# Chemical Kinetics

Equilibrium Thermodynamics tells us about the final state, yet, if I mix H_2 and O_2 together, they will remain unreacted even through equilibrium says they'll convert into water & heat. Well, they'll remain unreacted as long as there is no ignition source, at least. Combustion systems often do not achieve complete equilibrium because the conversion of reactants to products relies on chemical reactions with finite rates. Combustion is often concerned with the time-dependence of reactions, which thermodynamics can never tell us.

Law of Mass Action

For a single, forward reaction:

$$\sum_{i=1}^{m} \nu_i' M_i \xrightarrow{k_f} \sum_{i=1}^{m} \nu_i'' M_i$$
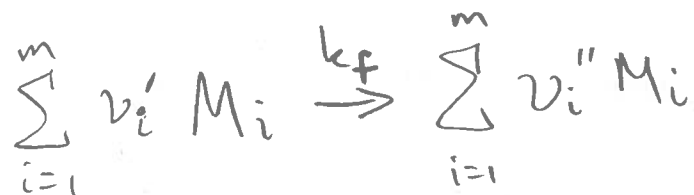
The consumption rate of reactant i is:

$$w_i = \frac{dc_i}{dt} \qquad \frac{moles}{volume \cdot second}$$

$$or \qquad = \frac{d[M_i]}{dt} \qquad \left(eg, \frac{d[H_2]}{dt}, etc \right)$$

The reaction constrains species concentrations to vary in a fixed way so as to conserve atoms:

$$\frac{w_i}{\nu_i'' - \nu_i'} = \frac{w_j}{\nu_j'' - \nu_j'} \equiv w$$

w is overall rate of reaction progress $\left(\frac{moles}{vol \cdot s} \right)$ similar to our definition of λ as a reaction progress variable in equilibrium chapter.
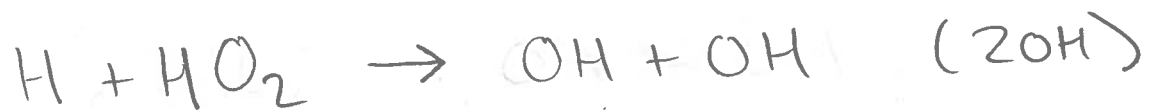
Law of Mass Action - II

An <u>elementary reaction</u> is one that can occur at a molecular level, ie, through a collision, and typically involves the breaking & formation of a single chemical bond.

For such elementary reactions, it can be shown that the rate of the reaction must depend on the collision frequency, which is proportional to the concentration of the reactants. This idea is given as a phenomenological law of mass action:

$$\omega = \underbrace{k_f(T)}_{\substack{\text{reaction} \\ \text{rate constant}}} \prod_{i=1}^{m} c_i^{\nu_i}$$

Law of Mass Action - Example

$$H + HO_2 \rightarrow OH + OH \quad (2OH)$$

Stoichiometry:

$$w = -\frac{d[H]}{dt} = -\frac{d[HO_2]}{dt} = \frac{1}{2}\frac{d[OH]}{dt}$$

$$\sum(\nu_i'' - \nu_i') = -1 \qquad \sum(\nu_i'' - \nu_i') = 2$$

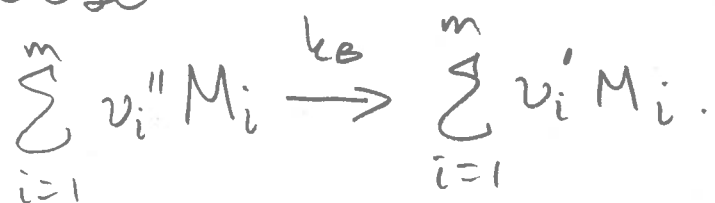**Law of Mass Action:**

$$w = k_f [H][HO_2].$$

We'll discuss k_f soon..

Reversible Reactions

For every reaction, we can write its reverse

$$\sum_{i=1}^{m} v_i'' M_i \xrightarrow{k_B} \sum_{i=1}^{m} v_i' M_i.$$

The net rate of a reaction will be the difference between the forward and reverse rates

$$W_i = W_{i,f} - W_{i,b} = (v_i'' - v_i')(w_f - w_b)$$

$$= (v_i'' - v_i') w$$

with w given by.

$$w = k_f \prod_{i=1}^{m} c_i^{v_i'} - k_b \prod_{i=1}^{m} c_i^{v_i''}$$

At equilibrium, $w \equiv 0$. (reaction in forward direction at same rate as in backward direction)

$$\therefore \quad \frac{k_f}{k_b} = \prod_{i=1}^{m} c_i^{(v_i'' - v_i')} = K_c(T).$$

Reversible Reactions - II

Thus
$$\omega = k_f \left(\prod_{i=1}^{m} c_i^{v_i'} - \frac{1}{K_c} \prod_{i=1}^{m} c_i^{v_i''} \right).$$

K_c comes from equilibrium and can be determined from thermodynamics to much higher accuracy than k_b, so this form is nearly always used.

Irreversible reactions

Reactions for which $\omega_b \ll \omega_f$ can be approximated by

$$\omega \cong k_f \prod_{i=1}^{m} c_i^{v_i'}$$

Such as reactions whose products are both radicals $c_{prod} \ll c_{reactants}$, or when products are rapidly consumed by subsequent reactions.

Multi-step Reactions

The reaction:

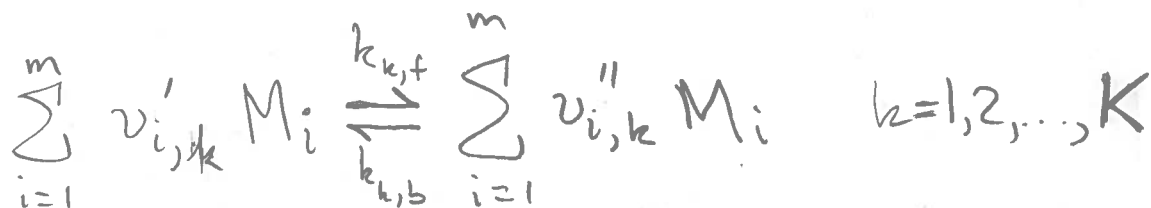$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

never happens. Well, maybe not _never_, but the probability of a single molecular collision (of 3 molecules simultaneously) breaking 6 bonds and forming 6 new ones in infinitessimally small.

There are many intermediate reactions between methane / oxygen and products.

For K total reactions, we can write

$$\sum_{i=1}^{m} v'_{i,k} M_i \underset{k_{k,b}}{\overset{k_{k,f}}{\rightleftharpoons}} \sum_{i=1}^{m} v''_{i,k} M_i \qquad k = 1, 2, \ldots, K$$

$\Big\{$ K reaction equations.

The Law of Mass Action is then:

$$W_k = k_{k,f} \prod_{i=1}^{m} C_i^{v'_{i,k}} - k_{k,b} \prod_{i=1}^{m} C_i^{v''_{i,k}} \qquad k = 1, 2, \ldots, K$$

$\uparrow$
rate of progress of kth rxn

Multi-step Reactions -II

Consumption/Production rate of ith species

$$w_i = \frac{dC_i}{dt} = \sum_{k=1}^{K} (v''_{i,k} - v'_{i,k}) w_k$$

is found by summing up rates from all elementary reactions.

Global / semi global Reactions.

Sometimes we want to approximate detailed kinetics for computational simplicity, such as in computational fluid dynamics simulations of turbulent combustion
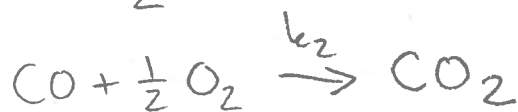
We can write

$$CH_4 + 2O_2 \xrightarrow{k} CO_2 + 2H_2O.$$

with a reaction rate given by

$$w = k \prod_{i=1}^{m} c_i^{n_i}$$

n_i is the reaction __order__ with respect to species i and can't be found from stoichiometry for non-elementary reactions.

for semi-global reaction, can write, e.g.

$$CH_4 + \frac{3}{2}O_2 \xrightarrow{k_1} CO + 2H_2O$$

$$CO + \frac{1}{2}O_2 \xrightarrow{k_2} CO_2$$

Reaction Order and Molecularity

An elementary reaction has an associated __molecularity__ which is the # of atoms/molecules that interact during the collision. Most reactions have molecularities of 2, as 2-body collisions are more common than 3 or more.

Reactions such as

$$H + O_2 \rightarrow HO_2$$

cannot conserve both momentum and energy, thus need to be written as

$$H + O_2 + M \rightarrow HO_2 + M$$

where M is any third-body species, typically only major species are considered.

The order of a global reaction depends on net effect of many intermediate steps and thus the n_i can be fractional. Since reactions of molecularity of 3 a higher are usually recombination reactions that retard progress, the overall reaction order should usually be less than 2.

Chemical Kinetic Rates

We can use our model of kinetic theory to assess the rate of chemical reactions.

We will consider only binary reactions of the type

$$A + B \rightleftharpoons C + D$$

$$O + H_2 \rightleftharpoons OH + H$$
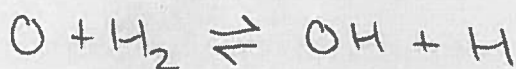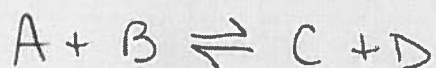
Modeling the Combustion of H_2, the simplest fuel, requires including 20 different reversible reactions of this type. For methane, we have > 100 reactions, and gasoline, > 1000!

This reaction represents swapping atoms from one molecule to the other and thus must be the result of a molecular collision.

The rate of the reaction is given by the law of mass action:

rate of forward reaction: $r_f = k_f [A][B]$

The rate is proportional to the concentrations of both species and a rate constant, k_f.

$$\text{rate of reverse reaction} = k_B[C][D]$$

At equilibrium, the 2 rates equal each other

$$k_f[A][B] = k_B[C][D]$$

$$K_C = \frac{k_f}{k_B} = \frac{[C][D]}{[A][B]}$$

↳ Equilibrium constant.

Once we know K_C, we only need to find either k_f or k_B.

$$r_f = k_f[A][B]$$

The rate of reaction is the rate of collisions times the fraction of collisions with sufficient energy to overcome the energy barrier to chemical reaction.

The collision rate between A & B is.

$$Z_{AB}\left[\frac{collisions}{cm^3\ s}\right] = \pi\, n_A n_B\, \sigma_{AB}^2 \left(\frac{8kT}{\pi\mu}\right)^{1/2}$$

We need to find the fraction of collisions with sufficient energy to make a reaction happen
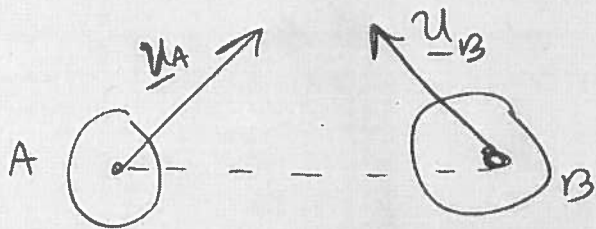
It is the velocity along the line of centers that will act in favor of chemical reaction.
The sideswiping energy will not contribute.

fraction of molecules with velocity in x-direction between u_x and $u_x + du_x$ is:

$$f(u_x) du_x = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{m}{2kT} u_x^2\right) du_x.$$

$$f(E_x) dE_x = 2\left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{E_x}{kT}\right) \frac{dE_x}{\sqrt{2mE_x}}$$

$$E_x = \frac{1}{2} m u_x^2 \qquad dE_x = \underbrace{m u_x}_{\sqrt{2mE_x}} du_x$$

$$u_x = \sqrt{\frac{2E_x}{m}}$$

We multiplied by 2 to account for both + and − u_x.

$$f(E_x) dE_x = \left(\frac{1}{\pi kT}\right)^{1/2} \frac{1}{E_x^{1/2}} \exp\left(-\frac{E_x}{kT}\right) dE_x.$$

Can verify using $\displaystyle\int_0^\infty f(E_x) dE_x = 1$

The fraction of collisions with energy along the impact direction with energy E_A to $E_A + dE_A$ and E_B to $E_B + dE_B$ is:

$$f(E_A) f(E_B) \, dE_A dE_B = \frac{1}{\pi kT} \frac{1}{\sqrt{E_A E_B}} \exp\left[-\frac{E_A + E_B}{kT}\right] dE_A dE_B$$

We are interested in collisions whose total energy exceeds a critical value

Total Energy = $\quad E = E_A + E_B$

$$E_A = E - E_B$$

$$f(E) f(E_B) \, dE \, dE_B = \left(\frac{1}{\pi kT}\right) \frac{1}{(E - E_B)^{1/2} E_B^{1/2}} \exp\left[-\frac{E}{kT}\right] dE \, dE_B$$

Integrate over all values of E_B: (E_B can vary from 0 to E).

$$f(E) dE = \frac{1}{\pi kT} \exp\left[-\frac{E}{kT}\right] dE \int_0^E \frac{1}{(E - E_B)^{1/2}} \frac{1}{E_B^{1/2}} \, dE_B$$

$$E_B = E \sin^2 \alpha. \qquad E - E_B = E(1 - \sin^2 \alpha)$$
$$\qquad\qquad\qquad\qquad = E \cos^2 \alpha.$$
$$dE_B = E \, 2 \sin \alpha \cos \alpha \, d\alpha.$$

When

$$E_B = E \qquad \sin^2 \alpha = 1 \qquad \alpha = \frac{\pi}{2}$$

$$f(E)dE = \frac{1}{\pi kT} \exp\left[-\frac{E}{kT}\right] dE \int_0^{\pi/2} \frac{1}{\sqrt{E}\cos\alpha} \frac{1}{\sqrt{E}\sin\alpha} 2E \sin\alpha \cos\alpha \, d\alpha.$$

$$\underbrace{\phantom{\int_0^{\pi/2} \frac{1}{\sqrt{E}\cos\alpha} \frac{1}{\sqrt{E}\sin\alpha} 2E \sin\alpha \cos\alpha \, d\alpha.}}$$

$$\int_0^{\pi/2} 2 \frac{\sin\alpha \cos\alpha}{\cos\alpha \sin\alpha} \, d\alpha$$

$$2\left(\frac{\pi}{2}\right) = \pi.$$

$$\boxed{f(E)dE = \frac{1}{kT} \exp\left[-\frac{E}{kT}\right] dE}$$

The fraction of collisions with energy greater than some energy, E_0 is

$$\int_{E_0}^{\infty} f(E)dE = \left(\frac{1}{kT}\right) \int_{E_0}^{\infty} \exp\left[-\frac{E}{kT}\right] dE$$

$$= \left(\frac{1}{kT}\right)(-kT) \exp\left(-\frac{E}{kT}\right)\Bigg|_{E_0}^{\infty}$$

$$\boxed{\int_{E_0}^{\infty} f(E)dE = + \exp\left[-\frac{E_0}{kT}\right]}$$

The reaction rate is this fraction times the rate of collisions.

$$r = Z_{AB} \exp\left(-\frac{E_0}{kT}\right) \qquad \left(\frac{\text{reacting collisions}}{\text{volume time}}\right)$$

$$\text{in} \left(\frac{\text{moles}}{V\ s}\right) \qquad r = \frac{Z_{AB}}{N_A} \exp\left(-\frac{E_A}{RT}\right) \qquad \begin{array}{l}\text{activation}\\ \text{energy}\\ \text{per}\\ \text{mole.}\end{array}$$

$$[E_A] = \frac{kJ}{\text{mole}}.$$

$$r = \pi \frac{n_A n_B}{N_A} \sigma_{AB}^2 \left(\frac{8kT}{\pi\mu}\right)^{1/2} \exp\left(-\frac{E_A}{RT}\right)$$

$$n_A = [A] N_A \qquad n_B = [B] N_A.$$

$$r = \underbrace{\pi N_A \sigma_{AB}^2 \left(\frac{8kT}{\pi\mu}\right)^{1/2} \exp\left(-\frac{E_A}{RT}\right)}_{} [A][B].$$

Modified Arrhenius rate law: $k = A T^n \exp\left(-\frac{E_A}{RT}\right)$

$$A = \pi N_A \sigma_{AB}^2 \left(\frac{8k}{\pi\mu}\right)^{1/2} \qquad n = 1/2.$$
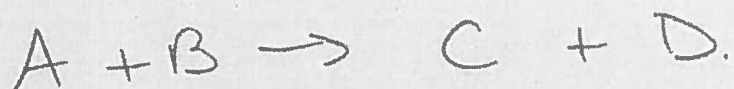
Thus, the Activation Energy represents the energy required to break the chemical bonds in a collision, while the temperature exponent is a consequence of the binary collision rate.

Kinetic theory has shown us why the Arrhenius rate law should describe gas-phase reactions!
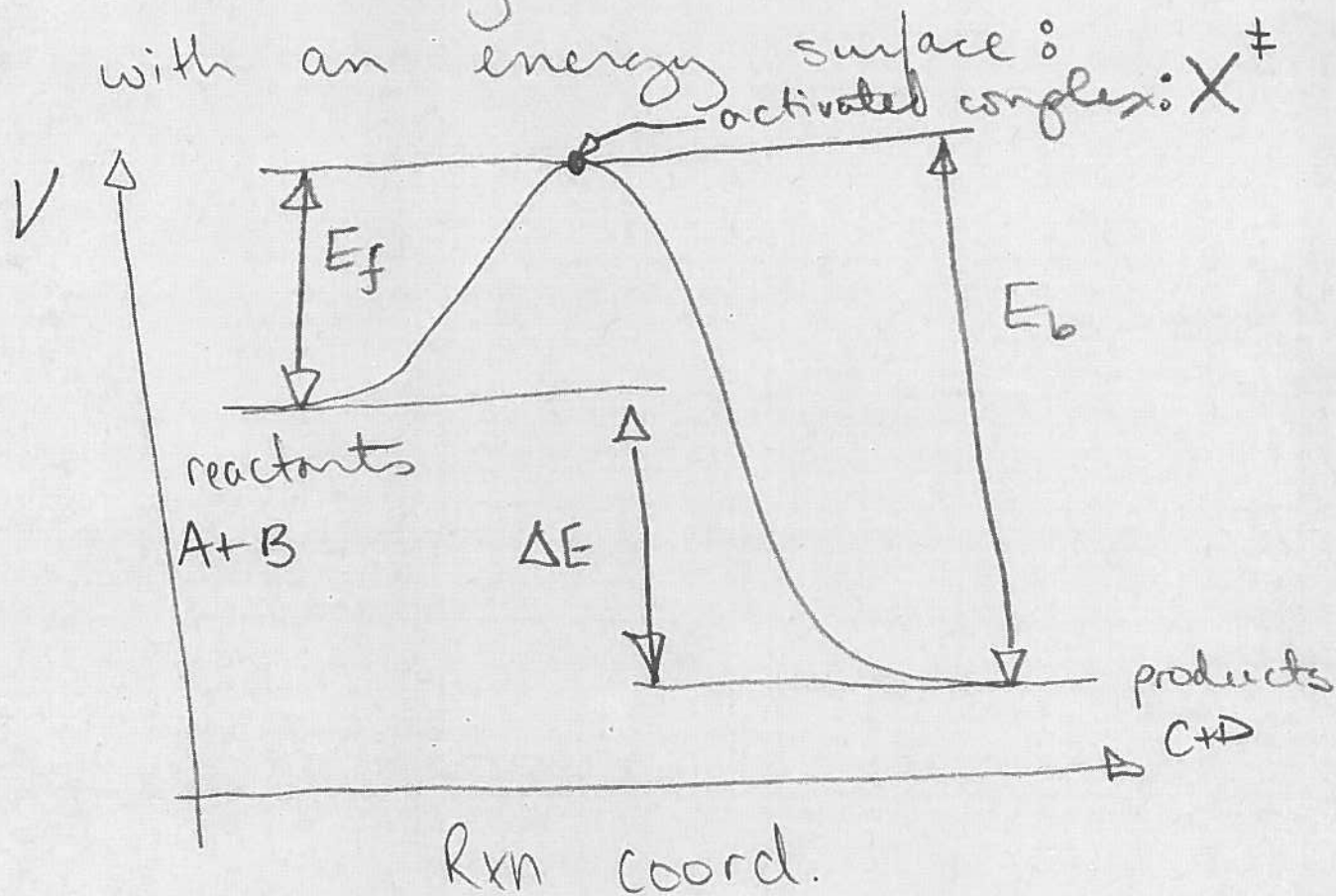
Transition - State Theory of Chemical Reactions.

Assume reaction:

$$A + B \rightarrow C + D.$$

Occurs along a reaction coordinate with an energy surface:

activated complex: $X^{\ddagger}$

V

E_f

E_b

reactants
$A + B$

ΔE

products
$C + D$

Rxn coord.

That has an activation energy barrier along its path.

We would like a better theory than our collision model to describe the rates of such reactions when there are internal energy modes that can suck up energy, as the collision model will predict too high of rates.

We assume:

- rxn progresses along a preferred direction (rxn coord.) & that an activated complex forms @ the top of the hill. E_f & E_b are the forward & backward activation energies needed to form the complex $X^{\neq}$

- The rxn rate in forward or backward directions is equal to the rate at which activated complexes pass along the rxn coord.

- The activated complex becomes products by converting an unstable vibrational mode to kinetic energy (translation).

Thus $A + B \rightarrow C + D$

$$A + B \rightleftharpoons X^{\ddagger}$$
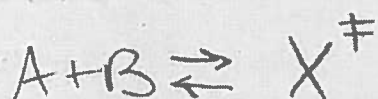
Concentration of $X^{\ddagger}$

$$K_c^{\ddagger} = \frac{[X^{\ddagger}]}{[A][B]}$$

Rate of rxn is proportional to $[X^{\ddagger}]$

and the frequency at which the unstable bond is vibrating, ν_D. (One period of oscillation takes us to products).

$$r = \nu_D [X^{\ddagger}] = \nu_D K_c^{\ddagger} [A][B].$$

$\therefore$ Because from Law of Mass Action

$$r = k_f [A][B]$$

Transition State Theory – non statistical thermo

My notes on TST from Advanced thermo are general up to page TST4, where we show

$$k_f = \nu_D K_c^{\ddagger}$$

frequency of vibration of unstable bond

The vibrational energy of the unstable bond is converted into kinetic energy of C & D

Equating these energy modes

$$\varepsilon_{VIB} = \varepsilon_{tr}$$

$$h\nu_D = 2\left(\frac{1}{2}k_B T\right)$$

Vibrational energy is ⌐   2 molecules   translational energy per molecule

Planck's constant $\times$ frequency.

$$\nu_D = \frac{k_B T}{h}$$

TST - classical - II

Thus
$$k_f = \left(\frac{k_B T}{h}\right) K_c^{\ddagger}.$$

$$K_c^{\ddagger} = \frac{K_p^{\ddagger}}{(R_u T)^{\Sigma \nu_i}}$$

$$\Sigma \nu_i = \underbrace{1}_{\text{product}} - \underbrace{n}_{\text{reaction order/molecularity}}$$

$$X^{\ddagger}$$

$$K_c^{\ddagger} = K_p^{\ddagger} (R_u T)^{n-1}$$

$$K_p^{\ddagger} = \exp\left(-\frac{\Delta G_0^{\ddagger}}{R_u T}\right)$$

$$\Delta G_0^{\ddagger} = \Delta H_0^{\ddagger} - T \Delta S_0^{\ddagger}$$

$$k_f = \left(\frac{k_B T}{h}\right)(R_u T)^{n-1} \exp\left(\frac{\Delta S_0^{\ddagger}}{R_u}\right) \exp\left(\frac{-\Delta H_0^{\ddagger}}{R_u T}\right).$$

Compare to Arrhenius form

$$k = Z \psi \exp\left(-\frac{E_a}{R_u T}\right)$$

collision frequency

steric factor

We see that

$$Z = \left(\frac{k_B T}{h}\right)(R_u T)^{n-1}$$

$$\psi = \exp\left(\frac{\Delta S_0^{\ddagger}}{R_u}\right)$$

$$E_a = \Delta H_0^{\ddagger}$$

Thus, the activation energy is the difference in enthalpy of formation of the activated complex compared to that of the reactants, as expected.
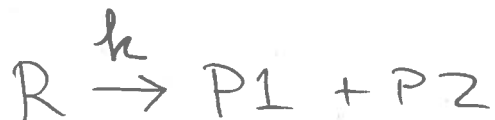
TST - Clasical - IV

The steric factor depends on entropy difference between TS and reactants. Since TS is less molecules than were reactants, $\Delta S_0^{\ddagger}$ is always negative $\psi < 1$ and rates are slower than predicted by basic collision theory.

Lindemann Theory of Unimolecular Reactions.

A unimolecular decomposition reaction, such as

$$R \xrightarrow{k} P1 + P2$$

$$\{ CH_4 \rightarrow CH_3 + H \}$$

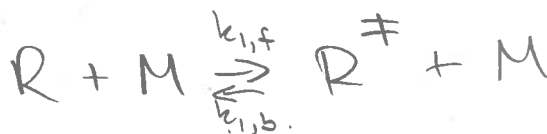Looks as if it has a molecularity of 1. However, in order for the reactant to have sufficient energy to decompose to products, it needs to be activated by a collision with other species.

Thus, we should write it as:

$$R + M \rightarrow P1 + P2 + \ldots + M$$

in case there are more product species.

Or, we write it as two steps, similar to the TST approach

$$R + M \underset{k_{1,b}}{\overset{k_{1,f}}{\rightleftarrows}} R^{\ddagger} + M$$

$$R^{\ddagger} \xrightarrow{k_2} P_1 + P_2 + \ldots$$

Reaction rates for R and $R^{\ddagger}$ are:

① $\quad \dfrac{dc_R}{dt} = -k_{1,f}\, c_R c_M + k_{1,b}\, c_R^{\ddagger} c_M$

② $\quad \dfrac{dc_{R^{\ddagger}}}{dt} = k_{1,f}\, c_R c_M - k_{1,b}\, c_{R^{\ddagger}} c_M - k_2\, c_{R^{\ddagger}}$

We now assume that the rates of activation & deactivation of R to $R^{\ddagger}$ are so fast that the concentration of $R^{\ddagger}$ is approximately constant in time (steady state approximation).

Thus $\quad \dfrac{dc_{R^{\ddagger}}}{dt} = 0$

From ②: $\quad c_{R^{\ddagger}} = \dfrac{k_{1,f}\, c_R c_M}{k_{1,b}\, c_M + k_2}$

Put into ①:

$$\dfrac{dc_R}{dt} = -k_{1,f}\, c_R c_M + k_{1,b} \left(\dfrac{k_{1,f}\, c_R c_M}{k_{1,b}\, c_M + k_2} \right) c_M .$$

$$\frac{dC_R}{dt} = \frac{-k_{1,f}\,C_R C_M \left(\cancel{k_{1,b}} C_M + k_2\right) + k_{1,b}\left(k_{1,f}\cancel{C_R C_M}\right) C_M}{k_{1,b} C_M + k_2}$$

$$\frac{dC_R}{dt} = - \frac{k_2\left(k_{1,f}\right) C_M C_R}{k_{1,b} C_M + k_2}$$

$$\frac{dC_R}{dt} = - \underbrace{\frac{k_2\left(k_{1,f}/k_{1,b}\right)}{1 + \left[k_2/(k_{1,b} C_M)\right]}}_{k} C_R$$

C_M is proportional to the overall gas pressure.

$$p\forall = n R_u T \qquad\qquad C_M = \frac{n}{\forall}$$

$$C_M = \frac{P}{R_u T}$$

As $p \to \infty$ $\quad$ $c_M \to \infty$.

$$k_\infty = k_2 \left(\frac{k_{1,f}}{k_{1,b}} \right) \neq f(p).$$

The high-pressure limit of a unimolecular reaction is of order one.

As $c_M \to 0$ $\quad (p \to 0)$.

$$k_0 = k_{1,f} \, c_M. \qquad (2^{nd} \text{ order})$$

$$k_0 \propto P.$$

$$\frac{1}{k} = \frac{1}{k_\infty} + \frac{1}{k_0}$$

Think of $1/k$ as being a resistance to a chemical reaction and these are 2 reactions in series.

We have the simple result:

$$k_f = \nu_D K_c^{\ddagger}$$

What is $K_c^{\ddagger}$?

$$K_c^{\ddagger} = \frac{n_{x^{\ddagger}}}{n_A n_B} = \frac{\phi_{x^{\ddagger}}}{\phi_A \phi_B} \exp\left(\frac{D_{0x^{\ddagger}} - D_{0A} - D_{0B}}{kT}\right)$$

$$\phi_i = Z_i / V$$

Write it in terms of moles:

$$K_c^{\ddagger} = \frac{N_A \phi_{x^{\ddagger}}}{\phi_A \phi_B} \exp\left(-\frac{\Delta E_0}{kT}\right)$$

$$\Delta E_0 = D_{0A} + D_{0B} - D_{0x^{\ddagger}}$$

ΔE_0 is chemical energy needed to form the activated complex at $T \to 0$.

Need $\phi_{X^{\ddagger}}$, which is tough Modern analysis searches for a saddle in the multidimensional Pot. Energy "surface" to find the activated complex.

Here, we assume.

$$\phi_{X^{\ddagger}} = \phi^{\ddagger} \phi_D$$

$\phi^{\ddagger}$ is the partition function / volume associated with all energy modes (translation, rotation & other vib. modes) but the rxn coord.

ϕ_D is the Z/V for the unstable vibrational mode associated with the rxn coordinate

For the bond to be weak & allow reaction
$\overset{\wedge}{unstable}$

$$\frac{\Delta \mathcal{E}}{kT} = \frac{h\nu}{kT} << 1.$$

$$\phi_D = \lim_{\frac{h\nu}{kT} \to 0} \left(Z_{vib} \right) = \lim_{h\nu/kT \to 0} \left(1 - e^{-h\nu/kT} \right)^{-1} = \frac{kT}{h\nu_D}$$

$$\therefore \quad K_c^{\ddagger} = N_A \left(\frac{kT}{h \nu_D}\right) \frac{\phi^{\ddagger}}{\phi_A \phi_B} \exp\left(-\frac{\Delta E_0}{kT}\right)$$

$$k = K_c^{\ddagger} \nu_D$$

$$k = N_A \left(\frac{kT}{h}\right) \frac{\phi^{\ddagger}}{\phi_A \phi_B} \exp\left(-\frac{\Delta E_0}{kT}\right)$$

$$\therefore \quad \boxed{E_a = \Delta E_0.}$$

$$AT^n = N_A \left(\frac{kT}{h}\right) \frac{\phi^{\ddagger}}{\phi_A \phi_B}$$

$$\boxed{n = 1}$$

$$\boxed{A = N_A \left(\frac{k}{h}\right) \frac{\phi^{\ddagger}}{\phi_A \phi_B}}$$

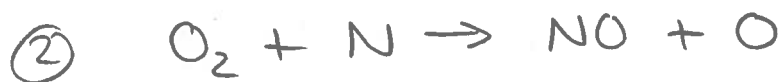Hard part is to figure out what $X^{\ddagger}$ is & what its energy modes are to find $\phi^{\ddagger}$.

Oxidation Mechanisms.

See slides for treatment of this section, as well as textbook.

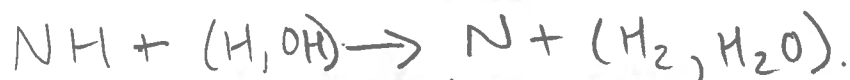# Mechanism of NO formation

Thermal, or Zel'dovich, mechanism :

    ① $N_2 + O \rightarrow NO + N$

    ② $O_2 + N \rightarrow NO + O$

    ③ $N + OH \rightarrow NO + H$

① is the rate-limiting step and is highly temperature dependent due to strength of $N \equiv N$ bond.

Prompt, or Fenimore, mechanism :

Initiation:

      $N_2 + CH \rightarrow NCN + H.$

      $N_2 + CH_2 \rightarrow HCN + NH.$

Generation of N: $HCN + O \rightarrow NCO + H$

      $HCN + (H, OH) \rightarrow CN + (H_2, H_2O)$

      $NCO + H \rightarrow NH + CO$

      $NH + (H, OH) \rightarrow N + (H_2, H_2O).$

      $CN + O \rightarrow N + CO$

Production of NO from N:

from thermal mechanism
$$\{$$

② $O_2 + N \rightarrow NO + O$

③ $N + OH \rightarrow NO + H.$
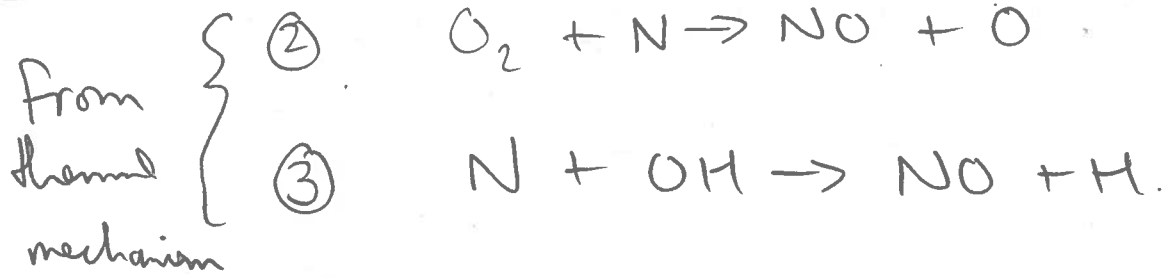
Similar process for NCN. oxidation to NO.