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ABSTRACT

The elementary reactions occurring in an H_2-F_2 explosion are given with each vibrational level of H_2 and HF considered as a separate reacting species. Rate coefficients for all the elementary reactions are either estimated or calculated, and the major assumptions entering into the determination of each rate coefficient are given. The effect of non-Maxwell distributions in the translational energies of some of the species is estimated. For strong pulses of F atoms, the explosion is complete before any appreciable contribution to the rate is made by thermal dissociation of F_2 or H_2.

The chemical change that produces lasing energy in H_2-F_2-HF systems has recently been modeled on computers.[1-5] The purpose of such computations is to gain insight into the processes that determine the amount of lasing power available and to try to reproduce gross (as compared to the detail of the model), macroscopic observations. The chemical change takes place by a series of elementary chemical reactions (such as those given in a thorough account by Cohen[6]) in which each vibrational state of H_2 and HF is necessarily considered as a separate species. However, in these models[1-5] other nonequilibrium effects in the chemistry have generally been neglected, and the transferability of thermal rate coefficients from one system to another has been implicitly accepted.

The kinetics model described here differs from previous models: (1) The rate coefficients for

$$F + H_2(0) \rightarrow HF(v) + H$$
$$H + F_2 \rightarrow HF(v) + F$$

are obtained for reactions taking place with a mixture of " hot" and thermal atoms. (2) The reactions of

$$F + H_2(v=1,2,3,4) \rightarrow HF(v'=0,1,...7) + H$$

are included and are shown to have an appreciable effect on the chemical change. (3) In an explosion initiated by a pulse of F atoms the rate of the overall reaction is shown to be fast compared with the vibrational relaxation of F_2 and H_2. The distribution of F_2 and H_2 over vibrational states is unaffected by the rise in translational temperature. The rates of dissociation of F_2, H_2, and HF are negligible during the explosion. Also, the distribution of HF(v) from $H + F_2 \rightarrow HF(v) + F$ is primarily from $H + F_2(0) \rightarrow HF(v) + F$. (4) The distribution of H atoms over translational energies is shown to be much different from a Maxwell distribution. When one is characterizing H-atom reactions in the H_2-F_2 explosion, this distribution over translational energies rather than the thermal distribution, should be used in future trajectory calculations. (5) The rates of V-R,T relaxation by H and F atoms of the higher vibrational states in HF are based on trajectory calculations and not on the harmonic oscillator approximation. The rates of V-R,T relaxation of HF($v>1$) by HF and H_2 are estimated from the rates of relaxation by F atoms as determined by trajectory calculations. (6) Qualitative assessments of the effect of rotational excitation are made when possible.

Many assumptions are made. For example, the rate coefficients for the V-R,T self-relaxation of the higher vibrational states of HF are based on at least five assumptions: (1) The V dependence is the same as that for V-R,T relaxation by F atoms. (2) All HF(v′) have the same efficiency in relaxing HF(v). (3) The relaxation is described by single-quantum transitions. (4) The effect of rotation excitation on the relaxation rate is taken to be negligible. (5) The temperature dependence of the relaxation rates for the higher V states is the same as that for the v = 1 state.

The model applies to a reaction initiated by a strong pulse of F atoms, and the time dependence of the concentration of F atoms in the initiating pulse can be modeled to fit experimental data. Although oxygen is used to stabilize experimental H_2-F_2 mixtures, our model contains no reactions of H or F atoms with O_2 because the rates of these reactions are negligible compared to the rates of the chain-carrying reactions H + F_2 and F + H_2. The kinetics in the self-explosion of H_2-F_2-O_2 mixtures, however, depends strongly on reactions of atoms with O_2.

The elementary reactions and the rate coefficients are given in Table I. The table also gives free-energy terms for reactions in which the vibrational states of H_2 and HF are specified. These terms modify the usual thermochemical free-energy change and are necessary for the determination of the rates of reverse reactions. Reverse reactions are included for all reactions except (23)-(30), where the reverse reactions are strongly endothermic, and (157)-(178), where the reverse rates are low because the diatoms are not vibrationally excited by the translational environment. The relaxation of HF by He, reactions (136)-(142), is included so that the model can be used with systems moderated with inert gas. The rates of the recombination reactions (157)-(186) and of the branching reactions (187)-(195) [where a choice of v is offered in H_2(v) and HF(v)] are negligible in a fast explosion, but the reactions are included for use in studies on explosion limits.

Some rate coefficients, not directly applicable to an exploding H_2-F_2 system, are calculated as an approximation to the rates present in the experimental system, and also for the purpose of comparing and assessing different methods of obtaining rate coefficients. The reverse reactions (-2)-(-22) take place with hot H atoms in the experimental system. Initially, however, we obtained the rates of these reactions by two methods for thermal distributions of H atoms but not for the distribution of H atoms actually present in the system. The thermal rate coefficients for (-2)-(-22) were obtained from equilibrium constants and the rates of the forward (near-thermal) reactions, where the forward rates were obtained from a combination of experimental results and trajectory calculations. The thermal rate coefficients for (-2)-(-22) were also obtained directly from trajectory calculations. Although not directly applicable to our model, the two sets of rate coefficients are necessary as a first approximation and also are needed in any attempt to assess the accuracy of various methods of calculation. Rate constants for (-2)-(-22) are presently being obtained from trajectory calculations, using for H atoms the distributions of velocity that we think are present in the experimental system.

Similarly, some quantities such as the translational distributions of F atoms are calculated to obtain a better picture of the physical system, although such distributions may not affect the rate coefficients importantly.

The relative importance of reactions involving atoms or other " intermediates" in determining the concentrations of HF(v) can be realized only when the concentrations of the atoms or intermediates are known. We have justified the use of some reactions in our model by obtaining their contributions from computer runs in which the explosion was simulated and in which the reactions were shown to significantly affect the concentrations of HF(v). These computations used earlier and different values for rate coefficients, but we consider the conclusions to be qualitatively correct. Computer runs using the present set of rate coefficients are now being carried out.

The kinetics model consists of Table I, which lists the elementary reactions and rate coefficients, and Table II, which lists the vibrational energy levels of H_2 and HF. The main body of this report comprises the " Notes" referred to in Table I and discussed at length immediately following Table II. In these Notes we attempt to justify our choice of reactions and our methods of obtaining the rate

TABLE I

RATE COEFFICIENTS USED IN SIMULATING THE EXPLOSIVE REACTION OF H_2 WITH F_2 WHEN THE EXPLOSION IS INITIATED BY A STRONG PULSE OF F ATOMS

Reaction No.	Reaction		Rate Coefficients[a] (cm^3/mole-sec and cm^6/mole^2-sec)	ΔE_v (cm^{-1})	Note[b]
(1)	F + H_2(0) = HF(0) + H		RK(1) = 0	0	1,2,4
(2)	(1)		(2) = 1.75 x 10^{13} $10^{-349/T}$	-3961.6	5
(3)	(2)		(3) = 4RK(2)	-7751.0	
(4)	(3)		(4) = 2.4RK(2)	-11,373.0	
(5)	F + H_2(1) = HF(1) + H		RK(5) = 2.1 x 10^{13}	+198.8	3,4,5
(6)	(2)		(6) = 1.09RK(5)	-3590.6	
(7)	(3)		(7) = 2.36RK(5)	-7212.6	
(8)	(4)		(8) = 4.63RK(5)	-10,671.5	
(9)	F + H_2(2) = HF(2) + H		RK(9) = 2.44 x 10^{13}	+333.4	3,4,5
(10)	(3)		(10) = 1.62 RK(9)	-3288.6	
(11)	(4)		(11) = 3.37RK(9)	-6747.4	
(12)	(5)		(12) = 6.5RK(9)	-10,046.8	
(13)	F + H_2(3) = HF(3) + H		RK(13) = 7.5 x 10^{13}	+405.3	3,4,5
(14)	(4)		(14) = RK(13)	-3053.5	
(15)	(5)		(15) = 1.57RK(13)	-6352.8	
(16)	(6)		(16) = 2.78RK(13)	-9495.7	
(17)	(7)		(17) = 0.78RK(13)	-12,484.2	
(18)	F + H_2(4) = HF(3) + H		RK(18) = 1.07 x 10^{13}	+3872.7	3,4,5
(19)	(4)		(19) = 4RK(18)	+413.8	
(20)	(5)		(20) = 7RK(18)	-2885.5	
(21)	(6)		(21) = 13RK(18)	-6028.3	
(22)	(7)		(22) = 25RK(18)	-9016.9	
(23)	H + F_2 → HF(0) + F		RK(23) = 0	0	6,7
(24)	(1)		(24) = 3.2 x 10^{11} $10^{-570/T}$	-3961.6	
(25)	(2)		(25) = 55RK(24)	-7751.0	
(26)	(3)		(26) = 177RK(24)	-11,373.0	
(27)	(4)		(27) = 220RK(24)	-14,831.9	
(28)	(5)		(28) = 309RK(24)	-18,131.2	
(29)	(6)		(29) = 166RK(24)	-21,274.0	
(30)	(7)		(30) = 72RK(24)	-24,262.6	
	HF + HF = HF + HF	F			
(31)	1 + 1 = 0 + 2	1.	RK(31) = 2.5 x 10^{13}	+172	8
(32)	1 + 2 = 0 + 3	0.63	RK(32) = 0.63RK(31)	+339	
(33)	1 + 3 = 0 + 4	0.4	etc.	+503	
(34)	1 + 4 = 0 + 5	0.2		+662	
(35)	1 + 5 = 0 + 6	0.12		+819	
(36)	1 + 6 = 0 + 7	0.11		+973	
(37)	2 + 2 = 1 + 3	3.		+167	
(38)	2 + 3 = 1 + 4	1.8		+331	
(39)	2 + 4 = 1 + 5	1.		+490	
(40)	2 + 5 = 1 + 6	0.54		+647	
(41)	2 + 6 = 1 + 7	0.28		+801	
(42)	3 + 3 = 2 + 4	6.		+163	
(43)	3 + 4 = 2 + 5	3.5		+322	
(44)	3 + 5 = 2 + 6	1.9		+480	
(45)	3 + 6 = 2 + 7	1.1		+633	
(46)	4 + 4 = 3 + 5	10.		+159	
(47)	4 + 5 = 3 + 6	5.7		+316	
(48)	4 + 6 = 3 + 7	3.1		+470	
(49)	5 + 5 = 4 + 6	16.		+156	
(50)	5 + 6 = 4 + 7	8.7		+310	
(51)	6 + 6 = 5 + 7	23.		+154	

Reaction No.	Reaction		Rate Coefficients[a] (cm^3/mole-sec and cm^6/mole^2-sec)	ΔE_v (cm^{-1})	Note[b]
	$HF + H_2 = HF + H_2$				
(52)	0 + 1 = 1 + 0	1.	RK(52) = 1.1 x 10^{12}	+199	9
(53)	1 + 1 = 0 + 2	3.6	RK(53) = 3.6RK(52)	+38	
(54)	1 + 2 = 0 + 3	2.3	etc.	+268	
(55)	1 + 3 = 0 + 4	1.3		+494	
(56)	1 + 4 = 0 + 5	0.75		+720	
(57)	1 + 5 = 0 + 6	0.33		+947	
(58)	1 + 6 = 0 + 7	0.2		+1179	
(59)	1 + 1 = 2 + 0	1.		+371	
(60)	1 + 2 = 2 + 1	5.2		+135	
(61)	2 + 2 = 1 + 3	9.		+96	
(62)	2 + 3 = 1 + 4	4.9		+322	
(63)	2 + 4 = 1 + 5	2.6		+548	
(64)	2 + 5 = 1 + 6	1.4		+755	
(65)	2 + 6 = 1 + 7	0.63		+1007	
(66)	2 + 1 = 3 + 0	0.8		+538	
(67)	2 + 2 = 3 + 1	4.1		+302	
(68)	2 + 3 = 3 + 2	14.		+72	
(69)	3 + 3 = 2 + 4	14.		+155	
(70)	3 + 4 = 2 + 5	7.5		+380	
(71)	3 + 5 = 2 + 6	3.6		+608	
(72)	3 + 6 = 2 + 7	1.8		+840	
(73)	3 + 1 = 4 + 0	0.58		+702	
(74)	3 + 2 = 4 + 1	2.9		+465	
(75)	3 + 3 = 4 + 2	10.		+235	
(76)	3 + 4 = 4 + 3	32.		+8	
(77)	4 + 4 = 3 + 5	19.		+217	
(78)	4 + 5 = 3 + 6	9.6		+445	
(79)	4 + 6 = 3 + 7	4.5		+677	
(80)	4 + 1 = 5 + 0	0.4		+861	
(81)	4 + 2 = 5 + 1	1.9		+625	
(82)	4 + 3 = 5 + 2	6.9		+395	
(83)	4 + 4 = 5 + 3	2.2		+168	
(84)	5 + 4 = 4 + 5	42.		+58	
(85)	5 + 5 = 4 + 6	22.		+285	
(86)	5 + 6 = 4 + 7	10.5		+517	
(87)	5 + 1 = 6 + 0	0.27		+1017	
(88)	5 + 2 = 6 + 1	1.4		+781	
(89)	5 + 3 = 6 + 2	4.7		+551	
(90)	5 + 4 = 6 + 3	14.9		+324	
(91)	5 + 5 = 6 + 4	45.		+99	
(92)	6 + 5 = 5 + 6	47.		+129	
(93)	6 + 6 = 5 + 7	21.		+361	
(94)	6 + 1 = 7 + 0	0.2		+1172	
(95)	6 + 2 = 7 + 1	0.8		+935	
(96)	6 + 3 = 7 + 2	3.1		+705	
(97)	6 + 4 = 7 + 3	9.5		+479	
(98)	6 + 5 = 7 + 4	28.		+253	
(99)	6 + 6 = 7 + 5	84.		+26	
(100)	7 + 6 = 6 + 7	46.5		+206	
	$HF(v) + M_1 = HF(v-1) + M_1$ M_1 = all HF				10
(101)	1 = 0		RK(101) = 8.2 x 10^{8}T+1.2 x 10^{17} T^{-2}	+3961.	
(102)	2 = 1		(102) = 3RK(101)	+3789.	
(103)	3 = 2		(103) = 5.8RK(101)	+3622.	
(104)	4 = 3		(104) = 9.7RK(101)	+3459.	
(105)	5 = 4		(105) = 13.RK(101)	+3299.	
(106)	6 = 5		(106) = 17.5RK(101)	+3143.	
(107)	7 = 6		(107) = 22.RK(101)	+2988.	

Reaction No.	Reaction	Rate Coefficients[a] (cm^3/mole-sec and cm^6/mole^2-sec)	ΔE_v (cm^{-1})	Note[b]
	$HF(v) + M_2 = HF(v-1) + M_2$			
	M_2 = all H_2			11
(108)	1 = 0	RK(108) = $1.61\times10^{11}\times T\times10^{-42.9/T^{\frac{1}{3}}}$	+3961.	
(109)	2 = 1	(109) = 3RK(108)	+3789.	
(110)	3 = 2	(110) = 5.8RK(108)	+3622.	
(111)	4 = 3	(111) = 9.7RK(108)	+3459.	
(112)	5 = 4	(112) = 13RK(108)	+3299.	
(113)	6 = 5	(113) = 17.5RK(108)	+3143.	
(114)	7 = 6	(114) = 22RK(108)	+2988.	
	$HF(v) + F = HF(v-1) + F$			
(115)	1 = 0	RK(115) = $3.99\times10^{10}\times T\times10^{-14.9/T^{\frac{1}{3}}}$	+3961.	12
(116)	2 = 1	(116) = 3RK(115)	+3789.	
(117)	3 = 2	(117) = 5.8RK(115)	+3622.	
(118)	4 = 3	(118) = 9.7RK(115)	+3459.	
(119)	5 = 4	(119) = 13RK(115)	+3299.	
(120)	6 = 5	(120) = 17.5RK(115)	+3143.	
(121)	7 = 6	(121) = 22RK(115)	+2988.	
	$HF(v) + H = HF(v-1) + H$			
(122)	1 = 0	RK(122) = 1.6×10^{13}	+3961	13
(123)	2 = 1	(123) = 3.RK(122)	+3789.	
(124)	3 = 2	(124) = 4.RK(122)	+3622.	
(125)	4 = 3	(125) = 12.RK(122)	+3459.	
(126)	5 = 4	(126) = 20.RK(122)	+3299.	
(127)	6 = 5	(127) = 30.RK(122)	+3143.	
(128)	7 = 6	(128) = 50.RK(122)	+2988.	
	$HF(v) + F_2 = HF(v-1) + F_2$			
(129)	1 = 0	RK(129) = $5.06\times10^{10}\times T\times10^{-48.6/T^{\frac{1}{3}}}$	+3961.	14
(130)	2 = 1	(130) = 3RK(129)	+3789.	
(131)	3 = 2	(131) = 5.8RK(129)	+3622.	
(132)	4 = 3	(132) = 9.7RK(129)	+3459.	
(133)	5 = 4	(133) = 13.RK(129)	+3299.	
(134)	6 = 5	(134) = 17.5RK(129)	+3143.	
(135)	7 = 6	(135) = 22.RK(129)	+2988.	
	$HF(v) + He = HF(v-1) + He$			
(136)	1 = 0	RK(136) = $5.41\times10^{11}\times T\times10^{-37.9/T^{\frac{1}{3}}}$	+3961.	15
(137)	2 = 1	(137) = 3RK(136)	+3789.	
(138)	3 = 2	(138) = 5.8RK(136)	+3622.	
(139)	4 = 3	(139) = 9.7RK(136)	+3459.	
(140)	5 = 4	(140) = 13RK(136)	+3299.	
(141)	6 = 5	(141) = 17.5RK(136)	+3143.	
(142)	7 = 6	(142) = 22RK(136)	+2988.	
	$H_2(v) + M_3 = H_2(v-1) + M_3$			
	M_3 = all but H_2 and H			
(143)	1 = 0	RK(143) = $5.05\times10^{10}\times T\times10^{-43.4/T^{\frac{1}{3}}}$	+4160.	16
(144)	2 = 1	(144) = 2RK(143)	+3924.	
(145)	3 = 2	(145) = 3RK(143)	+3694.	
(146)	4 = 3	(146) = 4RK(143)	+3467.	
(147)	5 = 4	(147) = 5RK(143)	+3242.	
(148)	6 = 5	(148) = 6RK(143)	+3014.	
(149)	7 = 6	(149) = 7RK(143)	+2782.	
	$H_2(v) + M_4 = H_2(v-1) + M_4$			
	$M_4 = H_2 + H$			
(150)	1 = 0	RK(150) = $2.10\times10^{11}\times T\times10^{-43.4/T^{\frac{1}{3}}}$	+4160.	17
(151)	2 = 1	(151) = 2RK(150)	+3924.	
(152)	3 = 2	(152) = 3RK(150)	+3694.	
(153)	4 = 3	(153) = 4RK(150)	+3467.	
(154)	5 = 4	(154) = 5RK(150)	+3242.	
(155)	6 = 5	(155) = 6RK(150)	+3014.	
(156)	7 = 6	(156) = 7RK(150)	+2782.	

Reaction No.	Reaction	Rate Coefficients[a] (cm^3/mole-sec and cm^6/mole^2-sec)	ΔE_v (cm^{-1})	Note[b]
(157)	$2F + He \rightarrow F_2 + He$	RK(157) = 4.6×10^{12}	0	18
(158)	$2F + F_2 \rightarrow F_2 + F_2$	(158) = 1.21×10^{13}	0	
(159)	$2F+M_2 \rightarrow F_2+M_2, M_2$=all H_2	(159) = 0	0	
(160)	$2F+M_1 \rightarrow F_2+M_1, M_1$=all HF	(160) = RK(161)	0	
(161)	$2F + F \rightarrow F_2 + F$	(161) = 6×10^{15}	0	
(162)	$2F + H \rightarrow F_2 + H$	(162) = 0	0	
(163)	$2H + M_6 \rightarrow H_2(0) + M_6$	RK(163) = 2×10^{14}	0	19
	$M_6 \rightarrow$ all except H			
(164)	$\rightarrow 1$	(164) = RK(163)	-4160.	
(165)	$\rightarrow 2$	(165) = RK(163)	-8084.	
(166)	$\rightarrow 3$	(166) = RK(163)	-11,778.	
(167)	$\rightarrow 4$	(167) = RK(163)	-15,245.	
(168)	$\rightarrow 5$	(168) = RK(163)	-18,487.	
(169)	$\rightarrow 6$	(169) = RK(163)	-21,501.	
(170)	$\rightarrow 7$	(170) = RK(163)	-24,283.	
(171)	$2H + H \rightarrow H_2(0) + H$	RK(171) = 10RK(163)	0	19
(172)	$\rightarrow 1$	(172) = 10RK(163)	-4160.	
(173)	$\rightarrow 2$	(173) = 10RK(163)	-8084.	
(174)	$\rightarrow 3$	(174) = 10RK(163)	-11,778.	
(175)	$\rightarrow 4$	(175) = 10RK(163)	-15,245.	
(176)	$\rightarrow 5$	(176) = 10RK(163)	-18,487.	
(177)	$\rightarrow 6$	(177) = 10RK(163)	-21,501.	
(178)	$\rightarrow 7$	(178) = 10RK(163)	-24,283.	
(179)	$H + F + M_5 \rightarrow HF(0) + M_5$	RK(179) = 1.25×10^{14}	0	20
(180)	$\rightarrow 1$	(180) = 1.25×10^{14}	-3962.	
(181)	$\rightarrow 2$ M_5 = all species	(181) = 1.25×10^{14}	-7751.	
(182)	$\rightarrow 3$	(182) = 1.25×10^{14}	-11,373.	
(183)	$\rightarrow 4$	(183) = 1.25×10^{14}	-14,831.	
(184)	$\rightarrow 5$	(184) = 1.25×10^{14}	-18,131.	
(185)	$\rightarrow 6$	(185) = 1.25×10^{14}	-21,274.	
(186)	$\rightarrow 7$	(186) = 1.25×10^{14}	-24,262.	
(187)	$HF(4) + F_2 \rightarrow HF(0) + 2F$	RK(187) = 7×10^{6}	+14,832.	21
(188)	$5 \rightarrow 0$	(188) = 0	+18,131.	
(189)	$6 \rightarrow 0$	(189) = 0	+21,274.	
(190)	$7 \rightarrow 0$	(190) = 0	+24,263.	
(191)	$H_2(0) + F_2 \rightarrow HF(0) + H + F$	RK(191) = 0	0	21
(192)	$1 \rightarrow 0$	(192) = 10^{5}	+4160.	
(193)	$2 \rightarrow 0$	(193) = 0	+8084.	
(194)	$3 \rightarrow 0$	(194) = 0	+11,778.	
(195)	$4 \rightarrow 0$	(195) = 0	+15,245.	

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[a] RK indicates values used in the kinetics model.

[b] These Notes are discussed immediately following Table II.

coefficients, most of which have not been measured experimentally. The accuracy of the model depends on the reactions chosen and the accuracy of the values of the rate coefficients. It is obvious that the values for most of the rate coefficients are uncertain, but this report may have some value in that the detailed descriptions of our assumptions and methods may be useful as a basis for further work. Despite the amount of experimental and theoretical (trajectory calculation) work that has been completed, the determination of rate coefficients is unfortunately necessarily made from work that is not directly applicable. We have tried to cite all references that bear directly on the reactions used, but for the large number of references on the experimental determinations of the V-R,T relaxation of HF(v) by HF and by F we refer to the recent paper of Blair, Breshears, and Schott.[7] All rate coefficients and relaxation times are converted to cm^3/mole-sec or cm^6/mole^2-sec; the symbol " RK" is used only for the values that we use in the kinetics model.

Reverse reactions are included for all reactions except (23)-(30) and (157)-(178), and the rate constants are given by

$$RK_r(i) = RK_f(i) \times K(i), \qquad (1)$$

where K(i) is an equilibrium constant calculated from JANAF tables. Equilibrium constants pertain to systems in which reactants and products are in complete thermodynamic equilibrium, but the reactions considered here involve H_2 and HF in individual vibrational levels. However, in the 1000-to-3000°K temperature range of interest here (and at lower temperatures as well), equilibrium distributions of H_2 or HF contain less than 10% of the molecules in vibrational levels $v > 0$. For reactions where H_2 or HF, or both, are in the 0th vibrational levels, the reverse rate constant is then given with little error by Eq. (1); see Note 4. For these cases (H_2 or HF in 0th vibrational levels) the equilibrium constant may be written

$$K(i) = 10^{-\Delta G/2.302RT},$$

where $\Delta G = \Delta G_f$(reactants) minus ΔG_f(products). For reactions involving H_2 or HF in higher vibrational states, an additional free-energy term is necessary so that

$$K(i) = 10^{-(\Delta G+\Delta E_V)/2.302RT},$$

where ΔE_v = vibrational energy in reactants minus vibrational energy in products. A value of ΔE_v for each reaction is given in Table I. The values of ΔG are only weakly dependent on temperature, and we have taken ΔG to be independent of temperature and equal to the value of 2000°K for all reactions except (157)-(162). The values of ΔG are

	Reaction No.	ΔG (cm/sec)
ΔG_1	(1)-(22)	10,700
ΔG_2	(23)-(30)	36,050
ΔG_3	(157)-(162)	12,240 $(1-1.25\times10^{-4}T)$
ΔG_4	(163)-(170)	34,550
ΔG_5	(179)-(186)	45,000
ΔG_6	(187)-(190)	$-\Delta G_3$
ΔG_7	(191)-(195)	$\Delta G_3-\Delta G_4-\Delta G_3$

The value of R in cms^{-1}/deg is 0.6950.

Table II gives the energy levels that determine the values of ΔE_v. Levels for H_2 were obtained from Wooley, Scott, and Brickwedde,[8] and for HF from Mann et al.[9]

TABLE II

VIBRATIONAL ENERGY LEVELS FOR HF AND H_2

v	H_2 (cm^{-1})	HF (cm^{-1})
0	0	0
1	4160.4	3961.6
2	8084.4	7751.0
3	11778.3	11373.0
4	15245.7	14831.9
5	18487.4	18131.2
6	21501.6	21274.0
7	24283.7	24262.6

NOTES

1. The rate of the thermal reaction

$$F + H_2(0) \rightarrow HF(v) + H \qquad (a)$$

is taken to be the mean of the two values

$$k = 1.6 \times 10^{14} \cdot 10^{-349/T} \quad \text{(Ref. 10)}$$

$$k = 0.59 \times 10^{14} \cdot 10^{-349/T} \quad \text{(Ref. 11)} .$$

The latter was obtained from a single value near room temperature combined with the temperature dependence of Ref. 10. Then for a thermal distribution of F atoms and $H_2(0)$ molecules

$$k_a = 1.1 \times 10^{14} \cdot 10^{-349/T} \text{ cm}^3\text{/mole-sec.} \qquad (2)$$

In an H_2-F_2 explosion however, the species do not have a Maxwell distribution over translation energy. The $H_2(0)$ molecules reacting in Reaction (a) probably have a Maxwell distribution, but the F atoms that are formed by a photolytic flash, by irradiation with electrons, or by chemical reaction are initially hot (having translational energy sufficiently high that the energy that can enter into excitation in an $F + H_2$ collision is greater than the activation energy, 1.6 kcal). Since the fraction of translational energy that can enter into excitation is $M_{H_2}/(M_{H_2} + M_F) = 0.095$, the initial energy, if the atom is hot, must be ≥ 16.8 kcal. It can be shown from the kinetic theory of hot atoms[12] that in a 1:1::H_2:F_2 mixture about 20% of the F atoms from a photolytic flash (absorption centered at about 2800 Å to produce F atoms with initial translational energies of 32 kcal/mole) collide with H_2 while hot.

TABLE III

RELATIVE RATES k(v) OF PRODUCTION OF HF(v) AND THE TRANSLATIONAL ENERGY OF F ATOMS E_T(F) FROM THE THERMAL REACTION $H + F_2 \rightarrow HF(v) + F$ AT ROOM TEMPERATURE

v	k(v) (Ref. 13)	E_T(F) (Ref. 13) (kcal/mole)	k(v) (Ref. 14)	k(v) (Ref. 15)
0	<0.1	—	0.04	
1	0.12	43	0.09	
2	0.13	38	0.11	
3	0.25	32	0.13	0.4
4	0.35	28	0.45	0.9
5	0.78	23	0.89	1.85
6	1.00	19	1.00	1.00
7	0.40	15	0.45	
8	0.26	12	0.20	
9	<0.16	—	<0.04	

The major part of the F atoms entering into reactions (1)-(4) is produced by reactions (23)-(30). The relative reaction rates in (23)-(30) and the distribution of initial [as formed in (23)-(30)] translational energies of F atoms were determined experimentally near room temperature for a thermal distribution of H atoms,[13] and are given in Table III. Although not stated in Ref. 13, the reaction is primarily with F_2 in the 0th vibrational state (see Note 6). Table III also shows the distributions k(v) obtained experimentally by Jonathan et al.[14] and theoretically by Wilkins.[15]

The translational energy in products can also be obtained from the work of Blais,[16] who determined theoretically the vibrational distributions for HF(v) from $H + F_2(0) \rightarrow HF(v) + F$ at fixed relative velocities $V_R = 4.57 \times 10^5$, 5.97×10^5, 7.09×10^5, 8.20×10^5, and 1.05×10^6 cm/sec. These velocities correspond to the most effective relative velocities for reaction of Maxwell distributions at roughly 400, 1000, 1500, 1800, and 2500°K. The translational energies in the F atoms, as shown in Table IV, were obtained by subtracting the energy in vibration and rotation in the products from the total energy available and then dividing by two. The energy in rotation in the products was assumed to be independent of the relative velocity of the reactants and equal to 3 kcal/mole.[13] The energy available to products was taken to be $\Delta E_0^\circ + \frac{1}{2} mV_R^2 + RT$, where RT was taken as 2 kcal/mole. Our assumptions about the amount of energy in rotation have a negligible effect on the distribution of the translational energies of the F atoms.

Although the distributions k(v) from Blais' theoretical work[16] for $V_R = 4.6 \times 10^5$ cm/sec and from Polanyi's experimental work[13] at 300°K are in only moderate agreement, the average values of E_T(F) are in good agreement. Blais' work shows that an appreciable fraction of translational energy in the H atom is carried over into translational energy of the F atom and that many distributions of translational energies are present.

TABLE IV

RELATIVE RATES k(v) OF PRODUCTION OF HF(v) AND THE TRANSLATIONAL ENERGY OF F ATOMS $E_T(F)$ FROM THE REACTION $H + F_2 \rightarrow HF(v) + F$

(Data taken from Figs. 5 through 9 of Ref. 16)

	$10^6\ V_R$							
	4.6		5.97		8.20		10.5	
v	k(v)	$E_T(F)$ (kcal/mole)	k(v)	$E_T(F)$ (kcal/mole)	k(v)	$E_T(F)$ (kcal/mole)	k(v)	$E_T(F)$ (kcal/mole)
0	0	50	0	50.5	0	52.5	0	55
1	0	44	0	45	0	47	0	49.5
2	0	39	0	40	0	41.5	0.055	44
3	0.006	34	0.02	35	0.075	36.5	0.177	39
4	0.199	29	0.21	30	0.25	30.5	0.220	33
5	0.265	24	0.31	25	0.375	26.5	0.309	29
6	0.331	19	0.36	20	0.225	22	0.166	24.5
7	0.199	16	0.10	16	0.075	17	0.072	19.5

However, the hot F atoms have little effect on the rate coefficient for $F + H_2(0) \rightarrow HF(v) + H$. Blais' work[17] on this reaction indicates that the cross section increases only 40% as the relative translational energy increases from 1 to 8 kcal/mole. We increase the rate coefficient by 20% (well within the experimental error) and use

$$RK(1) + RK(2) + RK(3) + RK(4) = 1.3 \times 10^{14} \cdot 10^{-349/T}.$$

A negligible number of super-hot atoms is formed by such reactions as

$$F + H_2\ (v > 0) \rightarrow HF\ (v = 0) + H^*,$$

$$H^* + F_2 \rightarrow HF(0) + F^*,$$

$$F^* + H_2\ (v > 0) \rightarrow HF(v = 0) + H^{**},$$

etc.

The temperature T is computed from the instantaneous heat release of all the reactions and from the sum of the instantaneous rotational and translational heat capacities. The rotational and translational temperatures are assumed to be equal. However, the rate of the self-rotational relaxation of H_2 is slow.[18] A rough extrapolation of the rates reported[18] for 77 to 170°K to temperatures of interest here (~1000°K) would indicate that the number of H_2-H_2 collisions is about 100 for relaxation of the excess rotational energy by a factor of e^{-1}. The rate of rotational relaxation of H_2 by HF or F_2 would not be expected to be greater. The rotational temperature of H_2 may therefore lag the translational temperature by about 100 collisions (~10^{-8} sec in a system at 1 atm). If the activation energy for (1)-(4) lies in rotation, then T should properly be a rotational temperature, and our computed values of T at any instant are too high. If the activation energy lies in translation, then T should refer to a translational temperature, and our computed values of T at any instant are too low.

2. The relative rates of production of HF(v) from the reaction of thermal F atoms,

$$F + H_2(0) \rightarrow HF(v) + H,$$

as determined by various workers, are given in Table V.

TABLE V

RELATIVE RATES OF PRODUCTION OF HF(v) FROM $F + H_2(0) \rightarrow HF(v) + H$

v	Ref. 19[a]	Ref. 20[a]	Ref. 21[a]	Ref. 17[b,c]	Ref. 22[b,d]	Ref. 23[b]	Ref. 24[b,e]
0	0	0	0	0	0	0	0
1	0.31	0.29	-0.18	0.33	0.14	0.03	~0.21
2	1.00	1.00	1.00	1.00	1.00	1.00	1.00
3	0.47	0.76	<1.33	1.66	0.58	1.07	0.49

---

[a] Experimental values at room temperature.

[b] Theoretical values.

[c] Average ratios calculated from the ratios obtained at fixed relative translational energies E_R = 1.0, 2.0, 4.0, 8.0 kcal/mole. The ratios of cross sections, $\sigma(3)/\sigma(2)$, at these relative energies are 1.54, 1.61, 1.72, 1.92, respectively. The energies correspond to average energies for Maxwell distributions at 330, 660, 1300, and 2600°K. A different method of assigning HF to vibrational levels gives $\sigma(3)/\sigma(2) \doteq 1.0$ independent of the relative energy.

[d] Calculated for relative velocity, $V_R = 4 \times 10^5$ cm/sec, J = 3.

[e] Thermal rate constants are given for k(v) in the range 100 to 1000°K. The ratio k(3)/k(2) is independent of temperature; k(1)/k(2) = 0.21 at 1000°K, and

k(1) = 10^[illegible] 10^-[illegible]/T
k(2) = 10^[illegible] 10^-[illegible]/T
k(3) = 10^[illegible] 10^-[illegible]/T .

The results of Blais[17] and Wilkins[24] indicate only a slight temperature dependence for k(3)/k(2); the experimental ratios[19,20] are in good agreement with two of the theoretical values.[22,24] Coombe and Pimentel[25] have recently shown experimentally that there is a small temperature dependence for k(3)/k(2) and k(1)/k(2) in the range 200 to 400°K: $k(3)/k(2) = 0.39 \exp(+117/RT)$, $k(1)/k(2) = 0.47 \exp(-254/RT)$. We use k(3)/k(2) = 0.60 and k(1)/k(2) = 0.25, and consider both ratios to be independent of temperature. We use the experimental temperature dependence[10] for the overall rate -- and not the theoretical temperature dependence, as would be given by the weighted sum of k(v) of Ref. 24. The rate constants are given in Table VI.

TABLE VI

RATE CONSTANTS FOR REACTIONS (1)-(4), $F + H_2(0) \rightarrow HF(v) + H$

Reaction No.	v	k(v)/k(2)	RK[a]
(1)	0	0	0
(2)	1	0.25	$1.75 \times 10^{13} \times 10^{-349/T}$
(3)	2	1.00	4 RK(2)
(4)	3	0.6	2.4 RK(2)

---

[a] RK indicates values used in the kinetics model.

About 15 to 20% of the F atoms react while hot, and we consider their effect on the relative rates to be small.

3. There are no experimental data for the rates of $F + H_2(v > 0) \rightarrow HF(v') + H$. The rates for v = 0, 1, 2, 3, as given in Table VII, were taken from Blais and Truhlar[22] and were determined for a fixed relative translational velocity $V_R = 4 \times 10^5$ cm/sec and J = 3.

TABLE VII

VIBRATIONAL ENERGY DISTRIBUTIONS AND REACTION CROSS SECTIONS FOR $F + H_2(v) \rightarrow HF(v') + H$ AT $V_R = 4 \times 10^5$ cm/sec, J = 3

	Fraction of HF with given v′								σ_R, Å^2
v\v′	0	1	2	3	4	5	6	7	
0	0	0.08	0.58	0.34	0	0	0	0	2.7
1	0.03	0.08	0.12	0.26	0.47	0.04	0	0	7.9
2	0	0	0.08	0.13	0.27	0.47	0.05	0	12.7
3	0.02	0.02	0.02	0.08	0.14	0.22	0.39	0.11	22.3

Rate constants for $F + H_2(v)$ were calculated from the cross sections in Table VII by using $k = V_R \cdot 10^{16}\, \sigma_R \cdot N_A$, where N_A is Avogadro's number. The results are given in Table VIII. The value of k(0) corresponds to the rate at T ≅ 1200°K as given by Eq. (2). The rates k(v) for v = 1, 2, 3, as given in Table VIII, are then obtained relative to the experimental rate at 1200°K and are taken to be independent of temperature. Although the rates k(v) and the relative rates for production of HF(v′) (as shown in Table VII) are given for fixed V_R and J, we assume these values in our calculations. Where the rate of production of HF(v′) (Table VII) is very low, we have added that rate to the rate for the neighboring (v′-1) or (v′+1) state to obtain the fractional contributions given in Table IX. The total rate for v = 4 as given in Table IX was taken to be equal to the total rate for v = 3, and the relative rates for production of HF(v′) were estimated from the relative rates (Table VII) in k(2) and k(3).

TABLE VIII

RELATIVE RATES FOR $F + H_2(v) \rightarrow HF + H$

v	σ_R (Å^2)	k(v) (cm^3/mole-sec)
0	2.7	0.65×10^{14}
1	7.9	1.90×10^{14}
2	12.7	3.05×10^{14}
3	22.3	5.36×10^{14}

TABLE IX

RATE CONSTANTS FOR REACTIONS (5)-(22), $F + H_2(v) \rightarrow HF(v') + H$

Reaction No.	v	v′	Fraction of HF with v′	RK[a] (cm^3/mole-sec)
(5)	1	1	0.11	2.1×10^{13}
(6)	1	2	0.12	1.09 RK(5)
(7)	1	3	0.26	2.36 RK(5)
(8)	1	4	0.51	4.63 RK(5)
(9)	2	2	0.08	2.44×10^{13}
(10)	2	3	0.13	1.62 RK(9)
(11)	2	4	0.27	3.37 RK(9)
(12)	2	5	0.52	6.5 RK(9)
(13)	3	3	0.14	7.5×10^{13}
(14)	3	4	0.14	RK(13)
(15)	3	5	0.22	1.57 RK(13)
(16)	3	6	0.39	2.78 RK(13)
(17)	3	7	0.11	0.78 RK(13)
(18)	4	3	0.02	1.07×10^{13}
(19)	4	4	0.08	4. RK(18)
(20)	4	5	0.14	7. RK(18)
(21)	4	6	0.26	13. RK(18)
(22)	4	7	0.50	25. RK(18)

---

[a] RK indicates values used in the kinetics model.

The $H_2(v)$ molecules that react in (5)-(22) are formed by V-V transfers from $HF(v')$ or by reactions (-5)-(-22), and initially have a nonthermal distribution over rotational states. The rate of self-rotational relaxation of H_2 is low.[18] As stated in Note 1, a rough extrapolation of the rates reported[18] for 77 to 170°K to temperatures of interest here (~1000°K) would indicate that the number of H_2-H_2 collisions is about 100 for relaxation of the excess rotational energy by a factor of e^{-1}. An appreciable fraction of the $H_2(v)$ molecules then collides with F atoms [$(F)/(H_2) \cong 0.01$ in an explosion] while still rotationally excited. Our rate constants for (5)-(22) were determined for $J = 3$ and are good approximations to the rates in an explosion only if the cross sections are not dependent on J. Muckerman's[26] trajectory calculations show a decrease of about 75% in cross section for $F + H_2(0)$ as J increases from 1 to 3. Later work by Blais and Truhlar,[27] however, shows little dependence of the cross section for $0 \le J \le 6$, and in view of current data we do not correct our rate coefficients for rotational excitation.

The importance of reactions (5)-(22) in carrying the chemical reaction can be estimated from the relative rates given in Table X. The relative concentrations of $H_2(v)$ were taken from the results of a computer-simulated explosion of H_2-F_2. The initial conditions for the computation were 300 torr F_2, 300 torr H_2, 40 torr O_2, 300°K, 1% of the F_2 dissociated in a 4.8-nsec pulse; the rate constants used in these computations were different from the rates proposed here, but the relative rates in Table X are probably not far out of line. The values in Table X indicate that at 1000 and 2400°K the contributions of $F + H_2(v > 0)$ to the total $HF(v')$ produced by $F + H_2(v) \rightarrow HF(v') + H$ are 13 and 30%, respectively.

TABLE X

RELATIVE CONCENTRATIONS $H_2(v)/H_2(0)$ AND RELATIVE RATES $k(v) \cdot H_2(v)/k(0) \cdot H_2(0)$ AT 1000 AND 2400°K IN A SIMULATED EXPLOSION

	1000°K		2400°K	
v	$H_2(v)/H_2(0)$	$k(v) \cdot H_2(v)/k(0) \cdot H_2(0)$	$H_2(v)/H_2(0)$	$k(v) \cdot H_2(v)/k(0) \cdot H_2(0)$
0	1	1	1	1
1	0.012	0.036	0.05	0.15
2	0.002	0.01	0.016	0.08
3	0.0115	0.094	0.017	0.14
4	0.0016	0.013	0.007	0.06

4. From detailed balancing, the rates of the reverse reactions (-2)-(-22) may be obtained in terms of the rate of (-1). If $\varepsilon_1, \varepsilon_2, \varepsilon_3, \cdots$ and $h_1, h_2, h_3, \cdots$ are energy differences between successive vibrational levels of HF and H_2, respectively, then

$$k_{-2} = k_2 \frac{k_{-1}}{k_1} \exp(\varepsilon_1/RT)$$

$$k_{-3} = k_3 \frac{k_{-1}}{k_1} \exp(\varepsilon_2/RT).$$

$$\vdots$$

$$k_{-5} = k_5 \frac{k_{-1}}{k_1} \exp(\varepsilon_1 - h_1)/RT, \text{ etc.}$$

$$\vdots$$

The ratio k_1/k_{-1} and the thermodynamic equilibrium constant K are defined by

$$\frac{k_1}{k_{-1}} \equiv \frac{(HF(0)) \cdot (H)}{(H_2(0)) \cdot (F)} ,$$

$$K \equiv \frac{[(HF(0)) + (HF(1)) + \ldots (HF(n))] \cdot (H)}{[(H_2(0)) + (H_2(1)) + \ldots (H_2(n))] \cdot (F)} ,$$

where the concentrations are those at thermodynamic equilibrium. The relative equilibrium concentrations $(HF(1))/(HF(0))$ and $(H_2(1))/(H_2(0))$ at 1000, 2000, and 3000°K are 0.003, 0.06, 0.15 and 0.0025, 0.05, 0.136, respectively, so that, with little error, the ratio k_1/k_{-1} may be replaced by K. Then

$$k_{-2} = k_2 \cdot K \cdot \exp(\varepsilon_1/RT), \text{ etc.} \qquad (3)$$

The equilibrium constant is a function of temperature $K(T) = 10^{-\Delta G/RT}$, and we take ΔG to be independent of temperature and equal to 10,600 cm^{-1}. The additional free energies that contribute to each reaction, ε_1, ε_2, $\varepsilon_1 - h_1$, etc., are given as ΔE_v in Table I. Only some of the reverse reactions in (-2)-(-22) are sufficiently near thermoneutrality to have significantly large rate coefficients; the values of these at 1000 and 2000°K (Table XI) were calculated to determine if these rates compete significantly with other reactions.

TABLE XI

VALUES OF RATE COEFFICIENTS FOR SOME REACTIONS OF NEAR-THERMAL DISTRIBUTIONS OF H ATOMS, $H + HF(v) \rightarrow H_2(v') + F$, AS CALCULATED FROM THE FORWARD REACTIONS

v	v′	Reaction No.	RK[a] 1000°K (cm³/mole-sec)	RK[a] 2000°K (cm³/mole-sec)
2	0	(-3)	4.5×10^{12}	5.6×10^{12}
3	0	(-4)	4.2×10^{13}	4.2×10^{13}
3	1	(-7)	3.3×10^{13}	4.1×10^{12}
4	1	(-8)	9.7×10^{13}	9.7×10^{13}
4	2	(-11)	2.76×10^{11}	4.8×10^{12}
5	2	(-12)	6.2×10^{13}	1×10^{14}
6	3	(-16)	3.67×10^{13}	8.7×10^{13}
7	3	(-17)	7.5×10^{13}	2.1×10^{14}
7	4	(-22)	2.3×10^{13}	7.9×10^{13}

---

[a] RK indicates values used in the kinetics model.

These rates are calculated from forward rates in which there is little hot-atom effect; the values in Table XI are therefore determined for a near-thermal distribution of H atoms, but in the explosive system a large fraction is very hot (see Note 6).

Wilkins[28] calculated rate coefficients for thermal, translational, and rotational distributions in the reaction $H + HF(v) \rightarrow H_2(v') + F$ in the temperature range 100 to 1000°K. Rate coefficients as estimated from his Fig. 1 are given in Table XII.

TABLE XII

RATE COEFFICIENTS FOR $H + HF(v) \rightarrow H_2(v') + F$

v	v′	Ref. 28 1000°K (10^{12} cm³/mole-sec)	Ref. 28 2000°K (10^{12} cm³/mole-sec)	Present Work 1000°K (10^{12} cm³/mole-sec)	Present Work 2000°K (10^{12} cm³/mole-sec)
6	0	3	3.5		
6	1	4	5		
6	2	9	10		
5	0	3	4		
5	1	6	8		
4	0	4	4		
4	1	3	4	97.	97.
3	0	5.5	7	42.	42.

Two significant differences between our values and those of Wilkins are shown in Tables XI and XII: (1) our values are a factor of 7 to 30 larger than those of Wilkins, and (2) our rate coefficients increase markedly with the exothermicity of the reaction, and Wilkins' do not. We have obtained preliminary values of the rate coefficients for (-2)-(-22) by trajectory calculations; these values are lower than the values in Table XI by factors of 5 to 10.

Our rate coefficients for (-2)-(-22) as calculated from Eqs. (3) are for reactions of thermal distributions of HF over J, but the HF molecules, as initially formed in reactions (2)-(30), have nonthermal distributions[13,16,17,19,24] over J with rotational excitation as high as J = 20. There are no experimental data for the rates of rotational relaxation of HF. Polanyi and Woodall,[29] however, modeled HCl chemiluminescence experiments to obtain upper limits for transition probabilities $P^{J}_{J+\Delta J}$ as a function of J and ΔJ for both upward and downward transitions in HCl. For $\Delta J = 1$, over the range $1 < J < 20$, which accounts for an appreciable fraction of the downward transitions, $P^{J}_{J+\Delta J}$ for downward transitions varies between 0.015 and 0.07. If we assume the same upper limits for probabilities for transitions in $HF-H_2$ collisions, then [with $(H)/H_2) \sim 0.01$ in a typical explosion initiated by a burst of F atoms] an appreciable fraction of the HF molecules collides with H atoms while still rotationally excited. Rotational self-relaxation of HCl takes place in about seven collisions.[30] If we assume that rotational self-relaxation of HF is equally rapid, then [with $(HF)/(H) \sim 30$ at 1000°K in a typical explosion] an appreciable fraction of excited HF still collides with H atoms. Relaxation in $HF-F_2$ collisions would be expected to be slower than that in $HF-H_2$ collisions. We conclude that rotationally excited HF molecules are colliding with H atoms and that our rate coefficients may have an added uncertainty if the rates of (-2)-(-22) depend appreciably on rotational excitation.

The following reactions are not included in the model because they are endothermic:

$$F + H_2(v) \rightarrow HF(v') + H$$

$$0 \rightarrow 4,5,6,7$$

$$1 \rightarrow 5,6,7$$

$$2 \rightarrow 6,7 \quad .$$

As pointed out by Cohen,[6] the reverse reactions, however, are exothermic and occur to some extent. But, as indicated by Wilkins' results in Table XII, reactions with large quantum jumps are not as important as those with small quantum jumps. And the rates are probably more uncertain.

5. It is of interest to consider the relative importance of reactions (-2)-(-22) in competing for H atoms and in degrading vibrational energy in HF(v).

The rate coefficients for $H + F_2 \rightarrow HF + F$, as calculated from Eq. (4), see Note 6, are 8.6×10^{13} and 1.65×10^{14} cm^3/mole-sec at 1000 and 2000°K. From a computation of a simulated explosion (initial conditions given previously), the ratios $HF(3)/F_2$, $HF(4)/F_2$, $HF(5)/F_2$, $HF(6)/F_2$, and $HF(7)/F_2$ at 1000 and 2000°K are 0.033, 0.025, 0.019, 0.012, 0.0055, and 0.09, 0.07, 0.05, 0.038, 0.027, respectively. These figures, when taken with the rate coefficients in Table XI indicate that in an H_2-F_2 explosion at 1000°K less than 5% of the H atoms react with HF(v), and at 2000°K less than 10% of the H atoms react with HF(v).

One of the most important reactions for V-R,T de-excitation of HF(v) is

$$HF(v) + HF \rightarrow HF(v-1) + HF. \qquad (b)$$

For a given v, the reaction among (-2)-(-22) that competes with Reaction (b) in degrading vibrational energy is

$$H + HF(v) \rightarrow H_2(v') + F. \qquad (c)$$

The efficiency of Reaction (c) relative to that of Reaction (b) in degrading vibrational energy in an H_2-F_2 explosion was calculated by using

$$\frac{R(c)}{R(b)} = \frac{(v-v')k_c}{k_b} \frac{(H)}{(HF)}$$

for those Reactions (c) where k_c is large. The values of k_c were obtained from Table XI, the requisite values of k_b from the coefficients RK(101)-RK(107), and the concentrations (H) and (HF), where (HF) is the sum of concentrations of all vibrational levels of HF, were obtained from a computed simulated explosion (initial conditions given previously). The ratios (H)/(HF) at 1000 and 2000°K were 0.025 and 0.0113, respectively. The relative efficiencies are given in Table XIII. If our rate coefficients for (-2)-(-22) are approximately correct, then the values in Table XIII indicate that some of these reactions are very important in degrading the vibrational energy. However, our rate coefficients in Table XI may overestimate the rates of (-2)-(-22), and these rates would not be appreciable if we used lower values of the rate coefficients from the Wilkins results shown in Table XII, or the values obtained from our trajectory calculations.

TABLE XIII

RELATIVE EFFICIENCIES R(c)/R(b) FOR DEGRADATION OF VIBRATIONAL ENERGY BY REACTIONS $HF(v) + HF \rightarrow HF(v-1) + HF$ (b) AND $H + HF(v) \rightarrow H_2(v') + F$ (c) IN AN H_2-F_2 EXPLOSION

		R(c)/R(b)	
v	v′	1000°K	2000°K
2	0	0.01	0.02
3	0	0.6	0.14
4	1	0.8	0.2
5	2	0.4	0.15
6	3	0.2	0.1

6. The rate of $H + F_2 \rightarrow HF + F$ for thermal H atoms was taken from

$$k = 1.2 \times 10^{14}\ 10^{-525/T} \qquad \text{(Ref. 31)}$$

$$k = 2.0 \times 10^{14}\ 10^{-570/T} \qquad \text{(Ref. 11).}$$

We use the temperature dependence of Rabideau, Hecht, and Lewis[11] and take the rate coefficient for thermal H atoms to be

$$k = 1.6 \times 10^{14}\ 10^{-570/T}.$$

The fact that the activation energy (2600 kcal = 912 cm^{-1}) is about equal to the difference in vibrational levels of F_2 (892 cm^{-1}) suggests that the rate can be attributed solely to

$$H + F_2(1) \rightarrow HF + F.$$

However, trajectory calculations have shown that

$$H + F_2(0) \rightarrow HF + F$$

has an appreciable cross section compared to that for $H + F_2(1)$.[14,16] The major part of the reaction near room temperature is carried by $F_2(0)$ because 98.6% of the F_2 molecules are in the 0th vibrational state. The distribution of $HF(v')$ over v' depends strongly on v in $F_2(v)$,[16] and thus would change markedly with temperature as the reaction progressed if the F_2 relaxed vibrationally. However, the rate of relaxation of F_2 into upper vibrational states is slow compared to the rate of reaction — as shown by Table XIV. The rate at which the translational temperature changes, as given in Table XIV, was taken from a computation in which the initial conditions were such as to produce a rather low rate, i.e., 0.1% F_2 dissociated over a 144-nsec interval.

The rate of transfer of vibrational energy into F_2 by V-V processes can also be shown to be too slow compared to the rate of the overall reaction. An upper limit, $k < 2 \times 10^9$ cm³/mole-sec, was obtained experimentally[34] for the rate coefficient for either or both of the processes:

$$HF(1) + F_2(0) \rightarrow HF(0) + F_2(v)$$

$$HF(1) + F_2(0) \rightarrow HF(0) + F_2(0).$$

The fractional rate per microsecond is

$$+\frac{dF_2(v)}{F_2(0)dt} < 2 \times 10^9 \cdot HF(v) \cdot 10^{-6}$$

$$< 2 \times 10^3 \cdot HF(v) .$$

In a system with initial conditions 300 torr H_2, 300 torr F_2, the sum of concentrations of $HF(v)$ for $v \geq 1$ does not exceed 5×10^{-6} before lasing ceases (computation of simulated explosion). The fractional increase in $F_2(v)$ is less than 0.01/μsec, and this rate is far exceeded by the rate of temperature increase. The rate of V-V transfer by

$$H_2(v) + F_2(0) \rightarrow H_2(v-1) + F_2(v')$$

might also be expected to be slow.

We take the $F_2(0):F_2(1)$ ratio to be unchanged at its 300°K value during the reaction, and the production of $HF(v')$ to be due to the reaction

$$H + F_2(0) \rightarrow HF(v') + F .$$

TABLE XIV

VIBRATIONAL RELAXATION TIMES OF F_2 COMPARED TO RATES OF REACTION IN AN H_2-F_2 EXPLOSION

(Values for dT/dt were taken from a computation of a simulated explosion, and the initial conditions for the computation were 300 torr H_2, 300 torr F_2, 0.1% F_2 dissociated in a 144-nanosecond pulse)

Temp. (°K)	$\tau P(F_2-F_2)$ (Refs. 32,33) (μsec-atm)	dT(translational)/dt (from simulated explosion) (deg/μsec)
300	11.27	1000 (at 400°K)
1000	0.71	6000
2000	0.204	~20,000
3000	0.110	~20,000

The relative rates of production of $HF(v)$ from $H + F_2 \rightarrow HF(v) + F$ are given in Table III for a reaction of thermal H atoms near room temperature. These results and the above equation for the rate coefficient for $H + F_2$ as a function of temperature are not applicable to an exploding H_2-F_2 mixture, and are given only for orientation, comparison, and for possible use in heavily moderated systems.

The applicable rates and the distributions of $HF(v)$ over v are obtained from a consideration of the translational energies of H actually present in an exploding system.

The H atoms in reactions (23)-(30) are formed in reactions (2)-(22) with high translational energy, and a fraction of them react while hot (defined as having translational energy greater than E_a = 2600 kcal). The distribution of initial translational energies of the H atoms depends on the relative rates in the exploding system of the reactions

$$F + H_2(v) \rightarrow HF(v') + H.$$

The relative rate coefficients, as obtained for a <u>fixed relative velocity</u> equal to the arithmetical average velocity for a Maxwell distribution at 1200°K, are obtained from the rate coefficients in Table VIII and are given in Table XV. The relative concentrations of $H_2(v)$, obtained near the peak of lasing in computer simulated explosions, are also given in Table XV. From these the relative rates are calculated.

TABLE XV

RELATIVE RATES OF F + $H_2(v)$

[k(v)/k(0) from Ref. 22, $H_2(0)/H_2(v)$ at T = 1860°K from a computed simulated explosion with initial conditions 300 torr H_2, 300 torr F_2, 1% F_2 dissociated in 4.8 nsec]

v	k(v)/k(0)	$H_2(v)/H_2(0)$	Rate k_v $H_2(v)$/ Rate k_0 $H_2(0)$
0	1.00	1.00	1.00
1	2.9	0.033	0.096
2	4.7	0.01	0.047
3	8.3	0.016	0.133

The values in Table XV were obtained for a fixed relative translational velocity (corresponding to the arithmetical average velocity of a Maxwell distribution at 1200°K) and for a ratio $H_2(v)/H_2(0)$ that is present at the peak of lasing at 1860°K. However, we assume that the relative rates in Table XV apply to translational distributions of F and $H_2(v)$ present during most of the lasing period in an exploding H_2-F_2 system. When the relative rates of production of HF(v´) from a given $H_2(v)$ (as shown in Table VII) are multiplied by the relative rates of reaction of each v, the relative rates of production of HF(v´) are obtained for all

$$F + H_2(v = 0,1,2,3) \rightarrow HF(v' = 0...7) + H ,$$

and are given in Table XVI.

TABLE XVI

RELATIVE RATES OF PRODOCTION OF HF(v´) FROM $H_2(v) + F \rightarrow HF(v') + H$ IN A LASING SYSTEM

v/v´	0	1	2	3	4	5	6	7
0	0	0.08	0.58	0.34	0	0	0	0
1	0.003	0.007	0.011	0.025	0.045	0.004	0	0
2	0	0	0.004	0.006	0.012	0.022	0.002	0
3	0.002	0.002	0.002	0.01	0.018	0.029	0.05	0.014

The values in Table XVI indicate that about 21% of the H atoms are formed from

$$H_2(v > 0) + F \rightarrow HF(v') + H ,$$

and the distributions of HF(v´) are shifted to higher v´ when compared to the distribution from

$$H_2(v = 0) + F \rightarrow HF(v') + H.$$

The shift in v´ is almost proportional to the increase in v of $H_2(v)$; if there is no strong dependence on v of the amount of rotational energy in the products, the distribution of translational energies of the H atoms from the $H_2(v > 0)$ reactions is then not greatly different from that from the $H_2(0)$ reactions. To obtain the initial translational energies of the H atoms we then consider only F + $H_2(0)$ reactions and use the relative rates as given in Table VI. The translational energies of the H atoms, as given in Table XVII, are average values obtained from Fig. 10 of Ref. 19, and are for a room-temperature experiment. The extra 2 or 3 kcal/mole that might arise from translational energy of the reactants at higher temperatures are neglected.

TABLE XVII

AVERAGE INITIAL TRANSLATIONAL ENERGIES (AITE) OF H ATOMS IN AN H_2-F_2 EXPLOSION AT ROOM TEMPERATURE

v	k(v)/k(2)	AITE of H Atoms (kcal/mole)
0	0	--
1	0.25	20
2	1.00	10
3	0.6	2

We assumed that the atoms with 2-kcal/mole energy H_{th} react with a thermal rate, and we calculated rate constants for those H atoms, H^*, that had initial energies of 10 kcal/mole, and for those, H^{**}, that had initial energies of 20 kcal/mole. We assumed H^* and H^{**} to be separate species, each with a distribution of discrete velocities. The distribution was obtained by considering that the initial energies were either 10 or 20 kcal/mole and that the energy of the atom was always reduced by 21% (the average fraction lost) in collisions with H_2.[35] The discrete velocities of the H atom were then v, v´, v´´ .... We took these to be equal to the relative velocities in collisions with F_2. The cross sections σ_v, $\sigma_{v'}$, $\sigma_{v''}$, etc., of H atoms with these relative velocities were obtained from Fig. 3 of Ref. 16, and were determined using a classical distribution of J at 1000°K. The rate of rotational relaxation of heavy molecules (such as F_2) is fast enough[36] so that we can consider the rotational and translational temperatures of F_2 to be about equal and the F_2 to attain a rotational temperature of 1000°K during an explosion. The effective rate constant for each species, H^* and H^{**}, was calculated from

$$k = N_A[f \cdot v \cdot \sigma_v + f' \cdot v' \cdot \sigma_{v'} + f'' \cdot v'' \cdot \sigma_{v''} + \ldots .]$$

where f, f′, f″.... are the fractions of H^* and H^{**} reacting while at velocities v, v′, v″, etc., and N_A is Avogadro's number. About 65% of the H^* atoms and about 85% of the H^{**} react with F_2 before being reduced to thermal (<2.6 kcal/mole) energies. The rate constants obtained for the atoms at 10 and 20 kcal/mole were, respectively,

$$k_h = 5.5 \times 10^{14} \text{ cm}^3\text{/mole-sec}$$

$$k_h' = 9.9 \times 10^{14} \text{ cm}^3\text{/mole-sec.}$$

In the program we combined all H atoms into one species and calculated an effective rate constant k_{eff};

$$k_{th}(H_{th})(F_2) + k_h(H^*)(F_2) + k_h'(H^{**})(F_2)$$
$$= k_{eff}(H) \cdot (F_2).$$

The value of k_{eff} is given by

$$k_{eff} = \frac{1}{\frac{x}{k_{th}} + \frac{x_1}{k_h} + \frac{1-x-x_1}{k_h'}} ,$$

where x is the fraction of H atoms that reacts with a thermal rate constant, x_1 is the fraction that started as H^* and reacted with rate constant k_h, and $(1-x-x_1)$ is the fraction that started as H^{**} and reacted with rate constant k_h'. Because 65% of the H^* and 85% of the H^{**} react while hot, the fractional contributions in Table XVII are corrected to $x = (0.6 + 0.35(1.00) + 0.15(0.25))/1.85 = 0.53$, $x_1 = 0.65/1.85 = 0.35$, and $1-x-x_1 = 0.12$. When these and the values for k_{th}, k_h, and k_h' are used in the above equation for k_{eff}, the net effect is $k_{eff} = 2\, k_{th}$;

$$k_{eff} = 3.2 \times 10^{14}\ 10^{-570/T} . \qquad (4)$$

We use

$$\sum_{i=23}^{30} RK(i) = 3.2 \times 10^{14}\ 10^{-570/T} .$$

The initial velocities of the 10- and 20-kcal H atoms are 9.1×10^5 and 1.29×10^6 cm/sec, respectively. About half the H atoms reacting in the system have velocities close to these values. To obtain the relative values of the rate coefficients among reactions (23)-(30) we used Blais' distribution (Ref. 16, Fig. 9) of HF(v) over v as calculated for $V_R = 1.08 \times 10^6$ cm/sec:

$RK(23) = 0$
$(24) = 3.2 \times 10^{11} \cdot 10^{-570/T}$
$(25) = 55\ RK(24)$
$(26) = 177\ RK(24)$
$(27) = 220\ RK(24)$
$(28) = 309\ RK(24)$
$(29) = 166\ RK(24)$
$(30) = 72\ RK(24)$.

7. The rate coefficients for reactions (-23)-(-30) are taken to be zero. All the reactions are strongly endothermic and the probability is negligible that a hot F atom collides with an HF molecule with sufficiently high vibrational energy ($v \geq 6$) to overcome the energy barrier. In a computed simulated explosion, the concentrations of the F_2 molecules were about a factor of 10 to 20 larger than the concentrations of HF($v \geq 6$), and were sufficiently high to moderate the F atoms before they collided with HF($v \geq 6$).

8. The rates of V-V transfer reactions among HF molecules, all measured near room temperature, are summarized in Table XVIII. The rate of $1 + 1 \rightarrow 0 + 2$ was measured by Bott[37] by monitoring the rate of appearance of the V = 2 level. The rates of $V + 0 \rightarrow (V - 1) + 1$ were determined[38,39,40]

from the rate of disappearance of the V level with the assumption that the major process was the V-V transfer and not the V-R,T transfer. The three values of the rate coefficients for 1 + 1 → 2 + 0 are in good agreement. Bott and Cohen[41] have shown that the rate coefficient for

TABLE XVIII

MEASURED VALUES OF HF-HF V-V TRANSFER RATES

Reaction No.	Reaction	Temp (°K)	k (cm³/mole-sec)	Ref.
(31)	1 + 1 → 0 + 2	295	2.2×10^{13}	37
	2 + 0 → 1 + 1	290	1.19×10^{13}	38
	3 + 0 → 2 + 1	290	2.88×10^{13}	39
	2 + 0 → 1 + 1	300?	1.12×10^{13}	40
	3 + 0 → 2 + 1	300?	1.20×10^{13}	40
	4 + 0 → 3 + 1	300?	$>3.2 \times 10^{13}$	40
	5 + 0 → 4 + 1	300?	$>4.9 \times 10^{13}$	40
(31)	1 + 1 → 2 + 0	290	2.8×10^{13}	38
(31)	1 + 1 → 2 + 0	300?	2.6×10^{13}	40[a]
(32)	2 + 1 → 3 + 0	300?	6.1×10^{13}	40[a]
(33)	3 + 1 → 4 + 0	300?	$>3.5 \times 10^{14}$	40[a]
(34)	4 + 1 → 5 + 0	300?	$>1.17 \times 10^{13}$	40[a]

---

[a] Calculated from the reverse reaction to obtain the rate of the exothermic reaction.

$$HF(1) + DF(0) \rightarrow HF(0) + DF(1)$$

decreases by about 50% as the temperature increases from 300 to 700°K and that there may be a minimum near 700°K with the rate coefficient increasing as T increases above 700°K. The work of Ahl and Cool[42] at 300 and 350°K indicates that the rate coefficient for this reaction may decrease as T increases. For reaction (31) we consider the temperature dependence to be slight and we use

$$RK(31) = 2.5 \times 10^{13} \text{ cm}^3\text{/mole-sec}$$

at all temperatures.

The rates of (32)-(51) relative to (31) were calculated from R(i) = F(i)•R(31) where the factor F(i) is

$$F(i) = \frac{[(\lambda+1)\cdot\ell]_i}{[(\lambda+1)\cdot\ell]_{31}} \cdot \frac{f_i}{f_{31}} ,$$

and where the ratio $[(\lambda+1)\cdot\ell]_i/[(\lambda+1)\cdot\ell]_{31}$ is obtained from theory[43]

$$P^{\lambda\rightarrow\lambda+1}_{\ell\rightarrow\ell-1} = (\lambda+1)\cdot\ell \, P^{0\rightarrow1}_{1\rightarrow0} \quad .$$

The factor f_i/f_{31} is used on the assumption that an energy defect between products and reactants reduces the rate.[44] Straight-line plots of the logarithm of measured V-V energy transfer probability vs energy defect for the 1 → 0, 0 → 1 transition are in the literature for HF-diatomic, DCl-diatomic, HBr-diatomic, and HCl-diatomic systems,[45] for HF-diatomic systems,[41] for various diatomic systems,[46] and for the HCl-hydrogen halide systems[47,48,49] (the HCl-hydrogen halide plots from the same data). The data in Ref. 45 for the HF-diatomic system are for HF and nonpolar molecules and are perhaps not a close approximation to the effects in HF-HF V-V transfer. We considered originally that the effect of the energy defect on HF-HF V-V transfer might be approximated best by the HCl-hydrogen halide systems, and we obtained the factors f_i/f_{31} from Fig. 3 of Ref. 47. The same factors f_i/f_{31} were obtained from later data[42] when a straight-line plot was made using the two points defined by

$$HF(1) + HF(1) \rightarrow HF(0) + HF(2)$$

$$E_d = 172 \text{ cm}^{-1} \quad k = 2.5 \times 10^{13} \text{ cm}^3\text{/mole-sec}$$

$$HF(1) + DF(0) \rightarrow HF(0) + DF(1)$$

$$E_d = 1055 \text{ cm}^{-1} \quad k = 2 \times 10^{12} \text{ cm}^3\text{/mole-sec.}$$

Similar, but not identical, factors would be obtained from the points for these two reactions as given by Bott and Cohen[41] in their Fig. 12. The factors F(i) which give the rates of (32)-(51) relative to that of (31) are given in Table XIX.

Multiquantum transitions are not included, since there are no hard experimental data, although theoretical[50,51] work indicates that such transitions may be significant.

The rates of reactions (32), (33), and (34) as obtained from Table XIX are much lower than those measured by Airey and Smith[40] and given in Table

TABLE XIX

FACTORS RELATING RK(32)-RK(51) TO RK(31)

Reaction No.	HF + HF → HF + HF	E_d (cm^{-1})	$(\lambda+1)\cdot\ell$	f_i	F(i)
(31)	1 + 1 = 0 + 2	172	2	1.	1.
(32)	1 + 2 = 0 + 3	339	3	0.42	0.63
(33)	1 + 3 = 0 + 4	503	4	0.2	0.4
(34)	1 + 4 = 0 + 5	662	5	0.08	0.2
(35)	1 + 5 = 0 + 6	819	6	0.04	0.12
(36)	1 + 6 = 0 + 7	973	7	0.03	0.11
(37)	2 + 2 = 1 + 3	167	6	1.	3.
(38)	2 + 3 = 1 + 4	331	8	0.45	1.8
(39)	2 + 4 = 1 + 5	490	10	0.2	1.0
(40)	2 + 5 = 1 + 6	647	12	0.09	0.54
(41)	2 + 6 = 1 + 7	800	14	0.04	0.28
(42)	3 + 3 = 2 + 4	164	12	1.	6.
(43)	3 + 4 = 2 + 5	322	15	0.46	3.5
(44)	3 + 5 = 2 + 6	480	18	0.21	1.9
(45)	3 + 6 = 2 + 7	633	21	0.095	1.1
(46)	4 + 4 = 3 + 5	159	20	1.	10.
(47)	4 + 5 = 3 + 6	316	24	0.48	5.7
(48)	4 + 6 = 3 + 7	470	28	0.22	3.1
(49)	5 + 5 = 4 + 6	156	30	1.1	16.
(50)	5 + 6 = 4 + 7	310	35	0.5	8.7
(51)	6 + 6 = 5 + 7	154	42	1.1	23.

XVIII. Some of the experimentally determined rate coefficients in Table XVIII, even for reactions with large energy defects, are higher than gas-kinetic collision rates. We have assumed that the relationship between energy defect and rate holds for higher vibrational states, but this may not be correct. It then appears that the only reasonably sure value among the rates of (31)-(51) is RK(31). The others must be considered to be estimates.

9. The reported values of the rate of (52) and (-52) are given in Table XX. The measured temperature dependence of k_{52} in the range 300 to 1000°K is slight.[41] We use, at all temperatures,

$$RK(52) = 1.1 \times 10^{12}\ cm^3/mole\text{-}sec.$$

There are no experimental data on reactions (53)-(100). We assume that each rate constant RK(i) can be obtained from RK(i) = F(i)•RK(52) where

$$F(i) = \frac{[(\lambda+1)\cdot\ell]_i}{[(\lambda+1)\cdot\ell]_{52}} \cdot \frac{f_i}{f_{52}} .$$

TABLE XX

MEASURED VALUES OF THE RATE CONSTANTS FOR REACTIONS (52) AND (-52)

Temp. (°K)	k_{-52} (cm^3/mole-sec)	k_{52} (cm^3/mole-sec)	Ref.
294	--	1.15×10^{12}	52
294	4.4×10^{11}	1.1×10^{12} [a]	45,52
298	4.4×10^{11}	1.1×10^{12} [a]	53
295	3.05×10^{11}	8.1×10^{11} [a]	41

---

[a] Calculated from $k_{52} = k_{-52}\cdot 10^{199/1.6T}$.

The factors f_i/f_{52} were obtained from Fig. 3 of Ref. 45 where the V-V exchange probability is plotted as a function of energy defect using data for the systems $HF\text{-}H_2$, $HF\text{-}D_2$, and $HF\text{-}N_2$. The factors F(i) that are used in the program are given in Table XXI.

10. The V-R,T relaxation rate of

$$HF(1) + HF(0) \rightarrow 2HF(0) \qquad (d)$$

was recently measured in the range 600 to 2400°K and near 300°K by Blair, Breshears, and Schott.[7] Their work contains a summary of the results of previous investigations. In obtaining an equation for the rate coefficient of Reaction (d), we weighted their work heavily. Our rate coefficient

$$k_a = 8.2 \times 10^6\cdot T + 1.2 \times 10^{17}\ T^{-2}$$

reproduces the values of τP given in Fig. 7 of their paper within about 5% in the range 400 to 2400°K, and at 300°K gives a value of τP about 20% higher than that of Ref. 7, but a value that is still centered within values obtained by other workers. There are no data on the rates of V-R,T relaxation of HF(1) by HF in higher vibrational states. We assume that all states have the same effectiveness as HF(0). For the reaction

$$HF(1) + M_1 \rightarrow HF(0) + M_1 , \qquad \text{[Reaction (101)]}$$

TABLE XXI

RELATIVE RATE CONSTANTS FOR REACTIONS (53)-(100)

Reaction No.	$HF + H_2 \rightarrow HF + H_2$	E_d (cm^{-1})	$(\lambda+1)\cdot\ell$	f_i	F(i)
(52)	0 + 1 = 1 + 0	199	1	1.	1.
(53)	1 + 1 = 0 + 2	37	2	1.8	3.6
(54)	1 + 2 = 0 + 3	268	3	0.76	2.3
(55)	1 + 3 = 0 + 4	494	4	0.32	1.3
(56)	1 + 4 = 0 + 5	720	5	0.13	0.75
(57)	1 + 5 = 0 + 6	947	6	0.056	0.33
(58)	1 + 6 = 0 + 7	1180	7	0.028	0.2
(59)	1 + 1 = 2 + 0	370	2	0.52	1.
(60)	1 + 2 = 2 + 1	135	4	1.3	5.2
(61)	2 + 2 = 1 + 3	96	6	1.5	9.
(62)	2 + 3 = 1 + 4	322	8	0.62	4.9
(63)	2 + 4 = 1 + 5	548	10	0.26	2.6
(64)	2 + 5 = 1 + 6	755	12	0.12	1.4
(65)	2 + 6 = 1 + 7	1007	14	0.045	0.63
(66)	2 + 1 = 3 + 0	538	3	0.27	0.8
(67)	2 + 2 = 3 + 1	302	6	0.68	4.1
(68)	2 + 3 = 3 + 2	72	9	1.6	14.
(69)	3 + 3 = 2 + 4	155	12	1.2	14.
(70)	3 + 4 = 2 + 5	380	15	0.5	7.5
(71)	3 + 5 = 2 + 6	608	18	0.2	3.6
(72)	3 + 6 = 2 + 7	840	21	0.085	1.8
(73)	3 + 1 = 4 + 0	702	4	0.145	0.58
(74)	3 + 2 = 4 + 1	465	8	0.36	2.9
(75)	3 + 3 = 4 + 2	235	12	0.86	10.
(76)	3 + 4 = 4 + 3	8	16	2.	32.
(77)	4 + 4 = 3 + 5	217	20	0.94	19.
(78)	4 + 5 = 3 + 6	445	24	0.4	9.6
(79)	4 + 6 = 3 + 7	677	28	0.16	4.5
(80)	4 + 1 = 5 + 0	860	5	0.08	0.4
(81)	4 + 2 = 5 + 1	625	10	0.19	1.9
(82)	4 + 3 = 5 + 2	395	15	0.46	6.9
(83)	4 + 4 = 5 + 3	168	20	1.1	2.2
(84)	5 + 4 = 4 + 5	58	25	1.7	42.
(85)	5 + 5 = 4 + 6	285	30	0.72	22.
(86)	5 + 6 = 4 + 7	517	35	0.3	10.5
(87)	5 + 1 = 6 + 0	1017	6	0.045	0.27
(88)	5 + 2 = 6 + 1	780	12	0.11	1.4
(89)	5 + 3 = 6 + 2	550	18	0.26	4.7
(90)	5 + 4 = 6 + 3	324	24	0.62	14.9
(91)	5 + 5 = 6 + 4	99	30	1.5	45.
(92)	6 + 5 = 5 + 6	130	36	1.3	47.
(93)	6 + 6 = 5 + 7	360	42	0.52	21.
(94)	6 + 1 = 7 + 0	1170	7	0.025	0.2
(95)	6 + 2 = 7 + 1	935	14	0.06	0.8
(96)	6 + 3 = 7 + 2	705	21	0.15	3.1
(97)	6 + 4 = 7 + 3	480	28	0.34	9.5
(98)	6 + 5 = 7 + 4	253	35	0.8	28.
(99)	6 + 6 = 7 + 5	26	42	2.	84.
(100)	7 + 6 = 6 + 7	206	49	0.95	46.5

where M_1 includes all vibrational states of HF, we use

$$RK(101) = k_a \ .$$

A recent theoretical calculation of the rate of Reaction (d) is that of Berend and Thommarson.[52] A mechanism that reproduces the temperature dependence of the relaxation rate of HF has been given by Thompson.[53]

The rate of V-R,T relaxation of the v = 2 state by HF(0) is twice the rate of relaxation of the v = 1 state.[37,38,54] There is evidence that the v = 3 state also relaxes with a rate proportional to v.[39] However, trajectory calculations[55] on the rates of relaxation of higher vibrational states in a somewhat similar reaction

$$HF(v) + F \rightarrow HF(v-1) + F$$

indicate that if all the vibrational energy transfer is ascribed to single-quantum transfers, then the rate of reaction is proportional, roughly, to $v^{1.6}$ (see Note 12). In lieu of any other information on the self-relaxation of higher v states in HF we considered the relaxation rate to be proportional to $v^{1.6}$, and we used the following rate coefficients

$$RK(102) = 3\ RK(101)$$

$$RK(103) = 5.8\ RK(101)$$

$$RK(104) = 9.7\ RK(101)$$

$$RK(105) = 13\ RK(101)$$

$$RK(106) = 17.5\ RK(101)$$

$$RK(107) = 22\ RK(101) \ .$$

Blais and Thompson[56] showed that rotational excitation considerably enhances the cross section for vibrational relaxation by F atoms:

$$HF(v) + F \rightarrow HF(v') + F \ .$$

The same effect should be expected in reactions (102)-(107), where rotationally excited HF(v) would be colliding with HF.

11. There are virtually no experimental data on the rate of

$$HF(1) + H_2(0) \rightarrow HF(0) + H_2(0) \ .$$

Upper limits of $k = 1.1 \times 10^{10}$ cm^3/mole-sec and 1.8×10^{10} cm^3/mole-sec at room temperature are given, respectively, by Bott and Cohen[41] and by Hancock and Green.[45,57] Vasil'ev et al.[58] obtained a value of 9×10^8 cm^3/mole-sec, but this is for a mixed process, V-V and V-R,T transfer; Hinchen[59] assumed a value 7.3×10^{10} cm^3/mole-sec. Kapralova et al.[60] obtained a theoretical value of 2.7×10^9 cm^3/mole-sec. There are no data at higher temperatures. For

$$HF(1) + M_2 \rightarrow HF(0) + M_2 \ , \qquad \text{[Reaction (108)]}$$

where M_2 includes all the vibrational states of H_2, we used for all temperatures the rate obtained by Bott and Cohen[61] in the 1350-to-3000°K range for

$$HF(1) + D_2 \rightarrow HF(0) + D_2 \ .$$

Thus,

$$RK(108) = 1.61 \times 10^{11} \cdot T \cdot 10^{-42.0/T^{\frac{1}{3}}} \ .$$

All vibrational states of H_2 are assumed to have the same effectiveness as D_2. The rate as given by RK(108) is about a factor of 7 to 10 greater than the rates of the V-R,T process in HF-He in the range 1350 to 3000°K, and would seem to be reasonable for V-R,T transfer in H_2 in the same temperature range. At 300°K the above expression for RK(108) gives 2.6×10^7 cm^3/mole-sec, which is somewhat lower than the upper limit of $k < 7 \times 10^8$ cm^3/mole-sec, as determined at 300°K for HF-He V-R,T relaxation;[45] it is also considerably lower than the upper limits (given above) that were obtained by Bott and Cohen[41] and by Hancock and Green[45,57] for HF-H_2 V-R,T relaxation. The correct value is very likely $2.6 \times 10^7 < RK(108) < 1.1 \times 10^{10}$ cm^3/mole-sec. We take the rates of relaxation from the upper vibrational states to be

$$RK(109) = 3 \ RK(108)$$

$$RK(110) = 5.8 \ RK(108)$$

$$RK(111) = 9.7 \ RK(108)$$

$$RK(112) = 13 \ RK(108)$$

$$RK(113) = 17.5 \ RK(108)$$

$$RK(114) = 22 \ RK(108) \ .$$

Relaxation rates would probably be enhanced by the rotational excitation of HF(v).

12. The rate of

$$HF(1) + F \rightarrow HF(0) + F$$

was measured by Blair, Breshears, and Schott[7] in the range 1500 to 2500°K, by Bott and Cohen,[62] and by Solomon et al.[63] Blair et al. found that F atoms are about 2 to 5 times more efficient than HF in relaxing HF, while Bott and Cohen and Solomon found that they were about 20 times more efficient. We use

$$RK(115) = 3.99 \times 10^{10} \cdot T \cdot 10^{-14.9/T^{\frac{1}{3}}} \ ,$$

which reproduces within 0.5% the measured relaxation rates of Ref. 7. Although 10 to 20% of the hot F atoms collide with HF(v) before being moderated, we make no correction to the thermal rate. Thompson[55] and Wilkins[64] calculated the rates theoretically. The rate coefficients are compared in Table XXII.

TABLE XXII

RATE COEFFICIENTS FOR $HF(1) + F \rightarrow HF(0) + F$
(NOT INCLUDING ATOM EXCHANGE REACTIONS) AS
DETERMINED BY TRAJECTORY CALCULATIONS

Temp. (°K)	(10^{12} cm^3/mole-sec) RK(115)	k(Wilkins)[a]	k(Thompson)[b]
1000	1.29	0.7	3.5
1500	2.98	1.	4.5
2000	5.19	~1.2	6.8
2500	7.88	~1.3	---

---

[a] As read from Fig. 1 of Ref. 64.

[b] Reference 55.

There are no experimental data on relaxation of higher vibrational states of HF by F. In some of Thompson's trajectories amounts of vibrational energy corresponding to several quanta were transferred. When rate coefficients were calculated by attributing all the energy transferred to one-quantum transfers, he obtained the values given in Table XXIII.

TABLE XXIII

RATE COEFFICIENTS FOR HF(v) + F → HF(v-1) + F AS TAKEN FROM TABLE II OF REF. 55

Temp. (°K)	(10^{12} cm^3/mole-sec) $k_{1\to 0}$	$k_{3\to 2}$	$k_{5\to 4}$
1000	3.5	15.5	
1500	4.5	26.1	75.4
2000	6.8	30.3	119.

As Thompson points out, the rapid increase in k with v (greater than the theory[43] $k_{v\to v-1} \simeq v k_{1\to 0}$) suggests that multiquantum transfers took place. Wilkins[64] also found in his trajectory calculations that amounts of energy corresponding to several quanta were transferred out of vibration. He interpreted his calculations in two ways: (1) He partitioned the continuum states of the products into discrete quantum states and reported rate constants as a function of temperature for the individual processes

$$HF(v') + F \to HF(v) + F$$

for the cases 3→2, 3→1, 6→5, 6→4, 6→3, 6→2. (2) He (as did Thompson) also attributed all the energy transferred to single-quantum transfers and calculated the rates for these processes. There is some question about the validity of partitioning the products into discrete states. We report Wilkins' results in Table XXIV as read from Figs. 1 and 6 of his paper,[64] and as calculated on the assumption of single-quantum transfers.

TABLE XXIV

RATE COEFFICIENTS FOR HF(v) + F → HF(v-1) + F AS DETERMINED IN REF. 64

Temp. (°K)	(10^{12} cm^3/mole-sec) $k_{1\to 0}$	$k_{2\to 1}$	$k_{3\to 2}$	$k_{6\to 5}$ [a]
1000	0.7	1.	2.	25.
1500	1.	1.5	2.8	36.
2000	~1.2	1.6	3.2	43.

---

[a] Recalculated from the results in Fig. 6 of Ref. 64 to obtain rates on the assumption of single-quantum transfers. We took Wilkins' values for the rate coefficients k' as he reported them for the individual transitions F + HF(v) → HF(v') + F (including atom exchange reactions), and then calculated $k_{6\to 5}$ (in which all the change in vibrational energy, previously distributed among the individual transitions, is now attributed to the 6 → 5 transition),

$$k_{6\to 5} = k'_{6\to 5} + 2k'_{6\to 4} + 3k'_{6\to 3} + 4k'_{6\to 4} .$$

Blais and Thompson[56] have shown that the cross sections for relaxation by atom exchange and by inelastic scattering are about equal. To account for relaxation by both processes, the rate coefficients of Wilkins and Thompson in Table XXII, those in Table XXIII, and the values of $k_{1\to 0}$, $k_{2\to 1}$, $k_{3\to 2}$ in Table XXIV should be doubled.

Thompson's results for the 1 → 0 transition are in good agreement with the experimental data, and his results for higher v states indicate that if the approximation of single-quantum transfers is made, then the rate coefficients increase with v at a rate greater than $k_{v\to v-1} = v k_{1\to 0}$, predicted by theory.[43] From Thompson's results we take the rate coefficients for the higher vibrational states to be

$$k_v = v^{1.6} k_{1\to 0} \quad ,$$

and our rate coefficients are

$$\begin{aligned} RK(116) &= 3\ RK(115) \\ (117) &= 5.8\ RK(115) \\ (118) &= 9.7\ RK(115) \\ (119) &= 13.\ RK(115) \\ (120) &= 17.5\ RK(115) \\ (121) &= 22.\ RK(115) \quad . \end{aligned}$$

If an appreciable fraction of HF collides with H atoms while the HF molecules are rotationally excited (Note 4), a similar fraction collides with F atoms. Blais and Thompson[56] showed that rotational excitation considerably enhances the cross section for vibrational relaxation by F atoms, and our rates as written above may be low.

13. There are no experimental data for the rate of

$$HF(1) + H \rightarrow HF(0) + H.$$

Thompson,[65] by trajectory calculations, obtained rates for this reaction and also for relaxation from higher states. His Table II is copied here as Table XXV.

TABLE XXV

RATE COEFFICIENTS FOR H-ATOM VIBRATIONAL RELAXATION OF HF, AS CALCULATED FROM CLASSICAL TRAJECTORIES (REF. 65)

T (°K)	$k_{1\to 0}$	$k_{3\to 2}$	$k_{5\to 4}$	$k_{7\to 6}$
	(10^{12} cm³/mole-sec)			
600	1.4	2.3		
1000	2.3	6.7	75.5	324.
1500	5.0	15.1	99.8	
2000	10.7	64.0	151.	348.

Wilkins[28] reported rate constants as a function of temperature in the range 100 to 1000°K for each of the processes

$$HF(v) + H \rightarrow HF(v') + H .$$

We recalculated his results for 1000°K, as read from his Fig. 3 and assuming single-quantum transfers. We used his values for $k'_{v\to v'}$, the rate coefficients for the individual transitions HF(v) → HF (v'), to obtain values of the rate coefficients k_v, in which all the change in vibrational energy is attributed to single-quantum transfers,

$$k_v = k'_{v\to v-1} + 2k'_{v\to v-2} \cdots\cdot + vk'_{v\to 0} .$$

The results are in Table XXVI. The values in Table XXVI correspond roughly to values that would be obtained from Blais' potential-energy surface (used by Thompson) for a system at a temperature slightly greater than 2000°K.

TABLE XXVI

RATE COEFFICIENTS FROM TRAJECTORY CALCULATIONS (REF. 28, T = 1000°K)

(10^{12} cm³/mole-sec)

$k_{1\to 0}$	$k_{2\to 1}$	$k_{3\to 2}$	$k_{4\to 3}$	$k_{5\to 4}$	$k_{6\to 5}$
8.	47.	90.	105.	190.	250.

If we assume that the probability of the 1 → 0 relaxation per collision is the same for H atoms as for F atoms, we can obtain approximate rates for relaxation by H atoms based on the experimental data for relaxation by F atoms [Ref. 7 and RK(115)]. For thermal H atoms the collision rate would be greater than that for F atoms by about a factor of three. By using the values of RK(115) in Table XXII we obtain the rate coefficients for thermal H atoms seen in Table XXVII.

TABLE XXVII

RATE COEFFICIENTS FOR H + HF(1) → H + HF(0) OBTAINED FROM EXPERIMENTAL VALUES FOR F + HF(1) → F + HF(0)

Temp. (°K)	k(122) = 3RK(115) (10^{12} cm³/mole-sec)
1000	3.9
1500	9.
2500	23.

These rates are about a factor of two larger than Thompson's, and the rate for 1000°K is one-half that given by Wilkins. The velocity distribution of H atoms in an H_2-F_2 explosion, however, is part thermal and part peaked at 9 x 10^5 cm/sec (10 kcal/mole) and 1.3 x 10^6 cm/sec (20 kcal/mole). Trajectory calculations were made for V_R = 9 x 10^5 cm/sec and rotational temperature = 2000°K to obtain k(122) = 5.3 x 10^{13} cm³/mole-sec. The rate coefficient for thermal atoms is about 1 x 10^{13} cm³/mole-sec (Tables XXV, XXVI, XXVII). About 53% of the H atoms are thermal and 47% are hot (Note 6). Then, by combining the rate coefficients by using the equation in Note 6 we obtain RK(122) = 1.6 x 10^{13} cm^3/mole-sec.

Both Thompson's and Wilkins' results indicate that if we attribute all the change in vibrational energy to single-quantum transfers, the dependence of the rate on v is much stronger than $k_{v\to v-1} = vk_{1\to 0}$. We use the following rates, as estimated from Tables XXV and XXVI

$$\begin{aligned} RK(123) &= 3\ RK(122) \\ (124) &= 4\ RK(122) \\ (125) &= 12\ RK(122) \\ (126) &= 20\ RK(122) \\ (127) &= 30\ RK(122) \\ (128) &= 50\ RK(122)\ . \end{aligned}$$

An appreciable fraction of rotationally excited HF molecules collides with H atoms (Note 4). As with F atoms, the V-R,T relaxation rate is probably enhanced over the rates given for (122)-(128).

14. An upper limit has been reported[34] for the rate of relaxation of HF by F_2 at 350°K, $k < 2 \times 10^9$ cm^3/mole-sec; the relaxation was either V-R,T or V-V. There are no other data for

$$HF(1) + F_2 \rightarrow HF(0) + F_2 .$$

The rate of relaxation of HCl by Cl_2 molecules is reported[66] to be 1/2000th the rate of relaxation by Cl atoms. We take the chemical affinity between F_2 and HF to be slight and take the rate at all temperatures to be given by the rate expression determined at 1350 to 4000°K for Ar,[61]

$$RK(129) = 5.06 \times 10^{10} \cdot T \cdot 10^{-48.6/T^{\frac{1}{3}}} .$$

The equation for RK(129) gives 2.26 x 10^6 cm^3/mole-sec at 350°K, which can be compared to the upper limit $k < 2 \times 10^9$ cm^3/mole-sec. The rates of relaxation of the upper states are taken to be proportional to $v^{1.6}$. The HF(v) collide with F_2 molecules while rotationally excited, and the rates are probably greater than those we use.

15. The rate of

$$HF(1) + He \rightarrow HF(0) + He$$

was measured by Bott and Cohen[61] in the range 1350 to 3500°K. An upper limit of 7 x 10^8 cm^3/mole-sec at 294°K was determined by Green and Hancock.[45] We take the rate expression determined from the results of Bott and Cohen to be applicable at all temperatures and we use

$$RK(136) = 5.41 \times 10^{11} \cdot T \cdot 10^{-37.9/T} .$$

This expression gives RK(136) = 3.2 x 10^5 cm^3/mole-sec at 294°K. The rates of relaxation from higher vibrational states are taken to be proportional to $v^{1.6}$.

Again, the rates are probably greater than those we use because of rotational excitation of HF.

16. There are no experimental data for the rates of V-R,T relaxation of H_2 by F_2 or by F atoms. There are room-temperature data for the V-R,T relaxation by HF,

$$H_2(1) + HF(0) \rightarrow H_2(0) + HF(0) . \qquad (e)$$

Hinchen[59] estimates $k = 5 \times 10^{11}$ cm^3/mole-sec. Lower values of upper limits for the rate coefficient are given by other workers: Bott and Cohen,[41] $k = 3 \times 10^{10}$ cm^3/mole-sec; Hancock and Green,[67] $k = 2.2 \times 10^{10}$ cm^3/mole-sec; Osgood,[68] $k = 5 \times 10^{10}$ cm^3/mole-sec. A comparison of the rate of this reaction (based on these upper limit values) with the rate of

$$HF(1) + HF(0) \rightarrow 2HF(0)$$

in a computed simulated H_2-F_2 explosion shows that the rate of Reaction (e) is lower than the rate of self-relaxation of HF by a factor of about 300. Reaction (e) is then not important in the degradation of the vibrational energy in the system. We assumed that F_2, F, and HF (all vibrational states) have the same efficiency for V-R,T relaxation of H_2 as does Ar, which rate was determined in the range 1500 to 2700°K as 0.24 times the rate of relaxation by H_2.[69] For

$$H_2(1) + M_3 \rightarrow H_2(0) + M_3 \ ,$$

where M_3 means all species except H_2 and H, we then use for all temperatures

$$RK(143) = 5.05 \times 10^{10} \cdot T \cdot 10^{-43.4/T^{\frac{1}{3}}}$$

$$= 0.24\ RK(150).$$

The rate of relaxation of H_2 in Ar was measured[70] at 300°K and found to be about 40% lower than the value obtained from the above equation. We take the rates of relaxation of the higher states to be proportional to v.

17. The rate of relaxation

$$H_2(1) + H_2(0) \rightarrow H_2(0) + H_2(0) \qquad (f)$$

was measured in the range 1100 to 2700°K.[69] The rate coefficient was

$$k_f = 2.105 \times 10^{11} \cdot T \cdot 10^{-43.4/T^{\frac{1}{3}}} \ .$$

We assume that H atoms and all vibrational states of H_2 are equally effective in relaxing $H_2(1)$ and that the above equation is valid at all temperatures of interest. We use

$$RK(150) = k_f$$

for the reaction

$$H_2(1) + M_4 \rightarrow H_2(0) + M_4 \ ,$$

where M_4 represents H atoms and H_2 in all vibrational levels. The equation for RK(150) gives $k = 2.08 \times 10^7$ cm³/mole-sec at 300°K. A measured value at 300°K is 7.94×10^6 cm³/mole-sec.[71,72] The rate of

$$H_2(1) + H \rightarrow H_2(0) + H$$

at 300°K has been measured as $k = 1.2 \times 10^8$ cm³/mole-sec.[73] Should the rate of relaxation by H atoms be greater by a factor of five to six than that by H_2, our calculations are not significantly affected; the concentration of H atoms is always less than a few percent of the concentration of H_2 molecules, and the rate of V-R,T relaxation of $H_2(v)$ is low compared to the dominant rate of V-R,T relaxation in the system, that of HF. We take the rates of relaxation of the higher v states to be proportional to v.

18. For reactions (157)-(162) we obtain the recombination rate from the dissociation rate and the equilibrium constant. The rates of dissociation of F_2 by Ar and by F_2 were recently measured, and the rate of dissociation of F_2 by F was estimated in the range 1400 to 2600°K by Breshears and Bird.[74] (Their paper also contains references to previous work.) We assume the rate of dissociation in He to be the same as that in Ar. Then, using their rates:

$$RK(157) = 4.6 \times 10^{12} \text{ cm}^6/\text{mole}^2\text{-sec}$$

$$RK(158) = 1.21 \times 10^{13} \text{ cm}^6/\text{mole}^2\text{-sec}$$

$$RK(161) = 6 \times 10^{13} \text{ cm}^6/\text{mole}^2\text{-sec} \ .$$

The rate coefficient for (159) is taken to be zero because of the high reactivity of F with H_2. The rate coefficient for (160) is taken to be equal to that for (161),[75] and all vibrational states of HF are taken to be equally effective:

$$2F + M_1 \rightarrow F_2 + M_1 \qquad M_1 = \text{all HF}$$

[Reaction (160)]

$$RK(160) = RK(161) \ .$$

In explosions initiated by 10- to 100-nsec pulses of F atoms, the rates of both the forward and reverse reactions for (157)-(162) are negligible.

19. In explosions initiated by pulses of F atoms the rates of the forward and reverse reactions for (163)-(178) are also negligible. The forward reactions are included because they might contribute to the overall reaction in other types of explosions. Recombination rates are given by Shui and Appleton[76] and by Stepukhovich and Umanskii.[77] We assume that the rates of recombination into all vibrational levels are equal and we use, as obtained from Shui and Appleton's Fig. 2,

$$RK(163) = 2 \times 10^{14} \text{ cm}^6/\text{mole}^2\text{-sec}$$

for

$$2H + M_6 \rightarrow H_2(0) + M_6 \; ,$$

where M_6 is all species except H. There is some evidence[77] that H is more efficient as a third body than is H_2. We take

$$RK(171) = 10\ RK(163)$$

and the rates of recombination into all vibrational states to be the same. The dissociation rate of H_2 is taken to be zero; the rate of vibrational excitation is probably too low to be excited by T-R,V transfers, and the rate of dissociation from lower levels ($v \leq 6$) is low because of the high activation energy.

20. The comments on the recombination and dissociation of H_2 apply to the recombination of H and F atoms into HF. We estimate

$$RK(179) = 1.25 \times 10^{14}\ cm^6/mole^2\text{-sec}$$

and assume that the rates of recombination into all vibrational levels are equal. The rate of dissociation of HF is taken to be zero. M_5 is all species.

21. Analysis[78] of experimental data [79,80] on the explosion limits of $H_2 + F_2$ has shown that the two reactions

$$HF(v) + F_2 \rightarrow 2F + HF$$

$$H_2(v) + F_2 \rightarrow H + F + HF$$

contribute to branching. These do not contribute to a pulse-initiated explosion but are included so that the program can be used to study explosion limits of H_2-F_2 mixtures.

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