O + SH \rightarrow OS + H$	93 ± 1	23 ± 10 [b]	-1
HO_2	OOH	$O + OH \rightarrow O_2 + H$	69.9 ± 0.3	5 ± 2 [c]	-1
HS_2	SSH	$S + SH \rightarrow S_2 + H$	99.6 ± 1.2	33 ± 5 [b]	-1
H_2N	HNH	$H + NH \rightarrow HN + H$	142 ± 4	46 ± 2 [c]	-1
H_2O	HOH	$H + OH \rightarrow HO + H$	61.4 ± 0.3	-57.8 ± 0.001 [c]	-1
H_2S	HSH	$H + SH \rightarrow HS + H$	85.4 ± 1.2	-4.9 ± 0.2 [c]	-1
NOS	NOS	$N + OS \rightarrow NO + S$	114 ± 1	149 ± 21 [b]	7
NOS	OSN	$O + SN \rightarrow OS + N$	123 ± 10	166 ± 39 [b]	7
NOS	ONS	$O + NS \rightarrow ON + S$	123 ± 10	49 ± 10 [b]	-1
NO_2	NOO	$N + O_2 \rightarrow NO + O$	113 ± 1	136 ± 17 [b]	7
NO_2	ONO	$O + NO \rightarrow ON + O$	81.1 ± 0.4	7.9 ± 0.2 [c]	-1
NS_2	NSS	$N + S_2 \rightarrow NS + S$	144 ± 1	164 ± 32 [b]	7
NS_2	SNS	$S + NS \rightarrow SN + S$	129 ± 10	90 ± 20 [b]	-1
N_2O	NNO	$N + NO \rightarrow N_2 + O$	135 ± 1	19.6 ± 0.1 [c]	-1
N_2O	NON	$N + ON \rightarrow NO + N$	135 ± 1	209 ± 27 [b]	7
N_2S	NNS	$N + NS \rightarrow N_2 + S$	176 ± 11	61 ± 10 [b]	-1
N_2S	NSN	$N + SN \rightarrow NS + N$	176 ± 11	244 ± 31 [b]	7
N_3	NNN	$N + N_2 \rightarrow N_2 + N$	113 ± 1	171 ± 13 [b,c,e]	7
S_2O	OSS	$O + S_2 \rightarrow OS + S$	90.4 ± 0.2	-14 ± 8 [c]	-1
S_2O	SOS	$S + OS \rightarrow SO + S$	67.5 ± 0.3	36.5 ± 1.0 [b]	-1
SO_2	SOO	$S + O_2 \rightarrow SO + O$	66.29 ± 0.01	35.3 ± 0.7 [b]	-1
SO_2	OSO	$O + SO \rightarrow OS + O$	60.8 ± 0.3	-70.95 ± 0.05 [c]	-1
O_3	OOO	$O + O_2 \rightarrow O_2 + O$	59.55 ± 0.02	34.1 ± 0.4	-1
S_3	SSS	$S + S_2 \rightarrow S_2 + O$	97.1 ± 0.2	65 ± 1 [b]	-1

[e] The $\Delta H^o_f(XYZ)$ includes an additional 60 ± 6 kcal/mol for spin forbidden reaction.

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Table 4. VALUES USED IN CALCULATING RATE CONSTANTS[a]

Empirical Formula of Triatomic Intermediate XYZ	Reaction	$\log_{10}A/$ $[cm^3\ mol^{-1}\ s^{-1}]$	C/(kcal/mol)	$\log_{10}k/[cm^3\ mol^{-1}\ s^{-1}]$ at 1500 K
CHN	C + HN $\rightarrow$ CH + N	11.8	8.0	12.2
	N + HC $\rightarrow$ NH + C	12.0	13.9	11.6
	H + CN $\rightarrow$ HC + N	12.8	12.8	-0.1
	N + CH $\rightarrow$ NC + H	11.8	0	13.4
	H + NC $\rightarrow$ HN + C	13.0	104.8	-0.7
	C + NH $\rightarrow$ CN + H	11.8	0	13.4
CHO	C + HO $\rightarrow$ CH + O	11.9	29.4	9.2
	O + HC $\rightarrow$ OH + C	11.8	8.0	12.2
	C + OH $\rightarrow$ CO + H	11.8	0	13.4
	H + OC $\rightarrow$ HO + C	13.3	154.5	-7.6
	H + CO $\rightarrow$ HC + O	13.4	174.9	-10.6
	O + CH $\rightarrow$ OC + H	11.8	0	13.4
CHS	C + HS $\rightarrow$ CH + S	11.6	12.1	11.5
	S + HC $\rightarrow$ SH + C	11.8	8.0	12.2
	C + SH $\rightarrow$ CS + H	11.8	0	13.4
	H + SC $\rightarrow$ HS + C	13.3	97.1	0.6
	H + CS $\rightarrow$ HC + S	13.1	101.2	-0.1
	S + CH $\rightarrow$ SC + H	11.8	0.8	13.4
CH_2	C + H_2 $\rightarrow$ CH + H	12.2	31.2	9.3
	H + HC $\rightarrow$ H_2 + C	11.8	8.0	12.2
	H + CH $\rightarrow$ HC + H	11.8	0	13.4
CNO	C + NO $\rightarrow$ CN + O	11.8	0	13.4
	O + NC $\rightarrow$ ON + C	12.1	28.9	9.5
	C + ON $\rightarrow$ CO + N	11.8	8.0	12.2

[a]Values of $\log_{10}A$, C, and $\log_{10}k$ at 1500 K in the equation $\log_{10}k/(cm^3\ mol^{-1}\ s^{-1})$ = $AT^{0.5}\exp(-C/RT)$ for all the reactions of the type X + YZ $\rightarrow$ XY + Z where X, Y, and Z are atoms of the elements carbon, hydrogen, nitrogen, oxygen and sulfur.

Table 4 (continued). VALUES USED IN CALCULATING RATE CONSTANTS

Empirical Formula of Triatomic Intermediate XYZ	Reaction	$\log_{10} A /$ [cm^3 mol^{-1} s^{-1}]	$C/(kcal/mol)$	$\log^{10} k /$ [cm^3 mol^{-1} s^{-1}] at 1500 K
CNS	N + OC → NO + C	12.7	113.9	-2.3
	N + CO → NC + O	12.5	77.1	2.8
	O + CN → OC + N	11.8	0	13.4
	C + NS → CN + S	11.8	0	13.4
	S + NC → SN + C	12.3	63.6	4.6
	C + SN → CS + N	11.8	8.0	12.2
	N + SC → NS + C	12.6	73.9	3.5
	N + CS → NC + S	12.1	2.3	13.4
	S + CN → SC + N	11.8	0	13.4
CN_2	C + N_2 → CN + N	12.1	45.2	7.1
	N + NC → N_2 + C	11.8	0	13.4
	C + NC → CN + C	11.8	0	13.4
COS	C + OS → CC + S	11.8	0	13.4
	S + OC → SO + C	12.6	132.2	-5.1
	C + SO → CS + O	11.8	0	13.4
	O + SC → OS + C	12.2	57.5	5.4
	O + CS → OC + S	11.8	0	13.4
	S + CO → SC + O	12.1	74.7	2.8
CO_2	C + O_2 → CO + O	11.8	0	13.4
	O + OC → O_2 + C	12.0	137.7	-6.4
	O + CO → OC + O	11.8	0	13.4
CS_2	C + S_2 → CS + S	11.8	0	13.4
	S + SC → S_2 + C	12.2	80.4	2.1
	S + CS → SC + S	11.8	0	13.4
C_2H	C + CH → C_2 + H	11.8	0	13.4
	H + C_2 → HC + C	13.2	60.5	6.0
	C + HC → CH + C	11.8	8.0	12.2

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Table 4 (continued). VALUES USED IN CALCULATING RATE CONSTANTS

Empirical Formula of Triatomic Intermediate XYZ	Reaction	$\log_{10} A / [cm^3 \; mol^{-1} \; s^{-1}]$	$C/(kcal/mol)$	$\log_{10} k / [cm^3 \; mol^{-1} \; s^{-1}]$ at 1500 K
C_2N	$C + CN \rightarrow C_2 + N$	11.4	38.3	7.4
	$N + C_2 \rightarrow NC + C$	11.8	0	13.4
	$C + NC \rightarrow CN + C$	11.8	0	13.4
C_2O	$C + CO \rightarrow C_2 + O$	12.0	115.3	-3.2
	$O + C_2 \rightarrow CO + C$	11.8	0	13.4
	$O + CO \rightarrow OC + O$	11.8	0	13.4
C_2S	$C + CS \rightarrow C_2 + S$	11.7	40.6	7.4
	$S + C_2 \rightarrow SC + C$	11.8	0	13.4
	$C + SC \rightarrow CS + C$	11.8	0	13.4
C_3	$C + C_2 \rightarrow C_2 + C$	11.8	0	13.4
HNO	$H + NO \rightarrow HN + O$	12.7	75.9	3.2
	$O + NH \rightarrow ON + H$	11.8	0	13.4
	$H + ON \rightarrow HO + N$	12.4	48.6	6.9
	$N + OH \rightarrow NO + H$	11.8	0	13.4
	$N + HO \rightarrow NH + O$	12.1	35.3	8.5
	$O + HN \rightarrow OH + N$	11.8	8.0	12.2
HNS	$H + NS \rightarrow HN + S$	12.4	41.2	8.0
	$S + NH \rightarrow SN + H$	11.8	0	13.4
	$H + SN \rightarrow HS + N$	12.4	31.2	9.5
	$N + SH \rightarrow NS + H$	11.8	0.8	13.4
	$N + HS \rightarrow NH + S$	11.8	18.0	10.8
	$S + HN \rightarrow SH + N$	11.8	8.0	12.2
HN_2	$H + N_2 \rightarrow HN + N$	13.3	150.9	-7.2
	$N + NH \rightarrow N_2 + H$	11.8	0	13.4
	$N + HN \rightarrow NH + N$	11.8	8.0	12.2
HOS	$H + OS \rightarrow HO + S$	12.6	22.3	10.9
	$S + OH \rightarrow SO + H$	11.8	0	13.4
	$H + SO \rightarrow HS + O$	12.8	39.6	8.6

Table 4 (continued). VALUES USED IN CALCULATING RATE CONSTANTS

Empirical Formula of Triatomic Intermediate XYZ	Reaction	$\log_{10}A/$ $[\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}]$	$C/(\text{kcal}/\text{mol})$	$\log_{10}k/[\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}]$ at 1500 K
	O + SH → OS + H	11.8	0	13.4
	O + HS → OH + S	11.8	8.0	12.2
	S + HO → SH + O	12.1	25.2	10.0
HO$_2$	H + O$_2$ → HO + O	13.1	16.8	12.2
	O + OH → O$_2$ + H	11.8	0	13.4
	O + HO → OH + O	11.8	8.0	12.2
HS$_2$	H + S$_2$ → HS + S	12.9	16.6	12.0
	S + SH → S$_2$ + H	11.8	0	13.4
	S + HS → SH + S	11.8	8.0	12.2
H$_2$N	H + HN → H$_2$ + N	11.8	8.0	12.2
	N + H$_2$ → NH + H	12.4	37.2	8.6
	H + NH → HN + H	11.8	0	13.4
H$_2$O	H + HO → H$_2$ + O	11.8	8.0	12.2
	O + H$_2$ → OH + H	12.1	9.9	12.3
	H + OH → HO + H	11.8	0	13.4
H$_2$S	H + HS → H$_2$ + S	11.8	8.0	12.2
	S + H$_2$ → SH + H	12.4	27.1	10.0
	H + SH → HS + H	11.8	0	13.4
H$_3$	H + H$_2$ → H$_2$ + H	11.8	8.0	12.2
NOS	N + OS → NO + S	11.8	8.0	12.2
	S + ON → SO + N	11.6	34.3	8.2
	S + NO → SN + O	12.0	34.7	8.6
	O + NS → ON + S	11.8	0	13.4
	O + SN → OS + N	11.8	8.0	12.2
	N + SO → NS + O	12.2	16.4	11.4
NO$_2$	N + O$_2$ → NO + O	11.8	8.0	12.2
	O + ON → O$_2$ + N	11.1	39.8	6.9
	O + NO → ON + O	11.8	0	13.4

Table 4 (concluded).   VALUES USED IN CALCULATING RATE CONSTANTS

Empirical Formula of Triatomic Intermediate XYZ	Reaction	$\log_{10}A/$ $[cm^3\ mol^{-1}\ s^{-1}]$	$C/(kcal/mol)$	$\log_{10}k/[cm^3\ mol^{-1}\ s^{-1}]$ at 1500 K
NS_2	$N + S_2 \to NS + S$	11.8	8.0	12.2
	$S + SN \to S_2 + N$	11.3	21.6	9.8
	$S + NS \to SN + S$	11.8	0	13.4
N_2O	$N + NO \to N_2 + O$	11.8	0	13.4
	$O + N_2 \to ON + N$	12.4	75.0	3.0
	$N + ON \to NO + N$	11.8	8.0	12.2
N_2S	$N + NS \to N_2 + S$	11.8	0	13.4
	$S + N_2 \to SN + N$	12.6	109.7	-1.8
	$N + SN \to NS + N$	11.8	8.0	12.2
N_3	$N + N_2 \to N_2 + N$	11.8	8.0	12.2
OS_2	$O + S_2 \to OS + S$	11.8	0	13.4
	$S + SO \to S_2 + O$	11.8	22.9	10.0
	$S + OS \to SO + S$	11.8	0	13.4
O_2S	$O + OS \to O_2 + S$	11.3	5.5	12.0
	$S + O_2 \to SO + O$	11.8	0	13.4
	$O + SO \to OS + O$	11.8	0	13.4
O_3	$O + O_2 \to O_2 + O$	11.8	0	13.4
S_3	$S + S_2 \to S_2 + S$	11.8	0	13.4

For the reactions in the H/N/O system, the experimental rate constants evaluated by the Leeds group[1,2] and the estimated rate constants are compared in Appendix A. The rest of this section compares the estimated rate constants with experimental data for reactions involving carbon and sulfur atoms that were not covered previously and with more recent data for the reaction of hydrogen atoms with nitric oxide and oxygen atoms with nitric oxide. The reactions of interest and the estimated rate parameters are given in Table 5.

For each reaction in Table 5, the experimental and estimated results have been compared. Boden and Thrush[9] have measured the rate of reaction (16)

$$O + CN \longrightarrow OC + N \tag{16}$$

between 570 and 687 K. The only rate constant reported by Boden and Thrush was $10^{13.0}$ cm^3 mol^{-1} s^{-1} at 687 K. Albens, Schmatjko, Wagner, and Wolfrum[10] recently reported a rate constant of $10^{13.1}$ cm^3 mol^{-1} s^{-1} independent of temperature at 298, 400, and 500 K. The experimental and estimated values are compared in Figure 3.

Hancock and Smith[11] have studied reaction (17).

$$O + CS \longrightarrow OC + S \tag{17}$$

They measured a rate constant of $10^{12.8}$ cm^3 mol^{-1} s^{-1} at 298 K and reported a previous measurement of $10^{14.1}$ cm^3 mol^{-1} s^{-1} at 1100 K by Homann, Krome, and Wagner.[12] The experimental results are compared with estimated values in Figure 3.

Flower, Hanson, and Kruger[13] recently completed a study of reaction (18) in a shock tube between 2400 and 4500 K.
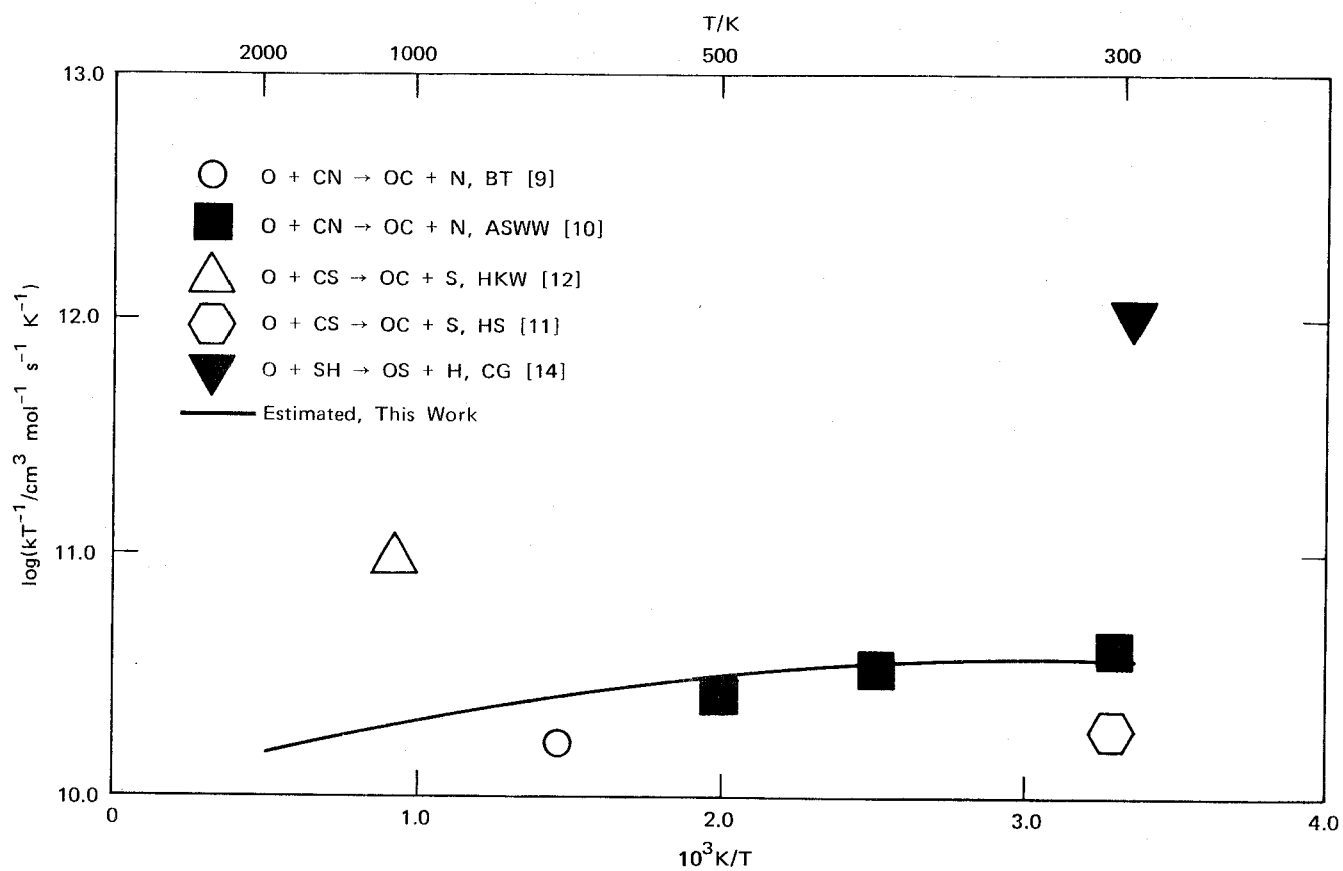
$$H + ON \longrightarrow HO + N \tag{18}$$
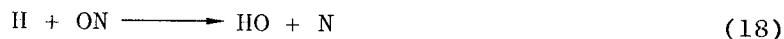
The experimental and estimated results are compared in Figure 4.

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Table 5. ESTIMATED RATE PARAMETERS AND RATE CONSTANTS[a]

Empirical formula of XYZ	Reaction	$\log[A/(cm^3\ mol^{-1}\ s^{-1})]$	$C/(kcal/mol)$	$\log[k/(cm^3\ mol^{-1}\ s^{-1})]$ at 1000 K
CNO	O + CN → OC + N	11.8	0	13.4
COS	O + CS → OC + S	11.8	0	13.4
HNO	H + ON → HO + N	12.4	48.6	6.9
HOS	O + SH → OS + H	11.8	0	13.4
HS_2	S + SH → S_2 + H	11.8	0	13.4
H_2S	H + HS → H_2 + S	11.8	8.0	12.2
NO_2	O + ON → O_2 + N	11.1	40.1	6.9
SO_2	S + O_2 → SO + O	11.8	0	13.4

[a]Estimated rate parameters of the equation $k = AT^{0.5} \exp(-C/RT)$ and rate constants at 1000 K for some reactions of the type X + YZ → XY + Z, where X, Y, and Z are atoms of the elements carbon, hydrogen, nitrogen, oxygen, and sulfur.

FIGURE 3   COMPARISON OF MEASURED AND ESTIMATED RATE CONSTANTS
FOR REACTIONS OF OXYGEN ATOMS

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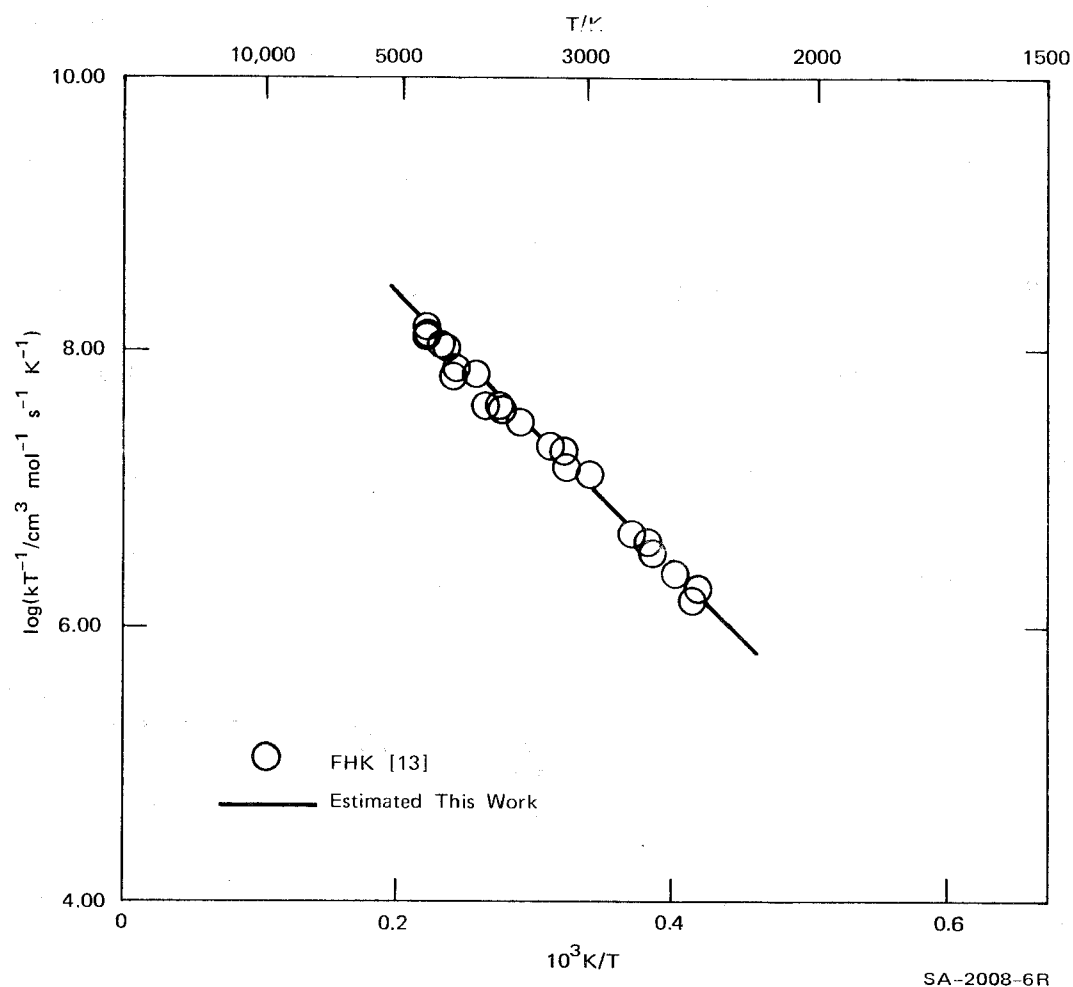
23

FIGURE 4   COMPARISON OF MEASURED AND ESTIMATED RATE CONSTANTS
FOR THE REACTION H + ON → HO + N

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Cupitt and Glass[14] have studied the reaction of atomic oxygen with hydrogen sulfide by esr spectroscopy. The variation in the concentration of free radicals was measured, and the results were interpreted in terms of a mechanism consisting of seven elementary reactions. One of the reactions was

$$O + SH \longrightarrow OS + H \tag{19}$$

The experimental results were consistent with a rate constant of $10^{14.5}$ cm^3 mol^{-1} s^{-1} at 295 K for reaction (19). This rate constant is compared with the estimated one in Figure 3.

Mihelcic and Schindler[15] have studied the sulfur analog of reaction (19)

$$S + SH \longrightarrow S_2 + H \tag{20}$$

by the same method as Cupitt and Glass. The rate constant of reaction (20) at 300 K was found to be $10^{13.4}$ cm^3 mol^{-1} s^{-1}. This rate constant is compared with the estimated one in Figure 5.

Using the same system as was used to study reaction (19), Cupitt and Glass measured the rate constant at 295 K for reaction (21)
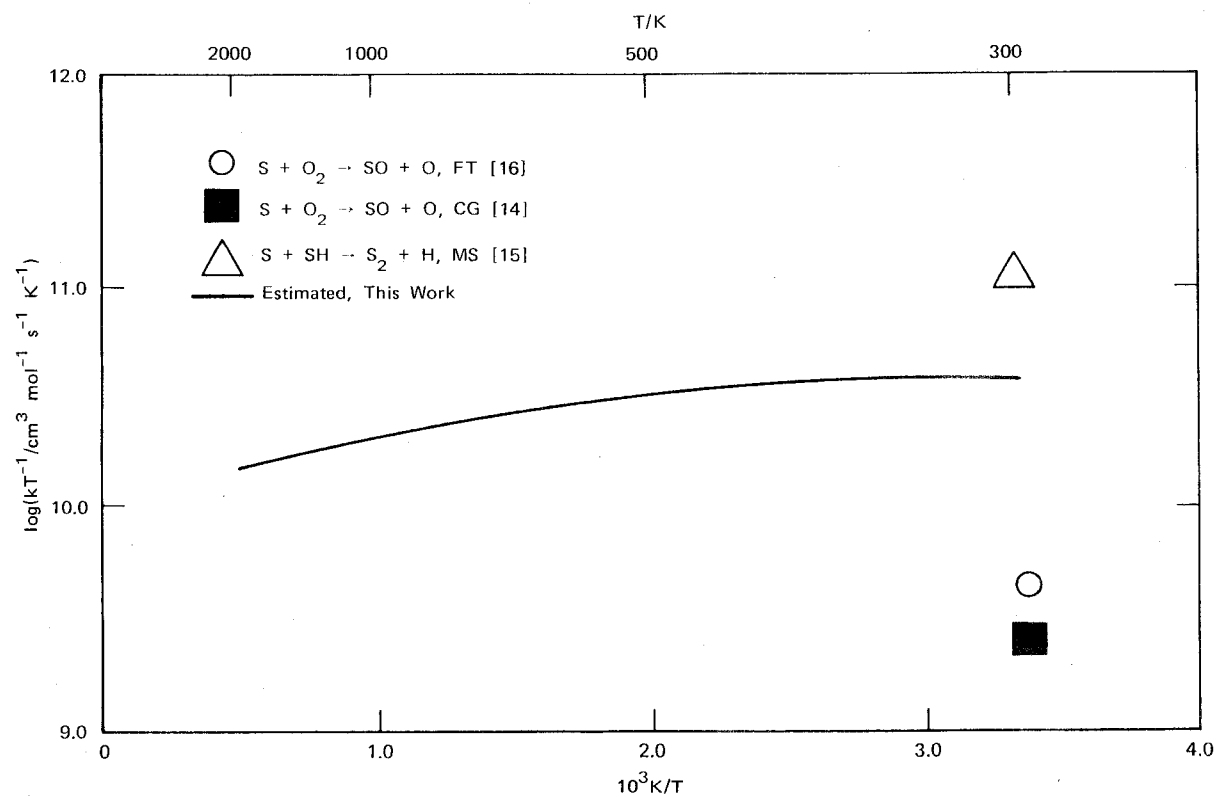
$$H + HS \longrightarrow H_2 + S \tag{21}$$

to be $10^{13.9}$ cm^3 mol^{-1} s^{-1}. This rate constant is compared with the estimated one in Figure 6.

Hanson, Flower, and Kruger[17] recently investigated the decomposition of nitric oxide in a shock tube in the range of 2500 to 4100 K. From their rate measurements, they derived the rate constants for reaction (22)

$$O + ON \longrightarrow O_2 + N \tag{22}$$

shown in Figure 7 with rate constants measured by other workers[18-21] and with the estimated rate constants.

FIGURE 5   COMPARISON OF MEASURED AND ESTIMATED RATE CONSTANTS
FOR REACTIONS OF SULFUR ATOMS

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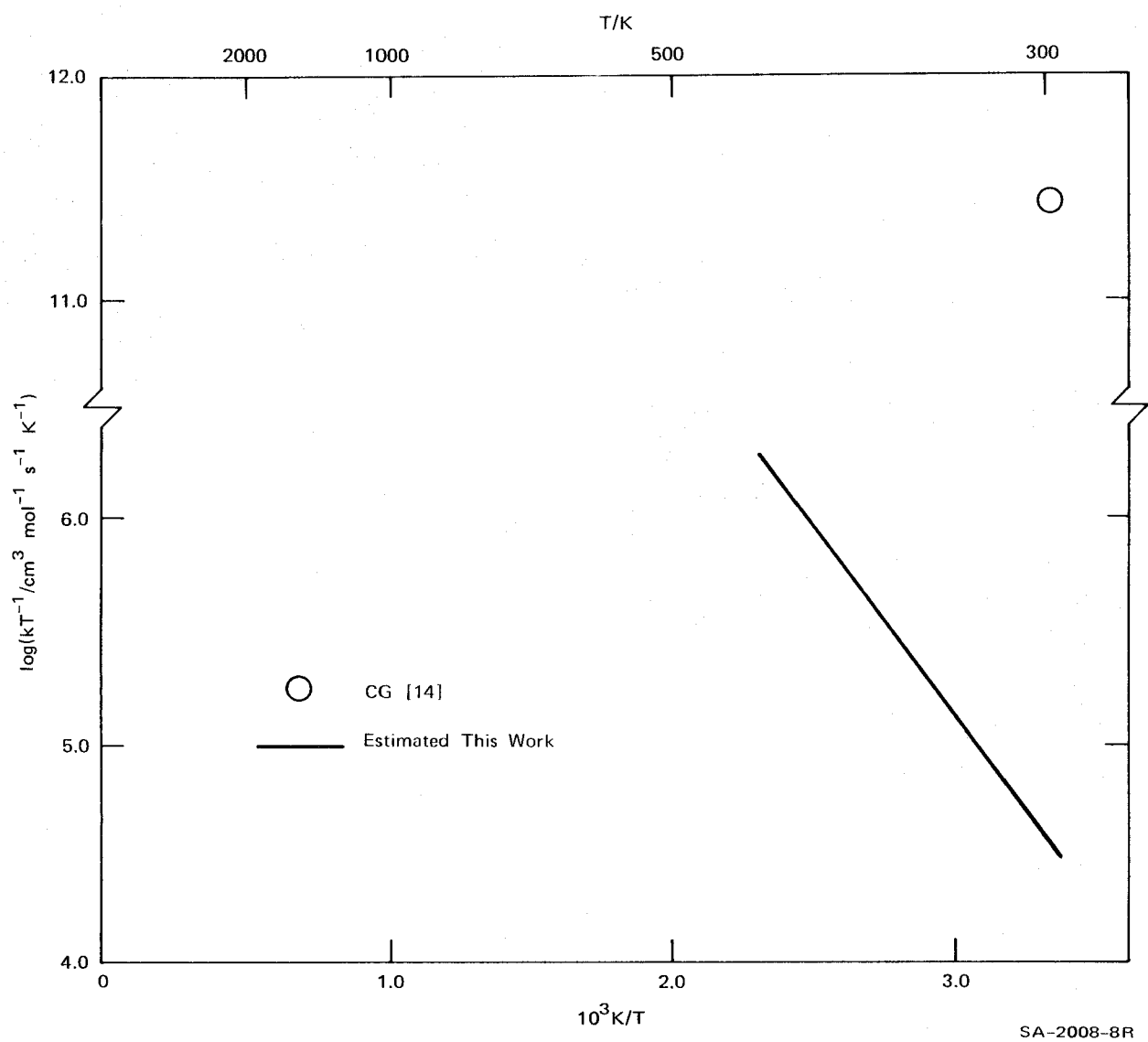FIGURE 6   COMPARISON OF MEASURED AND ESTIMATED RATE CONSTANTS
FOR THE REACTION H + HS → H_2 + S

27
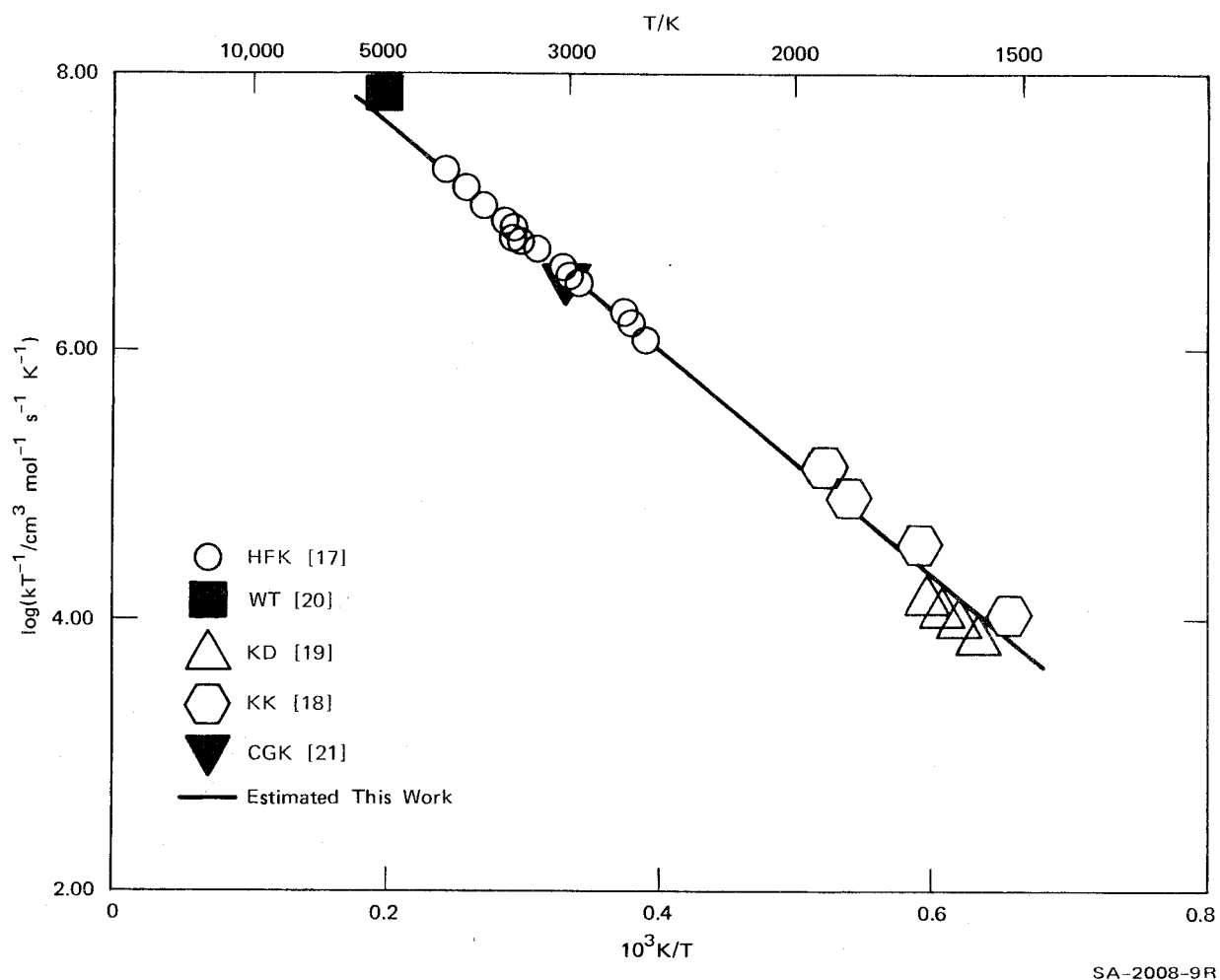
FIGURE 7 COMPARISON OF MEASURED AND ESTIMATED RATE CONSTANTS
FOR THE REACTION O + ON → O_2 + N

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Reaction (23)

$$S + O_2 \longrightarrow SO + O \qquad (23)$$

has been studied by Cupitt and Glass,[14] who found $k_{23} = 10^{11.9}$ cm^3 mol^{-1} s^{-1} at 295 K, and by Fair and Thrush,[16] who found $k_{23} = 10^{12.1}$ cm^3 mol^{-1} s^{-1} at 298 K. The experimentally determined rate constants are compared with the estimated ones in Figure 5.

The agreement between measured and estimated rate constants for H, N, O reactions is excellent, as shown in Figures 4 and 7. For reactions involving carbon and sulfur atoms, there is enough experimental evidence to suggest that the method of estimation is at least a good first approximation.

Consider reactions of the type

$$O + YZ \longrightarrow OY + Z \qquad (24)$$

shown in Figure 3. At first sight it appears that the worst agreement between measured and estimated values is for reaction (19)

$$O + SH \longrightarrow OS + H \qquad (19)$$

However, if all the difference between measured and estimated rate constants is attributed to activation energy, as is likely, then the difference between observed and calculated rate constants for reaction (19) corresponds to less than 2 kcal/mol, whereas the difference is 3 kcal/mol for reaction (17)

$$O + CS \longrightarrow CO + S \qquad (17)$$

These differences are not large for combustion reactions.

Similarly, for reactions of the type

$$S + YZ \longrightarrow SY + Z \qquad (25)$$

where Y is an sulfur or an oxygen atom, the difference between estimated

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and observed rate constants at 300 K corresponds to a difference of about 2 kcal/mol, as shown in Figure 5. However, when Y is a hydrogen atom, as in reaction (-21)

$$S + H_2 \longrightarrow SH + H \qquad (-21)$$

$$H + HS \longrightarrow H_2 + S \qquad (21)$$

there is a big discrepancy (about 7 powers of 10) between the rate constants at 300 K. This discrepancy in the rate constants for reaction (21) corresponds to about 10 kcal/mol in the activation energies. There is only one experimental value for reaction (21), but the other two rate constants in the same experiment, namely, for reactions (19) and (23)

$$O + SH \longrightarrow OS + H \qquad (19)$$

$$S + O_2 \longrightarrow SO + O \qquad (23)$$

are in good agreement with other experimental work and with the estimates. On the other hand, this one value for reaction (21) is the only example, out of all available experimental data for the CHNOS system, where the estimated and experimental data are not in agreement. There is no room for adjusting the estimated value, because the thermochemistry is too well known for reaction (21) to be anything other than exothermic. Furthermore, since the atom being transferred is a hydrogen atom, there is no need to estimate the heat of formation of the transition state. Clearly, more work is required on this reaction.

SECTION V

ESTIMATES OF RATE CONSTANTS FOR SPECIFIC REACTIONS
REQUESTED BY EPA AND ITS CONTRACTORS

During the course of this research, estimates of rate constants for reactions outside the limits of Table 1 were made by telephone, by letter, and during visits in response to requests on specific reactions by EPA and its contractors. The estimating techniques have been described previously.[7] The most recent estimates are given in Table 6. The other estimates have been published as part of a final report to EPA on a related project by Exxon.[22]

Table 6. HEATS OF REACTION AND ESTIMATED ARRHENIUS PARAMETERS FOR SOME REQUESTED REACTIONS

Reaction	ΔH^0_{298} (kcal/mol)	$\log_{10}$ $(A/(cm^3 mol^{-1}s^{-1}))$	E/(kcal/mol)	Comments
$HCN + N \rightarrow CH + N_2$	− 3.30	11.7	$[16 \pm 6]^a$	Spin retarded.
$HCO + N \rightarrow CH + NO$	41.58	14	48.6	Based on an estimate of E = 7 ± 3 kcal/mol for the back reaction.
$CH_2 + CN \rightarrow CH + HCN$	−22.70	12.5	5	
$HCN + O \rightarrow CH + NO$	71.72	14	$[72 \pm 2]$	Based on an estimate of E = 0 ± 2 kcal/mol for the back reaction.
$CN + NH \rightarrow CH + N_2$	−52.00	14	$[40 \pm 20]$	Four-center.
$CHO + HO \rightarrow H_2O + CO$		$10.5 + \log_{10}(T/K)$	0	
$CH_2 + N_2 \rightarrow HCN + NH$	29.30	14	$[70 + 20]$	Based on an estimate of E = 40 ± 20 kcal/mol for the back reaction.
$HCO + N \rightarrow HCN + O$	−30.14	14	$[0 \pm 2]$	No spin problem.
$CO_2 + H \rightarrow HCO + O$	110.5	14	$[11 \pm 2]$	Based on an estimate of E = 0 ± 2 kcal/mol for the back reaction.
$CO + HO_2 \rightarrow HCO + O_2$	30.4	12.5	37.4	Based on an estimate of E = 7 kcal/mol for the back reaction.
$CHO + O \rightarrow CO + HO$		$11.5 + \log_{10}(T/K)$	0.5	
$CH_3 + O_2 \rightarrow CH_2 + HO_2$	62.53	12.5	69.53	Based on an estimate of E = 7 kcal/mol for the back reaction.
$CH_3 + O_2 \rightarrow CH_3O + O$	27.8	12.5	30	
$CH_2O + N \rightarrow CH_2 + NO$	26.88	14	$[34 + 4]$	Based on an estimate of E = 7 ± 4 kcal/mol for the back reaction.
$CH_3O + M \rightarrow CH_2O + H + M$		$40.6 - 7.5 \log_{10}(T/K)$	22.6	Based on Hinshelwood-Lindemann theory.
$CH_3O + N \rightarrow CH_2O + NH$	−51.95	14	0	
$CH_3O + O \rightarrow CH_2O + HO$	−79.21	14	0	
$CH_3O + O_2 \rightarrow CH_2O + HO_2$	−23.95	12	6	
$CH_3O + H \rightarrow CH_2O + H_2$	−81.05	14	0	
$CH_3O + OH \rightarrow CH_2O + H_2O$	−96.05	13.5	0	
$CH_2 + CH_2O \rightarrow CH_3 + CHO$	−22.65	11.3	6.5	
$CH_3 + CH_2O \rightarrow CH_4 + CHO$	−17.75	11.3	6.5	
$CN + H_2 \rightarrow HCN + H$	−19.6	12.5	5	
$CN + HO \rightarrow HCN + O$	−21.4	12.5	3	
$O + CH + M \rightarrow CHO + M$	−192.6	$19 + \log_{10}(T/K)^b$	0	
$CHO + HO_2 \rightarrow CH_2O + O_2$	−40.0	14	3	
$CH_2 + H_2 \rightarrow CH_3 + H$	−5.5	12.5	7	
$CH + CH_3 \rightarrow 2 CH_2$	8.0	12.5	8.0	
$CH + CH_4 \rightarrow CH_2 + CH_2$	3.1	12	17.1	

[a] Estimates in square brackets are as given; others are ± 3 kcal/mol.

[b] $\log_{10}(A/cm^6 mol^{-2} s^{-1}))$; estimated error in $\log_{10}A$ is ± 0.5.

SECTION VI

THE COMPUTER PROGRAM

A computer program was written to calculate the rate constant at any temperature of any of the 75 reactions of the type $X + YZ \rightleftharpoons XY + Z$, where X, Y, and Z are atoms of the elements carbon, hydrogen, nitrogen, oxygen, and sulfur. The program, written in FORTRAN IV, is named CRATES for Chemical Reaction Rate Constants. Complete documentation for the program is inline in the form of FORTRAN comment cards. These cards are fully prepared to run on the UNIVAC 1108 computer under the EXEC-8 operating system. Only the RUN card needs to be changed to run the deck on the EPA installation.

A printout of the program and the deck of cards, containing the source deck for program CRATES and the data files, have been submitted to EPA. A 7-track, 556 bpi, unlabelled, BCD tape with one file was also submitted as a backup. This file has 84 characters per physical record (the last 4 characters are blanks) and is the source deck and data files for program CRATES but with no control cards. The tape can be converted to cards and the appropriate EXEC-8 control cards inserted by hand before executing the program.

Requests for copies of the program should be addressed to the Project Officer.

ESTIMATES OF RATE CONSTANTS FOR COMBINATION AND DISSOCIATION REACTIONS

Rate constants have been estimated for some of the combination and dissociation reactions of the type

$$X + Y + M \rightleftarrows XY + M \tag{26}$$

and

$$XY + Z + M \rightleftarrows XYZ + M \tag{27}$$
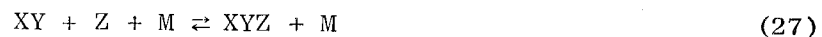
where X, Y, and Z are atoms of the elements hydrogen, nitrogen, and oxygen and M is N_2. The results are summarized in Section I, Conclusions, and are discussed in detail in the interim annual report[5] and in the Airlie House paper,[6] which is included as Appendix A.

SECTION VIII

VARIATION OF EQUILIBRIUM CONSTANT WITH TEMPERATURE

It has been pointed out[5,6,22] how useful it would be to have in analytical form the variation of the equilibrium constant with temperature. Rigorously,[7] the variation of the equilibrium constant with temperature is given by:

$$RT \ln K = -\Delta G_T^0 \tag{28}$$

where

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0 \tag{29}$$

$$\Delta G_T^0 = \Delta H_{300_T}^0 + \int_{300}^{T} \Delta C_p^0 dT - T\Delta S_{300}^0$$

$$-T \int_{300}^{} \Delta C_p^0 d \ln T \tag{30}$$

However, for estimating the equilibrium constants of the elementary reactions that are important in combustion systems, it is a very good approximation to use:

$$\Delta G_T^0 \approx \Delta H_{1500}^0 - T\Delta S_{1500}^0 \tag{31}$$

For reactions in which there is a change in the number of moles, for example, $N + O + M \rightarrow NO + M$, the equilibrium constant in units of concentration K_c is related to that in pressure units K_p by:

$$K_c = K_p (R'T)^{-\Delta n} \tag{32}$$

where R' is 82.057 cm^3 atm/(mol K) and Δn is the mole change in the reaction. For compatibility with the modified Arrhenius equation, which is:

$$k = AT^B \exp(-C/RT) \tag{33}$$

equation (32) can be put in the form:

$$K_c/(mol/cm^3)^{\Delta n} = (82)^{-\Delta n}[\exp(\Delta S^0_{1500}/R)]T^{-\Delta n} \exp[-\Delta H^0_{1500}/(RT)]$$

$$= A'T^{B'} \exp[-C'/(RT)] \tag{34}$$

where:

$$\log_{10}A' = -1.9\Delta n + [\Delta S^0_{1500}/(2.3R)]$$

$$B' = \Delta n$$

$$C' = \Delta H^0_{1500}.$$

SECTION IX

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SECTION X

APPENDICES

Appendix A

ESTIMATION OF RATE CONSTANTS AS A FUNCTION OF TEMPERATURE

FOR REACTIONS X + YZ $\rightleftarrows$ XY + Z, X + Y + M $\rightleftarrows$ XY + M, AND

X + YZ + M $\rightleftarrows$ XYZ + M, WHERE X, Y, AND Z ARE ATOMS   H, N, O

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ABSTRACT

Previously measured and evaluated rate constants for the reactions

$X + YZ \rightleftarrows XY + Z$, $X + Y + M \rightleftarrows XY + M$, and $X + YZ + M \rightleftarrows XYZ = M$,

where X, Y, and Z are the atoms H, N. and O, have been shown to fit the

form $k = AT^B \exp(-C/RT)$, where k is in mole, cm^3, sec units, and the

constants A, B, and C have the values listed below.

Reaction	$\log_{10}A$	B	C
$X + YZ \rightleftarrows XY + Z$	$16.6 + [\Delta S^{0\ddagger}_{300}/(2.3R)]$	0.5	$\Delta H^{0\ddagger}_{300} + 1$
$X + Y + M \rightarrow XY + M$	18	-1	0
$XY + M \rightarrow X + Y + M$	$16.1 + [\Delta S^{0\ddagger}_{1500}/(2.3R)]$	-2	ΔH^{0}_{1500}
$X + YZ + M \rightarrow XYZ + M$ (X and Z are both hydrogen atoms)	19	-1	0
$XYZ + M \rightarrow X + YZ + M$	$17.1 + [\Delta S^{0}_{1500}/(2.3R)]$	-2	ΔH^{0}_{1500}
$X + YZ + M \rightarrow XYZ + M$ (X and Z are not both hydrogen atoms)	20.2	-1.5	0
$XYZ + M \rightarrow X + YZ + M$	$18.3 + [\Delta S^{0}_{1500}/(2.3R)]$	-2.5	ΔH^{0}_{1500}

$\Delta S^{0\ddagger}_{300}$ is the entropy of activation at 300 K and is equal to -22

cal/(mole K) in the exothermic direction $(-22 + \Delta S^{0}_{300}$ cal/(mole K) in

the endothermic direction). $\Delta H^{0\ddagger}_{300}$ is the heat of activation at 300 K

and is equal to either (a) -1 kcal/mole for exothermic (-1 + ΔH^0_{300} kcal/ mole for endothermic) reactions that have a transition state preceded by an intermediate that is stable with respect to the reactants, or (b) 7 kcal/mole for exothermic (7 + ΔH^0_{300} kcal/mole for endothermic) reactions that are concerted or that have a transition state preceded by an intermediate that is unstable with respect to the reactants. The criterion for a stable intermediate is that its heat of formation must be at least 3 kcal/mole less than the sum of the heats of formation of the reactants.

It is suggested that the rate constants listed above may be useful in estimating rate constants for reactions that have not been studied experimentally, especially at temperatures above 1000 K.

A convenient form of the equilibrium constant, suitable for combustion reactions, is $K/(cm^3/mole) = 10^{1.9}(exp \Delta S^0_{1500}/R) \, T \, exp(-\Delta H^0_{1500}/RT)$.

INTRODUCTION

The aim of this research is to provide a computer program that will estimate rate constants of elementary chemical reactions for mathematical models of combustion processes. The models are being developed by the Combustion Research Section of the United States Environmental Protection Agency as tools to reduce air pollution and improve efficiency of utility burners. The chemical elements to be considered are carbon, hydrogen, nitrogen, oxygen, and sulfur. In the beginning, we selected the reactions of the atomic and diatomic species of hydrogen, nitrogen, and oxygen for their simplicity and because of the widely praised critical reviews by Baulch, Drysdale, Horne, and Lloyd.[1,2] * The species under consideration are H, N, O, H_2, N_2, O_2, HN, NO, and OH. For combinations, the "third body" M, is taken as N_2. The temperature range is 200 to 3000 K. The approach is to develop equations that will account for rate constants that have been measured and then use these equations to predict rate constants of reactions that have not been studied experimentally.

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* References are listed at the end of Appendix A.

TRANSFER REACTIONS

Transfer reactions were considered in this study first because they are simple and because of inspiration from Dryer, Naegeli, and Glassman's work[3] on the transfer reaction $CO + OH \rightarrow CO_2 + H$. The simplest transfer reactions are those between atoms and diatomics:

$$X + YZ \rightleftharpoons XY + Z \tag{1}$$

From transition state theory,[4] the rate constant, k, is given by:

$$k/[cm^3/(mole\ sec)] = \frac{82\kappa T^2}{h} \exp(-\Delta G_T^{o\ddagger}/RT) \tag{2}$$

where κ is Boltzmann's constant, h is Planck's constant, $\Delta G_T^{o\ddagger}$ is the standard free energy change (standard state of 1 atmosphere) at temperature T, going from the initial state to the transition state, R is the gas constant, and 82T is to express the rate constant in $cm^3/(mole\ sec)$.

$$\Delta G_T^{o\ddagger} = \Delta H_T^{o\ddagger} - T\Delta S_T^{o\ddagger} \tag{3}$$

where $\Delta H_T^{o\ddagger}$ and $\Delta S_T^{o\ddagger}$ are the enthalpy and entropy changes from the reactants to the transition state, and:

$$\Delta G_T^{o\ddagger} = \Delta H_{300}^{o\ddagger} + \int_{300}^{T} \Delta C_p^{o\ddagger} dT - T\Delta S_{300}^{o\ddagger} - T\int_{300}^{T} \Delta C_p^{o\ddagger} d\ln T \tag{4}$$

where $\Delta C_p^{o\ddagger}$ is the heat capacity change from the initial state to the transition state.

The heat capacity correction $\Delta C_p^{o\ddagger}$ is given by $\Delta C_p^{o\ddagger} = -3 \pm 1$ cal/(mole K). The reasoning is as follows: in a reaction X + YZ going to a transition state $X \cdots Y \cdots Z$, we can estimate the heat capacities of the

species X, YZ, and X···Y···Z (neglecting electronic heat capacities) as follows:

$$C_p^o (X) = 5R/2$$

$$C_p^o (YZ) = C_p^o (\text{translation}) + C_p^o (\text{rotation}) + C_p^o(\text{vibration})$$

$$= 5R/2 + R + C_p^o(\text{vib})$$

$$= 7R/2 + C_p^o(\text{vib})$$

$$C_p^{o\ddagger}(X \cdots Y \cdots Z) = C_p^o(\text{translation}) + C_p^o(\text{rotation}) + C_p^o(\text{vibration})$$

$$= 5R/2 + 3R/2 \text{ (nonlinear)} + C_p^o(\text{vib})$$

$$\therefore \Delta C_p^{o\ddagger}(X + YZ \rightarrow X \cdots Y \cdots Z) = 8R/2 + C_{p,\text{vib}}^o(X \cdots Y \cdots Z)^{\ddagger} - 12R/2 - C_{p,\text{vib}}^o(YZ)$$

X···Y···Z has 3n - 6 = 3 frequencies, one of which is the reaction frequency; one of which can be assumed equal to the Y-Z stretch in YZ; and the remaining one is the X···Y···Z bend.

$$\therefore \Delta C_p^{o\ddagger}(X + YZ \rightarrow X \cdots Y \cdots Z) = -2 R + C_p^o(X \cdots Y \cdots Z \text{ bend})$$

The C_p^o bend must lie between 0 and R and, therefore, has the value R/2 ± R/2:

$$\therefore \Delta C_p^{o\ddagger} = -3R/2 \pm 1R/2$$

$$= -3 \pm 1 \text{ cal/(mole K)}$$

Equation (4) can now be integrated directly, giving:

$$\Delta G_T^{o\ddagger} = \Delta H_{300}^{o\ddagger} - T\Delta S_{300}^o + \Delta C_p^{o\ddagger} [(T - 300) - T\ln(T/300)] \tag{5}$$

where $\Delta C_p^{o\ddagger}$ is -3 cal/(mole K).

Summarizing,

$$k/[\text{cm}^3/(\text{mole sec})] = \frac{82 \; K \; T^2}{h} \exp (-\Delta G_T^{o\ddagger}/RT) \tag{2}$$

Engleman[5] has pointed out that it would be more convenient to transpose equation (2) to the modified Arrhenius equation:

$$k = AT^B \exp(-C/RT) \tag{6}$$

The results follow.

In general,

$$A/(cm^3/(mole\ sec)) = \frac{82\ K}{\ln(300)^{(\Delta C_p^{o\ddagger}/R)}}\ \exp[\Delta S_{300}^{o\ddagger} - (\Delta C_p^{o\ddagger}/R)] \qquad (7)$$

$$B = 2 + (\Delta C_p^{o\ddagger}/R) \qquad (8)$$

$$C/(kcal/mole) = \Delta H_{300}^{o\ddagger} - .3\ \Delta C_p^{o\ddagger} \qquad (9)$$

where $\Delta C_p^{o\ddagger}$ is in units of $cal/(mole\ k)$.

Inserting the value of $\Delta C_p^{o\ddagger} = -3\ cal/(mole\ K)$, equations (7), (8), and (9) become:

$$A = 10^{16.6}\ \exp(\Delta S_{300}^{o\ddagger}/R) \qquad (10)$$

$$B = 0.5 \qquad (11)$$

$$C = \Delta H_{300}^{o\ddagger} + 1 \qquad (12)$$

That is,

$$k/[cm^3/(mole\ sec)] = 10^{16.6}\ \exp(\Delta S_{300}^{o\ddagger}/R)T^{0.5}\ \exp[-(\Delta H_{300}^{o\ddagger} + 1/RT] \qquad (13)$$

We have found empirically (Figures A-1 to A-8) that all the Leeds critically evaluated data[1,2] could be fitted by substituting the following values in equation (13). In the exothermic direction, $\Delta S_{300}^{o\ddagger} = -22\ cal/mole\ K)$, and $\Delta H_{300}^{o\ddagger} = -1$ or 7 kcal/mole. In the endothermic direction, $\Delta S_{300}^{o\ddagger} = -22 + \Delta S_{300}^{o}\ cal/(mole\ K)$, and $\Delta H_{300}^{o\ddagger} = (-1 + \Delta H_{300}^{o})$ or $(7 + \Delta H_{300}^{o})$ kcal/mole. References in the figures refer to the original compilation.

JANAF values[6] for the three atoms and six diatomic species in the H, N, O system are listed in Table A-1, and were used to calculate ΔS_{300}^{o} and ΔH_{300}^{o} for the nine reaction pairs of the H, N, O system in Table A-2. Unless otherwise noted, JANAF values are used throughout this paper. The values of A, B, and C used to calculate the rate constants in Figures A-1 to A-8 are given in Table A-3. The rate constants were calculated at 200 K, 300 K, 400 K, 500 K, 700 K, 1000 K, 2000 K, 3000 K, and 4000 K. A typical calculation for the reaction $O + H_2 \rightarrow OH + H$ is shown in Table A-4.
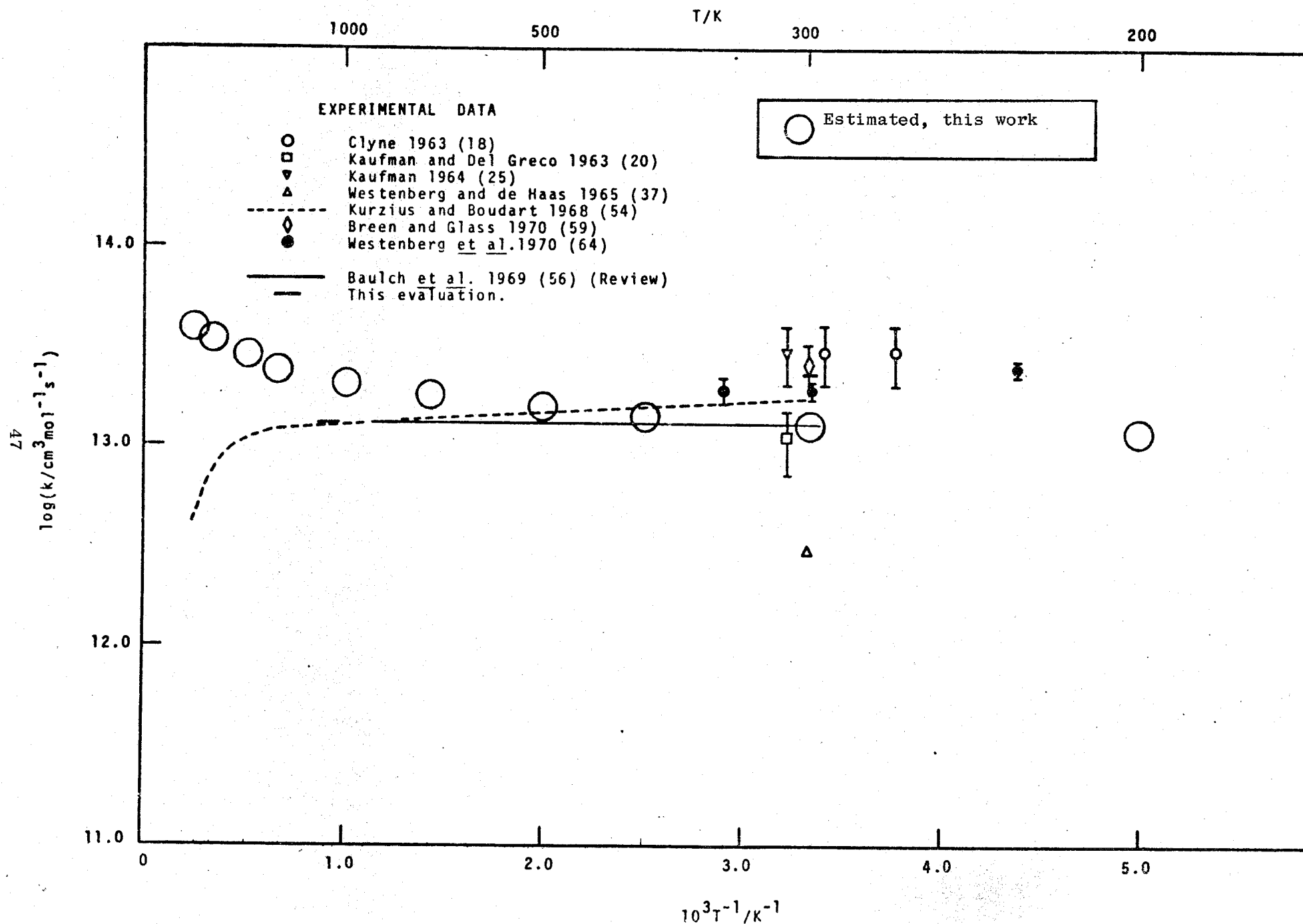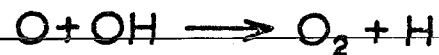
FIGURE A-1   O + OH → O₂ + H
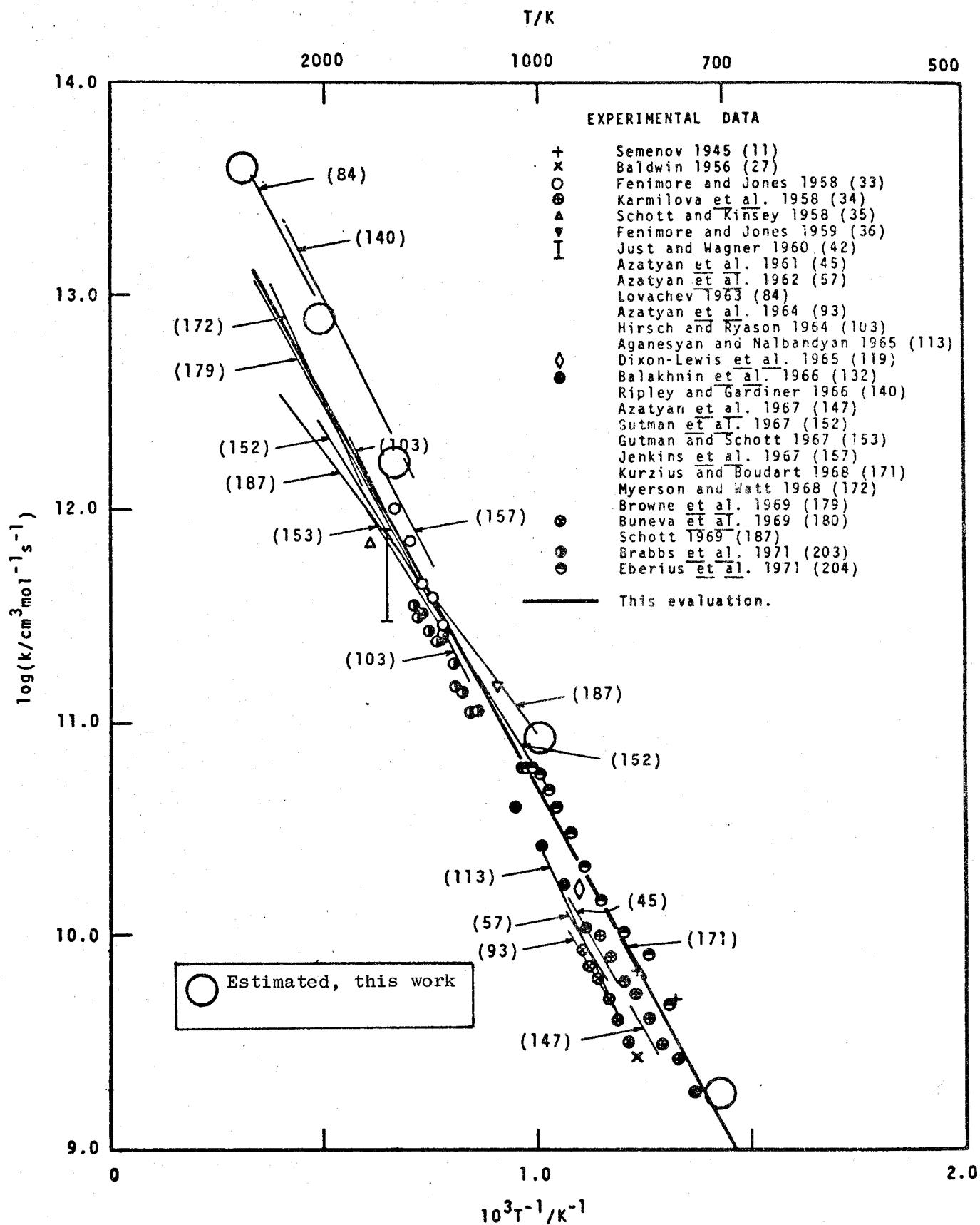
FIGURE A-2   H + O$_2$ $\rightarrow$ HO + O
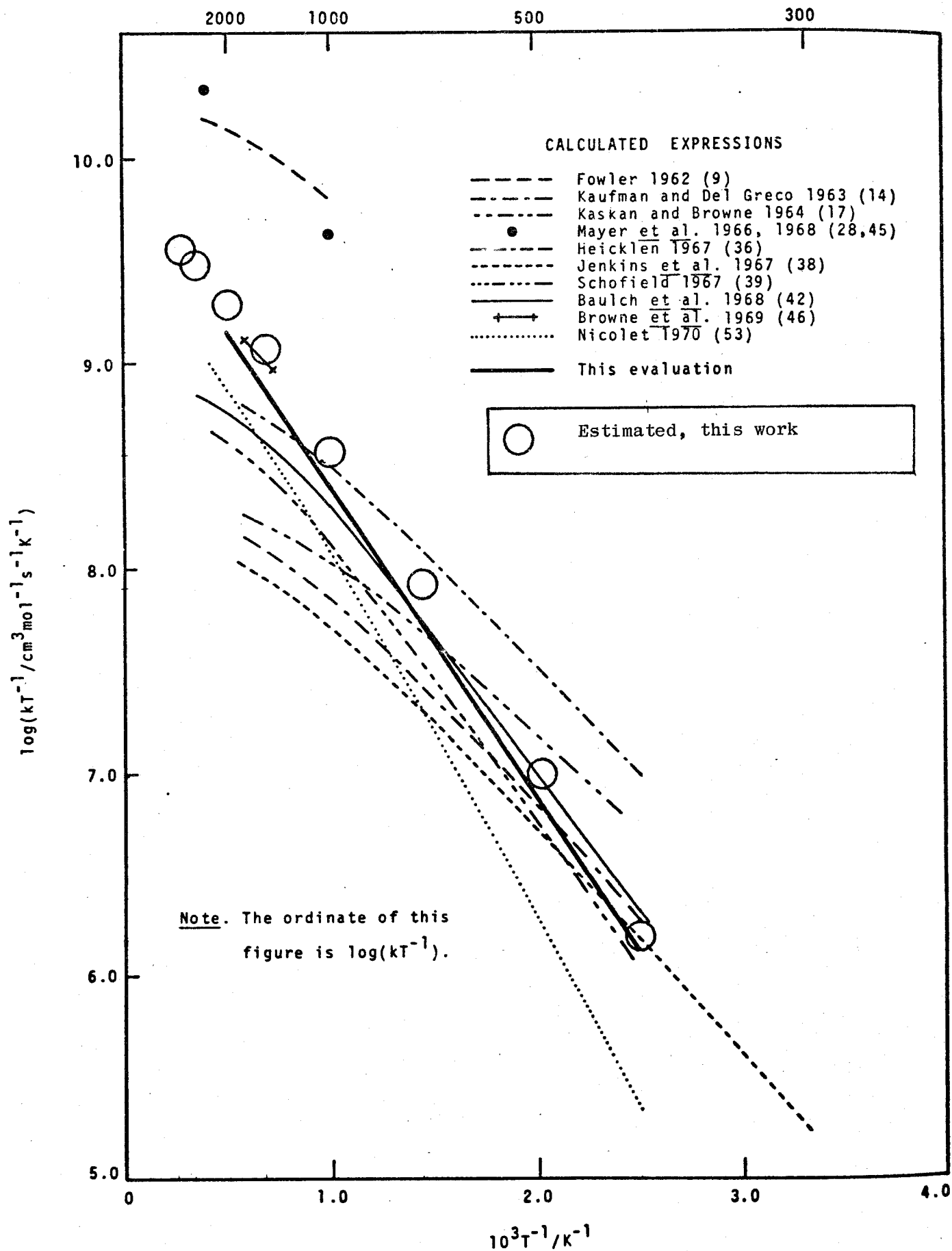
48

FIGURE A-3 H + OH → H₂ + O

CALCULATED EXPRESSIONS

— — — — Fowler 1962 (9)
—··—··— Kaufman and Del Greco 1963 (14)
—···—···— Kaskan and Browne 1964 (17)
● Mayer et al. 1966, 1968 (28,45)
—·—·— Heicklen 1967 (36)
---------- Jenkins et al. 1967 (38)
—··—··— Schofield 1967 (39)
———— Baulch et al. 1968 (42)
+————+ Browne et al. 1969 (46)
·············· Nicolet 1970 (53)

———— This evaluation

○ Estimated, this work

Note. The ordinate of this figure is log(kT⁻¹).

49

FIGURE A-4   O + H_2 → OH + H

50

NO + N ⟶ N₂ + O

December   1969

T(°K)
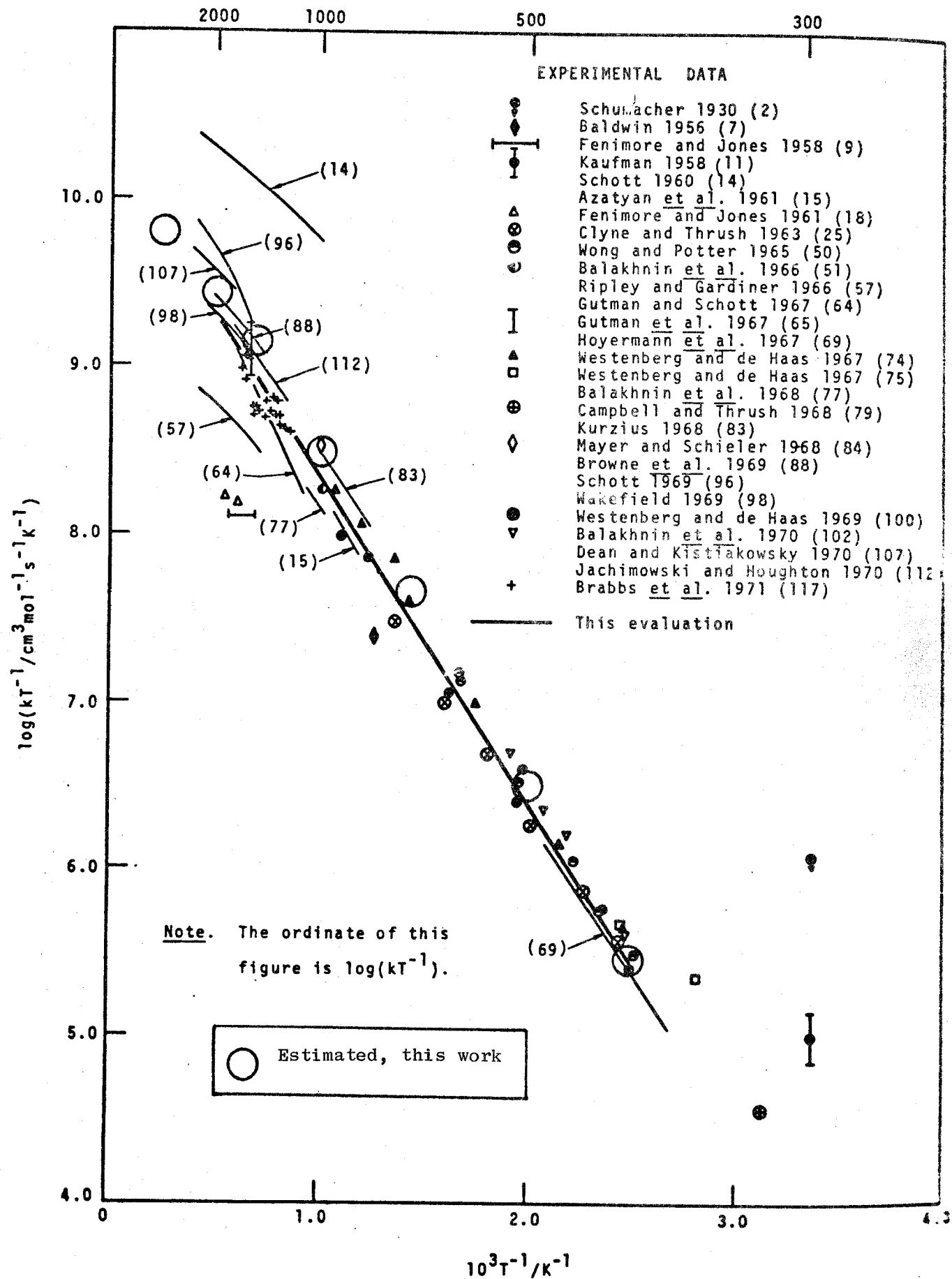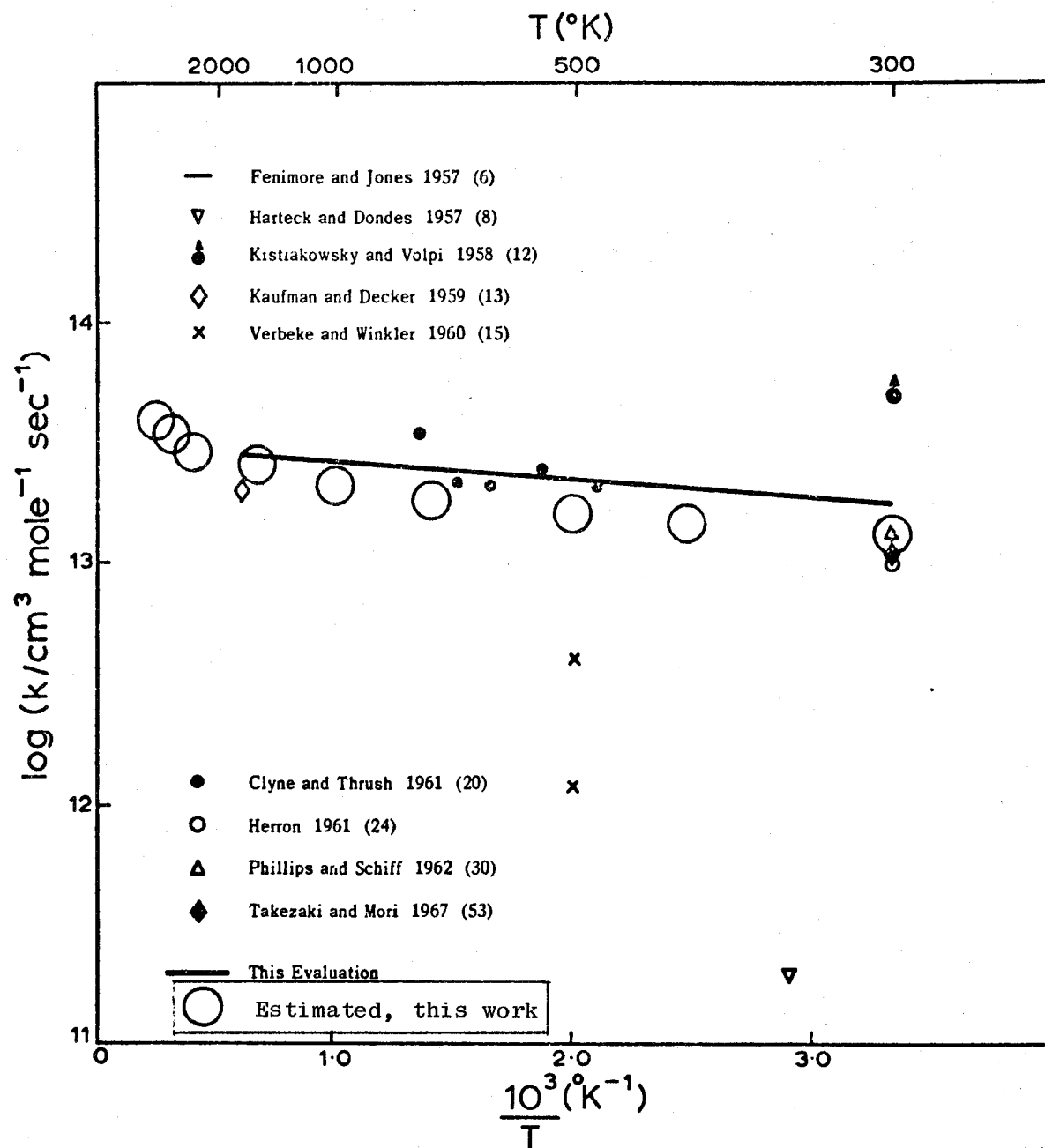
FIGURE A-5   N + NO → N₂ + O
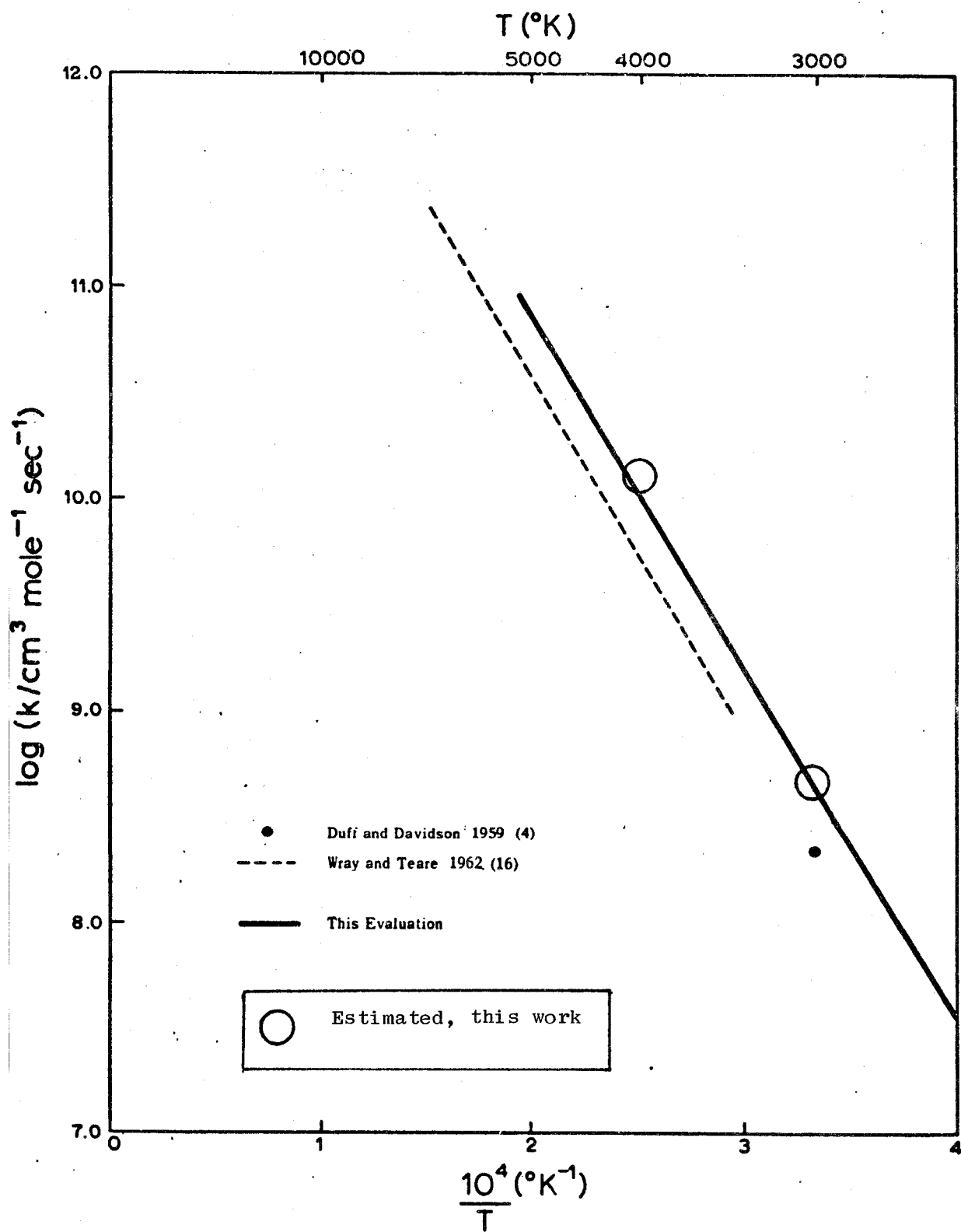
FIGURE A-6 $O + N_2 \rightarrow ON + N$

FIGURE A-7   N + O$_2$ $\rightarrow$ NO + O

$$NO + O \longrightarrow O_2 + N$$
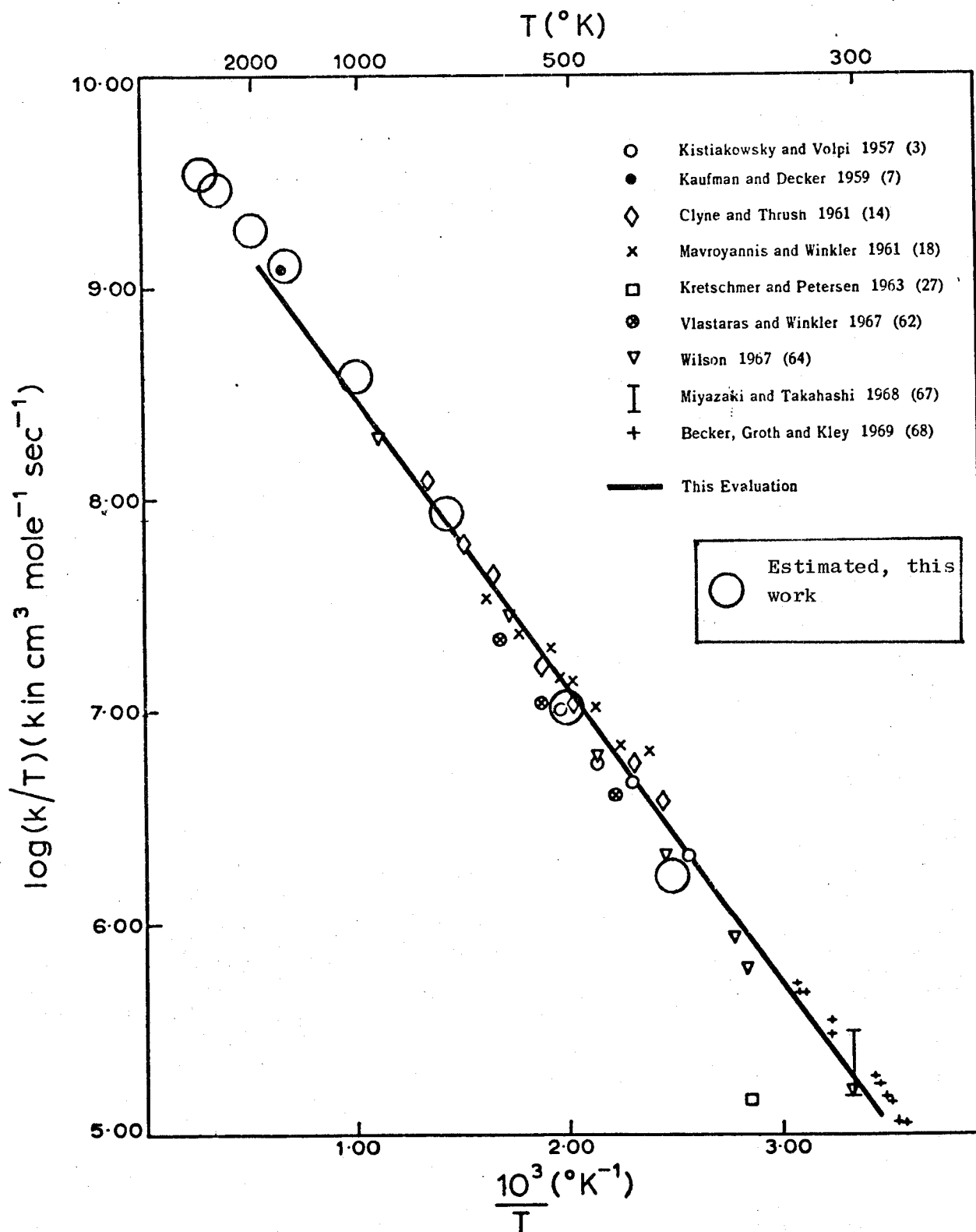
December 1969
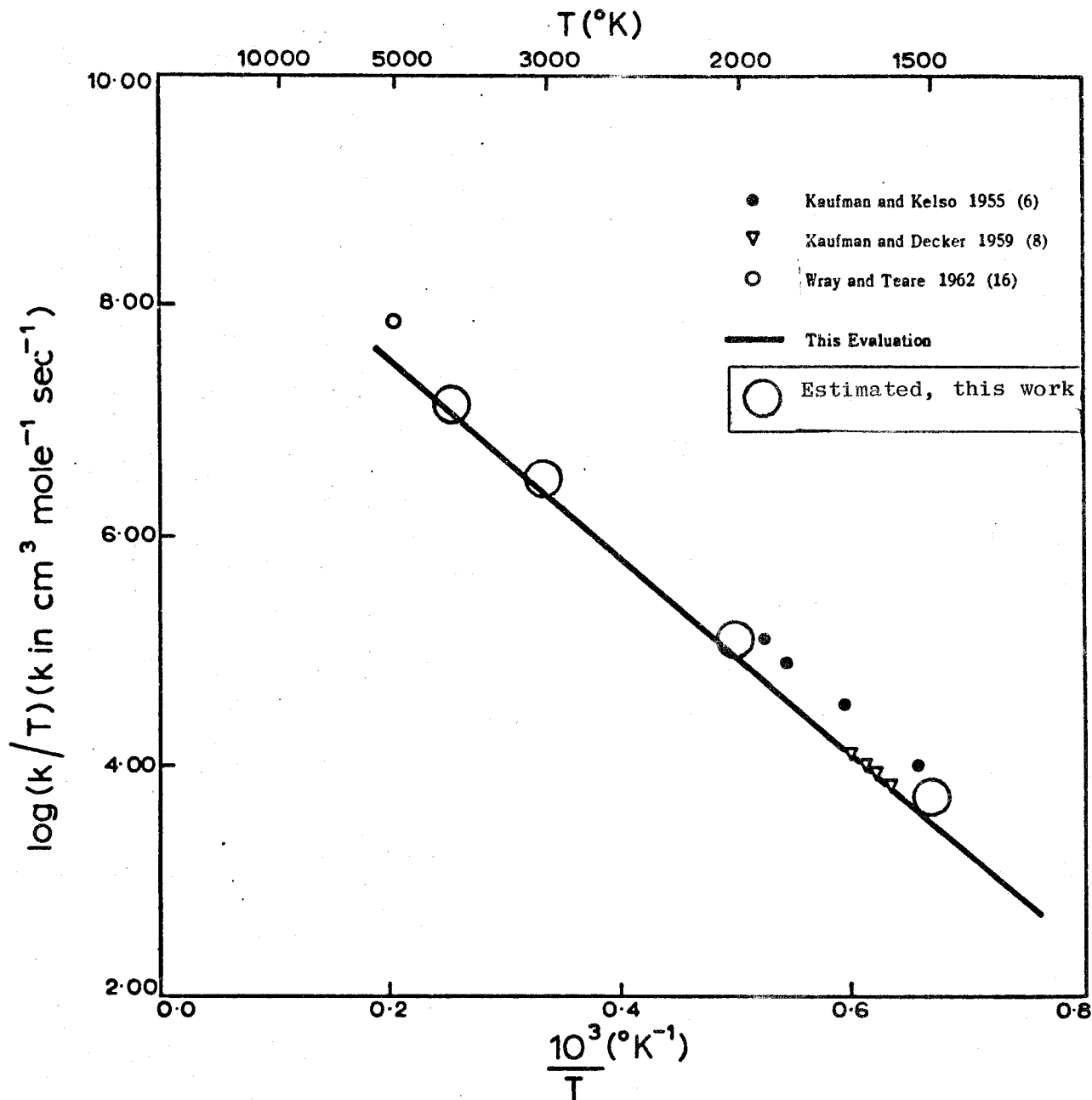
FIGURE A-8   O + ON $\rightarrow$ O$_2$ + N

Table A-1

THERMODYNAMIC PROPERTIES OF MONATOMIC

AND DIATOMIC SPECIES IN THE H, N, O SYSTEM[5]

		$\Delta H^o_{f300}/(kcal/mole)$	$S^o_{300}/[cal/(mole\ k)]$
Monatomic	H	52.1	27.42
	N	113.0	36.64
	O	59.6	38.50
Diatomic	HN	90.0	43.29
	HO	9.3	43.92
	H_2	0	31.25
	NO	21.6	50.39
	N_2	0	45.81
	O_2	0	49.05

Table A-2

OVERALL ENTROPIES AND HEATS FOR ALL CHEMICAL REACTION PAIRS

Reaction Pair	$\Delta S^0_{300}/[cal/(mole\ K)]$	$\Delta H^0_{300}/[kcal/mole]$
$O + NH \rightleftarrows NO + H$	4.0	-75.9
$O + HN \rightleftarrows HO + N$	1.2	-27.3
$N + OH \rightleftarrows NO + H$	2.8	-48.6
$N + NH \rightleftarrows N_2 + H$	6.7	-150.9
$O + OH \rightleftarrows O_2 + H$	6.0	-16.8
$H + HN \rightleftarrows H_2 + N$	2.8	-29.1
$H + HO \rightleftarrows H_2 + O$	1.6	-1.8
$N + O_2 \rightleftarrows NO + O$	-3.2	-31.8
$N + NO \rightleftarrows N_2 + O$	2.7	-75.0

Table A-3

Values of A, B, and C in $k/[cm^3/(mole\ sec)] = AT^B \exp(-C/RT)$ Used to Calculate Rate

Constants in Figures A-1 to A-8

Figure	Reaction	$\Delta S^{o\ddagger}_{300}/[cal/(mole\ K)]$	$\log_{10} A/[cm^3/mole\ sec)]$	B	$\Delta H^{o\ddagger}_{300}/(kcal/mole)$	C/(kcal/mole)
A-1	$O+OH \rightarrow O_2+H$	-22	11.8	0.5	-1	0
A-2	$H+O_2 \rightarrow HO+O$	$-22+\Delta S^o_{300} = -16.0$	13.1	0.5	$-1+\Delta H^o_{300} = 15.8$	16.8
A-3	$H+HO \rightarrow H_2+O$	-22	11.8	0.5	7	8
A-4	$O+H_2 \rightarrow OH+H$	$-22+\Delta S^o_{300} = -20.4$	12.1	0.5	$7+\Delta H^o_{300} = 8.8$	9.8
A-5	$N+NO \rightarrow N_2+O$	-22	11.8	0.5	-1	0
A-6	$O+N_2 \rightarrow ON+N$	$-22+\Delta S^o_{300} = -19.3$	12.4	0.5	$-1+\Delta H^o_{300} = 74.0$	75.0
A-7	$N+O_2 \rightarrow NO+O$	-22	11.8	0.5	7	8
A-8	$O+ON \rightarrow O_2+N$	$-22+\Delta S^o_{300} = -25.2$	11.1	0.5	$7+\Delta H^o_{300} = 38.8$	39.8

Table A-4

Calculation of the Rate Constant as a Function

of Temperature for $O + H_2 \rightarrow OH + H$ from

$$k/[cm^3/(mole\ sec)] = 10^{12.1}T^{0.5}\exp(-9.8/RT)$$

(See Figure A-4)

Temperature/K	1000K/T	$\log_{10}k/[cm^3/(mole\ sec)]$	$\log\left(\frac{k}{T}\right)\left[\frac{Kelvin}{cm^3/(mole\ sec)}\right]$
200	5.0	2.5	0.2
300	3.33	6.2	3.7
400	2.50	8.0	5.4
500	2.00	9.2	6.5
700	1.43	10.5	7.6
1000	1.00	11.5	8.5
1500	0.67	12.3	9.1
2000	0.50	12.7	9.4
3000	0.33	13.2	9.7
4000	0.25	13.4	9.8

The value of $\Delta S_{300}^{o\ddagger} = -22$ cal/(mole K) is very reasonable. Consider for example the reaction,

$$H + O_2 \rightarrow (H \cdots O \cdots O)^{\ddagger} \rightarrow HO + O \qquad (14)$$
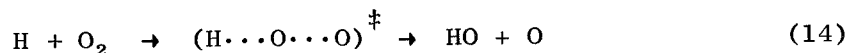
As a first approximation the triatomic transition state may be approximated by the molecule HO_2. The entropy of activation of 300 K is then given by the entropy change at 300 K for the reaction

$$H + O_2 \rightarrow HO_2 \qquad (15)$$

That is $\Delta S_{300}^{o\ddagger}$ (Reaction 14) $= \Delta S_{300}^{o}$ (Reaction 15) $= S_{300}^{o}(HO_2) - S_{300}^{o}(H) - S_{300}^{o}(O_2) = 54.4 - 27.4 - 49 - 0 = -22.0$ cal/(mole K). The exact agreement is fortuitous because in another example,

$$N + NO \rightarrow N \cdots N \cdots O \rightarrow N_2 + O \qquad (16)$$
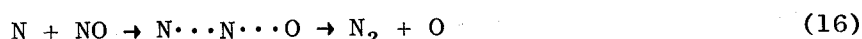
the activation reaction is approximated by

$$N + NO \rightarrow N_2O \qquad (17)$$

The entropy change for Reaction (17) is

$$
\begin{aligned}
\Delta S_{300}^{o}(17) &= S_{300}^{o}(N_2O) - S_{300}^{o}(N) - S_{300}^{o}(NO) \\
&= 52.6 - 36.6 - 50.4 \\
&= -34.4 \text{ cal/(mole K)}
\end{aligned}
$$

However the point is that the "universal" value of $\Delta S_{300}^{o\ddagger} = -22$ cal/(mole K) can be readily understood in terms of the entropy of the reactants and of the transition state.

The two values for $\Delta H_{300}^{o\ddagger}$ in the exothermic direction require more interpretation and discussion. The basic postulates are (a) that $\Delta H_{300}^{o\ddagger} = -1$ kcal/mole for reactions that have a transition state preceded by an intermediate that is stable with respect to the reactants and (b) that $\Delta H_{300}^{o\ddagger} = 7$ kcal/mole for reactions that are concerted or have a transition state preceded by an intermediate that is unstable with respect to the reactants.

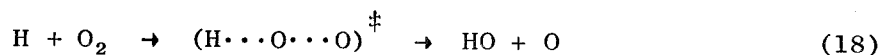For the general reaction

$$X + YZ \rightarrow (X \cdots Y \cdots Z)^{\ddagger} \rightarrow XY + Z \qquad (1)$$
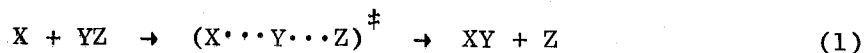
consider first the case where the transition state is preceded by a stable molecule intermediate as shown in Figure A-9. An example is the reaction

$$N + NO \rightarrow (N \cdots N \cdots O)^{\ddagger} \rightarrow N_2 + O \qquad (16)$$
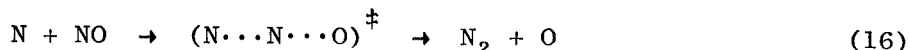
The stable molecule intermediate in this case is N_2O. The sum of the heats of formation of the reactants $N + NO$ is 134.6 kcal/mole compared to 19.6 kcal/mole for N_2O. That is, N_2O is 115 kcal/mole more stable than $N + NO$. If we allow 60-80 kcal to form the triplet state N_2O^3 it is still 40 ± 10 kcal more stable than reactants and $\Delta H^{0\ddagger}_{300}$ (Reaction 16) $= -1$ kcal/mole. Another example is

$$H + O_2 \rightarrow (H \cdots O \cdots O)^{\ddagger} \rightarrow HO + O \qquad (18)$$

In this case, the stable molecule intermediate is HO_2. The reaction

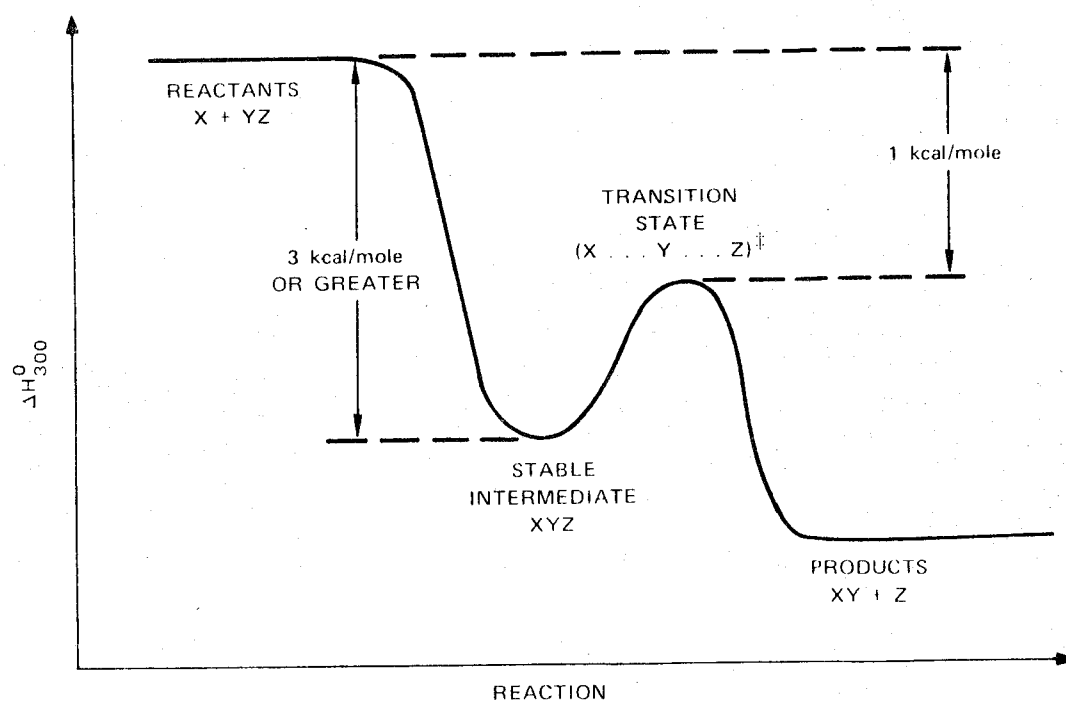$$H + O_2 \rightarrow HO_2 \qquad (19)$$

is 63.9 kcal/mole exothermic, hence ΔH^0_{300} (Reaction 18) $= -1$ kcal/mole.

Consider now the case where the reaction is concerted or has a transition state preceded by an intermediate that is unstable with respect to the reactants as shown in Figure A-10. An example of a concerted reaction is
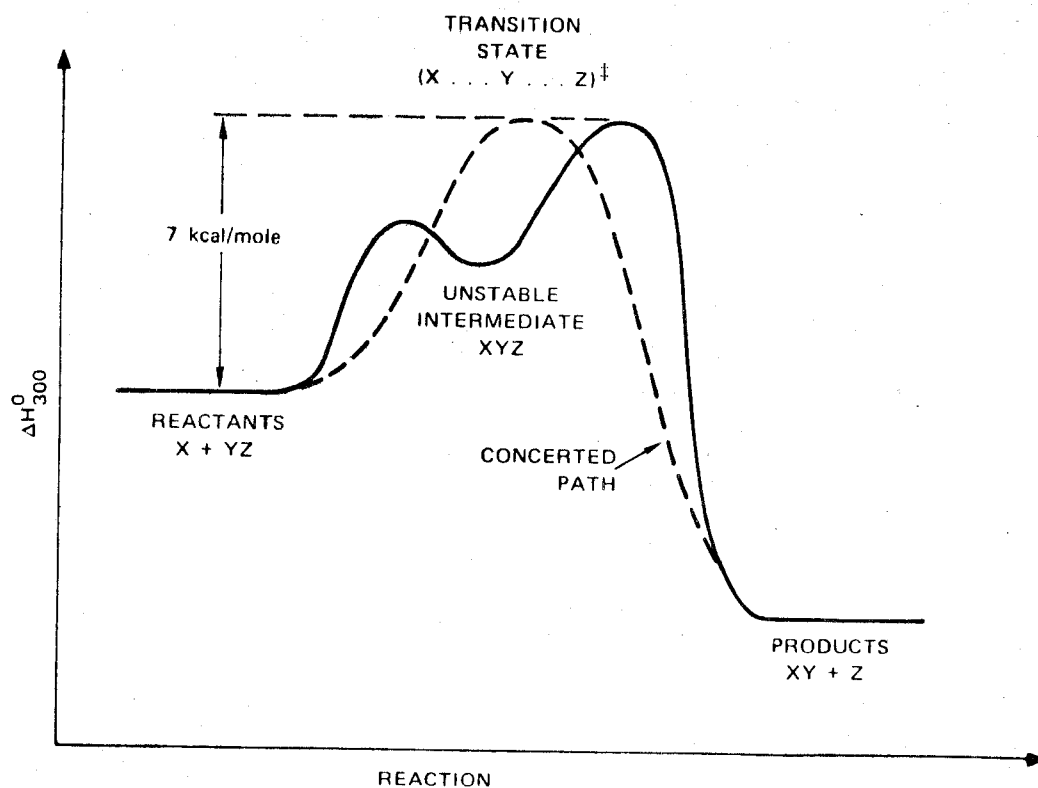
$$H + HO \rightarrow (H \cdots H \cdots O)^{\ddagger} \rightarrow H_2 + O \qquad (20)$$
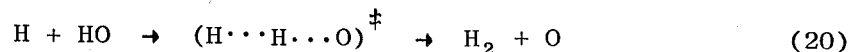
Therefore, in the case of Reaction (20), $\Delta H^{0\ddagger}_{300} = 7$ kcal/mole.

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FIGURE A-9   HEAT CHANGES FOR REACTIONS HAVING TRANSITION STATES
PRECEDED BY AN INTERMEDIATE THAT IS STABLE WITH
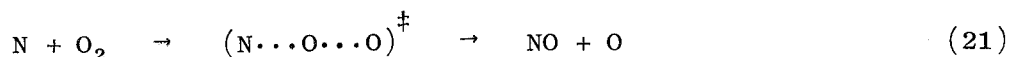RESPECT TO THE REACTANTS

In such cases $\Delta H^{0\ddagger}_{300}$ ~ -1 kcal/mole.

FIGURE A-10 HEAT CHANGES FOR REACTIONS THAT ARE CONCERTED OR THAT HAVE A TRANSITION STATE THAT IS PRECEDED BY AN INTERMEDIATE THAT IS UNSTABLE WITH RESPECT TO THE REACTANTS

In such cases $\Delta H_{300}^{0\ddagger} = 7$ kcal/mole.

An example of a reaction that has a transition state preceded by an
intermediate that is unstable with respect to the reactants is

$$N + O_2 \quad \rightarrow \quad (N \cdots O \cdots O)^{\ddagger} \quad \rightarrow \quad NO + O \qquad (21)$$

The intermediate is NOO produced by the reaction

$$N + O_2 \quad \rightarrow \quad NOO \qquad (22)$$

We have estimated (see later) that $\Delta H^o_{f300}(NOO)$ is 136 ± 16 kcal/mole.
The sum of the heats of formation of the reactants is 113 ± 1 kcal/mole,
therefore NOO is unstable with respect to $N + O_2$, and $\Delta H^{o\ddagger}_{300}$ (Reaction 22)
= 7 kcal/mole.

For a system of three elements, there are 18 ways to arrange linearly
the atoms. For example the empirical formula HNO can be HNO, HON, or
NHO. Thus there are 18 pairs of reactions: 9 pairs are chemical
reactions, for example

$$O + OH \quad \rightleftarrows \quad O_2 + H \qquad (23)$$

and 9 pairs are exchange reactions, for example

$$O^{18} + O^{16}O^{16} \quad \rightleftarrows \quad O^{18}O^{16} + O^{16} \qquad (24)$$
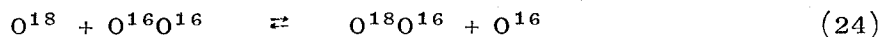
In order to estimate the rate constants of all 18 pairs of reactions,
it is necessary to assign values of $\Delta H^{o\ddagger}_{300}$ of either -1 or 7 kcal/mole
to the reaction in the exothermic direction. (The exchange reactions
are all thermoneutral, which is taken as exothermic for the purpose of
assigning a value of $\Delta H^{o\ddagger}_{300}$.) All reactions that involve transfer of a
hydrogen atom are concerted and have $\Delta H^{o\ddagger}_{300}$ = 7 kcal/mole. For the other
reactions it is necessary to know the heat of formation of the triatomic
intermediate and determine whether it is stable or unstable with respect
to the reactants. In some cases the heat of formation of the triatomic
is well known, for example HOH, OCO, HNO, and HO_2. In other cases the

heat of formation had to be estimated. In general the main estimating technique was to take the fully hydrogenated species and estimate the strengths of the bonds to the hydrogens. For example, the heat of formation of HNN was estimated from ΔH^0_{f300} (H_2NNH_2) assuming each N-H bond strength to be 95 kcal/mole. The details of the estimation are given in a separate paper[7] that considers the 75 triatomic species in the complete C, H, N, O, system but the results relevant to the present work are summarized in Table A-5.

It is interesting to compare the rate constants predicted by the above considerations with some experimental results not given as figures in the Leeds compilation. Reaction (25)

$$N + OH \rightarrow NO + H \tag{25}$$

has been studied by Campbell and Thrush,[8] and by Garvin and Broida.[9] Their results are shown in Figure A-11 along with some estimates by Tunder, Mayer, Cook, and Schieler.[10]

The exchange reactions are of limited practical importance, but their primary purpose here is to test the model described above with the available experimental data on isotopic exchange reactions. For example, Klein and Herron[11] and later Jaffe and Klein[12] showed that oxygen atoms will exchange with O_2 and NO at rate constants close to 10^9 M^{-1} sec^{-1} at 300 to 400 K, in fair agreement with our predicted values of 10^{10} M^{-1} sec^{-1} based on $\Delta H^{0\ddagger}_{300} = -1$ kcal/mole, $\Delta S^{0\ddagger}_{300} = -22$ cal/(mole K), and $\Delta C^0_{p,300} = -3$ cal/(mole K). In the case of H/H_2 exchange, Ridley, Schultz, and LeRoy[13] and Westenberg and de Haas[14] measured rate constants

Table A-5. Determination of values of $\Delta H^{0\ddagger}_{300}$ used to calculate rate constants
of atom-transfer reactions in the H, N, O system

Reaction pair in exothermic direction except when thermoneutral	Triatomic structure	Intermediate ΔH^0_{f300}/(kcal/mole)	species	Reactants ΔH^0_{f300}/(kcal/mole)	ΔH^0_{300}(Intermediate − reactants)/(kcal/mole)	$\Delta H^{0\ddagger}_{300}$/ (kcal/mole)
O + NH ⇌ ON + H	HNO	23.8[5]	O + NH	149.5 ± 4	126 ± 5	−1
O + HN ⇌ OH + N	concerted					7
N + OH ⇌ NO + H	NOH	77 ± 11	N + OH	122.3 ± 1.3	45 ± 12	−1
N + NH ⇌ N$_2$ + H	HNN	152 ± 16	H + N$_2$	203 ± 5	51 ± 21	−1
N + HN ⇌ NH + N	concerted					7
O + OH ⇌ O$_2$ + H	OOH	5 ± 2[5]	O + OH	68.9 ± 0.3	64 ± 3	−1
O + HO ⇌ OH + O	concerted					7
H + HN ⇌ H$_2$ + N	concerted					7
H + NH ⇌ HN + H	HNH	4.5 ± 1.5[5]	H + NH	142 ± 4	96 ± 6	−1
H + OH ⇌ HO + H	HOH	57.8[5]	H + OH	61.4 ± 0.3	119 ± 1	−1
H + HO ⇌ H$_2$ + O	concerted					7
N + O$_2$ ⇌ NO + O	NOO	136 ± 16	N + O$_2$	113 ± 1	−23 ± 17	7
O + NO ⇌ ON + O	ONO	7.9 ± 0.2[5]	O + NO	81.9 ± 0.4	73 ± 1	−1
N + NO ⇌ N$_2$ + O	NNO	19.6 ± 0.1[5]	N + NO	134.6 ± 1.4	115 ± 2	−1
N + ON ⇌ NO + N	NON	209 ± 26	N + ON	134.6 ± 1.4	−74 ± 28	7
H + H$_2$ ⇌ H$_2$ + H	concerted					7
N + N$_2$ ⇌ N$_2$ + N	NNN	111 ± 5	N + N$_2$	113 ± 1	2 ± 6	7
O + O$_2$ ⇌ O$_2$ + O	OOO	34.1 ± 0.4	O + O$_2$	59.55 ± 0.02	26 ± 1	−1

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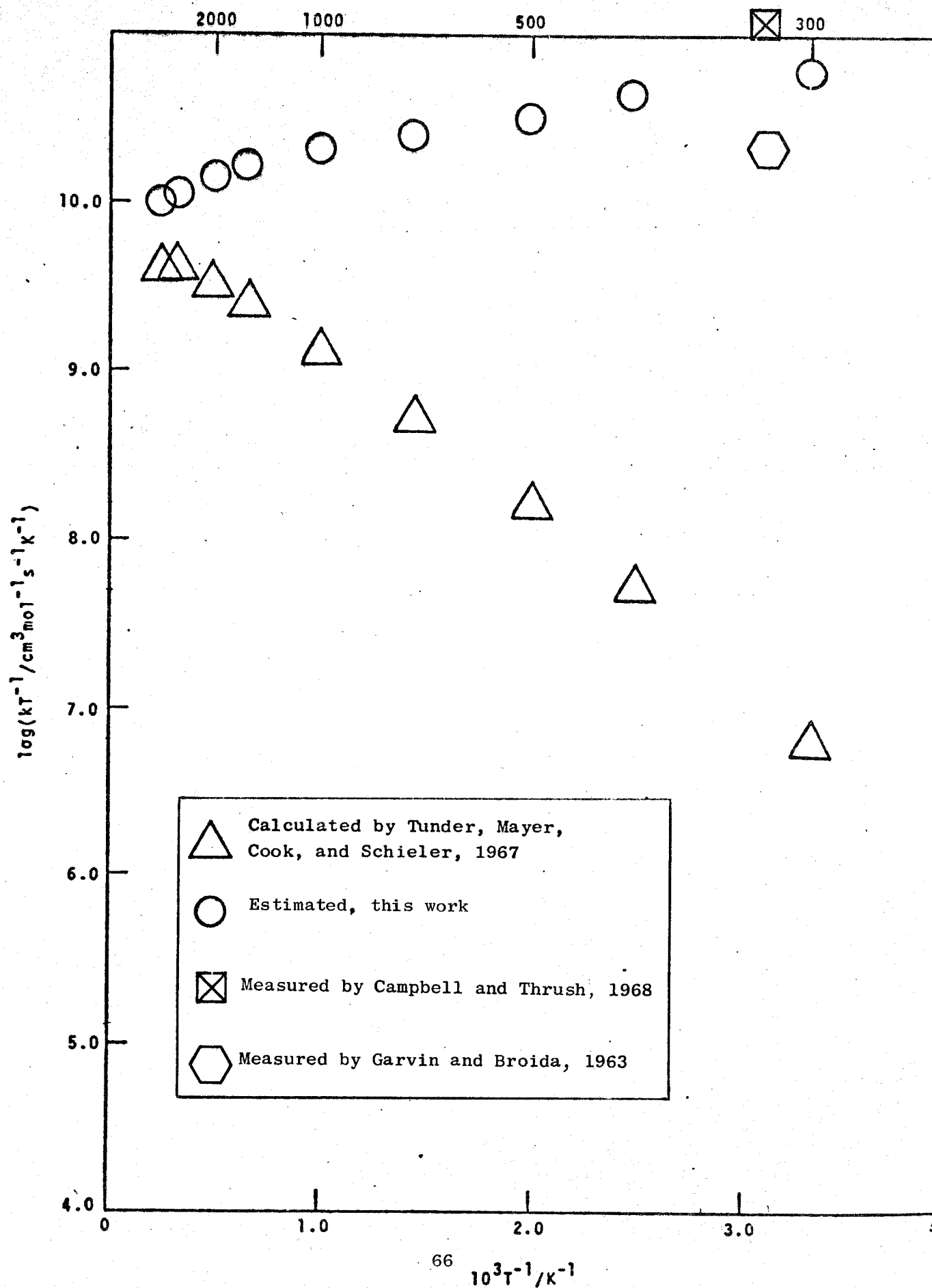
FIGURE A-11   NO + OH → NO + H

for $D + H_2 \rightarrow DH + H$. As shown in Figure A-12, their rate constants agree well with estimated values.

Another interesting test of the model is given by Reactions (26) and (27)

$$N(^4S) + O_2 \rightarrow NO + O(^3P) \tag{26}$$

$$N(^2D) + O_2 \rightarrow NO + O(^3P) \tag{27}$$
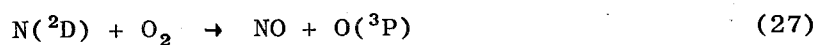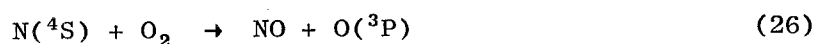
When ground state nitrogen atoms react with molecular oxygen as in Reaction (26), the intermediate NOO is unstable with respect to the reactants and $\Delta H^{o\ddagger}_{300} = 7$ kcal/mole (see Table A-5 and Figure A-7). However, when the nitrogen atom is in its upper excited state, $N(^2D)$, which is 55 kcal/mole above the ground state, the sum of the heats of formation of the reactants is now 163 kcal/mole compared with 136 ± 16 for the intermediate NOO so that intermediate is now stable with respect to the reactants, and $\Delta H^{o\ddagger}_{300} = -1$ kcal/mole. Slanger, Wood, and Black[15] have measured rate constants for Reaction (27) as shown in Figure A-13.

The good agreement between estimated and measured data suggests that equation (13) is a good approximation for reactions of the type $X + YZ \rightarrow XY + Z$ that have not been studied experimentally.

A computer program has been written in FORTRAN IV to estimate rate constants for the eight transfer reactions in the H_2/O_2 and N_2/O_2 systems. This program has been tested and is working in both batch and conversational modes on Stanford Research Institute's CDC 6400 computer. Requests for copies of the program should be addressed to W. Steven Lanier, Combustion Research Section, Clean Fuels and Energy Branch, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.
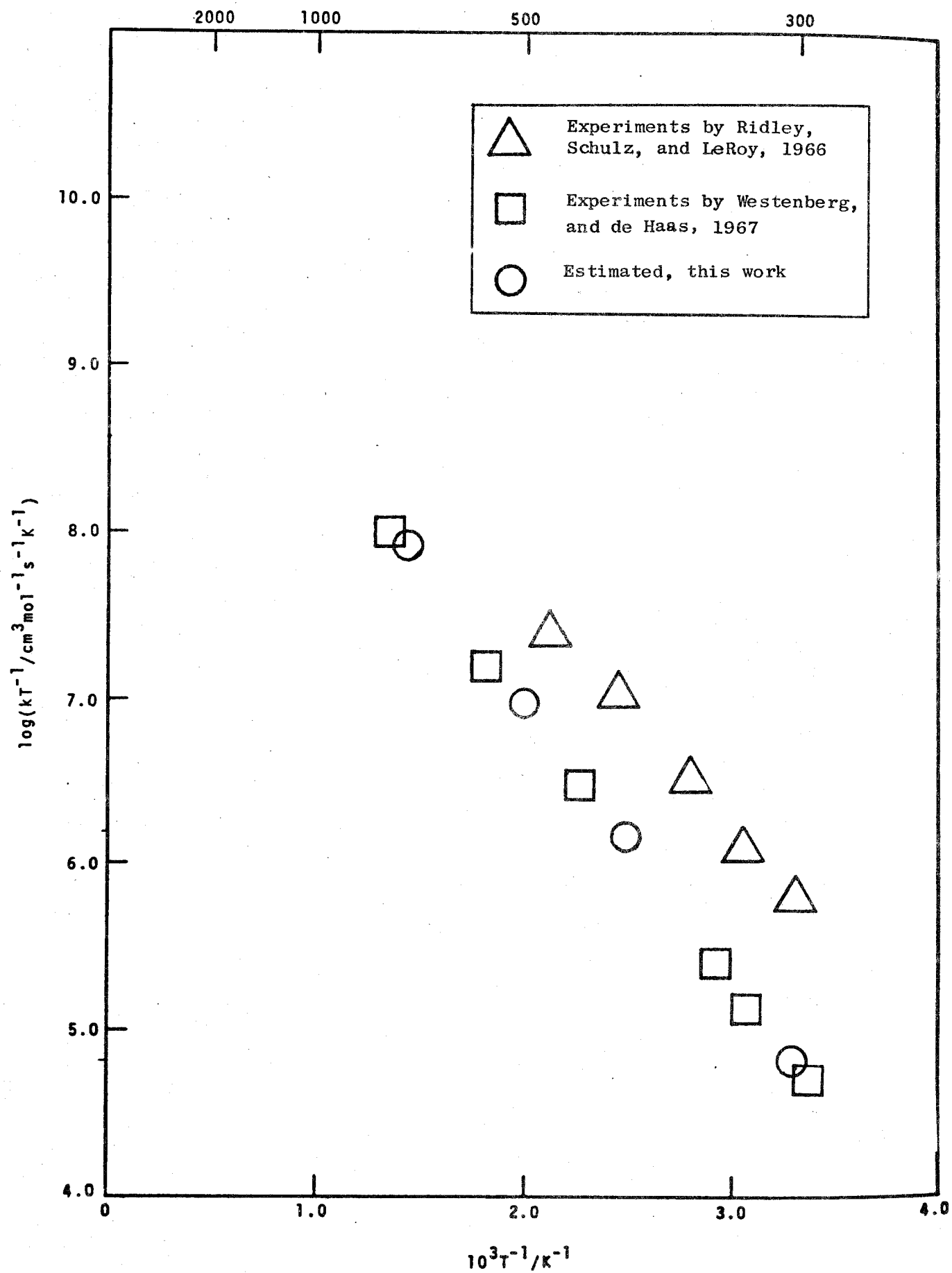
FIGURE A-12   D + H$_2$ → DH + H
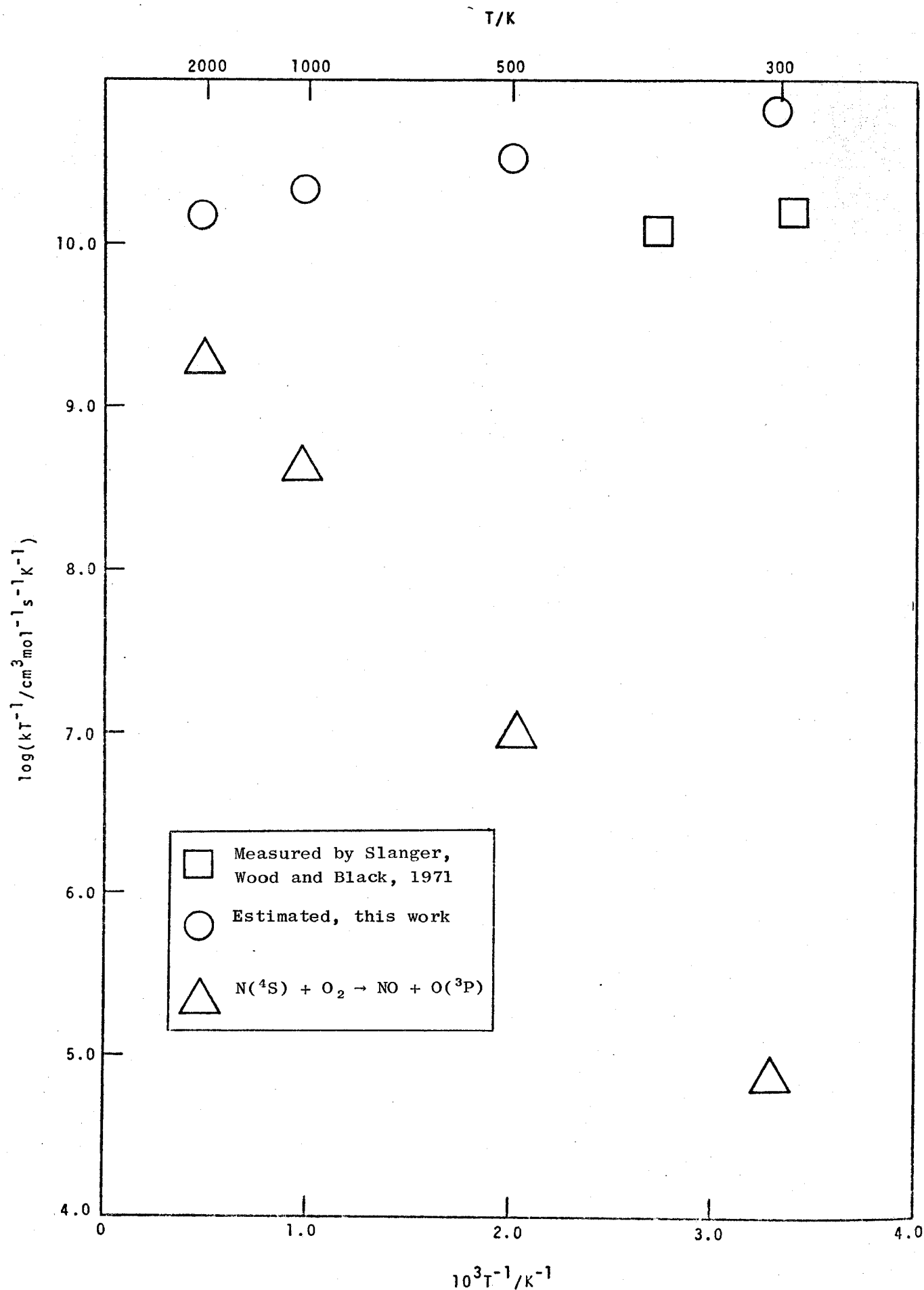
FIGURE A-13 N(^{2}D) + O$_2$ → NO + O(^{3}P)

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Variation of Equilibrium Constant with Temperature

V. Engleman[5] has pointed out how useful it would be to have in analytical form the variation of the equilibrium constant with temperature. Rigorously,[4] the variation of the equilibrium constant with temperature is given by:

$$RT\ln K = -\Delta G^o_T \tag{28}$$

where

$$\Delta G^o_T = \Delta H^o_T - T\Delta S^o_T \tag{29}$$

$$\Delta G^o_T = \Delta H^o_{300_T} + \int_{300}^T \Delta C^o_p dT - T\Delta S^o_{300}$$
$$-T\int_{300}^T \Delta C^o_p d\ln T \tag{30}$$

However, for the purpose of estimating the equilibrium constants of the elementary reactions that are important in combustion systems, it is a very good approximation to use:

$$\Delta G^o_T \approx \Delta H^o_{1500} - T\Delta S^o_{1500} \tag{31}$$

For reactions in which there is a change in the number of moles, for example, $N + O + M \rightarrow NO + M$, the equilibrium constant in units of concentration K_c is related to that in pressure units K_p by:

$$K_c = K_p(R'T)^{-\Delta n} \tag{32}$$

where R' is 82.057 cm^3 atm/(mole K) and Δn is the mole change in the reaction. For compatibility with the modified Arrhenius equation, which is:

$$k = AT^B \exp(-C/RT) \tag{6}$$

equation (32) can be put in the form:

$$K_c/(mole/cm^3) = (82)_{'}^{-\Delta n}[\exp(\Delta S^o_{1500}/R)]T^{-\Delta n} \exp[-\Delta H^o_{1500}/(RT)] \tag{33}$$
$$= A'T^{B'} \exp[-C'/(RT)]$$

where

$$\log_{10} A' = -1.9 \Delta n + [\Delta S^0_{1500}/(2.3R)]$$

$$B' = \Delta n$$

$$C' = \Delta H^0_{1500}$$

Reactions of the Type $XY + M \rightarrow X + Y + M$

In air-oxidized combustion, N_2 is by far the most abundant species. It is therefore a good first approximation to take N_2 as M. In all the following, M and N_2 may be used interchangeably:

$$XY + M \rightarrow X + Y + M \tag{34}$$

According to Benson,[4] most atom recombinations, back reaction (-34), have rate constants in the range $10^{15.5 \pm 0.5}$ $cm^6/(mole^2$ sec$)$ at 300 K. The rate constants are slightly more than a power of ten slower at 3000 K. We have empirically derived the following rate equation for reaction (-34) over the temperature range 200 K to 4000 K:

$$k_{-23}/[cm^6/mole^2 \ sec)] = 10^{18} \ T^{-1} \tag{35}$$

That is,

$$k_{-34}/[cm^6/(mole^2 \ sec)] = A_{-34} T^{B-34} \exp(-C_{-34}/RT) \tag{36}$$

where

$$\log_{10} A_{-34} = 18$$

$$B_{-34} = -1$$

$$C_{-34} = 0$$

and where the subscript -34 denotes the reverse of Reaction (34).

The rate constant of the forward Reaction (34) is related to k_{-34} the rate constant of the reverse reaction (-34) by the equilibrium constant K_{34}:

$$\frac{k_{34}}{k_{-34}} = K_{34} \tag{37}$$

that is,

$$k_{34} = K_{34}k_{-34} \tag{38}$$

As discussed previously, for high-temperature combustion, a good approximation for K_{34} is:

$$K_{34}/(cm^3/mole) = 10^{-1.9}[\exp(\Delta S^0_{1500}/R)]T^{-1}[\exp(-\Delta H^0_{1500}/RT)] \tag{39}$$

$$\therefore \quad k_{34}/[cm^3/(mole\ sec)] = 10^{18}\ T^{-1}\ 10^{-1.9}\ [\exp(\Delta S^0_{1500}/R)]\ T^{-1}[\exp(-\Delta H^0_{1500}/RT)$$

$$= 10^{16.1}\ [\exp(\Delta S^0_{1500}/R)T^{-2}[\exp(-\Delta H^0_{1500}/RT))] \tag{40}$$

where ΔS^0_{1500} and ΔH^0_{1500} are the entropy and heat changes in reaction (34) as written. In the modified Arrhenius form

$$k_{34}/[cc/mole\ sec)] = A_{34}T^{B_{34}}\exp(-C_{34}/RT) \tag{41}$$

where

$$\log_{10} A_{34} = 16.1 + [\Delta S^0_{1500}/(2.3R)]$$

$$B_{34} = -2$$

$$C_{34} = \Delta H^0_{1500}$$

The Leeds group [1,2] has critically evaluated rate data for three reactions of the type $XY + M \rightarrow X + Y + M$; namely, where XY is NO, H_2, or HO. The relevant data for calculating the rate constant from equations (35) and (41) are given in Table A-6.

MODIFIED ARRHENIUS PARAMETERS $\left[k = AT^B \exp(-C/RT) \right]$ FOR THE REACTION $XY + M \rightleftarrows X + Y + M$ (34)

AB	ΔS^0_{1500} [a]	ΔH^0_{1500} [b]	$\log_{10} [A_{34}]$ [c]	B_{34}	C_{34} [b]	$\log_{10} [A_{-34}]$ [c]	B_{-34}	C_{-34} [b]
NO	28.52	154.5	22.32	-2	154.5	18.0	-1	0
H_2	28.12	107.4	22.24	-2	107.4	18.0	-1	0
HO	26.49	105.4	21.88	-2	105.4	18.0	-1	0

Units are:　[a] cal/(mole K)

[b] kcal/mole

[c] $cm^3 deg^2$/(mole sec).

Examples of rate constant calculations for NO + M → N + O + M are given in Table A-7.

The calculated rate constants for reaction (34) where XY is NO, H_2, or HO are plotted on copies of the Leeds evaluations in Figures A-14 to A-19.

The good agreement between estimated and measured data suggests that equations (35) and (41) are good approximations for reactions of the type XY + M → X + Y + M that have not been studied experimentally.

Reactions of the Type XYZ + M → XY + Z + M

As in the previous case of XY + M → X + Y + M, M can be taken as N_2. For most reactions[4] of the type:

$$XYZ + M \rightarrow XY + Z + M \tag{42}$$

the rate constant k_{-42} is of the order of $10^{16.5}$ cc^2/(mole^2 sec) at 300 K. When X and Z are hydrogen atoms, for example, $H_2O + M \rightarrow HO + H + M$, the temperature dependence is close to T^{-1}, which is the same as for the diatomic series XY + M ⇌ X + Y + M. In the modified Arrhenius form of the rate constant:

$$k_{-42}/[cm^6/(mole^2 \ sec)] = A_{-42} \ T^{B-42} \exp(-C_{42}/RT) \tag{43}$$

where

$$\log_{10}(A_{-42}/[cm^6/(mole^2 \ sec)]) = 19$$
$$B_{-42} = -1$$
$$C_{-42}/(kcal/mole) = 0$$

Table A-7

CALCULATION OF RATE CONSTANTS FOR NO + M ⇄ N + O + M   (1)

T	$\log_{10} A_1$	$\log_{10} T^2$	$154.5/\theta$	$\log_{10} k_1$	$\log_{10} T^{1/2}$	$\log_{10} \frac{k_1}{T^{1/2}}$	$\log_{10} A_{-1}$	$\log_{10} T$	$\log_{10} k_{-1}$	$\log_{10} k_{-1} T^{1/2}$	$1000/T$
200					1.15		18.0	2.30	15.70	16.85	5.0
300					1.24		18.0	2.48	15.52	16.76	3.33
400					1.30		18.0	2.60	15.40	16.70	2.5
500					1.35		18.0	2.70	15.30	16.65	2.0
700					1.42		18.0	2.84	15.16	16.58	1.43
1000					1.50		18.0	3.00	15.00	16.50	1.00
1500					1.59		18.0	3.18	14.82	16.41	0.67
2000	22.32	6.60	16.88	-1.16	1.65	0.49	18.0	3.30	14.70	16.35	0.50
3000	22.32	6.96	11.26	4.10	1.74	5.84	18.0	3.48	14.52	16.26	0.33
4000	22.32	7.20	8.44	6.68	1.80	8.48	18.0	3.60	14.40	16.20	0.25

Units are: T, Kelvins
A_1, $cm^3 deg^2/(mole \ sec)$
θ, kcal/mole
k, $cm^3/(mole \ sec)$
A_{-1}, $cm^6 \ deg/(mole^2 \ sec)$
k_{-1}, $cm^6/(mole^2 \ sec)$.
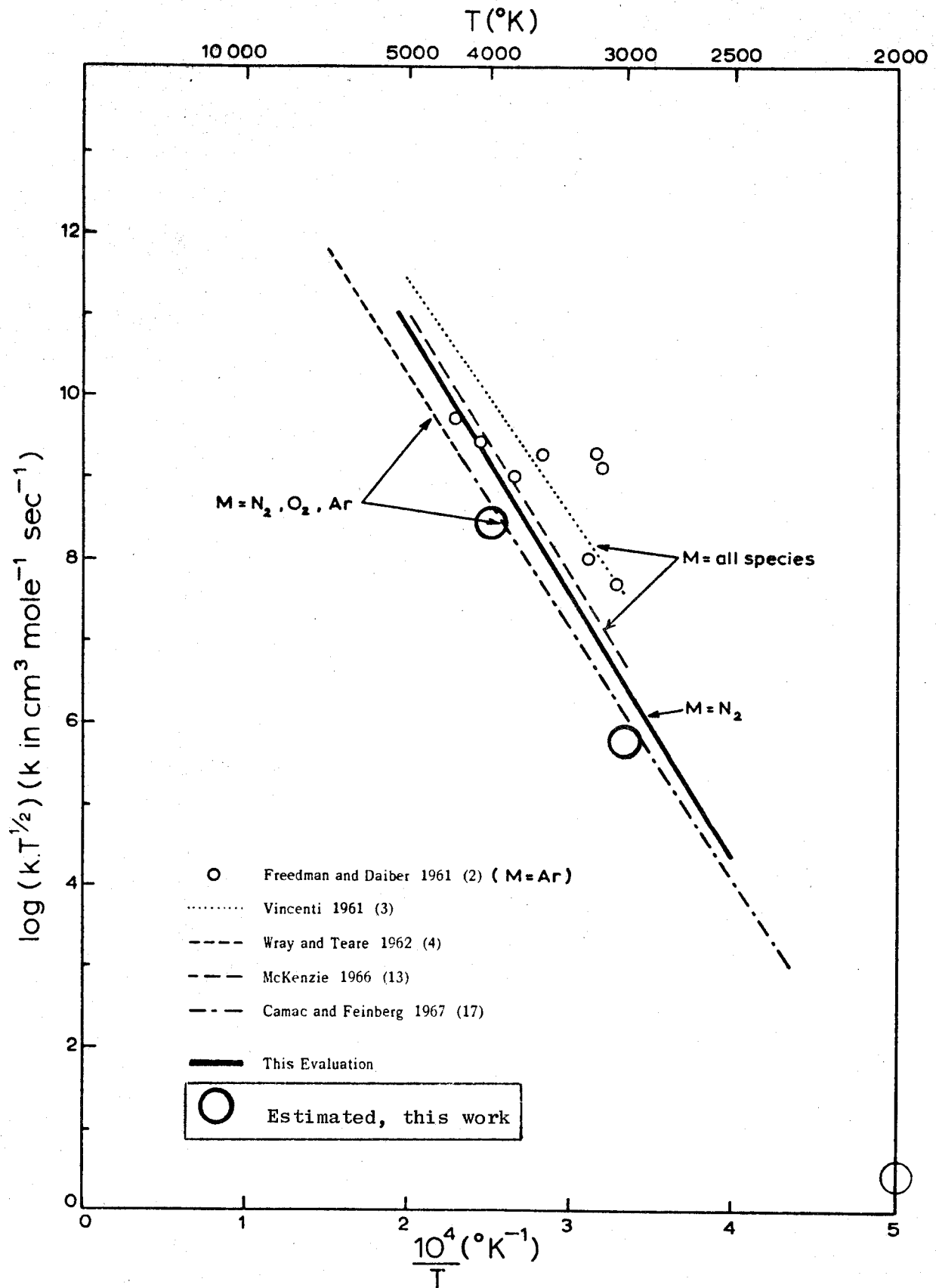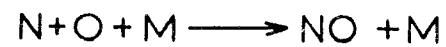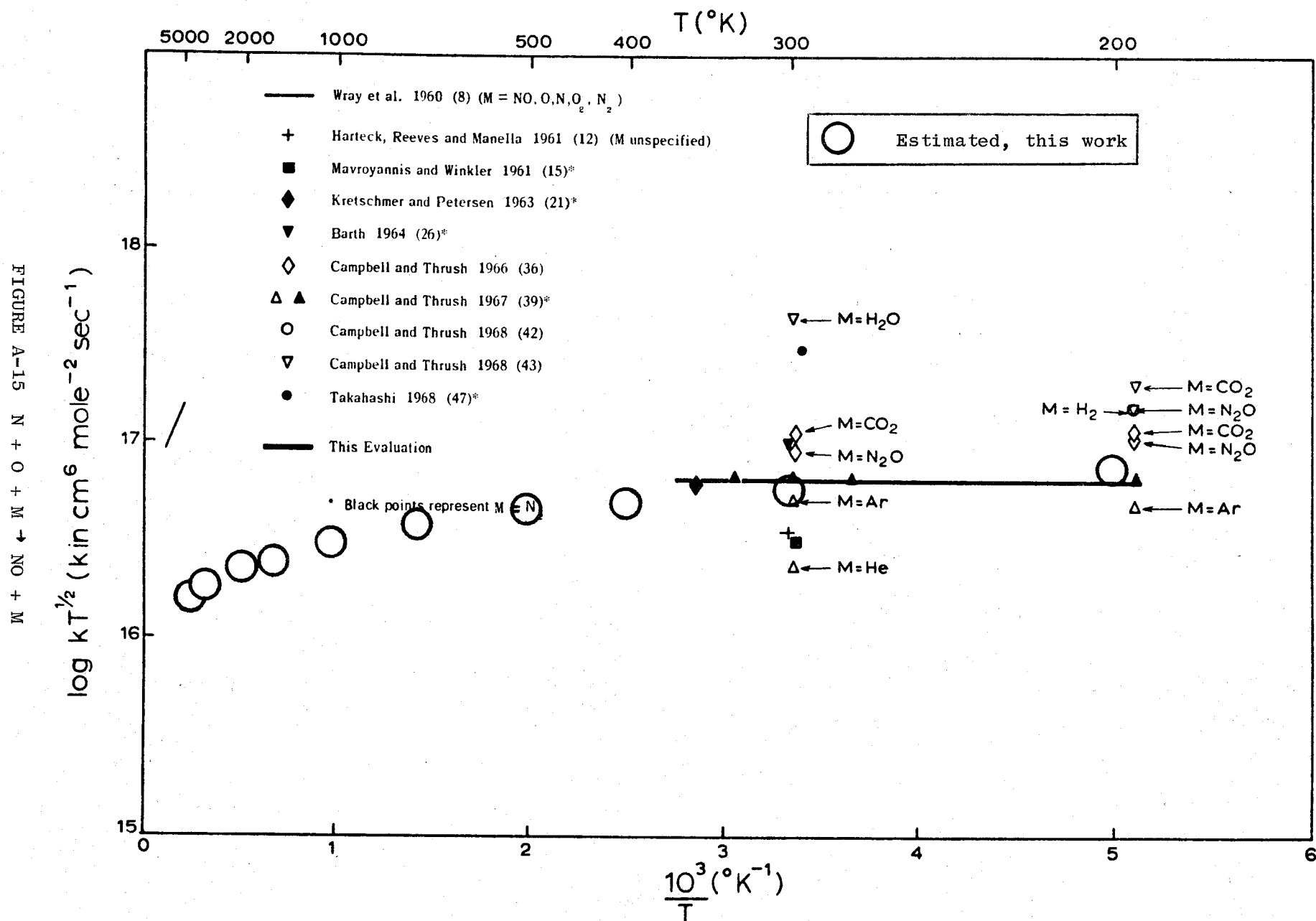
FIGURE A-14   NO + M $\rightarrow$ N + O + M

FIGURE A-15 N + O + M → NO + M
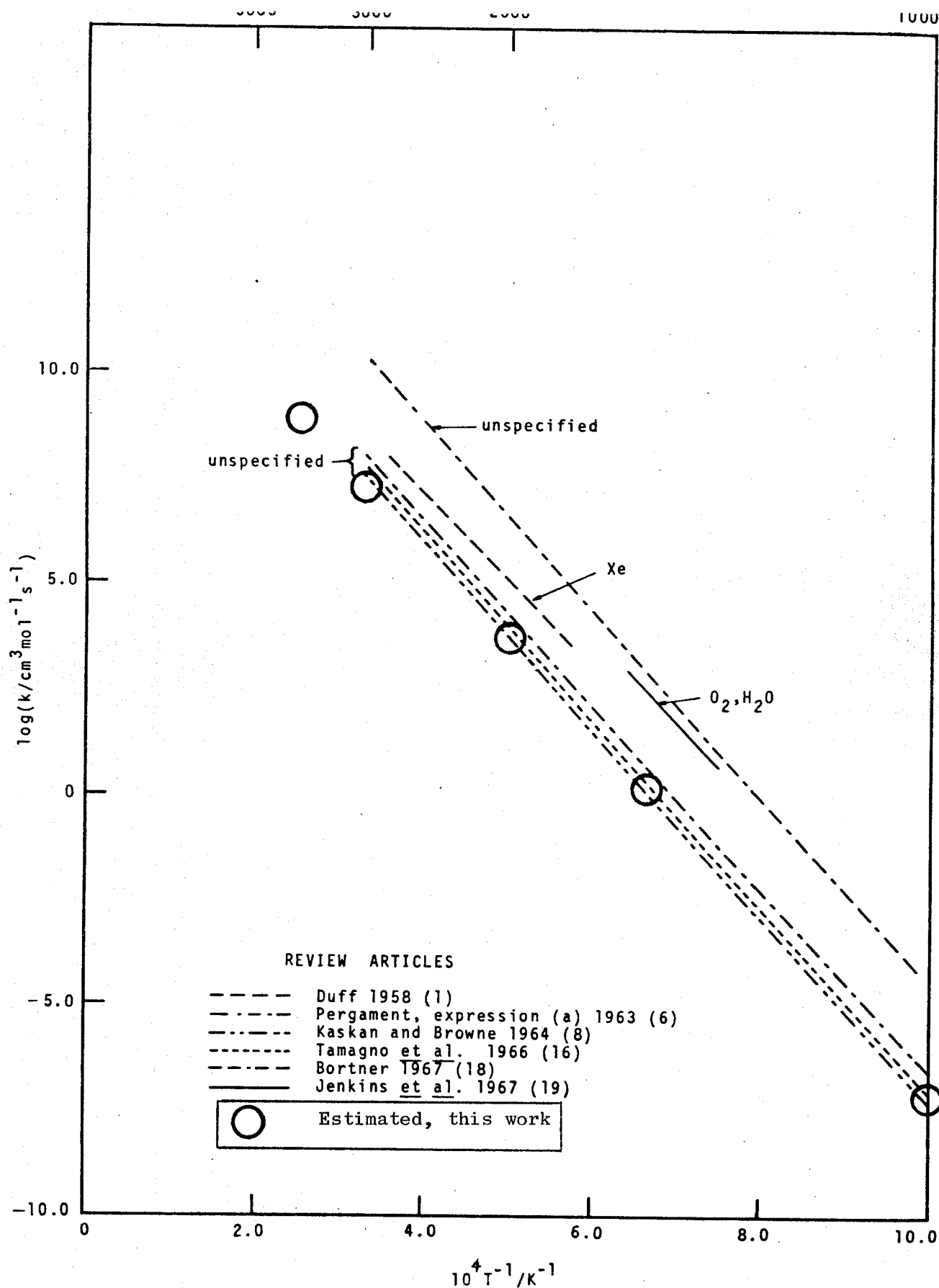
FIGURE A-16   OH + M → O + H + M
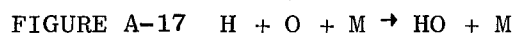
FIGURE A-17 H + O + M → HO + M
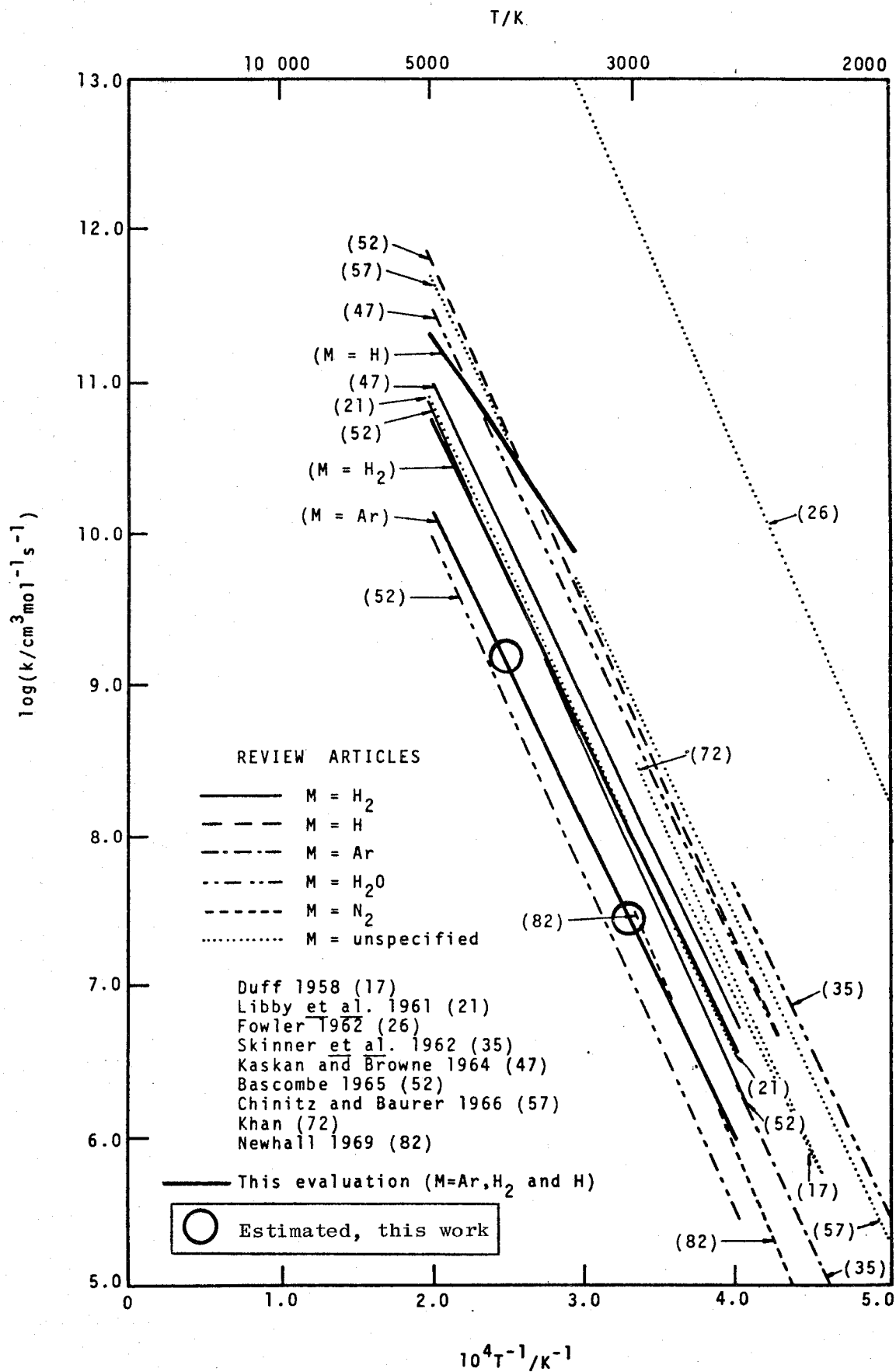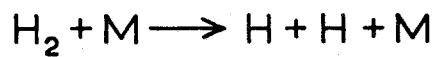
FIGURE A-18 $H_2 + M \rightarrow H + H + M$
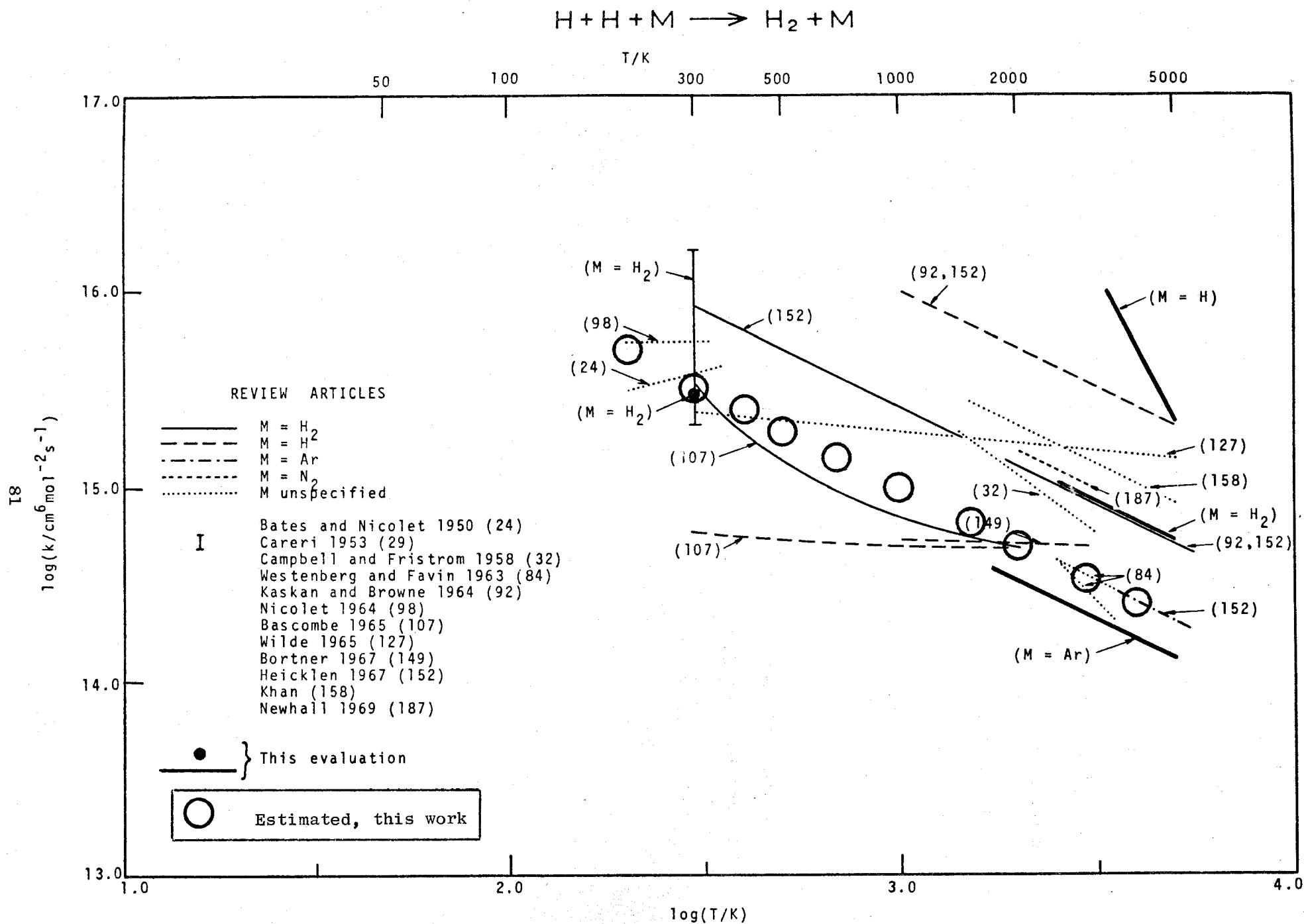
FIGURE A-19   H + H + M → H_2 + M

As discussed previously in the case of XY + M $\rightleftharpoons$ X + Y + M, the equilibrium constant is given by:

$$k_{42}/(cm^3/mole) = 10^{-1.9}[\exp(\Delta S^0_{1500}/R)]T^{-1}(-\Delta^0_{1500}/(RT))] \quad (44)$$

$$\therefore k_{42}/[cm^3/(mole\ sec)] = 10^{17.1}[\exp(\Delta S^0_{1500}/R)]T^{-2}[\exp(-\Delta^0_{1500}/(RT))] \quad (45)$$

In the modified Arrhenius form:

$$k_{42}/[cm^3/(mole\ sec)] = A_{42}T^{B_{42}}\exp(-C_{42}/RT) \quad (46)$$

where

$$\log_{10}(A_{42}/(cm^3/(mole\ sec)]) = 17.1 + [\Delta S^0_{1500}/(2.3R)]$$

$$B_{42} = -2$$

$$C_{42}/(kcal/mole) = \Delta H^0_{1500}$$

The calculated results for $H_2O + M \rightleftharpoons HO + H + M$ are compared in Figures A-20 and A-21 with the Leeds critically evaluated data.[1,2]

When X and Z are not both hydrogen atoms (for example, NO_2 or HO_2), the temperature variation of the combination rate constant is more nearly $T^{-1.5}$ than T^{-1}. So k_{-42} is given by:

$$k_{-42}/[cm^6/(mole^2\ sec)] = 10^{20.2}T^{-1.5} \quad (47)$$

In the modified Arrhenius form

$$k_{-42}/[cm^6/(mole^2\ sec)] = A_{-42}T^{B_{-42}}\exp(-C_{-42}/RT) \quad (48)$$

where

$$\log_{10}(A_{-42}/[cm^6/(mole^2\ sec)] = 20.2$$

$$C_{-42} = -1.5$$

$$C_{-42}/(kcal/mole) = 0$$

and for the forward reaction:

$$k_{42}/[cm^3/(mole\ sec)] = A_{42}T^{B_{42}}\exp(-C_{42}/RT) \quad (49)$$

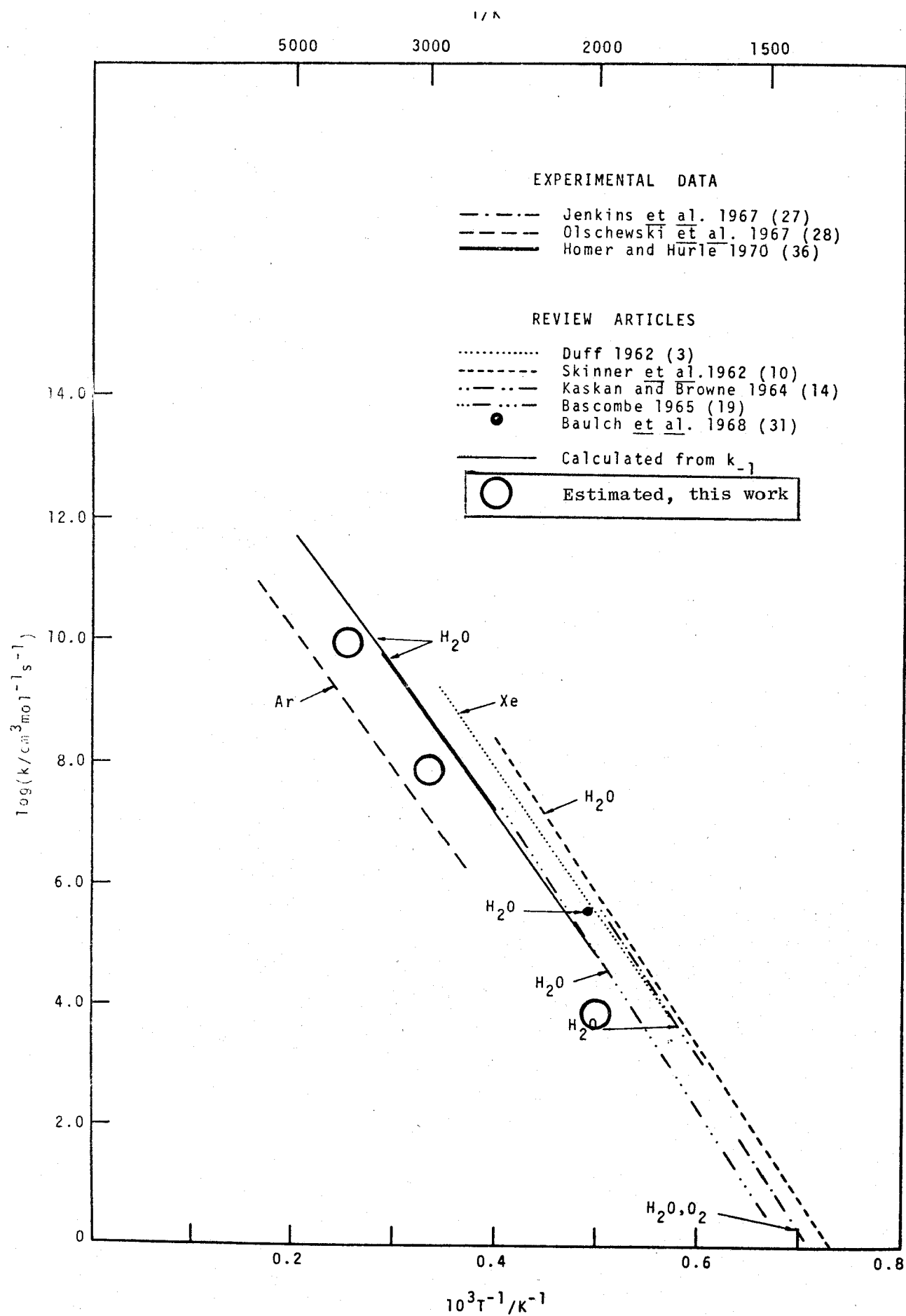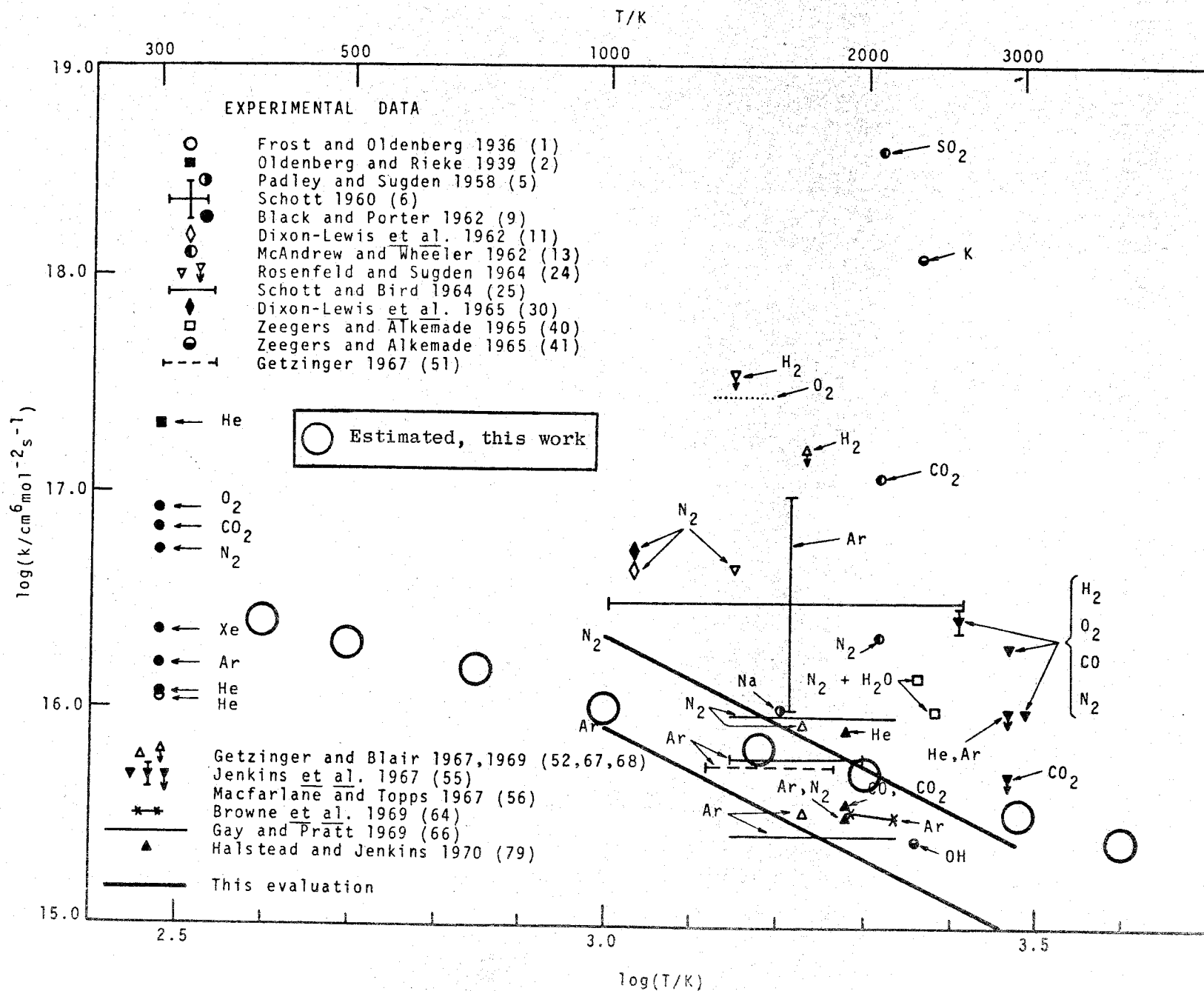FIGURE A-20 $H_2O + M \rightarrow H + OH + M$

H+OH+M $\longrightarrow$ H$_2$O+M

EXPERIMENTAL DATA

- ○   Frost and Oldenberg 1936 (1)
- ▣   Oldenberg and Rieke 1939 (2)
- ◐   Padley and Sugden 1958 (5)
- ⊢✚⊣   Schott 1960 (6)
- ●   Black and Porter 1962 (9)
- ◇   Dixon-Lewis et al. 1962 (11)
- ◑   McAndrew and Wheeler 1962 (13)
- ▽ ▽   Rosenfeld and Sugden 1964 (24)
- ⊢⊣   Schott and Bird 1964 (25)
- ◆   Dixon-Lewis et al. 1965 (30)
- □   Zeegers and Alkemade 1965 (40)
- ⊖   Zeegers and Alkemade 1965 (41)
- ⊢ - - ⊣ Getzinger 1967 (51)

Estimated, this work

Getzinger and Blair 1967,1969 (52,67,68)
Jenkins et al. 1967 (55)
Macfarlane and Topps 1967 (56)
Browne et al. 1969 (64)
Gay and Pratt 1969 (66)
Halstead and Jenkins 1970 (79)

This evaluation

84

where

$$\log_{10}(A_{42}/[cm^3/(mole\ sec)]) = 18.3 + [\Delta S_{1500}/(2.3R)]$$

$$B_{42} = -2.5$$

$$C_{42}/(kcal/mole) = \Delta H^0_{1500}$$

The data for calculating rate constants for XYZ + M → XY + Z + M

are summarized in Table A-8. (There was no Leeds figure for

HO_2 + M → H + O_2 + M, so rate constants were not calculated for the

forward reaction.)

The calculated rate constants are compared with the Leeds

critically evaluated experimental data[1,2] for XYZ = NO_2 in Figures A-22

and A-23, and for the reaction H + O_2 + M → HO_2 + M in Figure A-24.

The good agreement between estimated and measured data suggests that

equations (43) and (49) are good approximations for reactions of the

type XYZ + M ⇌ X + YZ + M that have not been studied experimentally.

A final warning is in order. Not all atom-metathesis reactions

will have activation energies of either 7 or -1 kcal/mole. Many such as

H + Cl_2 or F + H_2 will have each of the order of 2 or 3 kcal/mole. At

300 K, an extension of our scheme for these reactions will yield serious

discrepancies of many powers of 10. However, in flame systems at a

temperature of 2000 K, an error of 4 kcal/mole in estimating $\Delta H^{\ddagger}$ will

lead to an error of about a factor of 2 in a rate constant. This value

is crude but useful.

As regards extending the technique to species larger than atoms and

diatomic molecules, there appears to be no reason why the principles used

in the present work cannot be developed further. The form of the rate

Table A-8

MODIFIED ARRHENIUS PARAMETERS $\left[k = AT^B \exp(-C/RT) \right]$ FOR THE REACTION XYZ + M $\rightarrow$ XY + Z + M   (42)

ABC	ΔS^0_{1500} [a]	ΔH^0_{1500} [b]	$\log_{10}\left[A_{42}\right]$ [c]	B_{42}	C_{42} [b]	$\log_{10}\left[A_{-42}\right]$ [d]	B_{-42}	C_{-42} [b]
H_2O	31.13	122.6	23.89	-2	154.5	19.0	-1	0
NO_2	33.97	74.6	24.51	-2.5	74.6	20.2	-1.5	0
HO_2						20.2	-1.5	0

Units are:

a cal/(mole K).

b kcal/mole .

c $cm^3 deg^{-B}$/(mole sec).

d $cm^6 deg^{-B}$/(mole^2 sec).
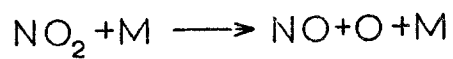
$NO_2 + M \longrightarrow NO + O + M$

July 1970
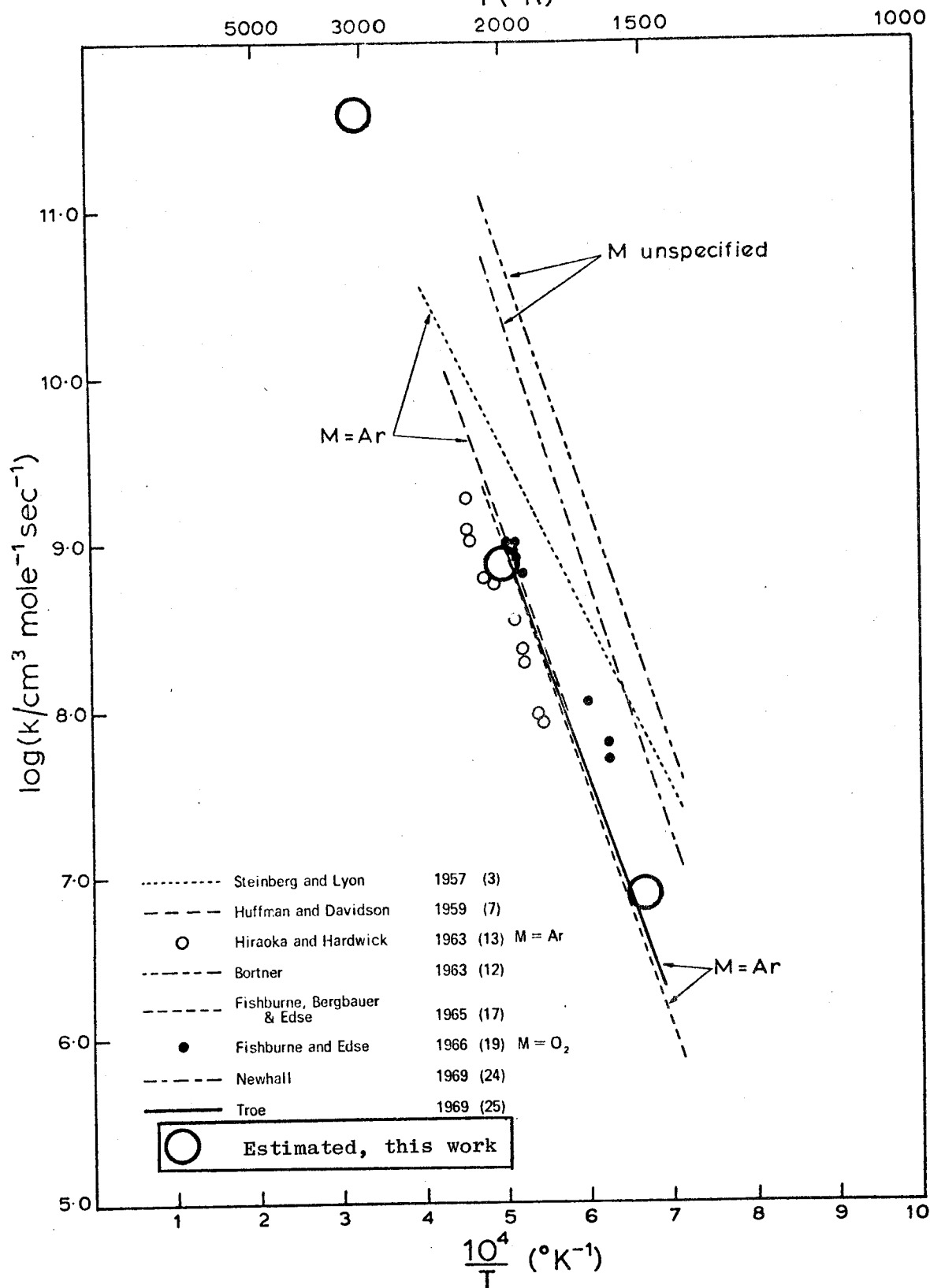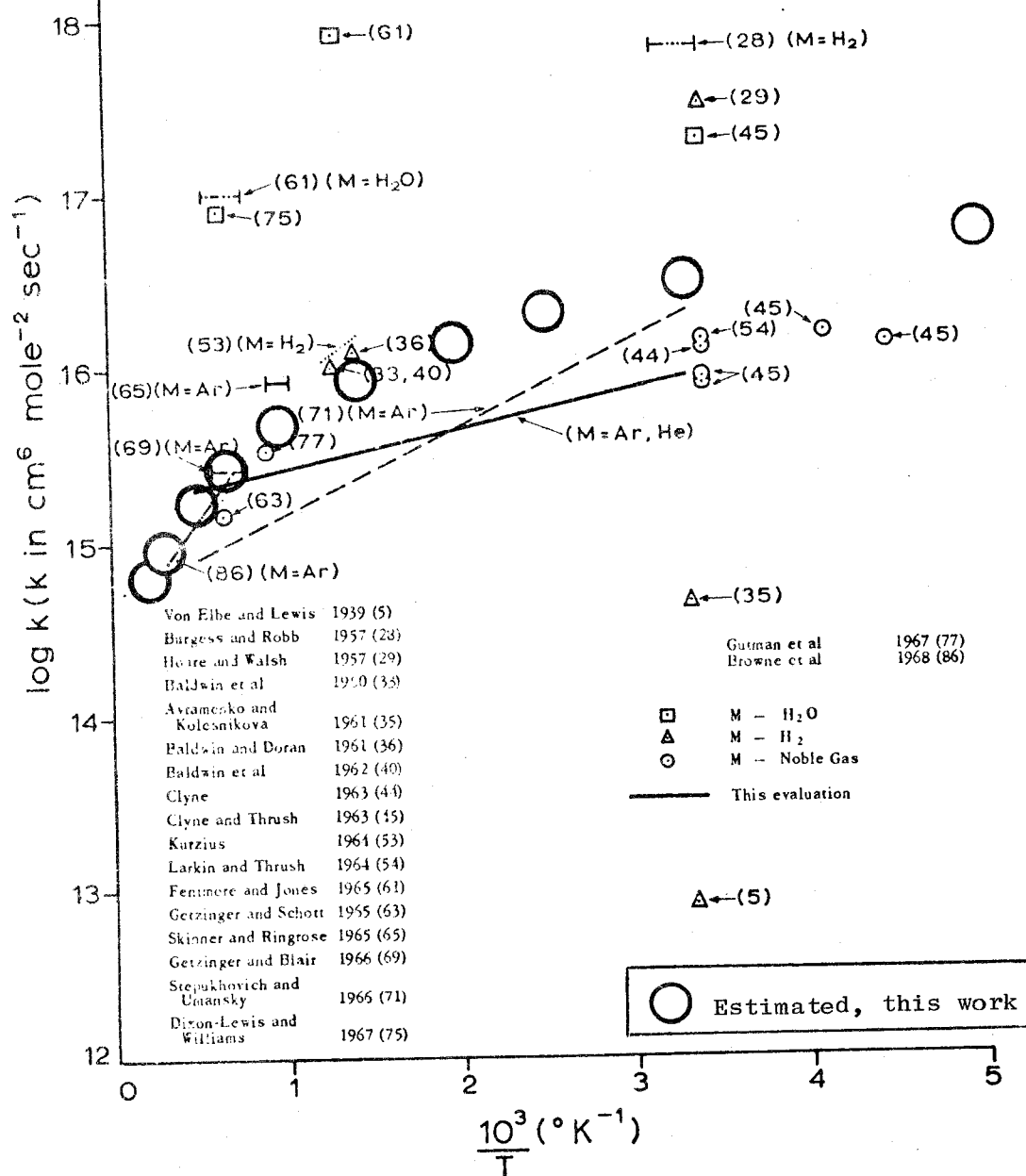
FIGURE A-22 $NO_2 + M \rightarrow NO + O + M$

87
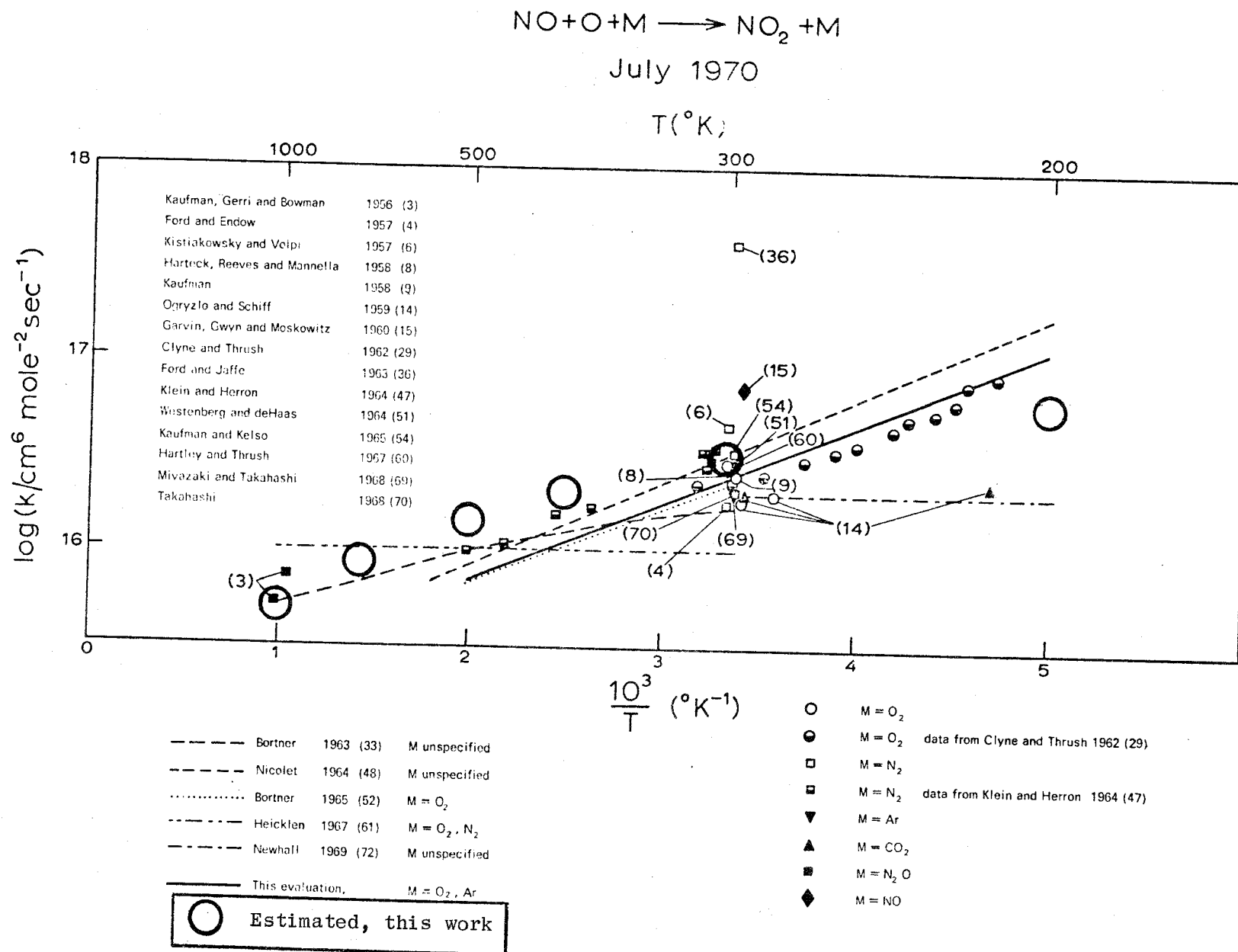
FIGURE A-23 NO + O + M → NO₂ + M

FIGURE A-24 $H + O_2 + M \rightarrow HO_2 + M$

constant for reactions of larger species should be similar to equation (2) although the values of $\Delta H^{o\ddagger}_{300}$, $\Delta S^{o\ddagger}_{300}$, and $\Delta C^{o\ddagger}_{p}$ may be different.

ACKNOWLEDGMENTS

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ESTIMATION OF HEATS OF FORMATION AT 300 K OF SOME TRIATOMIC SPECIES CONTAINING ATOMS OF THE ELEMENTS CARBON, HYDROGEN, NITROGEN, OXYGEN, AND SULFUR

As discussed in the main body of the report, to determine whether $\Delta H^{o\ddagger}_{300}$ is -1 or 7 kcal/mol, it is often necessary to know the heat of formation at 300 K of the triatomic intermediate XYZ in the reaction $X + YZ \rightarrow XY + Z$. In some cases, XYZ is a molecule whose heat of formation is well known; for example, ΔH^o_{f300} (H_2O) = -57.8 kcal/mol. In other cases, no data are available in the literature and an estimate is necessary. Table B-1 lists the known heats of formation of some molecules that were used in the estimates. The following estimates of bond dissociation energies were used: D(N-H) = 95 ± 5, D(C-H) = 95 ± 5, D(H-O) = 90 ± 5, and D(H-S) = 82 kcal/mol. All heats of formation are for a temperature of 300 K; the units are kcal/mol. Each estimate is discussed in detail below.

CNH

The method of estimation for ΔH^o_f(CHN) involved estimating the ΔH^o_f of CH_2=NH from the dehydrogenation of CH_3-NH_2 and removing two H-atoms to get ΔH^o_f (CNH).

$$CH_3-NH_2 \longrightarrow H_2 + CH_2=NH \qquad \Delta H = 21.5 \pm 1 \text{ (Reference 7)}$$

$$\Delta H^o_f(CH_2=NH) = 21.5 + \Delta H^o_f(CH_3-NH_2) = 16.0 \pm 1$$

Table B-1. HEATS OF FORMATION OF MONATOMIC, DIATOMIC, AND POLYATOMIC SPECIES USED TO ESTIMATE HEATS OF FORMATION OF TRIATOMIC SPECIES

(all values have units of kcal/mol)

Species	ΔH_f^o	Reference[a]
Monatomic		
C	170.89 ± 0.45	1
H	52.10 ± 0.001	1
N	113.0 ± 1	1
O	59.55 ± 0.02	1
S	66.29 ± 0.01	1
Diatomic		
C_2	200.2 ± 0.9	1
CH	142.0 ± 0.1	1
CN	104.0 ± 2.5	1
CO	-26.4 ± 0.6	1
CS	55.0 ± 5.0	1
H_2	0	1
NH	90.0 ± 4.0	1
HO	9.49 ± 0.04	1
HS	34.6 ± 4.0	1
N_2	0	1
NO	21.58 ± 0.04	1
NS	63.0 ± 10	1
O_2	0	1
SO	1.2 ± 0.3	1
S_2	30.8 ± 0.2	1
Polyatomic		
CH_3NH_2	-5.5 ± 0.1	2
CH_2CH_2	12.5 ± 0.1	2
CH_3OH	-48.1 ± 0.05	2
CH_3SH	-5.4 ± 0.1	2
CH_3NO	16.0 ± 2[b]	3
CH_3ONH_2 (liquid)	-13.0 ± 2[b]	1
CH_3OCH_3	-44.0 ± 0.1	2
CH_3SCH_3	-8.9 ± 0.1	2
HNCS	30.0 ± 2[b]	3
CH_3SSCH_3	-5.6 ± 0.2	2
CH_3CN	21.0 ± 1	4
$(CN)_2$	73.9 ± 0.4	1

Table B-1 (Concluded). HEATS OF FORMATION OF MONATOMIC, DIATOMIC, AND POLYATOMIC SPECIES USED TO ESTIMATE HEATS OF FORMATION OF TRIATOMIC SPECIES

(all values have units of kcal/mol)

Species	ΔH^o_f	Reference[a]
OCO	-94.05 ± 0.01	1
OCS	-33.1 ± 0.3	1
HNO	23.8 ± 1[b]	1
SCS	27.98 ± 0.19	1
CCO	68.5 ± 15.0	1
NH_2OH	-9.0 ± 1[b]	3
NH_2NH_2	22.8 ± 1[b]	3
CH_3OOCH_3	-30.0 ± 2[b]	3
HOO·	5.0 ± 2[b]	1,3
$CH_3O·$	3.5 ± 1	3
$CH_3S·$	29.0 ± 2	5
HOOH	-32.5 ± 1[b]	1,3,4
HSSH	$+2.5 \pm 2$[b]	6
ONO	7.9 ± 0.2	1
HOH	-57.8 ± 0.001	1
HSH	-4.9 ± 0.2	1
CH_3OOH	-31.5 ± 2[b]	3
HOOOH	-13.5 ± 1[b]	3
NNO	19.6 ± 0.1	1
HNNN	70.3 ± 2[b]	3
O_3	34.1 ± 0.4	1
HCO·	10.4 ± 2.0	1
$CH_3·$	34.81 ± 0.2	1

[a] References are listed at the end of Appendix B.
[b] Errors estimated for this report.

CNO

The $\Delta H_f^0(CNO)$ was estimated by removing three H-atoms from CH_3NO.

$$CH_3NO \longrightarrow 3H\cdot + CNO \qquad\qquad \Delta H = 285 \pm 15$$

$$\Delta H_f^0(CNO) = 285 \pm 15 + \Delta H_f^0(CH_3NO) - 3\left[\Delta H_f^0(H\cdot)\right] = 145 \pm 17$$

CON

The $\Delta H_f^0(CON)$ was estimated by removing five H-atoms from CH_3ONH_2 where the $\Delta H_f^0(CH_3ONH_2)$ was obtained from the liquid value and from an estimated $\Delta H_v(CH_3ONH_2)$ of 8 ± 1.

$$CH_3ONH_2(\ell) \longrightarrow CH_3ONH_3(g) \qquad\qquad \Delta H_v = 8 \pm 1$$
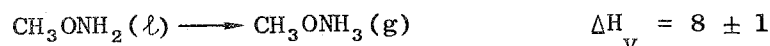
$$\Delta H_f^0(CH_3ONH_2)_g = 13 - \Delta H_f^0(CH_3ONH_2)_\ell = 5 \pm 3$$

$$CH_3ONH_2 \longrightarrow 5H\cdot + CON \qquad\qquad \Delta H = 475 \pm 25$$

$$\Delta H_f^0(CON) = 475 \pm 25 + \Delta H_f^0(CH_3ONH_2)_g - 5\left[\Delta H_f^0(H\cdot)\right] = 220 \pm 2.9$$

CNS

The $\Delta H_f^0(CNS)$ was estimated by noting that the difference between $\Delta H_f^0(NO)$ and $\Delta H_f^0(NS)$ was 41 ± 10. This value was added to the $\Delta H_f^0(CNO)$.

$$\Delta H_f^0(NS) - \Delta H_f^0(NO) = 41 \pm 10$$
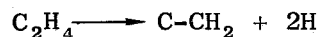
$$\Delta H_f^0(CNS) = \Delta H_f^0(CNO) + 41 = 186 \pm 25$$

CSN

The $\Delta H_f^0(CSN)$ was estimated from $\Delta H_f^0(CON)$ by noting that the substitution of an S-atom for an O-atom adds 35 to the heat of formation of methyl ether.

$$\Delta H_f^0(CH_3SCH_3) - \Delta H_f^0(CH_3OCH_3) = 35.1 \pm 0.2$$

$$\Delta H_f^0(CSN) = \Delta H_f^0(CON) + 35 = 250 \pm 29$$

$$C_2 + C_2H_4 \longrightarrow 2C\text{-}CH_2 \qquad\qquad \Delta H = 0 \pm 1 \text{ (assumed)}$$

$$\Delta H_f^o(C\text{-}CH_2) = [0 + \Delta H_f^o(C_2) + \Delta H_f^o(C_2H_4)]/2 = 106.4 \pm 2$$

$$C_2H_4 \longrightarrow C\text{-}CH_2 + 2H$$

$$\Delta H = \Delta H_f^o(C\text{-}CH_2) + 2[\Delta H_f^o(H \cdot)] - \Delta H_f^o(C_2H_4) = 198.1 \pm 2$$

$$CH_2{=}NH \longrightarrow 2H + CNH \qquad\qquad \Delta H = 198 \pm 2$$

$$\Delta H_f^o(CNH) = 198 + \Delta H_f^o(CH_2{=}NH) - 2[\Delta H_f^o(H \cdot)] = 110 \pm 3$$

COH

The $\Delta H_f^o(COH)$ was estimated by removing three H-atoms from CH_3OH.

$$CH_3OH \longrightarrow 3H \cdot + COH \qquad\qquad \Delta H = 285 \pm 15$$

$$\Delta H_f^o(COH) = 285 \pm 15 + \Delta H_f^o(CH_3OH) - 3[\Delta H_f^o(H \cdot)] = 81 \pm 15$$

CSH

The $\Delta H_f^o(CSH)$ was estimated by removing three H-atoms from CH_3SH.

$$CH_3SH \longrightarrow 3H \cdot + CSH \qquad\qquad \Delta H = 285 \pm 15$$

$$\Delta H_f^o(CSH) = 285 \pm 5 + \Delta H_f^o(CH_3SH) - 3[\Delta H_f^o(H \cdot)] = 123 \pm 15$$

HCS

The $\Delta H_f^o(HCS)$ was estimated by assuming that the bond dissociation energy $D(H\text{-}CS)$ was equal to $D(H\text{-}CO)$.

$$HCO \longrightarrow H \cdot + CO$$
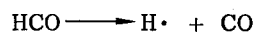
$$\Delta H = D(H\text{-}CO) = \Delta H_f^o(H \cdot) + \Delta H_f^o(HCO) = 15.3 \pm 2.6$$

$$D(H\text{-}CS) = D(H\text{-}CO) = 15.3 \pm 2.6$$

$$HCS \longrightarrow H \cdot + CS \qquad\qquad \Delta H = 15.3 \pm 2.6$$

$$\Delta H_f^o(HCS) = \Delta H_f^o(H \cdot) + \Delta H_f^o(CS) - 15.3 = 91.8 \pm 8$$

NCS

The ΔH_f^o(NCS) was estimated by removing an H-atom from HNCS.

$$\text{HNCS} \longrightarrow \text{NCS} + \text{H} \cdot \qquad \Delta H_R = 95 \pm 5$$

$$\Delta H_f^o(\text{NCS}) = 95 + \Delta H_f^o(\text{HNCS}) - \Delta H_f^o(\text{H}\cdot) = 73 \pm 7$$

Note: A value of 75 ± 5 kcal/mol for ΔH_f^o(NCS) has been estimated by

N. Barroeta.[8]

COS

Method I--The ΔH_f^o(COS) was estimated by adding 35.1 ± 0.2 for S-atom substitution (see CSN) to the ΔH_f^o(COO) (see COO).

$$\Delta H_f^o(\text{COS}) = \Delta H_f^o(\text{COO}) + 35 = 170 \pm 22$$

Method II--The ΔH_f^o(COS) was estimated by subtracting 12 ± 11 from ΔH_f^o(CSO) (See CSO).

11 ± 10 is the difference between ΔH_f^o(HOS) and ΔH_f^o(HSO)

$$\Delta H_f^o(\text{COS}) = \Delta H_f^o(\text{CSO}) - 12 = 152 \pm 30$$

Taking the average of methods I and II, $\Delta H_f^o(\text{COS}) = [170 + 152]/2 = 161 \pm 36$.

CSO

The ΔH_f^o(CSO) was assumed to be equal to the ΔH_f^o(CSS) (See CSS).

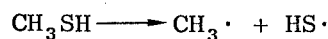$$\Delta H_f^o(\text{CSO}) = \Delta H_f^o(\text{CSS}) = 164 \pm 19$$

COO

The ΔH_f^o(COO) was estimated by removing four H-atoms from CH_3OOH.

$$\text{CH}_3\text{OOH} \longrightarrow \text{COO} + 4\text{H} \cdot \qquad \Delta H = 375 \pm 20$$

$$\Delta H_f^o(\text{COO}) = 375 + \Delta H_f^o(\text{CH}_3\text{OOH}) - 4[\Delta H_f^o(\text{H}\cdot)] = 135 \pm 22$$

CSS

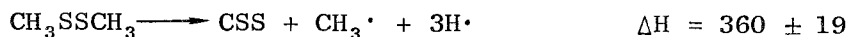The $\Delta H_f^o(CSS)$ was estimated by removing three H-atoms and a $CH_3\cdot$ from $CH_3-S-S-CH_3$.

$$CH_3SH \longrightarrow CH_3\cdot + HS\cdot$$

$$\Delta H = \Delta H_f^o(CH_3\cdot) + \Delta H_f^o(HS\cdot) - \Delta H_f^o(CH_3SH)$$

$$D(CH_3-SH) = \Delta H = 74.8 \pm 4$$

$$CH_3SSCH_3 \longrightarrow CSS + CH_3\cdot + 3H\cdot \qquad \Delta H = 360 \pm 19$$

$$\Delta H_f^o(CSS) = 360 + \Delta H_f^o(CH_3SSCH_3) - \Delta H_f^o(CH_3\cdot) - 3[\Delta H_f^o(H\cdot)]$$

$$\Delta H_f^o(CSS) = 164 \pm 19$$

CCN

Method I--The $\Delta H_f^o(CCN)$ was estimated by removing three H-atoms from CH_3CN.

$$CH_3CN \longrightarrow CCN + 3H\cdot \qquad \Delta H_f^o(CH_3CN) - 3[\Delta H_f^o(H\cdot)]$$
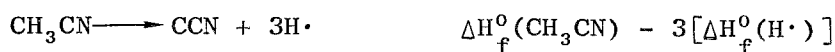
$$\Delta H_f^o(CCN) = 150 \pm 16$$

Method II--The $\Delta H_f^o(CCN)$ was estimated by removing an N-atom from $(CN)_2$ using a value for $D(C-N) = 180 \pm 4$ kcal/mol.

$$\cdot CN \longrightarrow C + N$$

$$D_{C-N} = \Delta H_f^o(C) + \Delta H_f^o(N) - \Delta H_f^o(\cdot CN) = 180 \pm 4$$

$$NCCN \longrightarrow N + CCN \qquad \Delta H = 180 \pm 4$$

$$\Delta H_f^o(CCN) = 180 + \Delta H_f^o(CN)_2 - \Delta H_f^o(N)$$
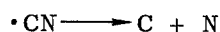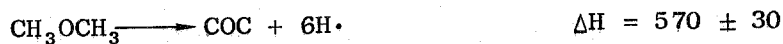
$$\Delta H_f^o(CCN) = 141.0 \pm 3.4$$

$\Delta H_f^o(CCN)$ was taken as the average of methods I and II.

$$\Delta H_f^o(CCN) = 146 \pm 16$$

COC

The $\Delta H^o_f(COC)$ was estimated by removing six H-atoms from CH_3OCH_3.

$$CH_3OCH_3 \longrightarrow COC + 6H\cdot \qquad\qquad \Delta H = 570 \pm 30$$

$$\Delta H^o_f(COC) = 570 + \Delta H^o_f(CH_3OCH_3) - 6[\Delta H^o_f(H\cdot)] = 213 \pm 30$$

CCS

The $\Delta H^o_f(CCS)$ was estimated by adding 61 to $\Delta H^o_f(CCO)$. 61 ± 0.4 is the difference between $\Delta H^o_f(CS_2)$ and $\Delta H^o_f(SCO)$ and also the difference between $\Delta H^o_f(SCO)$ and $\Delta H^o_f(CO_2)$.

$$\Delta H^o_f(CS_2) - \Delta H^o_f(SCO) = 61.1 \pm 0.5$$

$$\Delta H^o_f(SCO) - \Delta H^o_f(CO_2) = 61.0 \pm 0.3$$

$$\therefore \Delta H^o_f(CCS) = \Delta H^o_f(CCO) + 61 = 30 \pm 15$$

CSC

The $\Delta H^o_f(CSC)$ was estimated by adding the difference $[\Delta H^o_f(CH_3SCH_3) - \Delta H^o_f(CH_3OCH_3)]$ to $\Delta H^o_f(COC)$ (See COC).

$$\Delta H^o_f(CH_3SCH_3) - \Delta H^o_f(CH_3OCH_3) = 35.1 \pm 0.2$$

$$\Delta H^o_f(CSC) = \Delta H^o_f(COC) + 35 = 248 \pm 30$$

This is equivalent to removing 6 H-atoms from CH_3SCH_3.

HON

The $\Delta H^o_f(HON)$ was estimated by removing two H-atoms from NH_2OH.

$$H_2NOH \longrightarrow NOH + 2H\cdot \qquad\qquad \Delta H = 190 \pm 10$$

$$\Delta H^o_f(NOH) = 190 + \Delta H^o_f(NH_2OH) - 2[\Delta H^o_f(H\cdot)] = 77 \pm 11$$

HNS

The $\Delta H^o_f(HNS)$ was estimated by adding 41 ± 10, the difference between $\Delta H^o_f(NO)$ and $\Delta H^o_f(NS)$, to $\Delta H^o_f(HNO)$ (See CNS).

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$$\Delta H^o_f(NS) - \Delta H^o_f(NO) = 41 \pm 10$$

$$\Delta H^o_f(HNS) = \Delta H^o_f(HNO) + 41 = 65 \pm 11$$

HSN

The $\Delta H^o_f(HSN)$ was estimated by adding 35.1 ± 0.2, the increase in the ΔH^o_f of CH_3OCH_3 when an S-atom is substituted for an O-atom, to $\Delta H^o_f(HON)$.

$$\Delta H^o_f(CH_3SCH_3) - \Delta H^o_f(CH_3OCH_3) = 35.1 \pm 0.2 \quad \text{(See \underline{CSN})}$$

$$\Delta H^o_f(HSN) = \Delta H^o_f(HON) + 35 = 112 \pm 11 \quad \text{(See \underline{HON})}$$

HNN

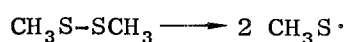The $\Delta H^o_f(HNN)$ was estimated by removing three H-atoms from H_2NNH_2.

$$H_2N-NH_2 \longrightarrow HNN + 3H\cdot \qquad \Delta H = 285 \pm 15$$

$$\Delta H^o_f(HNN) = 285 + \Delta H^o_f(N_2H_4) - 3[\Delta H^o_f(H\cdot)]$$

$$\Delta H^o_f(HNN) = 152 \pm 16$$

HOS

Method I--The $\Delta H^o_f(HOS)$ was estimated by obtaining D(S-OH) from $D(CH_3S-SCH_3)$ and $D(CH_3O-OCH_3)$. These were averaged (50.5), and 14.5 was added as the difference between D(HO-OH) and $D(CH_3O-OCH_3)$.

$$CH_3S-SCH_3 \longrightarrow 2\ CH_3S\cdot$$

$$D(CH_3S-SCH_3) = \Delta H = 2[\Delta H^o_f(CH_3S\cdot)] - \Delta H^o_f(CH_3SSCH_3) = 64 \pm 4$$
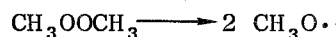
$$CH_3OOCH_3 \longrightarrow 2\ CH_3O\cdot$$

$$D(CH_3O-OCH_3) = \Delta H = 2[\Delta H^o_f(CH_3O\cdot)] - \Delta H^o_f(CH_3OOCH_3) = 37 \pm 4$$

$$D(CH_3S-OCH_3) = [D(CH_3S-SCH_3) + D(CH_3O-OCH_3)]/2 = 50.5 \pm 6$$

$$D(HO-OH) - CH_3O-OCH_3 = 14.5 \pm 5$$

$$\therefore \ D(HS-OH) = D(CH_3S-OCH_3)$$

$$HOS \qquad HO\cdot + S \qquad\qquad \Delta H = 65 \pm 11$$

$$\Delta H_f^0(HOS) = \Delta H_f^0(\cdot OH) + \Delta H_f^0(S) - 65 = 11 \pm 11$$

Method II--The $\Delta H_f^0(HOS)$ was estimated from $D(H-OS)$, which was obtained from $D(H-O_2)$.

$$HO_2 \ \rightarrow \ H\cdot + O_2$$
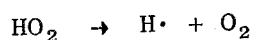
$$D(H-O_2) = \Delta H = \Delta H_f^0(H\cdot) + \Delta H_f^0(O_2) - \Delta H_f^0(HO_2) = 47.1 \pm 2$$

$$HOS \qquad H + OS \qquad\qquad \Delta H = 47.1 \pm 2$$

$$\Delta H_f^0(HOS) = \Delta H_f^0(H\cdot) + \Delta H_f^0(SO) - 47.1 = 6.2 \pm 2$$

Method III--The $\Delta H_f^0(HOS)$ was estimated by estimating $\Delta H_f^0(HOSH)$ from $\Delta H_f^0(HOOH)$ and $\Delta H_f^0(HSSH)$ and then estimating $D(H-SOH)$.

$$\Delta H_f^0(HOSH) = [\Delta H_f^0(HOOH) + \Delta H_f^0(HSSH)]/2 = -15 \pm 5$$

Since $\qquad D(H-OH) - D(H-OCH_3) = D(H-OCH_3) - D(H-OOH) = 14$

and $\qquad\qquad D(H-SH) - D(H-SCH_3) = 5 \pm 3$

$$\therefore \ D(H-SCH_3) - D(H-SSH) = 5 \pm 3$$

$$D(H-SSH) = D(H-SCH_3) - 5 = 82 \pm 5$$

$$HSOH \qquad HOS\cdot + H\cdot \qquad\qquad \Delta H = 82 \pm 5$$

$$\Delta H_f^0(HOS) = 82 + \Delta H_f^0(HSOH) - \Delta H_f^0(H\cdot) = 15 \pm 10$$

An average of methods I, II, and III gives

$$\Delta H_f^0(HOS) = 11 \pm 13$$

HSO

The ΔH^0_f(HSO) was estimated by first estimating the ΔH^0_f(HSOH) as an average of ΔH^0_f(HOOH) and ΔH^0_f(HSSH) and removing an H-atom from HSO-H.

$$\Delta H^0_f(\text{HOSH}) = [\Delta H^0_f(\text{HSSH}) + \Delta H^0_f(\text{HOOH})]/2 = -15 \pm 5$$

$$D(\text{H-OSH}) = 90 \pm 5$$

$$\text{HOSH} \longrightarrow \text{H}\cdot + \text{OSH} \qquad \Delta H = 90 \pm 5$$

$$\Delta H^0_f(\text{OSH}) = 90 + \Delta H^0_f(\text{HOSH}) - \Delta H^0_f(\text{H}\cdot) = 23 \pm 10$$

HSS

The ΔH^0_f(HSS) was estimated by removing an H-atom from HSSH.

$$\text{HSSH} \longrightarrow \text{H} + \text{SSH} \qquad \Delta H = 82 \pm 5$$

$$\Delta H^0_f(\text{SSH}) = 82 - \Delta H^0_f(\text{H}\cdot) + \Delta H^0_f(\text{HSSH}) = 33 \pm 5$$

NOS

The ΔH^0_f(NOS) was estimated by estimating the ΔH^0_f(H$_2$NOSH) and removing three H-atoms. ΔH^0_f(H$_2$NOSH) was estimated by inserting an S-atom in H$_2$NO-H using a value of 42, which was obtained from the difference between ΔH^0_f(HOH) and ΔH^0_f(HOSH) (See HOS).

$$\Delta H^0_f(\text{HOH}) - \Delta H^0_f(\text{HOSH}) = 42 \pm 5$$

$$\Delta H^0_f(\text{H}_2\text{NOSH}) = \Delta H^0_f(\text{H}_2\text{NOH}) + 42 = 33 \pm 6$$

$$\text{H}_2\text{NOSH} \longrightarrow \text{NOS} + 3\text{H}\cdot \qquad \Delta H = 272 \pm 15$$

$$\Delta H^0_f(\text{NOS}) = 272 + \Delta H^0_f(\text{H}_2\text{NOSH}) - 3[\Delta H^0_f(\text{H}\cdot)]$$

$$\Delta H^0_f(\text{NOS}) = 149 \pm 21$$

NSO

Method I--The $\Delta H^0_f(NSO)$ was estimated by adding 35 to $\Delta H^0_f(NOO)$. The 35 factor was obtained from the difference between $\Delta H^0_f(ROR)$ and $\Delta H^0_f(RSR)$. Note: also close to $\Delta H^0_f(NS) - \Delta H^0_f(NO) = 41$ and $\Delta H^0_f(RSH) - \Delta H^0_f(ROH) = 43$.

$$\Delta H^0_f(NSO) = \Delta H^0_f(NOO) + 35 = 171 \pm 20$$

Note: See <u>NOO</u> for estimates of $\Delta H^0_f(NOO)$.

Method II--The $\Delta H^0_f(NSO)$ was estimated by comparing ΔH^0_f of XSO and XOS

$$\Delta H^0_f(HSO) - \Delta H^0_f(HOS) = 11 \pm 10$$

$$\therefore \Delta H^0_f(NSO) - \Delta H^0_f(NOS) = 11 \pm 10$$

$$\Delta H^0_f(NSO) = \Delta H^0_f(NOS) + 11 = 160 \pm 31$$

The average of the two methods is

$$\Delta H^0_f(NSO) = 166 \pm 39$$

ONS

Method I--The $\Delta H^0_f(ONS)$ was estimated by adding 41, the difference between $\Delta H^0_f(NS)$ and $\Delta H^0_f(NO)$, to $\Delta H^0_f(ONO)$

$$\Delta H^0_f(NS) - \Delta H^0_f(NO) = 41 \pm 10$$

$$\Delta H^0_f(ONS) = \Delta H^0_f(ONO) + 41 = 49 \pm 10$$

Method II--The $\Delta H^0_f(ONS)$ was estimated by assuming $D(O-NS)$ was equal to $D(O-NO)$ (73.3 ± 0.6).

$$D(O-NS) = D(O-NO) = 73.3 \pm 0.6$$

$$ONS \longrightarrow O + NS \qquad \Delta H = 73.3 \pm 0.6$$

$$\Delta H^0_f(ONS) = \Delta H^0_f(O) + \Delta H^0_f(NS) - 73 = 49 \pm 10$$

Average of methods I and II: $\Delta H^o_f(ONS) = 49 \pm 10$.

NOO

The $\Delta H^o_f(NOO)$ was estimated by inserting an O-atom in H_2NOH and removing three H-atoms. The value for O-atom insertion was determined from $\Delta H^o_f(HOOH) - \Delta H^o_f(HOH)$ and $\Delta H^o_f(CH_3OOH) - \Delta H^o_f(CH_3OH)$.

$$\Delta H^o_f(HOOH) - \Delta H^o_f(HOH) = 25.3 \pm 1$$

$$\Delta H^o_f(CH_3OOH) - \Delta H^o_f(CH_3OH) = 16.6 \pm 2$$

Average value = 21 ± 2

$$\Delta H^o_f(H_2NOOH) = \Delta H^o_f(H_2NOH) + 21 = 12 \pm 3$$

$$H_2NOOH \longrightarrow NOO + 3H \cdot \qquad\qquad \Delta H = 280 \pm 15$$

$$\Delta H^o_f(NOO) = 280 + \Delta H^o_f(H_2NOOH) - 3[\Delta H^o_f(H\cdot)] = 136 \pm 17$$

$\Delta H^o_f(NSS)$ was estimated by comparing the differences between XOO and XSS compounds.

$$\Delta H^o_f(HSS) - \Delta H^o_f(HOO) = 28 \pm 7$$

$$\Delta H^o_f(CSS) - \Delta H^o_f(COO) = 28 \pm 41$$

The average is 28 ± 15

$$\therefore \Delta H^o_f(NSS) - \Delta H^o_f(NOO) = 7 \pm 15$$

$$\Delta H^o_f(NSS) = \Delta H^o_f(NOO) + 27 = 164 \pm 32$$

SNS

Method I--The $\Delta H^o_f(SNS)$ was estimated by using D(S-NO) and D(S-NS) and calculating D(S-NO) from $\Delta H^o_f(SNO)$.

$$SNO \longrightarrow S + NO$$

$$D_{S-NO} = \Delta H^o_f(S) + \Delta H^o_f(NO) - \Delta H^o_f(SNO)$$

Note: See <u>SNO</u> for estimate of $\Delta H_f^0(SNO)$.

$$D_{S-NO} = 9 \pm 10$$

$$SNS \longrightarrow NS + S \qquad\qquad \Delta H = 39 \pm 10$$

$$\Delta H_f^0(SNS) = \Delta H_f^0(NS) + \Delta H_f^0(S) - 39 = 90 \pm 20$$

Method II--The $\Delta H_f^0(SNS)$ was estimated by adding $2X[\Delta H_f^0(NS) - \Delta H_f^0(NO)]$, i.e., 82 ± 20, to $\Delta H_f^0(ONO)$.

$$\Delta H_f^0(NS) - \Delta H_f^0(NO) = 41 \pm 10$$

$$\Delta H_f^0 SNS = \Delta H_f^0(ONO) + 2(41) = 90 \pm 20$$

Average of methods I and II:

$$\Delta H_f^0(SNS) = 90 \pm 20$$

Note: These two methods are somewhat equivalent in that $\Delta H_f^0(SNO)$ was estimated from $\Delta H_f^0(ONO)$ and $\Delta H_f^0(NO)$ and $\Delta H_f^0(NS)$.

NON

The $\Delta H_f^0(NON)$ was estimated by removing four H-atoms from H_2NONH_2. The $\Delta H_f^0(H_2NONH_2)$ was estimated by replacing the OH group by an NH_2 group on NH_2OOH. $\Delta H_f^0(H_2NOOH)$ was estimated by inserting an O-atom into NH_2OH. (21 ± 2, see <u>NOO</u>). The value for replacing an OH by NH_2 was estimated from $\Delta H_f^0(H_2NOOH) - \Delta H_f^0(HOOOH)$.

$$\Delta H_f^0(HN_2OOH) = \Delta H_f^0(H_2NOH) + 21 \qquad (\text{See } \underline{NOO})$$

$$\Delta H_f^0(NH_2OOH) = 12 \pm 3$$

$$\Delta H_f^0(NH_2OOH) - \Delta H_f^0(HOOH) = 25.5 \pm 4$$

$$\Delta H_f^0(HN_2ONH_2) = \Delta H_f^0(NH_2OOH) + 25 = 37.5 \pm 7$$
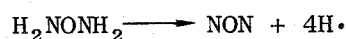
$$H_2NONH_2 \longrightarrow NON + 4H\cdot \qquad\qquad \Delta H = 380 \pm 20$$

$$\Delta H_f^0(NON) = 380 + \Delta H_f^0(H_2NONH_2) - 4[\Delta H_f^0(H\cdot)]$$

NNS

The $\Delta H_f^o(NNS)$ was estimated by adding 41, the difference between $\Delta H_f^o(NS)$ and $\Delta H_f^o(NO)$, to the $\Delta H_f^o(NNO)$.

$$\Delta H_f^o(NS) - \Delta H_f^o(NO) = 41 \pm 10$$

$$\Delta H_f^o(NNS) = \Delta H_f^o(NNO) + 41 = 61 \pm 10$$

NSN

The $\Delta H_f^o(NSN)$ was estimated by adding 35, the value for replacement of an O-atom by an S-atom (See CSN), to the $\Delta H_f^o(NON)$.

$$\Delta H_f^o(NSN) = \Delta H_f^o(NON) + 35 = 244 \pm 27$$

NNN

The $\Delta H_f^o(N_3)$ was estimated by removing an H-atom from HN_3.
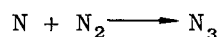
$$\Delta H_f^o(HN_3) = 70.3 \pm 2$$

$$HN_3 \longrightarrow H + N_3 \qquad\qquad \Delta H = 95 \pm 5$$

$$\Delta H_f^o(N_3) = 95 - \Delta H_f^o(H\cdot) + \Delta H_f^o(HN_3)$$

$$\Delta H_f^o(N_3) = 111 \pm 7$$

Note: JANAF gives value of 99 ± 5 for $\Delta H_f^o(N_3)$.

The reaction

$$N + N_2 \longrightarrow N_3$$

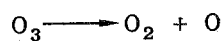is spin forbidden, and a value of 60 ± 6 must be added to $\Delta H_f^o(XYZ)$.

$$\Delta H_f^o(N_3) = \Delta H_f^o(N_3) + 60 = 171 \pm 13$$

SOO

The $\Delta H_f^o(SOO)$ was estimated by assuming that $D(SO-O) = D(OO-O)$ $D(OO-O)$ was calculated from $\Delta H_f^o(O_3)$

$$O_3 \longrightarrow O_2 + O$$

$$\Delta H_R = D(OO-O) = \Delta H_f^0(O_2) + \Delta H_f^0(O) - \Delta H_f^0(O_3)$$

$$D(OO-O = 25.5 \pm 0.4 = D(SO-O)$$

$$SOO \longrightarrow SO + O \qquad\qquad \Delta H = 25.5 \;\Delta\; 0.4$$

$$\Delta H_f^0(SOO) = \Delta H_f^0(SO) + \Delta H_f^0(O) - 25.5 = 35.3 \pm 0.7$$

SOS

The $\Delta H_f^0(SOS)$ was estimated by assuming that $D(S-OS) = D(S-OO)$. $D(S-OO)$ was calculated from $\Delta H_f^0(SOO)$ (see SOO).

$$SOO \longrightarrow S + O_2$$

$$\Delta H = D_{S-OO} = \Delta H_f^0(S) + \Delta H_f^0(S) + \Delta H_f^0(O_2) - \Delta H_f^0(SOO)$$

$$D(S-OO) = D(S-OS) = 31.0 \pm 0.7$$

$$SOS \longrightarrow SO + S \qquad\qquad \Delta H = 31.0 \pm 0.7$$

$$\Delta H_f^0(SOS) = \Delta H_f^0(SO) + \Delta H_f^0(S) - 31 = 36.5 \pm 1.0$$

SSS

The $\Delta H_f^0(S_3)$ was estimated by assuming that the increase in ΔH_f^0 in going from O_2 to O_3 would be the same as in going from S_2 to S_3.

$$\Delta H_f^0(O_3) - \Delta H_f^0(O_2) = 34.1 \pm 0.4$$

$$\therefore \text{ Let } \quad \Delta H_f^0(S_3) - \Delta H_f^0(S_2) = 34.1 \pm 0.4$$

$$\Delta H_f^0(S_3) = 34.1 + \Delta H_f^0(S_2) = 65 \pm 1$$

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16. ABSTRACT The report describes the rate estimation of some elementary chemical reactions that are important in combustion systems, including those involving the production and destruction of oxides of both nitrogen and sulfur. The estimates were made as part of a systematic effort to investigate the rate constants of reactions of species containing carbon, hydrogen, nitrogen, oxygen, and sulfur. The effort was concentrated on the atom transfer reactions between atoms and diatomic molecules containing these elements. All previously measured rate constants for these reactions were found to have the same value (plus or minus a factor of 3) in the exothermic direction at 2000 K. Rate constants in the endothermic direction are readily available from the equilibrium constants, all of which can be calculated. A FORTRAN computer program enables a user with no previous kinetics experience to estimate the rate constants at any temperature between 200 and 3000 K for any of the 75 pairs of atom transfer reactions involving the five elements.

17. KEY WORDS AND DOCUMENT ANALYSIS

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