Overhead Slides for

Chapter 11

of

Fundamentals of Atmospheric Modeling

by

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Lewis Symbols

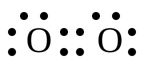
Element	Lewis Symbol	No. e^-	Val.	*m* g/mol
Hydrogen	H•	1	1	1.008
Carbon	•C• (4 •)	4	4	12.01
Nitrogen	N (5 •)	5	3	14.01
Oxygen	O (6 •)	6	2	16.00
Fluorine	F (7 •)	7	1	19.00
Sodium	Na•	1	1	22.99
Magnesium	•Mg•	2	2	24.30

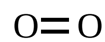
Aluminum	•Al• (3 •)	3	3	26.98
Silicon	Si (4 •)	4	4	28.09
Sulfur	S (6 •)	6	2	32.07
Chlorine	Cl (7 •)	7	1	35.45
Potassium	K•	1	1	39.10
Calcium	•Ca•	2	2	40.08
Bromine	Br (7 •)	7	1	79.90

Lewis Structures

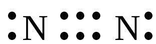
Molecular hydrogen

Molecular oxygen

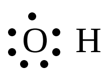




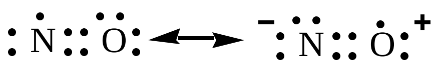
Molecular nitrogen

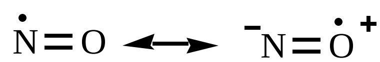


Hydroxyl radical

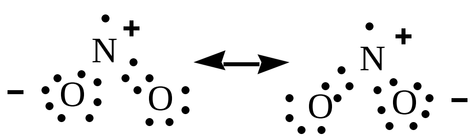


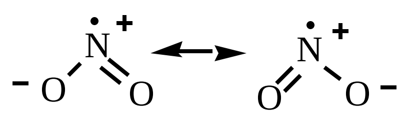
Nitric oxide



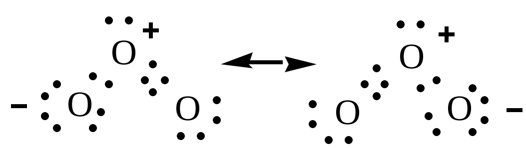


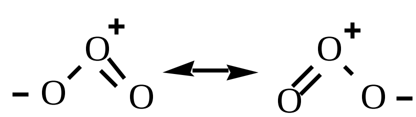
Nitrogen dioxide





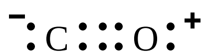
Ozone



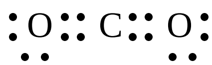


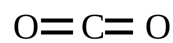
Lewis Structures

Carbon monoxide

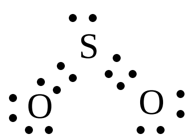


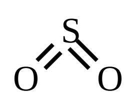
Carbon dioxide



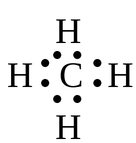


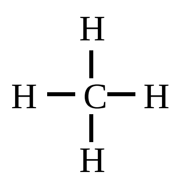
Sulfur dioxide



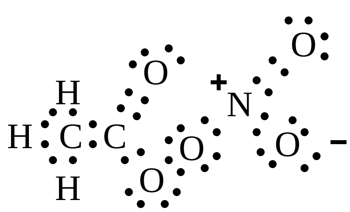


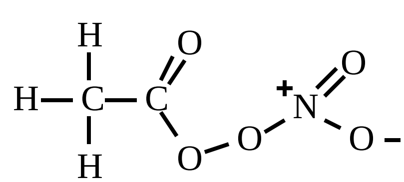
Methane





Peroxyacetyl nitrate (PAN)





Chemical Reactions

Elementary unimolecular photolysis reaction

$$\dot{N}O_2 + h\nu \longrightarrow \dot{N}O + \dot{O}\cdot \qquad \lambda < 410 \text{ nm} \qquad (11.1)$$

Elementary bimolecular thermal decomposition reaction

$$N_2O_5 + M \longrightarrow \dot{N}O_2 + \dot{N}O_3 + M \qquad (11.2)$$

Nonelementary bimolecular thermal decomposition reaction

$$N_2O_5 \xrightarrow{M} \dot{N}O_2 + \dot{N}O_3 \qquad (11.3)$$

Elementary bimolecular collision reaction

$$CH_4 + \dot{O}H \longrightarrow \dot{C}H_3 + H_2O \qquad (11.4)$$

Termolecular combination reaction

$$\dot{N}O_2 + \dot{N}O_3 + M \longrightarrow N_2O_5 + M \qquad (11.5)$$

-- derived from a pair of elementary bimolecular reactions

$$A + B \Leftrightarrow AB^* \qquad AB^* + M \rightarrow AB + M$$

Reaction Coefficients and Rates

Rates for reactions with first-, second-, third-order rate coefficients

$$\text{Rate} = k_F[A] \tag{11.8}$$

$$\text{Rate} = k_S[A][B]$$

$$\text{Rate} = k_T[A][B][C]$$

Rates for photolysis reaction

$$\text{Rate} = J[A] \tag{11.9}$$

Rate of Change of Reactant Concentration

Photolysis reaction, $A + h\nu \rightarrow D + G$

$$\frac{d[A]}{dt} = -\text{Rate} = -J[A] \qquad (11.10)$$

Nonelementary bimolecular reaction, $A \xrightarrow{M} D + E$

$$\frac{d[A]}{dt} = -\text{Rate} = -k_F[A] \qquad (11.11)$$

Nonelementary termolecular reaction, $A + B \xrightarrow{M} E$

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\text{Rate} = -k_S[A][B] \qquad (11.12)$$

Elementary bimolecular reaction, $A + A \rightarrow E + F$

$$\frac{d[A]}{dt} = -2\text{Rate} = -2k_S[A]^2 \qquad (11.13)$$

Elementary termolecular reaction, $A + B + C \rightarrow E + F$

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = \text{-Rate} = -k_T[A][B][C] \qquad (11.14)$$

Rate of Change of Concentration

Generalized reaction, $aA + bB \rightarrow eE + fF$

$$\text{Rate} = k_r[\text{A}]^a[\text{B}]^b \qquad (11.16)$$

Rate of change of reactant concentration

$$\frac{d[\text{A}]}{dt} = -a\text{Rate} = -ak_r[\text{A}]^a[\text{B}]^b \qquad (11.17)$$

$$\frac{d[\text{B}]}{dt} = -b\text{Rate} = -bk_r[\text{A}]^a[\text{B}]^b \qquad (11.17)$$

Rate of change of product concentration

$$\frac{d[\text{E}]}{dt} = e\text{Rate} = ek_r[\text{A}]^a[\text{B}]^b \qquad (11.18)$$

$$\frac{d[\text{F}]}{dt} = f\text{Rate} = fk_r[\text{A}]^a[\text{B}]^b \qquad (11.18)$$

Third Bodies

Elementary termolecular combination reaction

$$\mathrm{A} + \mathrm{B} + \mathrm{M} \rightarrow \mathrm{E} + \mathrm{M}$$

Rate of change of third body

$$\frac{d[\mathrm{M}]}{dt} = k_T[\mathrm{A}][\mathrm{B}][\mathrm{M}] - k_T[\mathrm{A}][\mathrm{B}][\mathrm{M}] = 0 \quad (11.19)$$

Number concentration of air molecules (molec. cm^{-3})

$$N_d = \frac{p_d}{k_B T} \quad (2.18)$$

Number concentration of nitrogen and oxygen molecules

$$[\mathrm{M}] = N_{N_2} = \chi_{N_2} N_d \qquad [\mathrm{M}] = N_{O_2} = \chi_{O_2} N_d \quad (11.20)$$

Example 11.1.

Calculate the number concentration of N_2 and O_2 when T = 278 K and p_d = 920 mb.

Solution

N_d = 2.40 x 10^{19} molec. cm^{-3}

N_{N_2} = 1.87x 10^{19} molec. cm^{-3}

N_{O_2} = 5.02 x 10^{18} molec. cm^{-3}

Rate Coefficients from Kinetic Analysis

Elementary bimolecular collision reaction

$$A + B \rightarrow D + F$$

Expose small quantity of A to large quantity of B --> maximum loss of B is [A].

Rate of loss of A

$$\frac{d[A]_t}{dt} = -k_F[A]_t = -k_S[A]_t[B]_0 \qquad (11.21)$$

Integrate

$$k_S = -\frac{1}{[B]_0 h} \ln \frac{[A]_{t=h}}{[A]_0} \qquad (11.22)$$

Unimolecular reactions

$$k_F = -\frac{1}{h} \ln \frac{[A]_{t=h}}{[A]_0} \qquad (11.23)$$

Termolecular reactions

$$k_T = -\frac{1}{[B]_0[C]_0 h} \ln \frac{[A]_{t=h}}{[A]_0} \qquad (11.23)$$

Arrhenius Equation

Temperature-dependence of a reaction rate

$$\frac{d(\ln k_r)}{dT} = \frac{E_r}{R^* T^2}, \qquad (11.24)$$

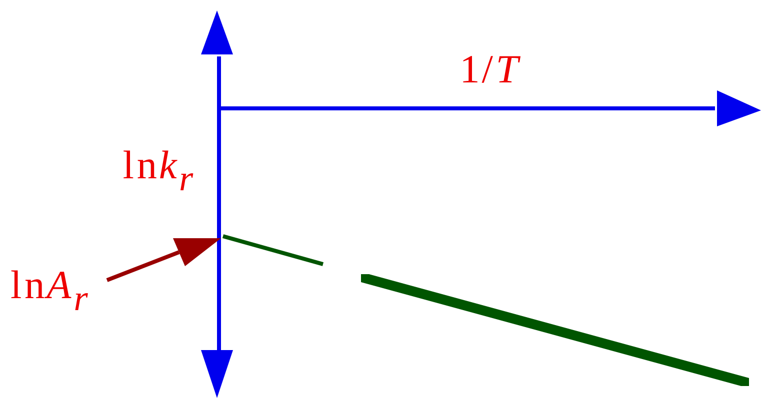
Activation energy

Smallest amount of energy required for reacting species to form an activated complex or transition state before products are formed

Integrate

$$\ln k_r = \ln A_r - \frac{E_r}{R^* T} \qquad (11.25)$$

Fig. 11.1. Measure k_r vs. T --> plot to find A_r and E_r.



Useful form of Arrhenius equation

$$k_r = A_r \exp\left(-\frac{E_r}{R^* T}\right) = A_r \exp\left(\frac{C_r}{T}\right) \qquad (11.26)$$

Temperature Dependence

$E_r \approx 0$ --> collisional prefactor strongly depends on T -->

$$k_r = A_r \left(\frac{300}{T}\right)^{B_r} \exp\left(\frac{C_r}{T}\right). \qquad (11.27)$$

B_r found by fitting equation to data

Example 11.2.

$$\dot{N}O + O_3 \longrightarrow \dot{N}O_2 + O_2$$

$$k_1 = 1.80 \times 10^{-12} \exp(-1370/T) = 1.81 \times 10^{-14}$$

cm^3 molec.$^{-1}$ s^{-1} at T = 298 K

$$\dot{O}\cdot + O_2 + M \longrightarrow O_3 + M$$

$$k_2 = 5.63 \times 10^{-34} (300/T)^{2.8} = 5.74 \times 10^{-34}$$

cm^6 molec.$^{-2}$ s^{-1} at T = 298 K.

Pressure-Dependence of Reactions

Rate of pressure-dependent reaction

$$k_r = \frac{k_{\infty,T} k_{0,T}[\mathrm{M}]}{k_{\infty,T} + k_{0,T}[\mathrm{M}]} F_c^{\left[1+\left(\log_{10}\frac{k_{0,T}[\mathrm{M}]}{k_{\infty,T}}\right)^2\right]^{-1}} \qquad (11.29)$$

Low pressure limit rate coefficient x M

$$k_{0,T}[\mathrm{M}] = \lim_{[\mathrm{M}] \to 0} k_r \qquad (11.30)$$

High pressure limit rate coefficient

$$k_{\infty,T} = \lim_{[\mathrm{M}] \to \infty} k_r \qquad (11.31)$$

Example 11.3.

$$\dot{\mathrm{O}}\mathrm{H} + \dot{\mathrm{N}}\mathrm{O}_2 \xrightarrow{\mathrm{M}} \mathrm{HNO}_3$$

p_a = 140 mb $\quad$ T = 216 K

$[\mathrm{M}] = N_d$ = 4.69 x 10^{18} molec. cm^{-3}

F_c = 0.43

$k_{0,T} = 2.60 \times 10^{-30} (300/T)^{2.9}$ cm^6 molec.$^{-2}$ s^{-1}

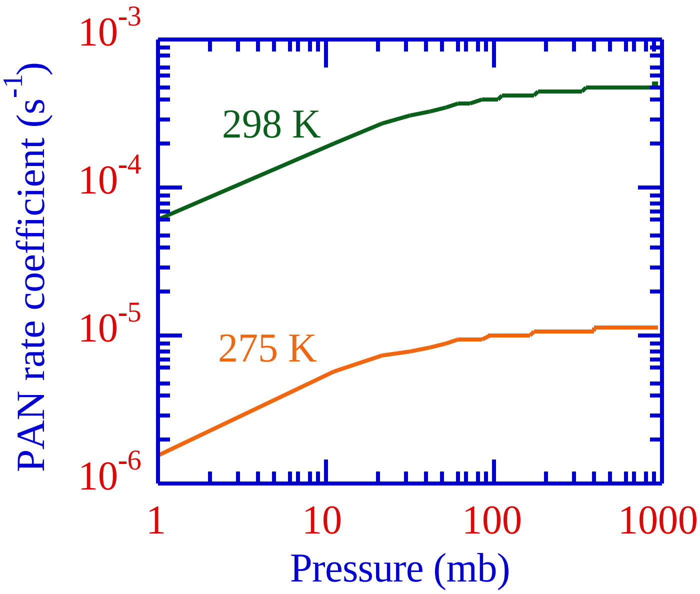
$k_{0,T}[\mathrm{M}]$ = 2.47 x 10^{-11} at T = 216 K

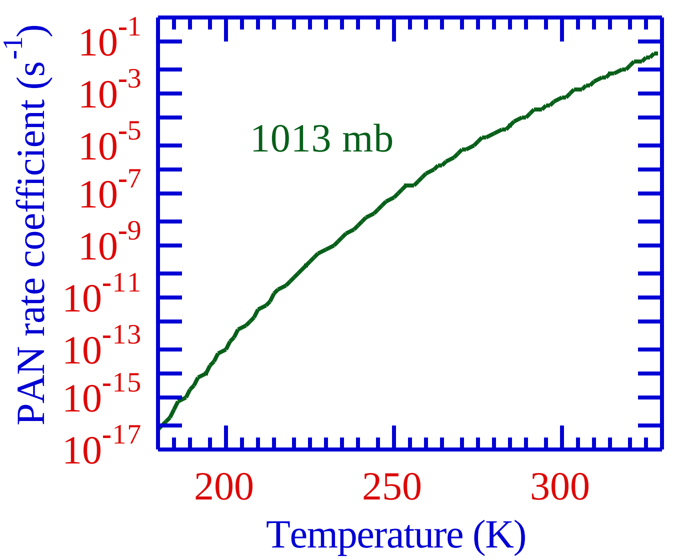
$k_{\infty,T}$ = 8.16 x 10^{-11} cm^3 molec.$^{-1}$ s^{-1}

k_r = 1.11 x 10^{-11} cm^3 molec.$^{-1}$ s^{-1}

PAN Rate Coefficient

Figs. 11.2 a and b. PAN rate coefficient as a function of pressure and temperature, respectively.





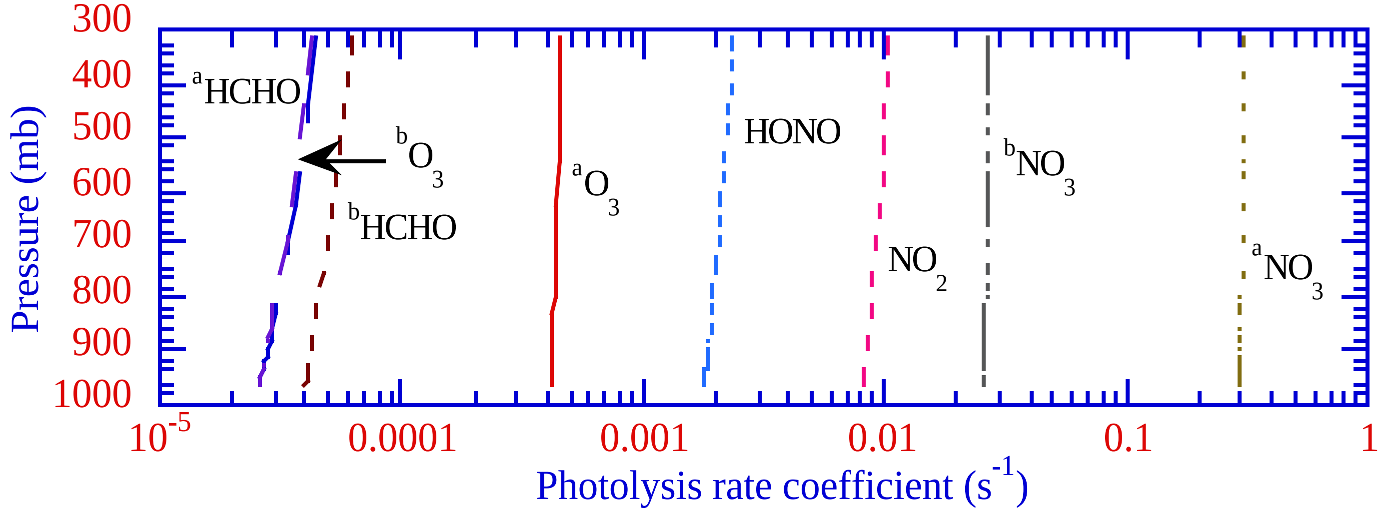
Photolysis Coefficients

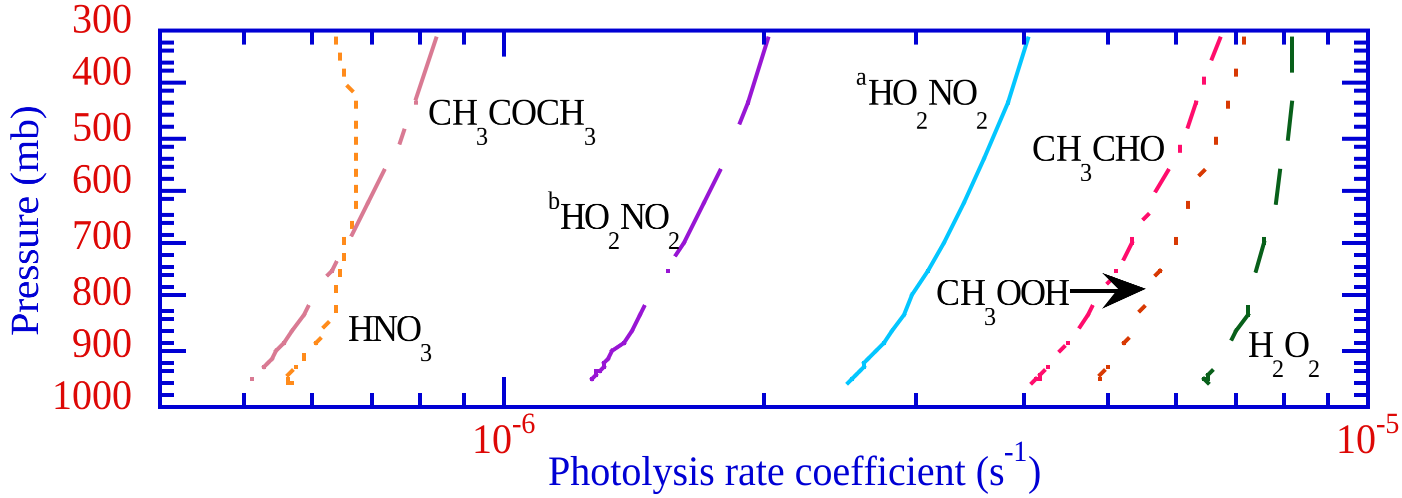
$$J_{q,p} = \int_0^{\infty} 4\pi I_{p,\lambda} b_{a,g,q,\lambda,T} Y_{q,p,\lambda,T} d\lambda \qquad (11.34)$$

Photoprocesses

$$\dot{N}\dot{O}_3 + h\nu \longrightarrow \begin{cases} \dot{N}O_2 + \dot{O}\cdot & 410\text{ nm} < \lambda < 670\text{ nm} \\ \dot{N}O + O_2 & 590\text{ nm} < \lambda < 630\text{ nm} \end{cases} \qquad (11.35)$$

Figs. 11.3 a and b. Predicted photolysis rate coefficients.





Sets of Reactions

Reactions

$$\dot{N}O + O_3 \longrightarrow \dot{N}O_2 + O_2 \qquad (11.36)$$

$$\dot{O}\cdot + O_2 + M \longrightarrow O_3 + M \qquad (11.37)$$

$$\dot{N}O_2 + h\nu \longrightarrow \dot{N}O + \dot{O}\cdot \qquad (11.38)$$

$$\dot{N}O_2 + O \longrightarrow \dot{N}O + O_2 \qquad (11.39)$$

Reaction rates

$$\text{Rate}_1 = k_1[NO][O_3] \qquad (11.36)$$

$$\text{Rate}_2 = k_2[O][O_2][M] \qquad (11.37)$$

$$\text{Rate}_3 = J[NO_2] \qquad (11.38)$$

$$\text{Rate}_4 = k_3[NO_2][O] \qquad (11.39)$$

Sets of Reactions

Resulting ODEs

$$\frac{d[NO]}{dt} = P_c - L_c = Rate_3 + Rate_4 - Rate_1 = J[NO_2] + k_3[NO_2][O] - k_1[NO][O_3]$$

(11.40)

$$\frac{d[NO_2]}{dt} = P_c - L_c = Rate_1 - Rate_3 - Rate_4 = k_1[NO][O_3] - J[NO_2] - k_3[NO_2][O]$$

(11.41)

$$\frac{d[O]}{dt} = P_c - L_c = Rate_3 - Rate_2 - Rate_4 = J[NO_2] - k_2[O][O_2][M] - k_3[NO_2][O]$$

(11.42)

$$\frac{d[O_3]}{dt} = P_c - L_c = Rate_2 - Rate_1 = k_2[O][O_2][M] - k_1[NO][O_3]$$

(11.43)

Production term for NO

$$P_c = J[NO_2] + k_3[NO_2][O] \qquad (11.44)$$

Loss term for NO

$$L_c = k_1[NO][O_3] \qquad (11.44)$$

E-folding Lifetimes

Overall lifetime (s)

$$\tau_A = \frac{1}{\frac{1}{\tau_{A1}} + \frac{1}{\tau_{A2}} + \ldots \frac{1}{\tau_{An}}} \qquad (11.45)$$

E-folding lifetime

Time a species takes to have its concentration reduced to 1/e its original value

Unimolecular reaction

$$\mathrm{A} \rightarrow \textit{products}$$

First derivative

$$\mathrm{d}[\mathrm{A}]/\mathrm{d}t = -k_\mathrm{F}[\mathrm{A}]$$

Solution

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_\mathrm{F} h}$$

E-folding lifetime occurs when

$$\frac{[\mathrm{A}]}{[\mathrm{A}]_0} = \frac{1}{e} = e^{-k_\mathrm{F} h} \qquad (11.46)$$

E-folding lifetime

$$\tau_{A1} = h = \frac{1}{k_\mathrm{F}}$$

E-folding Lifetimes

Bimolecular reaction

$$A + B \rightarrow \textit{products}$$

Loss rate of species A

$$\frac{d[A]}{dt} = -k_S[A][B]_0$$

E-folding lifetime

$$\tau_{A2} = \frac{1}{k_S[B]_0} \qquad (11.47)$$

Termolecular reaction

$$A + B + C \rightarrow \textit{products}$$

E-folding lifetime

$$\tau_{A3} = \frac{1}{k_T[B]_0[C]_0} \qquad (11.48)$$

Example of a Stiff System

Example 11.4.

$CH_4 + OH \rightarrow CH_3 + H_2O$

k = 6.2×10^{-15} cm^3 $molec^{-1}$ s^{-1} at 298K.

[OH·] = 5.0×10^5 molec. cm^{-3}

---> $\tau_{CH_4} = \frac{1}{k\left[OH^{\cdot}\right]}$ = 10.2 years

$O(^1D) + M \rightarrow O + M$

k = 2.6×10^{-11} cm^3 $molec^{-1}$ s^{-1} at 298K

[M] = $[N_2]$ = 1.9×10^{19} molec. cm^{-3}

---> $\tau_{O(^1D)} = \frac{1}{k[M]}$ = 2×10^{-9} seconds

---> stiff set of equations

Half-Lifetimes

Unimolecular reaction

Half-lifetime occurs when

$$\frac{[A]}{[A]_0} = \frac{1}{2} = e^{-k_F h}$$

Solve for half-lifetime

$$\tau_{(1/2)A1} = h = \frac{0.693}{k_F} \quad (11.49)$$

Bimolecular reaction

$$\tau_{(1/2)A2} = \frac{0.693}{k_S[B]_0} \quad (11.50)$$

Termolecular reaction

$$\tau_{(1/2)A3} = \frac{0.693}{k_T[B]_0[C]_0} \quad (11.50)$$