

## Chemical Nonequilibrium

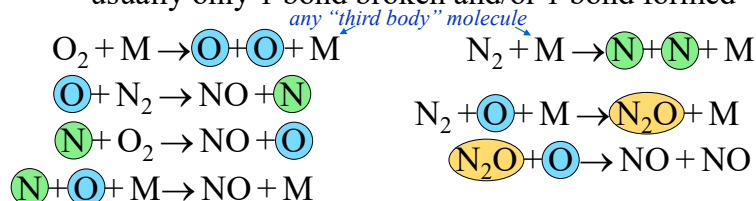
- If gas is not in chemical equilibrium, we can not use equilibrium state relations (e.g.,  $K_p$ ) to find composition
  - need to find **time rate of change of composition**
- Analogous to vibrational nonequilibrium
  - need  $dN_i/dt$  for each species  $i$  due to collisions which change the chemical composition
    - denote these collisions as **chemical reactions**
- Requires development of **chemical mechanism**
  - set of reactions (and species) necessary to capture dynamic behavior of composition under appropriate temperature and pressure conditions
  - usually developed by an “expert” in chemical kinetics

## Elementary Reactions

- To model nonequilibrium chemical processes
  - need to understand what reactions are important
- **Global reaction** (global mechanism)  $(\text{moles}/\text{cm}^3)/\text{sec}$   
*a very unlikely collision*  $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$   $dN_{\text{NO}}/dt = ?$   $d[\text{NO}]/dt = ?$

- **Elementary reactions**

- usually only 1 bond broken and/or 1 bond formed



*depend on intermediate species, often unstable radicals*

## Reaction Rate

- General elementary reaction  $\sum_{i=1}^n v'_i M_i \rightarrow \sum_{i=1}^n v''_i M_i$
- Reaction rate (RR)  $d[M_i]/dt = RR(v''_i - v'_i)$  (IV.C.1)

- Example  $N + N + O \rightarrow NO + N$

$$d[N]/dt = RR(1 - 2) = -RR$$

$$d[NO]/dt = RR$$

## Reaction Rate Constant

- From kinetic theory (or empirical evidence), reaction rate should be proportional to amount of each reactant

$$(IV.C.2) \quad RR = k \prod_i [M_i]^{v'_i} \quad \sum_{i=1}^n v'_i M_i \rightarrow \sum_{i=1}^n v''_i M_i$$

- Proportionality factor
  - reaction **rate constant,  $k$**

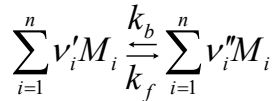
- Example  $N + N + O \rightarrow NO + N$

$$RR = k[N]^2[O] \Rightarrow \frac{d[N]}{dt} = -k[N]^2[O]$$

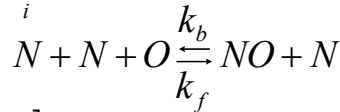
## Forward and Backward (Rev.) Rates

- In general, an elementary reaction can proceed in either direction

General Reaction  
Rate Equation



$$\frac{d[M_i]}{dt} = k_f \prod_i [M_i]^{\nu'_i} (\nu''_i - \nu'_i) + k_b \prod_i [M_i]^{\nu''_i} (\nu'_i - \nu''_i)$$



$$\frac{d[NO]}{dt} = k_f [N]^2 [O] - k_b [NO][N]$$

## Relationship: $k_f$ and $k_b$

- From Principle of Detailed Balance

$$\text{(IV.C.3)} \quad \boxed{\frac{k_f}{k_b} = K_c(T)} \quad \text{equilibrium constant for concentration} \quad K_c(T) = \frac{K_p(T)}{(\bar{R}T)^{\sum \nu_i}}$$

– so for a reaction, only 1 rate constant is independent

- e.g., for  $N+N+O \rightarrow NO+N$

$$\frac{d[NO]}{dt} = k_f [N]^2 [O] - \frac{k_f}{K_c} [NO][N] = k_f [N] \left\{ [N][O] - \frac{1}{K_c} [NO] \right\}$$

- Equilibrium constant is a thermodynamic property
  - but this relation valid even if not in *chemical equilibrium*
  - however,  $K_c$  based on *thermal equilibrium*
    - i.e., translations, rotations, vibrations in equilibrium

## Characteristic Reaction Times

- What is characteristic time for a given (single direction) reaction?
  - e.g., forward reaction  $O_2 + N \rightarrow NO + O$
  - define characteristic time by reaction rate and change in reactant concentration

$$\tau_{chem} \equiv \left| \frac{[N] - [N]_0}{d[N]/dt} \right| \leftarrow \frac{d[N]}{dt} = -k_f [O_2][N]$$

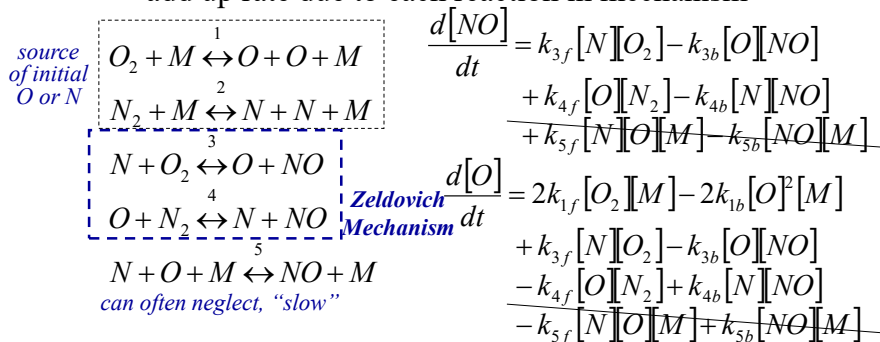
- as example for reaction in air, we might assume fractional  $[O_2]$  change much less than for  $[N]$  and little  $N$  initially

$$\tau_{chem} = \frac{[N] - 0}{k_f [O_2]_0 [N]} = \frac{1}{k_f [O_2]_0} \Rightarrow \frac{d[N]}{dt} = - \frac{[N]}{\tau_{chem}} = - \frac{d[NO]}{dt}$$

*for early times*

## Reaction Rates from Mechanisms

- Example: simple dry air (5 species, no H containing) for “low” temperatures (below ionization conditions)
  - add up rate due to each reaction in mechanism



**Note:** rx 3 + rx 4 =  
 $N_2 + O_2 \rightarrow 2NO$

How many of these rate expressions are independent? : for each species in mechanism

## Rate Equations

- So, we generally have
  - **S-N ODE's** ( $d[M_i]/dt$ ) and **N atom balances**
    - $S$  = number of species
    - $N$  = number of nuclei
- Goal is to solve this set of simultaneous equations (i.e., for composition vs. time)
  - because there are usually a wide range of species concentrations, get a wide range of time constants
    - ⇒ **“stiff” set of equations** – makes numerical solution tricky
- To solve, we also need to know the rate constants
  - usually from experiments (though simple reactions can be modeled using quantum theory and computer simulations)
  - but can model behavior with kinetic theory

## Model for $k$ in Bimolecular Reactions

- Chemical reaction due to inelastic collision; can relate bimolec. collision rate with activation energy to 2-body reaction rate

$$\bar{g} = \sqrt{8k_{\text{Boltz}} T / \pi \mu} \quad k = \frac{N_{\text{Av}} \bar{g}}{(kT)^2} \int_{\varepsilon_a}^{\infty} e^{-\varepsilon/kT} \sigma_{\text{rxn}}(\varepsilon) \varepsilon d\varepsilon$$

$$\sigma_{\text{rxn}} = \sigma_0 \text{fn}(\varepsilon) = N_{\text{Av}} \sigma_0 \bar{g} e^{-\varepsilon_a/\bar{R}T} F_n(T)$$

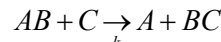
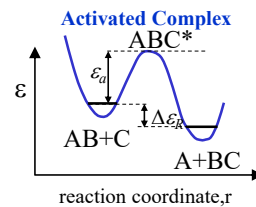
– lumping constants

$$k = AT^{1/2} F_n(T) e^{-\varepsilon_a/\bar{R}T}$$

- Common to use Modified **Arrhenius Rate** expression

$$(IV.C.4) \quad k = AT^b e^{-\varepsilon_a/\bar{R}T}$$

pre-expon. factor      temperature exponent      activation energy



$$\frac{d[BC]}{dt} = k[AB][C]$$

## Example High T Air Mechanism

REACTION	A (cm <sup>3</sup> /mol/s)	b	Ea (cal/mol)	REACTION	A (cm <sup>3</sup> /mol/s)	b	Ea (cal/mol)
N <sub>2</sub> +O=NO+N	7.0×10 <sup>13</sup>	0.	75000.	O <sup>+</sup> +N <sub>2</sub> =N <sub>2</sub> <sup>+</sup> +O	9.03×10 <sup>11</sup>	0.36	45304.
O <sub>2</sub> +N=NO+O	1.34×10 <sup>10</sup>	1.0	7080.	NO <sup>+</sup> +O=O <sub>2</sub> <sup>+</sup> +N	7.23×10 <sup>12</sup>	0.29	96568.
O <sub>2</sub> +M=O+O+M	3.62×10 <sup>18</sup>	-1.0	118000.	NO <sup>+</sup> +O <sub>2</sub> =O <sub>2</sub> <sup>+</sup> +NO	4.02×10 <sup>12</sup>	-0.09	35766.
N <sub>2</sub> /2/ O <sub>2</sub> /9/ O/25/				O <sub>2</sub> <sup>+</sup> +O=O <sup>+</sup> +O <sub>2</sub>	4.02×10 <sup>12</sup>	-0.09	35766.
N <sub>2</sub> +M=N+N+M	1.92×10 <sup>17</sup>	-0.5	224900.	O <sub>2</sub> <sup>+</sup> +N <sub>2</sub> =N <sub>2</sub> <sup>+</sup> +O <sub>2</sub>	9.94×10 <sup>12</sup>	0.0	80871.
N <sub>2</sub> /2.5/ N/0/				NO+O <sup>+</sup> =N <sup>+</sup> +O <sub>2</sub>	1.4×10 <sup>5</sup>	1.9	30401.
N <sub>2</sub> +N=N+N+N	4.1×10 <sup>22</sup>	-1.5	224900.	O <sub>2</sub> <sup>+</sup> +N=N <sup>+</sup> +O <sub>2</sub>	8.73×10 <sup>13</sup>	0.14	56828.
NO+M=N+O+M	4.0×10 <sup>20</sup>	-1.5	150000.	NO <sup>+</sup> +O=N <sup>+</sup> +O <sub>2</sub>	1.01×10 <sup>12</sup>	0.5	153396.
NO/20/ O/20/ N/20/				N+e <sup>-</sup> =N <sup>+</sup> +e <sup>-</sup> +e <sup>-</sup>	2.5×10 <sup>33</sup>	0.0	334213.
N+O=NO <sup>+</sup> +e <sup>-</sup>	5.32×10 <sup>12</sup>	0.0	63385.	O+e <sup>-</sup> =O <sup>+</sup> +e <sup>-</sup> +e <sup>-</sup>	3.9×10 <sup>33</sup>	-3.78	314940.
NO <sup>+</sup> +N=O <sup>+</sup> +N <sub>2</sub>	3.41×10 <sup>13</sup>	-1.08	25434.	O+O=O <sub>2</sub> <sup>+</sup> +e <sup>-</sup>	1.1×10 <sup>13</sup>	0.0	160152.
NO <sup>+</sup> +N=N <sub>2</sub> <sup>+</sup> +O	7.23×10 <sup>13</sup>	0.0	70539.	N+N=N <sub>2</sub> <sup>+</sup> +e <sup>-</sup>	2.0×10 <sup>13</sup>	0.0	134123.
N <sub>2</sub> <sup>+</sup> +N=N <sub>2</sub> +N <sup>+</sup>	7.83×10 <sup>10</sup>	0.5	0.				

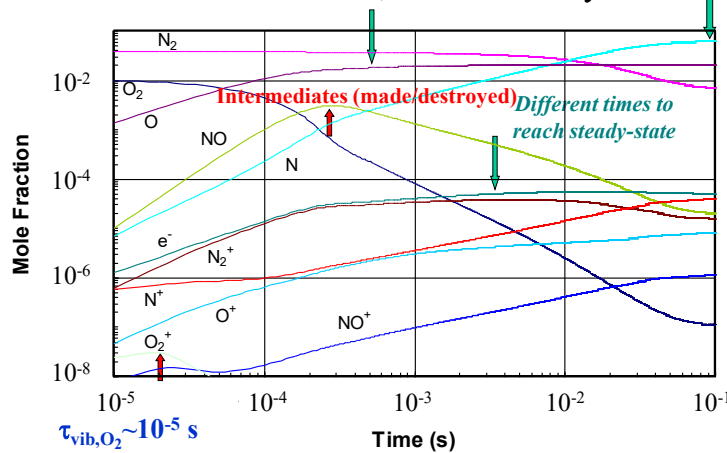
Modified version of Dunn mechanism, used only for illustrative purposes

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**AE 6050**

## Example Result

- 5%air/95%Ar at 0.1 atm,300K suddenly heated to 6000K



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## Chemical vs. Thermal Nonequilibrium

- Previous collision rate/Arrhenius model neglected rot./vibr. distributions or averaged over thermal distributions
  - while rotational equilibrium often occurs quickly, vibrational relaxation slower
  - previous example,  $\tau_{\text{vib}} < \tau_{\text{chem}}$  for many reactions
    - but significant O production occurring before vibr. equilibrium achieved
  - collisions involving excited vibr. states have lower activation energies
    - so if not in vibr. equilibrium, need to use vibr.-state-specific chemical reactions
- In some gas dynamic flows, may also need to consider translation or rotational distributions

