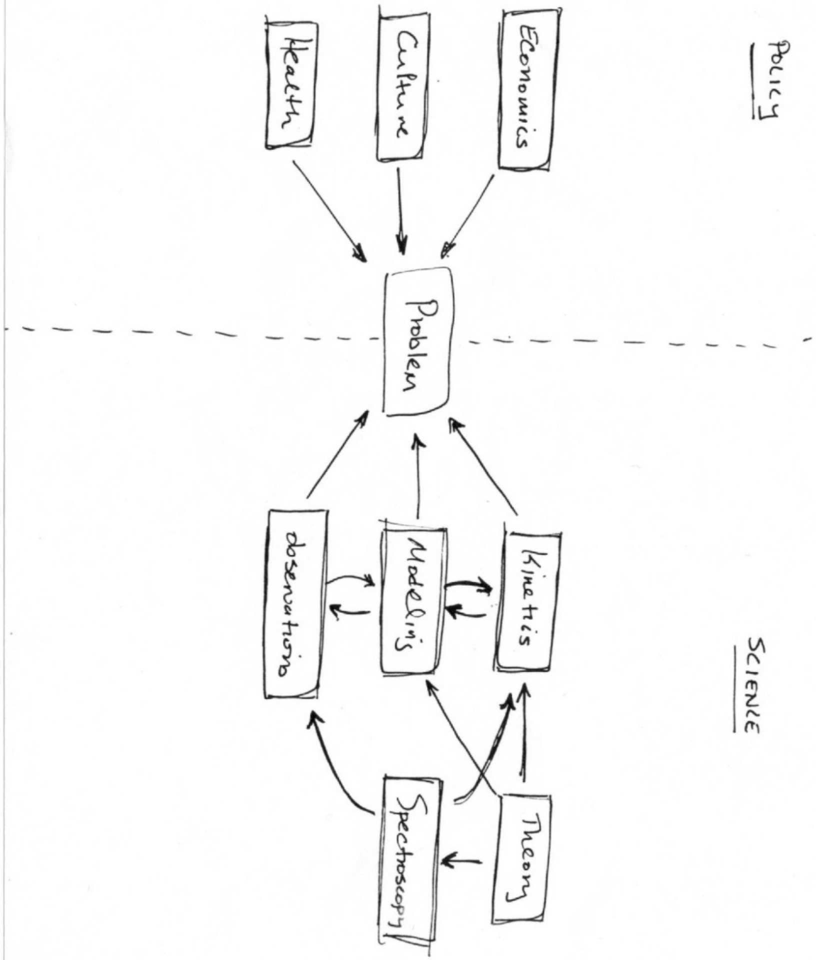


I. Kinetics:

$$A + BC \rightarrow AB + C \qquad (a)$$

$$A + B \xrightarrow{M} AB \qquad (b)$$

(1) Exothermic ?

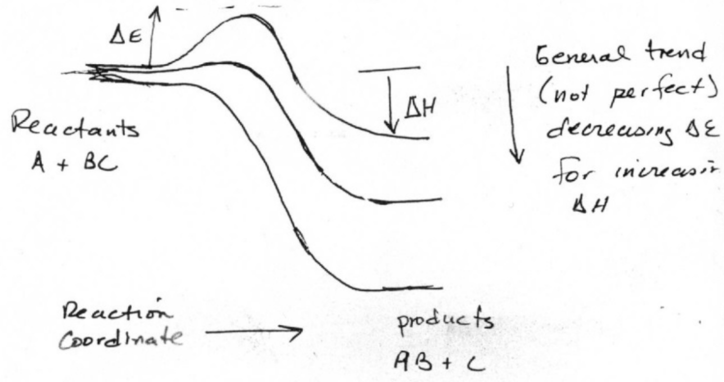
IF $\Delta H > 5$ Kcal/mole, likely unimportant

(2) Type: · Radical-Radical - (a) or (b)

· Radical-Molecule (a)

. Molecule-Molecule RARE!

(3) Potential energy surface - bimolecular reaction

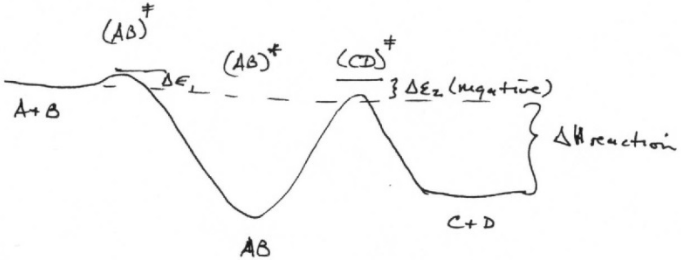


$$K = Ae^{-\Delta E/RT}$$

A = "Preexponential factor"

ΔE = "Activation Energy"

Mixed Behavior:



$$k^{II} = k_1 \left\{ \frac{k_2 + k_m[M]}{k_{-1} + k_2 + k_m[M]} \right\}$$

where:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (AB)^*$$

$(AB)^* + M \xrightarrow{k_m} AB$ "termolecular channel"

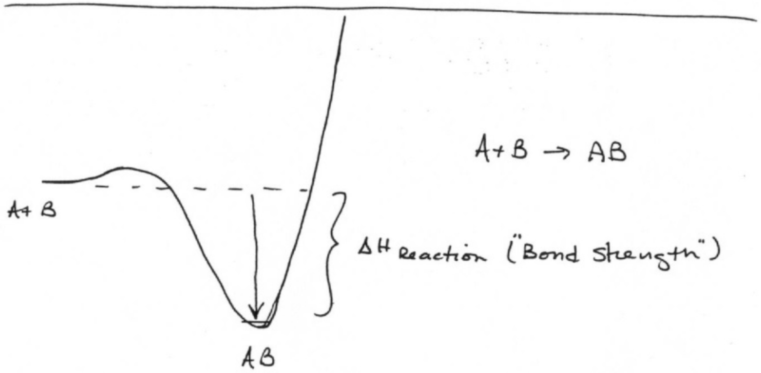
$(AB)^* \xrightarrow{k_2} C + D$ "bimolecular channel"

$k_1 = A_1 e^{-\Delta\varepsilon_1/RT}$

$k_2 = A_2 e^{-\Delta\varepsilon_2/RT}$

k_{-1} ~ T-independent (simple bond fission from excited-state complex)

(4) Potential Energy Surface, termolecular Reaction



$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (AB)^*$$

$$(AB)^* + M \xrightarrow{k_m} AB$$

$k^{II} = \dfrac{k_1 k_m[M]}{k_{-1} + k_m[M]}$ from steady-state $(AB)^*$

Where

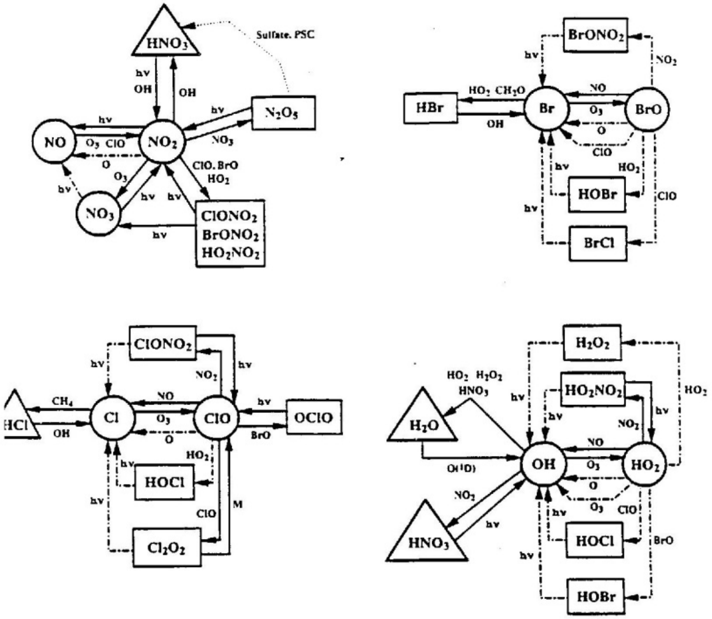
$$\frac{d(A)}{dt} = -k^{II}[A][B] \left(= -\frac{d[AB]}{dt} \right)$$

low P: $k^{II} \cong \dfrac{k_1 k_m}{k_{-1}}[M]$ linear in [M]

high P: $k^{II} \cong k_1$ (high Pressure limit)

DELING

Photochemistry: Stratosphere



- 21 photolysis Rates
- 33 reactions
- 28 species

} This will get you 90% of the result for most of Stratosphere.

△ = long-lived reservoir

○ = radical

(6) Photolysis

$$J(h,T,\phi)=\int_0^\infty F_{sun}(\lambda,h,\phi)\cdot\sigma(\lambda,T)\cdot\phi(\lambda,T,p)\,d\lambda$$

= photolysis rate (function of Temperature, altitude, solar zenith ang pressure.

F • Solar flux is dependent on the ozone column between point of interest and sun, so it depends on wavelength, altitude, and solar zenith angle.

σ • Cross section is a molecular property that depends on Temperature and wavelength (mainly)

φ • Quantum yield depends on wavelength (mainly) and to a much lesser extent on temperature & pressure

It is easy to estimate a photolysis Rate with tabulated values of solar flux. It is *hard* to calculate an accurate photolysis rate (x2) w/o a model that includes Rayleigh scatter, multiple Scattering, ozone distribution, etc.

Ozone destruction

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O_3 \rightarrow X + 2O_2$$
$$O_3 + O_3 \rightarrow O_2 + O_2 + O_2$$

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O \rightarrow X + O_2$$
$$O_3 + O \rightarrow O_2 + O_2$$

NOTE:

$$X + O_3 \rightarrow XO + O_2$$
$$O_3 + h\nu \rightarrow O_2 + O$$
$$O + XO \rightarrow X + O_2$$
$$O_3 + O_3 + h\nu \rightarrow O_2 + O_2 + O_2$$

Typically, $XO + O \rightarrow$ / $XO + O_3 \rightarrow$ are RATE-DETERMINING STEPS because $NO + XO \rightarrow NO_2 + X$ is FAST!

OZONE LOSS:

$$\begin{aligned}\text{Loss} = {} & 2k(O)(ClO) + 2k[ClO](HO_2) + 2k[ClO][BrO] \\ & + 2k[ClO](ClO) + 2k[HO_2]^2 + 2k[HO_2][BrO] \\ & + 2k[HO_2](O) + 2k[HO_2][O_3] + 2k[BrO](O) \\ & + 2k[NO_2][O] + 2k[O](O_3)\end{aligned}$$

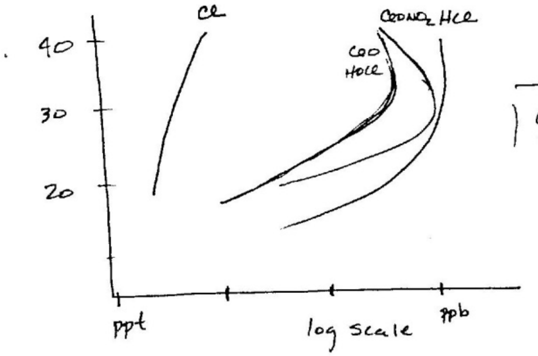
Typically,

$O + NO_2$	→	Most important overall
$HO_2 + O_3$ $HO_2 + O$	→	2nd Most important
$O + ClO$ $HO_2 + ClO$ $BrO + ClO$	→	3rd, but close to Ho
$O + O_3$	→	5% of ozone loss

Antarctica:

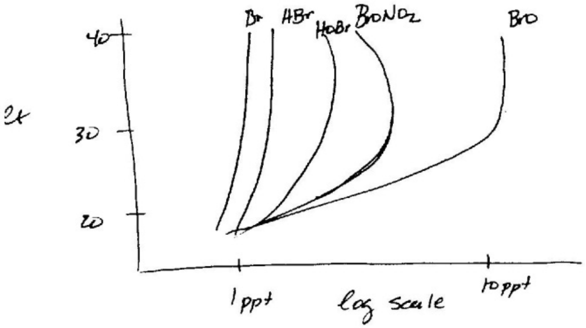
$ClO + ClO$	→	Cl_2O_2	~80% ozone los
$BrO + ClO$	→		~20% ozone lo

ERVATIONS:



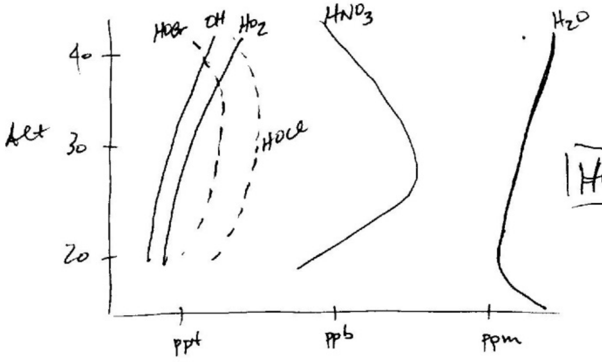
ClOx

Cl_2O_2 important
OCl in ~~polar~~ polar regions
in winter



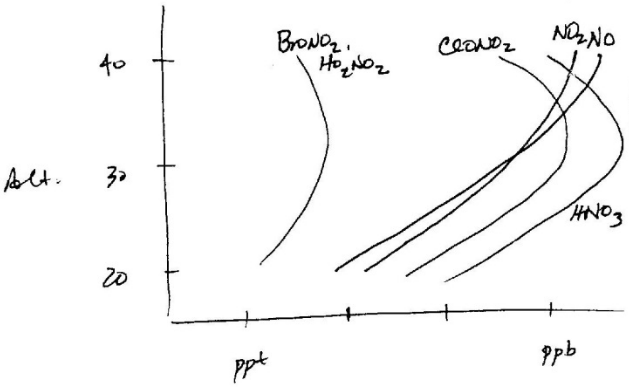
BrOx

BrCl important
in polar
regions in
winter.



HOx

HO_2NO_2 ?
H_2O_2 ?



NOx

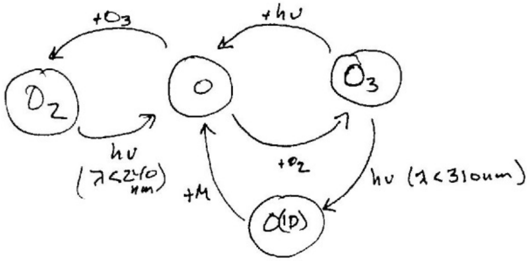
(N_2O_5, NO_3 only at night)

STEADY-STATE, (EXAMPLE)

$$\frac{[BrO]}{[Br]} = \frac{k[O_3]}{k[ClO]+k[O]+k[NO]}$$

(k's all different)

CHAPMAN:



Heterogeneous Chemistry

(Page 203)

"Sticking coefficient" (loosely)

$$k = \frac{\gamma}{4}\left(\frac{8kT}{\pi m_x}\right)^{1/2} \text{S.A.}$$

"Molecular speed"

aerosol surface area.

EXAMPLE:

$N_2O_5 + H_2O \rightarrow 2HNO_3$

$\gamma = 0.1$

$M_{N_2O_5} = 108$ AMU. ($= 1.79\times10^{-25}$ kg/molecule)

$K = 1.381\times10^{-23}$ J/K

at 220 K, $\left(\frac{8kT}{\pi m_x}\right)^{1/2} = 208$ m/s

$$k = \frac{0.1}{4}(208\ \text{m/s})\cdot \text{S.A.}$$

typical surface area ~ $1\ \mu m^2/cm^3$

So:

$$k = \frac{0.1}{4}(208\ \text{m/s})\cdot 1\ \mu m^2/cm^3$$

$$\boxed{k = 5.2\times10^{-6}\ s^{-1}}$$

(lifetime of N_2O_5 ~ 2 days)