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PLUME CHEMISTRY MODELS
SUMMARY OF A PLUME CHEMISTRY WORKSHOP

PHYSICAL DYNAMICS, INCORPORATED

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PLUME CHEMISTRY MODELS
SUMMARY OF A PLUME CHEMISTRY WORKSHOP

by

Edward R. Fisher

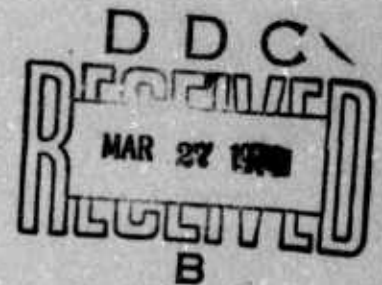
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13. ABSTRACT Two plume chemistry models are presented as a result of a workshop meeting in January, 1973. The first model characterizes the chemi-excitation and relaxation processes appropriate to an O/H/OH/H ₂ /O ₂ /H ₂ O system, while the second model characterizes the relaxation processes in a mixture of CO ₂ , H ₂ O, H ₂ , CO, N ₂ , O and H. These chemistry models are presented for baseline predictions on plume behavior.			

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INTRODUCTION

As the plume modeling capabilities continue to develop under the ARPA Plume Physics Program, a reliable set of "baseline" chemical mechanisms characterizing various fuel/atmospheric environments becomes increasingly important. This importance stems not only from providing direct comparisons between various flow field calculations using the same chemical models but also in establishing a basis upon which to judge improvements in reaction mechanisms and rate coefficients as new experimental and theoretical results become available. In this report, two chemical mechanisms with accompanying rate coefficients are presented: a chemi-excitation and vibrational relaxation mechanism for the APOLLO vehicle (H_2/O_2 System), and a general vibrational relaxation mechanism for a system consisting of H_2O , CO_2 , CO , N_2 , O , H and OH species. These reaction mechanisms are the outgrowth of a chemistry workshop held at Physical Dynamics, Inc., Berkeley, California on January 12, 1973. A list of attendees to this workshop are given in Appendix I. It should be noted that the collective input for all attending is represented in these two reaction mechanisms, particularly with respect to the magnitude of the proposed rate coefficients.

It will be clear upon reviewing the references accompanying the reaction mechanisms that many rate coefficients are very poorly known particularly for reactions involving atomic and radical species. Experiments underway at Wayne State University, AVCO and CALSPAN under the Plume Physics Program are expected to improve these estimates in the coming months.

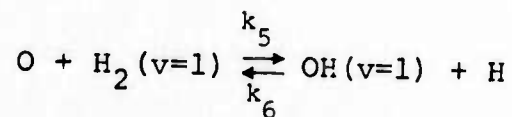
In proposing these baseline chemical mechanisms, it should be noted that an attempt was made to include all types of chemical reactions. Thus, reactions with relatively high activation energies generally limited in importance to high temperature regions of the plume are included as well as fast reactions involving reactive intermediates such as OH.

The mechanisms presented in this report should complement the "lumped parameter" hydrocarbon and amine combustion mechanisms recently proposed [Kummler, Fisher, Boynton (1972)] as well as the recent review of vibrational cross section data appropriate to rarified plume environments [Fisher (1972)].

CHEMICAL MODELS

The chemical reactions listed in Table I for the APOLLO system consist of both chemi-excitation and vibrational relaxation processes. To date there is no direct information on the rate coefficients for the chemi-excitation reactions [listed as reactions 1) through 18)] except for the overall reactions as reviewed in the Leed's reports [Baulch (1969)]. The rate coefficients for the reactions involving excited states have been estimated following a method of Boynton (1972) which most likely consists of an upper limit to these excited state reactions. The approach taken in these estimates is to assume that vibrational energy in the reactants [e.g., $H_2(v=1)$ as shown in reaction 3)] removes the experimentally observed overall activation energy as compiled in the Leed's reviews. Thus, the high temperature region (above about $1500^\circ K$) is dominated by the excited state reaction where $H_2(v=1)$ is present in relatively large concentrations while the low temperature reaction is dominated by the $H_2(v=0)$ reaction. By assuming a Boltzmann population of $H_2(v=1)$ at any given temperature, the additive contribution of reactions 1) and 3) are made to fit the measured overall reaction rate.

The reverse rate coefficients for reactions involving excited states have been calculated from the appropriate equilibrium constant as taken from the Leeds' review together with Boltzmann factors to account for the excited state populations. For example, the equilibrium constant for the reaction set



is related to the equilibrium constant for the overall reaction



as given in the Leeds reports by

$$K_{56} = \frac{e^{-E_1/KT}}{e^{-E_2/KT}} \frac{Q_2}{Q_1} K_{\text{Leeds}}$$

where E_1 = vibrational spacing of OH
 E_2 = vibrational spacing of H_2
 Q_1 = vibrational partition function of OH
 Q_2 = vibrational partition function of H_2
and K_{Leeds} = thermodynamic equilibrium constant for the overall reaction.

The reverse rate coefficients for chemical excitation reactions producing H_2O [i.e. reactions 7), 9), 11) and 13)] were calculated from the forward rate coefficients assuming that the H_2O is formed in the vibrational ground state. Note also that the energy transfer reactions [i.e. reactions 14) through 47) and Table II] are only listed in the forward direction. The reverse rate coefficients can be calculated from the Boltzmann factor involving the energy defect (energy available to the translational and rotational modes).

Table III lists the best available Einstein A Coefficients for incorporation into plume chemistry models. Of course the prediction of radiated energy in any given wavelength region depends not only on the total energy available from a given vibrational state as given by the A Coefficient, but also on the spectral shape of that band (i.e. the rotational distribution). A more extensive discussion of this point can be found elsewhere [Boynton, Fisher, Kummeler, Thomson (1973)].

TABLE I
APOLLO CHEMISTRY MODEL

<u>Reaction</u>	<u>Reference</u>	<u>Rate Constant</u> (cc/molecule-sec)
1) $O + H_2 \rightarrow OH + H$	(a,b)	$1.65^{-13} \exp(-2500/T)$
2) $H + OH \rightarrow O + H_2$	(c)	$6.9^{-14} \exp(-1425/T)$
3) $O + H_2(v=1) \rightarrow OH + H$	(d)	$1.3^{-10} \alpha$ ($\alpha = 0.9, 0.5$)
4) $H + OH \rightarrow O + H_2(v=1)$	(c)	$5.5^{-11} \alpha \exp(-4925/T)$
5) $O + H_2(v=1) \rightarrow OH(v=1) + H$	(d)	$1.3^{-10} (1 - \alpha)$
6) $H + OH(v=1) \rightarrow O + H_2(v=1)$	(c)	$5.5^{-11} (1 - \alpha) \exp(215/T)$
7) $OH + H_2 \rightarrow H_2O + H$	(d)	$3.8^{-11} \exp(-2600/T)$
8) $H + H_2O \rightarrow OH + H_2$	(c)	$1.5^{-10} \exp(-10075/T)$
9) $OH + H_2(v=1) \rightarrow H_2O + H$	(e)	1.5^{-10}
10) $H + H_2O \rightarrow OH + H_2(v=1)$	(c)	$5.8^{-10} \exp(-13475/T)$
11) $OH(v=1) + H_2 \rightarrow H_2O + H$	(e)	1.5^{-11}
12) $H + H_2O \rightarrow OH(v=1) + H_2$	(c)	$5.8^{-11} \exp(-12475/T)$
13) $OH + OH \rightarrow H_2O + O$	(a)	$9.6^{-12} \exp(-390/T)$
14) $O + H_2O \rightarrow OH + OH$	(a)	$9.5^{-11} \exp(-9000/T)$
15) $O + OH \rightarrow O_2 + H$	(f)	4^{-11}
16) $H + O_2 \rightarrow O + OH$	(c)	$6.9^{-10} \exp(-8400/T)$
17) $O + OH(v=1) \rightarrow O_2 + H$	(f)	4^{-11}
18) $H + O_2 \rightarrow O + OH(v=1)$	(c)	$6.9^{-10} \exp(-13400/T)$

ENERGY TRANSFER REACTIONS*

Vibration-Translation Processes:

19) $\text{H}_2(v=1) + \text{H} \rightarrow \text{H}_2 + \text{H}$	(g)	$3.2^{-11} \exp(-1400/T)$
20) $\text{H}_2(v=1) + \text{O} \rightarrow \text{H}_2 + \text{O}$	(e)	$3.0^{-13} \sqrt{T}$
21) $\text{H}_2(v=1) + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_2$	(h, i)	$1.5^{-7} \exp(-139/T^{1/3})$
22) $\text{H}_2(v=1) + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O}$	(e, j)	$1.5^{-7} \exp(-139/T^{1/3})$
23) $\text{N}_2(v=1) + \text{H} \rightarrow \text{N}_2 + \text{H}$	(u)	$1.9^{-6} \exp(-164/T^{1/3})$
24) $\text{N}_2(v=1) + \text{O} \rightarrow \text{N}_2 + \text{O}$	(k, l, m)	$1.2^{-13} \exp(-23/T^{1/3})$
25) $\text{N}_2(v=1) + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2$	(n)	$3.9^{-8} \exp(-164/T^{1/3})$
26) $\text{N}_2(v=1) + \text{H}_2\text{O} \rightarrow \text{N}_2 + \text{H}_2\text{O}$	(e, j)	$3.9^{-8} \exp(-164/T^{1/3})$
27) $\text{OH}(v=1) + \text{H} \rightarrow \text{OH} + \text{H}$	(e)	3^{-11}
28) $\text{OH}(v=1) + \text{O} \rightarrow \text{OH} + \text{O}$	(e)	3^{-11}
29) $\text{OH}(v=1) + \text{H}_2 \rightarrow \text{OH} + \text{H}_2$	(e)	1^{-11}
30) $\text{OH}(v=1) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2\text{O}$	(e)	3^{-12}
31) $\text{H}_2\text{O}(010) + \text{H} \rightarrow \text{H}_2\text{O}(000) + \text{H}$	(e)	1^{-11}
32) $\text{H}_2\text{O}(010) + \text{O} \rightarrow \text{H}_2\text{O}(000) + \text{O}$	(e)	1^{-11}
33) $\text{H}_2\text{O}(010) + \text{H}_2 \rightarrow \text{H}_2\text{O}(000) + \text{H}_2$	(e, o)	1^{-11}
34) $\text{H}_2\text{O}(010) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(000) + \text{H}_2\text{O}$	(p)	1^{-11}
35) $\text{H}_2\text{O}(020) + \text{H} \rightarrow \text{H}_2\text{O}(010) + \text{H}$	(t)	2^{-11}
36) $\text{H}_2\text{O}(020) + \text{O} \rightarrow \text{H}_2\text{O}(010) + \text{O}$	(t)	2^{-11}
37) $\text{H}_2\text{O}(020) + \text{H}_2 \rightarrow \text{H}_2\text{O}(010) + \text{H}_2$	(t)	2^{-11}
38) $\text{H}_2\text{O}(020) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(010) + \text{H}_2\text{O}$	(t)	2^{-11}

* Note that the reverse rate coefficient can be calculated directly from detailed balance.

- 39) $\text{H}_2\text{O}(001) + \text{H} \rightarrow \text{H}_2\text{O}(000) + \text{H}$ (e) 1^{-11}
 40) $\text{H}_2\text{O}(001) + \text{O} \rightarrow \text{H}_2\text{O}(000) + \text{O}$ (e) 1^{-11}
 41) $\text{H}_2\text{O}(001) + \text{H}_2 \rightarrow \text{H}_2\text{O}(000) + \text{H}_2$ (o) 2^{-13}
 42) $\text{H}_2\text{O}(001) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(000) + \text{H}_2\text{O}$ (q) 1^{-12}
 43) $\text{H}_2\text{O}(001) + \text{H} \rightarrow \text{H}_2\text{O}(020) + \text{H}$ (e) 1^{-11}
 44) $\text{H}_2\text{O}(001) + \text{O} \rightarrow \text{H}_2\text{O}(020) + \text{O}$ (e) 1^{-11}
 45) $\text{H}_2\text{O}(001) + \text{H}_2 \rightarrow \text{H}_2\text{O}(020) + \text{H}_2$ (e) 1^{-11}
 46) $\text{H}_2\text{O}(001) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(020) + \text{H}_2\text{O}$ (e) 1^{-11}

Vibration-Vibration Processes

- 47) $\text{H}_2(v=1) + \text{H}_2\text{O}(000)$
 $\rightarrow \text{H}_2(v=0) + \text{H}_2\text{O}(001)$ (r) $2.5^{-14} T^{5/6} \exp(-30.1/T^{1/3})$
 48) $\text{H}_2(v=1) + \text{OH}(v=0)$
 $\rightarrow \text{H}_2(v=0) + \text{OH}(v=1)$ (e) 1^{-12}
 49) $\text{N}_2(v=1) + \text{H}_2\text{O}(010)$
 $\rightarrow \text{N}_2(v=0) + \text{H}_2\text{O}(001)$ (e) 3^{-13}
 50) $\text{N}_2(v=1) + \text{H}_2\text{O}(000)$
 $\rightarrow \text{N}_2(v=0) + \text{H}_2\text{O}(010)$ (s) $9.4^{-11} \exp(-64/T^{1/3})$
 51) $\text{H}_2\text{O}(010) + \text{H}_2\text{O}(010)$
 $\rightarrow \text{H}_2\text{O}(020) + \text{H}_2\text{O}(000)$ (e) $1^{-12} \sqrt{T}$
 52) $\text{H}_2\text{O}(001)$ and $\text{H}_2\text{O}(100)$ assumed in quasi-equilibrium at the
 local translational temperature.

References (Apollo Model)

- a) D.L. Baulch, et. al., High Temperature Reaction Rate Data, Leeds University, (1969).
- b) F.P. Boynton, Semi Annual Technical Report No. 1, Physical Dynamics Report PD-72-020, February(1972).
- c) calculated from the forward rate coefficient and detailed balance, using the equilibrium constant as given in the Leeds review [(a) above].
- d) estimated from the Leeds review [(a) above] using a method outlined in (b) above.
- e) estimate
- f) W.E. Wilson Jr., J. Phys. Chem. Refer. Data 1, 535 (1972).
- g) R.F. Hiedner and V.V. Casper, Chem. Phys. Letters 15, 179(1972)
- h) J.H. Kieffer and R.W. Lutz, J. Chem. Phys. 44, 658(1966) 45, 3888(1966).
- i) C. Joffrin, J. Ducuing and J.P. Coffinet, Opt. Commun. 2, 245(1970).
- j) past measurements involving water presumably measure both VV and VT processes.
- k) W.D. Breshears and P.F. Bird, J. Chem. Phys. 48, 4768 (1968).
- l) R.J. McNeal, M.E. Whitson Jr. and G.R. Cook, preprint of work submitted to Chem. Phys. Letters(1972). Aerospace Report SPL 3303, July(1972).
- m) D.J. Eckstrom, Stanford Research Institute, unpublished results.
- n) D.R. White, J. Chem. Phys. 46, 2016(1967).
- o) estimate based on Marriott's cross section values see E.R. Fisher, AFCRL Special Report, 72-0539, August(1972).
- p) estimate based on all available data
- q) estimate based on analogy to HF VT relaxation

- r) estimate based on the modified Rapp model, J. Chem. Phys. 40, 573(1964); Fisher unpublished results.
- s) estimate based on data of C.W. Von Rosenberg, K.N.C. Bray and N.H. Pratt, J. Chem. Phys. 56, 3230(1972) and 13th Symp. (Intern.) on combustion p. 89, (1971).
- t) scaled from the analogous rate constant for exciting the lowest bending mode.
- u) estimated based on the rate for CO + H; see reference (o) under RELAXATION MODEL (2).

TABLE II
VIBRATIONAL RELAXATION MODEL

<u>Vibration-Translation Processes</u>	<u>Reference</u>	<u>Rate Constant (cc/molecule-sec)</u>
1) $H_2(v=1) + H \rightarrow H_2 + H$	(a)	$3.2^{-11} \exp(-1400/T)$
2) $H_2(v=1) + O \rightarrow H_2 + O$	(b)	$3.0^{-11} \sqrt{T}$
3) $H_2(v=1) + H_2 \rightarrow H_2 + H_2$	(c,d)	$1.5^{-7} \exp(-139/T^{1/3})$
4) $H_2(v=1) + H_2O \rightarrow H_2 + H_2O$	(b,e)	$1.5^{-7} \exp(-139/T^{1/3})$
5) $N_2(v=1) + H \rightarrow N_2 + H$	(y)	$1.9^{-6} \exp(-164/T^{1/3})$
6) $N_2(v=1) + O \rightarrow N_2 + O$	(f,g,h)	$1.2^{-13} \exp(-23/T^{1/3})$
7) $N_2(v=1) + H_2 \rightarrow N_2 + H_2$	(i)	$3.9^{-8} \exp(-164/T^{1/3})$
8) $N_2(v=1) + H_2O \rightarrow N_2 + H_2O$	(b,e)	$3.9^{-8} \exp(-164/T^{1/3})$
9) $OH(v=1) + H \rightarrow OH + H$	(b)	3^{-11}
10) $OH(v=1) + O \rightarrow OH + O$	(b)	3^{-11}
11) $OH(v=1) + H_2 \rightarrow OH + H_2$	(b)	1^{-11}
12) $OH(v=1) + H_2O \rightarrow OH + H_2O$	(b)	3^{-12}
13) $H_2O(010) + H \rightarrow H_2O(000) + H$	(b)	1^{-11}
14) $H_2O(010) + O \rightarrow H_2O(000) + O$	(b)	1^{-11}
15) $H_2O(010) + H_2 \rightarrow H_2O(000) + H_2$	(b,j)	1^{-11}
16) $H_2O(010) + H_2O \rightarrow H_2O(000) + H_2O$	(k)	1^{-11}
17) $H_2O(001) + H \rightarrow H_2O(000) + H$	(b)	1^{-11}
18) $H_2O(001) + O \rightarrow H_2O(000) + O$	(b)	1^{-11}
19) $H_2O(001) + H_2 \rightarrow H_2O(000) + H_2$	(j)	2^{-13}
20) $H_2O(001) + H_2O \rightarrow H_2O(000) + H_2O$	(l)	1^{-12}

21)	$\text{H}_2\text{O}(001) + \text{H} \rightarrow \text{H}_2\text{O}(020) + \text{H}$	(b)	1^{-11}
22)	$\text{H}_2\text{O}(001) + \text{O} \rightarrow \text{H}_2\text{O}(020) + \text{O}$	(b)	1^{-11}
23)	$\text{H}_2\text{O}(001) + \text{H}_2 \rightarrow \text{H}_2\text{O}(020) + \text{H}_2$	(b)	1^{-11}
24)	$\text{H}_2\text{O}(001) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(020) + \text{H}_2\text{O}$	(b)	1^{-11}
25)	$\text{CO}(v=1) + \text{H} \rightarrow \text{CO}(v=0) + \text{H}$	(o)	$5.3^{-7} \exp(-119/T^{1/3})$
26)	$\text{CO}(v=1) + \text{O} \rightarrow \text{CO}(v=0) + \text{O}$	(p)	$1^{-8} \exp(-96/T^{1/3})$
27)	$\text{CO}(v=1) + \text{H}_2 \rightarrow \text{CO}(v=0) + \text{H}_2$	(q)	$9^{-9} \exp(-119/T^{1/3})$
28)	$\text{CO}(v=1) + \text{H}_2\text{O} \rightarrow \text{CO}(v=0) + \text{H}_2\text{O}$	(b)	$9^{-9} \exp(-119/T^{1/3})$
29)	$\text{CO}_2(010) + \text{H} \rightarrow \text{CO}_2(000) + \text{H}$	(b)	$3.8^{-12} \exp(-7/T^{1/3})$
30)	$\text{CO}_2(010) + \text{O} \rightarrow \text{CO}_2(000) + \text{O}$	(p)	$2.3^{-9} \exp(-77/T^{1/3})$
31)	$\text{CO}_2(010) + \text{H}_2 \rightarrow \text{CO}_2(000) + \text{H}_2$	(r)	$7.6^{-12} \exp(-7/T^{1/3})$
32)	$\text{CO}_2(010) + \text{H}_2\text{O} \rightarrow \text{CO}_2(000) + \text{H}_2\text{O}$	(s)	1^{-11}
33)	$\text{CO}_2(010) + \text{CO}_2 \rightarrow \text{CO}_2(000) + \text{CO}_2$	(r)	$4.6^{-10} \exp(-77/T^{1/3})$
34)	$\text{CO}_2(001) + \text{H} \rightarrow \text{CO}_2(000) + \text{H}$	(t)	$6.7^{-8} \exp(-208/T^{1/3})$
35)	$\text{CO}_2(001) + \text{O} \rightarrow \text{CO}_2(000) + \text{O}$	(t)	$1^{-8} \exp(-96/T^{1/3})$
36)	$\text{CO}_2(001) + \text{H}_2 \rightarrow \text{CO}_2(000) + \text{H}_2$	(t)	$9^{-9} \exp(-119/T^{1/3})$
37)	$\text{CO}_2(001) + \text{H}_2\text{O} \rightarrow \text{CO}_2(000) + \text{H}_2\text{O}$	(t)	$9^{-9} \exp(-119/T^{1/3})$
38)	$\text{CO}_2(001) + \text{H} \rightarrow \text{CO}_2(030) + \text{H}$	(b)	$2.13^{17} T^{-6.34} \exp(-3013/T$ $-378.7/T^{1/3} + 1416/T^{2/3})$
39)	$\text{CO}_2(001) + \text{O} \rightarrow \text{CO}_2(030) + \text{O}$	(u)	$4.6^{24} T^{-5.89} \exp(-4223/T$ $-672.7/T^{1/3} + 2683/T^{2/3})$
40)	$\text{CO}_2(001) + \text{H}_2 \rightarrow \text{CO}_2(030) + \text{H}_2$	(v)	$4.27^{17} T^{-6.34} \exp(-3013/T$ $-378.7/T^{1/3} + 1416/T^{2/3})$

- 41) $\text{CO}_2(001) + \text{H}_2\text{O} \rightarrow \text{CO}_2(030) + \text{H}_2\text{O}$ (v) $4.71^{-40} T^{4.54} \exp(2081/T + 454/T^{1/3} - 1729/T^{2/3})$
- 42) $\text{CO}_2(001) + \text{CO}_2 \rightarrow \text{CO}_2(030) + \text{CO}_2$ (v) $9.16^{23} T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$
- 43) $\text{CO}_2(001) + \text{CO} \rightarrow \text{CO}_2(030) + \text{CO}$ (v) $6.87^{23} T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$
- 44) $\text{CO}_2(001) + \text{N}_2 \rightarrow \text{CO}_2(030) + \text{N}_2$ (v) $6.87^{23} T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$

Vibration-Vibration Processes

- 45) $\text{H}_2(v=1) + \text{H}_2\text{O}(000)$
 $\rightarrow \text{H}_2(v=0) + \text{H}_2\text{O}(001)$ (m) $2.5^{-14} T^{5/6} \exp(-30.1/T^{1/3})$
- 46) $\text{H}_2(v=1) + \text{OH}(v=0)$
 $\rightarrow \text{H}_2(v=0) + \text{OH}(v=1)$ (b) 1^{-12}
- 47) $\text{N}_2(v=1) + \text{H}_2\text{O}(010)$
 $\rightarrow \text{N}_2(v=0) + \text{H}_2\text{O}(001)$ (b) 3^{-13}
- 48) $\text{N}_2(v=1) + \text{H}_2(000)$
 $\rightarrow \text{N}_2(v=0) + \text{H}_2\text{O}(010)$ (n) $9.4^{-11} \exp(-64/T^{1/3})$
- 49) $\text{H}_2\text{O}(010) + \text{H}_2\text{O}(010)$
 $\rightarrow \text{H}_2\text{O}(020) + \text{H}_2\text{O}(000)$ (b) $1^{-12} \sqrt{T}$
- 50) $\text{CO}_2(001) + \text{H}_2\text{O}(000)$
 $\rightarrow \text{CO}_2(010) + \text{H}_2\text{O}(010)$ (b) 1^{-13}

- 51) $N_2(v=1) + CO_2(000)$
 $\rightarrow N_2(v=0) + CO_2(001)$ (r) Take the largest value $1.71^{-6} \exp(-175.3/T^{1/3})$
 $6.07^{-14} \exp(15.3/T^{1/3})$
- 52) $N_2(v=1) + CO(v=0)$
 $\rightarrow N_2(v=0) + CO(v=1)$ (v) Take the largest value $1.78^{-6} \exp(-210/T^{1/3})$
 $6.98^{-13} \exp(-25.6/T^{1/3})$
- 53) $CO_2(001) + CO(v=0)$
 $\rightarrow CO_2(000) + CO(v=1)$ (b) $1.56^{-11} \exp(-30.1/T^{1/3})$
- 54) $CO_2(101) + H_2O(000)$
 $\rightarrow CO_2(000) + H_2O(001)$ (b) $2^{-13} \sqrt{T}$
- 55) $CO_2(021) + H_2O(000)$
 $\rightarrow CO_2(000) + H_2O(001)$ (b) $2^{-13} \sqrt{T}$
- 56) $CO_2(101) + CO_2(000)$
 $\rightarrow CO_2(100) + CO_2(001)$ (b) $2^{-11} \sqrt{T}$
- 57) $CO_2(020) + CO_2(000)$
 $\rightarrow CO_2(010) + CO_2(010)$ (b) $4^{-13} \sqrt{T}$
- 58) $H_2O(020) + H \rightarrow H_2O(010) + H$ (w) 2^{-11}
- 59) $H_2O(020) + O \rightarrow H_2O(010) + O$ (w) 2^{-11}
- 60) $H_2O(020) + H_2 \rightarrow H_2O(010) + H_2$ (w) 2^{-11}
- 61) $H_2O(020) + H_2O \rightarrow H_2O(010) + H_2O$ (w) 2^{-11}
- 62) $CO_2(020) + H \rightarrow CO_2(010) + H$ (w) $7.6^{-12} \exp(-7/T^{1/3})$
- 63) $CO_2(020) + O \rightarrow CO_2(010) + O$ (w) $4.6^{-9} \exp(-77/T^{1/3})$
- 64) $CO_2(020) + H_2 \rightarrow CO_2(010) + H_2$ (w) $1.5^{-11} \exp(-7/T^{1/3})$
- 65) $CO_2(020) + H_2O \rightarrow CO_2(010) + H_2O$ (w) 2^{-11}

- 66) $\text{CO}_2(020) + \text{CO}_2 \rightarrow \text{CO}_2(010) + \text{CO}_2$ (w) $9.2^{-10} \exp(-77/T^{1/3})$
- 67) $\text{CO}_2(030) + \text{H} \rightarrow \text{CO}_2(020) + \text{H}$ (w) $1.2^{-11} \exp(-7/T^{1/3})$
- 68) $\text{CO}_2(030) + \text{O} \rightarrow \text{CO}_2(020) + \text{O}$ (w) $6.9^{-9} \exp(-77/T^{1/3})$
- 69) $\text{CO}_2(030) + \text{H}_2 \rightarrow \text{CO}_2(020) + \text{H}_2$ (w) $2.3^{-11} \exp(-7/T^{1/3})$
- 70) $\text{CO}_2(030) + \text{H}_2\text{O} \rightarrow \text{CO}_2(020) + \text{H}_2\text{O}$ (w) 3^{-11}
- 71) $\text{CO}_2(030) + \text{CO}_2 \rightarrow \text{CO}_2(020) + \text{CO}_2$ (w) $1.4^{-9} \exp(-77/T^{1/3})$
- 72) $\text{H}_2\text{O}(100)$ and $\text{H}_2\text{O}(001)$ assumed in quasi-equilibrium at the local translational temperature.
- 73) $\text{CO}_2(100) + \text{M} \rightarrow \text{CO}_2(020) + \text{M}$ (x)

References (Vibrational Relaxation Model)

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- (e) past measurements involving water presumably measure both VV and VT processes.
- (f) W.D. Breshears and P.F. Bird, J. Chem. Phys. 48, 4768 (1968).
- (g) R.J. McNeal, M.E. Whitson Jr. and G.R. Cook, preprint of work submitted to Chem. Phys. Letters (1972). Aerospace Report SPL 3303, July(1972).
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- (i) D.R. White, J. Chem. Phys. 46, 2016(1967).
- (j) estimate based on Marriott's cross section values see E.R. Fisher, AFCRL Special Report, 72-0539, August (1972).
- (k) estimate based on all available data
- (l) estimate based on analogy to HF VT relaxation
- (m) estimate based on the modified Rapp model, J. Chem. Phys. 40, 573(1964) Fisher unpublished results.
- (n) estimate based on data of C.W. Von Rosenberg, K.N.C. Bray and N.H. Pratt, J. Chem. Phys. 56, 3230(1972) and 13th Symp. (Intern.) on combustion p. 89, (1971).
- (o) C.N. Rosenberg, R. Taylor and D. Teare, J. Chem. Phys. 54, 1974(1971). Also assuming the $\text{CO}_2 + \text{H}_2$ activation energy, as shown in reaction 27).
- (p) unpublished data from AVCO.

- (q) W. J. Hoche and R. C. Millikan, J. Chem. Phys. 38, 214 (1963); and R. C. Millikan, J. Chem. Phys. 38, 2855 (1963).
- (r) R. Taylor and S. Bitterman, Rev. Mod. Phys. 41, 26 (1969).
- (s) M.I. Buckwald and S. H. Bauer, J. Phys. Chem. 76, 3108 (1972).
- (t) since direct VT relaxation of $\text{CO}_2(v_3)$ to ground state has not been unambiguously determined without competing VV processes, $\text{CO}_2(v_3)$ was assumed to relax like $\text{CO}(v=1)$.
- (u) estimate based on analogy with reaction 35).
- (v) estimate based on AVCO suggestion.
- (w) scaled from the analogous rate constant for exciting the lowest bending mode.
- (x) the Fermi resonance in CO_2 is assumed to couple the (100) and (020) modes with a gas kinetic efficiency independent of collision partner.
- (y) estimated based on the rate for $\text{CO} + \text{H}$, under (o) above.

TABLE III
RADIATIVE LIFETIMES

<u>SPECIES</u>	<u>t(sec)</u>
OH(v=1)	0.3
H ₂ O(100)	0.14
H ₂ O(010)	0.045
H ₂ O(001)	0.014
H ₂ O(020)	0.022
CO ₂ (010)	0.33
CO ₂ (001)	0.0025
CO ₂ (101)	0.091

SUMMARY

Two plume chemistry models are presented in this report together with the best available estimate of the rate coefficients. The intent of these models is to provide baseline chemical input to plume flow field calculations to both compare different flow field programs and to provide baseline radiation predictions in an actual plume configuration. As new rate coefficient data becomes available these models will be updated to continue to provide state-of-the-art chemistry mechanisms.

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APPENDIX I

Attendance List to Plume Chemistry Workshop
Held at Physical Dynamics, Inc., Berkeley, California
January 12, 1973

Frederick P. Boynton, Physical Dynamics

Philip E. Cassady, Lockheed-Palo Alto

Paul V. Davis, IDA

Edward R. Fisher, Physical Dynamics (Chairman)

Ralph H. Kummler, Physical Dynamics

Paul F. Lewis, AVCO EVERETT

C. Bradley Moore, University of California-Berkeley

J. Derek Teare, AVCO EVERETT

Kenneth Wilson, Lockheed-Palo Alto

Kurt L. Wray, Boston College