2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 20

Room 3-442
Friday, April 19, 11:00am - 1:00pm

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Systems with chemical reactions

Activated complex
Extension of the simple system model for large n

Necessary condition of chemical equilibrium
(from the maximum entropy principle)

Equilibrium and non-equilibrium forms of the
law of mass action

Turning reactions "on" and "off" does not affect the local properties

Given the instantaneous composition $(\boldsymbol{n}, n^*)$:

• **Neglect the contribution of the activated complex A^* to the mixtures properties** (indeed, for large n, we can assume $n^* \ll n$ because A^* is highly unstable and hence very short lived).

• Assume that the rate at which **non-chemical collisions** redistribute the excesses or defects in local kinetic energy caused by the chemical reactions, is much faster than the rate at which **chemically effective collisions** produce them. Thus, if we suddenly turn reactions "off", the mixture relaxes almost instantly to SE, and even when reactions are "on" the state (all the properties) is very close to the SES it would relax to if we turned them "off".

• Therefore, the instantaneous properties can be assumed equivalent to the SE properties of a mixture with the composition but with no active chemical reaction mechanisms, i.e., with reactions **turned "off"**. In particular,

$$S_{\boldsymbol{\epsilon}}^{\text{on}} = S_{\text{off}}(U, V, \boldsymbol{n}) = S_{\text{off}}(U, V, \boldsymbol{n}_a + \boldsymbol{\nu} \cdot \boldsymbol{\epsilon})$$

Family of partial SES's and chemical SES

The extended simple system model, assumes:

$$S_{\boldsymbol{\epsilon}}^{\mathrm{on}} = S_{\mathrm{off}}(U, V, \boldsymbol{n}(\boldsymbol{n}_a, \boldsymbol{\nu}, \boldsymbol{\epsilon})) \quad \text{with} \quad \boldsymbol{n}(\boldsymbol{n}_a, \boldsymbol{\nu}, \boldsymbol{\epsilon}) = \boldsymbol{n}_a + \boldsymbol{\nu} \cdot \boldsymbol{\epsilon}$$

This represents a z-parameter family of SES curves (z is the number of independent reaction coordinates) which spans the range of allowed energy and entropy values.

The maximum entropy principle requires that at SE, the system chooses the set of values of the reaction coordinates, $\boldsymbol{\epsilon}_o$ that satisfies

$$Y_j = \left(\frac{\partial S_{\boldsymbol{\epsilon}}^{\mathrm{on}}}{\partial \epsilon_j} \right)_{U, V, \boldsymbol{n}_a, \boldsymbol{\nu}, \epsilon_j'} = 0 \qquad \forall j$$

Y_j is called the **affinity of the j-th reaction**. It is zero at equilibrium.
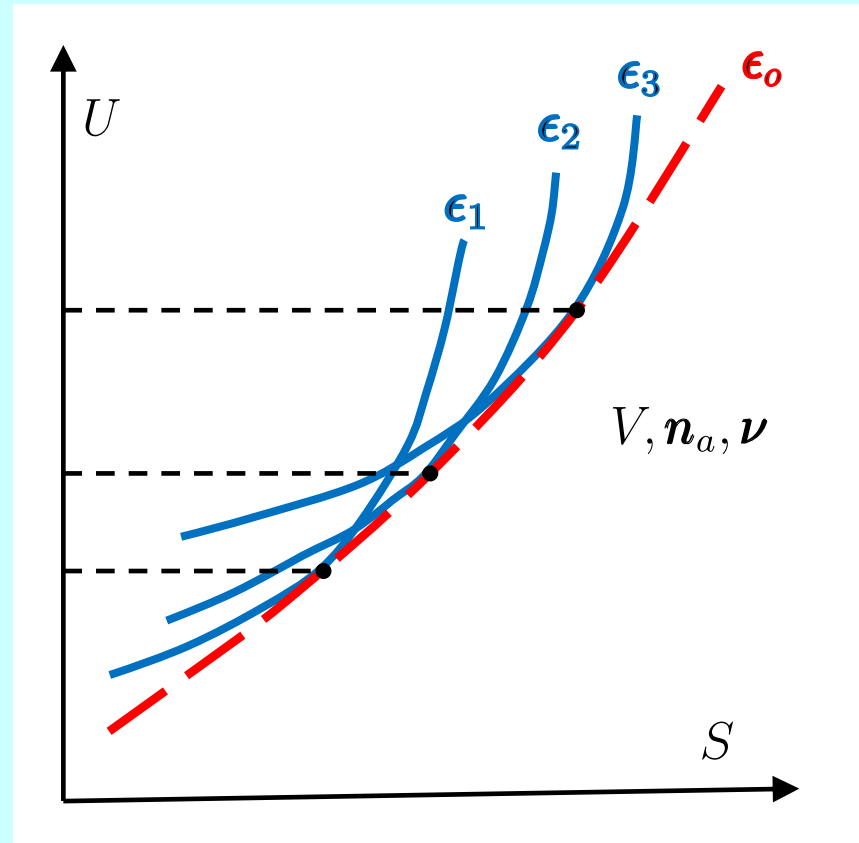
Affinities and the non-equilibrium law of mass action
here for a Gibbs-Dalton mixture of ideal gases

We assumed $\quad S_{\boldsymbol{\epsilon}}^{\mathrm{on}} = S_{\mathrm{off}}(U, V, \boldsymbol{n}_a + \boldsymbol{\nu} \cdot \boldsymbol{\epsilon})$

recall that $\quad \partial S_{\mathrm{off}}(U, V, \boldsymbol{n})/\partial n_i = -\mu_i^{\mathrm{off}}/T_{\mathrm{off}}$ and note that $\partial n_i/\partial \epsilon_j = \nu_i^{(j)}$

$$Y_j = \left(\frac{\partial S_{\mathrm{off}}}{\partial \epsilon_j} \right)_{U, V, \boldsymbol{n}_a, \boldsymbol{\nu}, \boldsymbol{\epsilon}_j'} = -\frac{1}{T_{\mathrm{off}}} \sum_i \nu_i^{(j)} \mu_i^{\mathrm{off}}$$

Assume ideal mixture of ideal gases $\quad \mu_i^{\mathrm{off}} = \mu_{ii}(T, p_o) + RT \ln \frac{p}{p_o} + RT \ln y_i$

Recall $\quad \Delta g_j^o(T) = \sum_i \nu_i^{(j)} \mu_{ii}(T, p_o) \qquad \nu^{(j)} = \sum_i \nu_i^{(j)}$

$$\sum_i \nu_i^{(j)} \ln y_i = \ln \prod_i (y_i)^{\nu_i^{(j)}} \qquad [N_i] = \frac{p}{RT} y_i$$
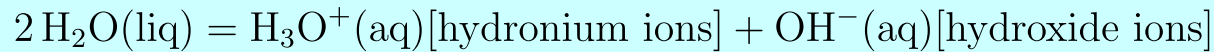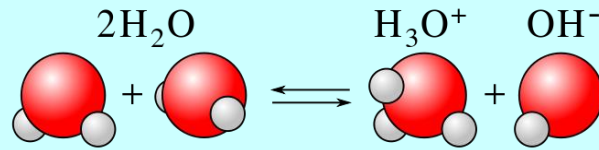
We obtain the **non-equilibrium law of mass action**

$$\prod_i (y_i)^{\nu_i^{(j)}} = K_j(T, p) \exp \left[-\frac{Y_j}{R} \right] \qquad K_j(T, p) = \left[\frac{p_o}{p} \right]^{\nu^{(j)}} \overbrace{\exp \left[-\frac{\Delta g_j^o(T)}{RT} \right]}^{K_j(T)}$$

$$\prod_i [N_i]^{\nu_i^{(j)}} = K_j^c(T) \exp \left[-\frac{Y_j}{R} \right] \qquad K_j^c(T) = \left[\frac{p_o}{RT} \right]^{\nu^{(j)}} \exp \left[-\frac{\Delta g_j^o(T)}{RT} \right]$$

Chemical equilibrium of self-ionization of pure liquid water

pH and pOH

$$2\,H_2O(liq) = H_3O^+(aq)[\text{hydronium ions}] + OH^-(aq)[\text{hydroxide ions}]$$

$$pH = -\log_{10}\frac{[H_3O^+]}{1\,\text{mol/liter}} \qquad pOH = -\log_{10}\frac{[OH^-]}{1\,\text{mol/liter}}$$

Assuming the molarity of water, $[H_2O]$ in mol/liter, is that of pure water (dilute solution, $y_1 \approx 1$)

$$[H_2O] = \frac{n}{V} = \frac{n}{m}\frac{m}{V} = \frac{\rho}{M} \quad \text{e.g., at 25°C } [H_2O] = \frac{997\,\text{g/liter}}{18\,\text{g/mol}} = 55.4\,\frac{\text{mol}}{\text{liter}}$$

$$\prod_i [N_i]^{\nu_i} = \frac{[H_3O^+][OH^-]}{[H_2O]^2} = K_c(T) \qquad [H_3O^+][OH^-] = K_c(T)\,[H_2O]^2 = K_w(T)$$

At 25 °C, $K_w = 1.01 \times 10^{-14}\,\text{mol}^2/\text{liter}^2$. Notice that this equilibrium condition implies that pH + pOH $\approx$ 14, even when (due to the presence of other ions in the solution) pH $\neq$ pOH. In the absence of other ions, for pure water at 25 °C, pH = pOH = pK_w $\approx$ 7.

| T	0°C	25°C	37°C	100°C
$K_w(T) \times 10^{14}$ in mol^2/liter^2	0.115	1.01	3.55	49.9
$pK_w = -\log_{10}\dfrac{K_w(T)}{1\,\text{mol}^2/\text{liter}^2}$	14.94	14.00	13.45	12.30
pH = pOH of neutral solution	7.47	7.00	6.72	6.15
ρ in g/liter	1000	997	993	959
$K_c(T) \times 10^{11}$	0.355	3.10	10.8	142

Systems with chemical reactions

Chemical kinetics

Potential energy surface and the activated complex (Eyring, 1935)

$$A + BC = ABC^* = AB + C$$
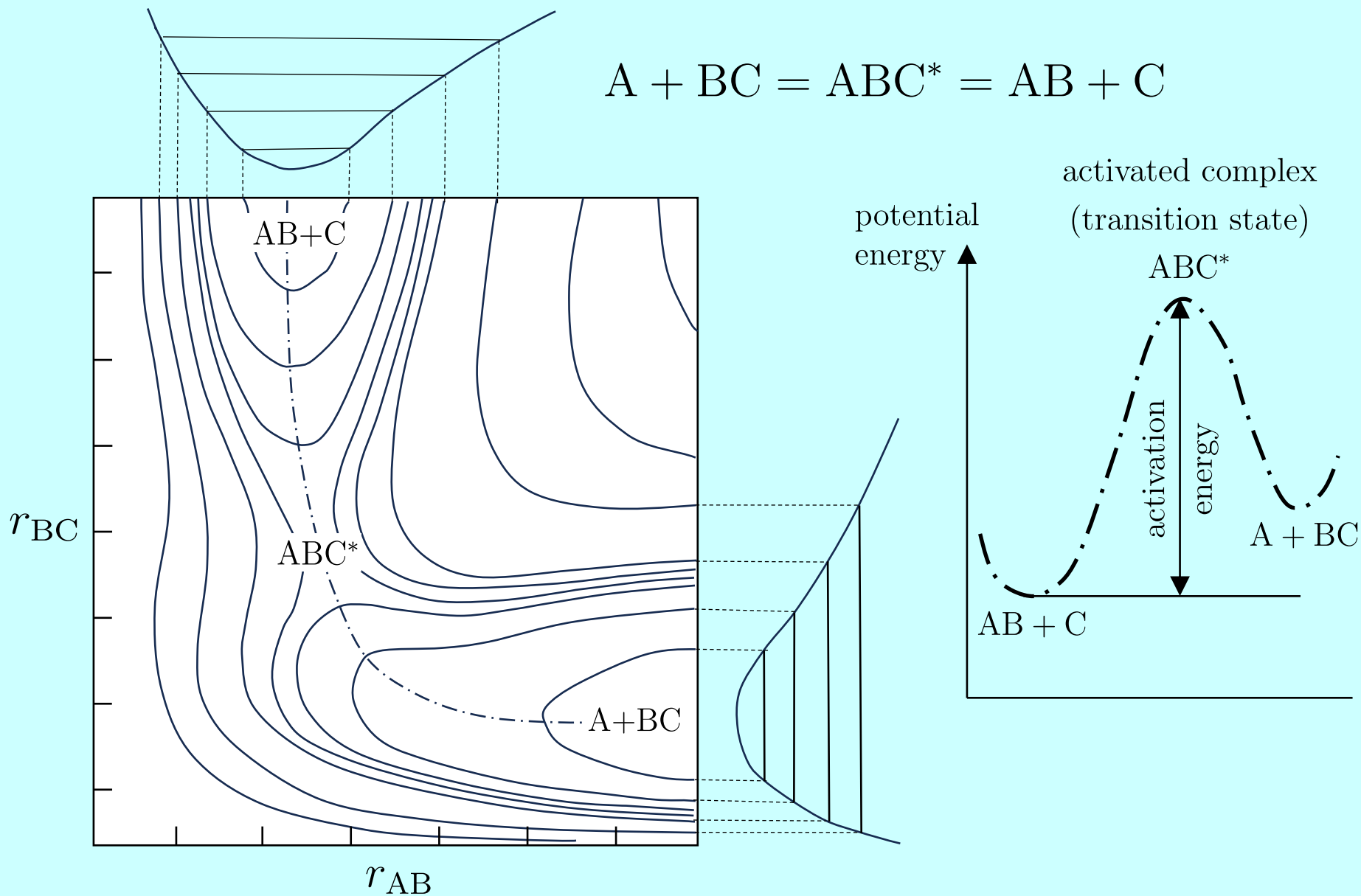
Maxwell-Boltzmann distribution of velocities at SES

determines the probability of collisions with sufficiently high kinetic energy to be chemically effective after which it is rapidly reestablished by non-chemical collisions
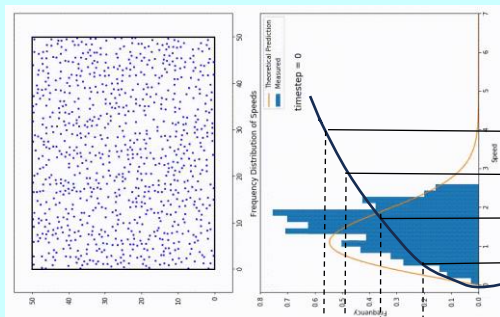
$$f(w) = \left[\frac{m}{2\pi k_{\mathrm{B}}T}\right]^{3/2} \exp\left[-\frac{mw^2}{2k_{\mathrm{B}}T}\right]$$

AB+C

ABC*

A+BC

r_{BC}

r_{AB}
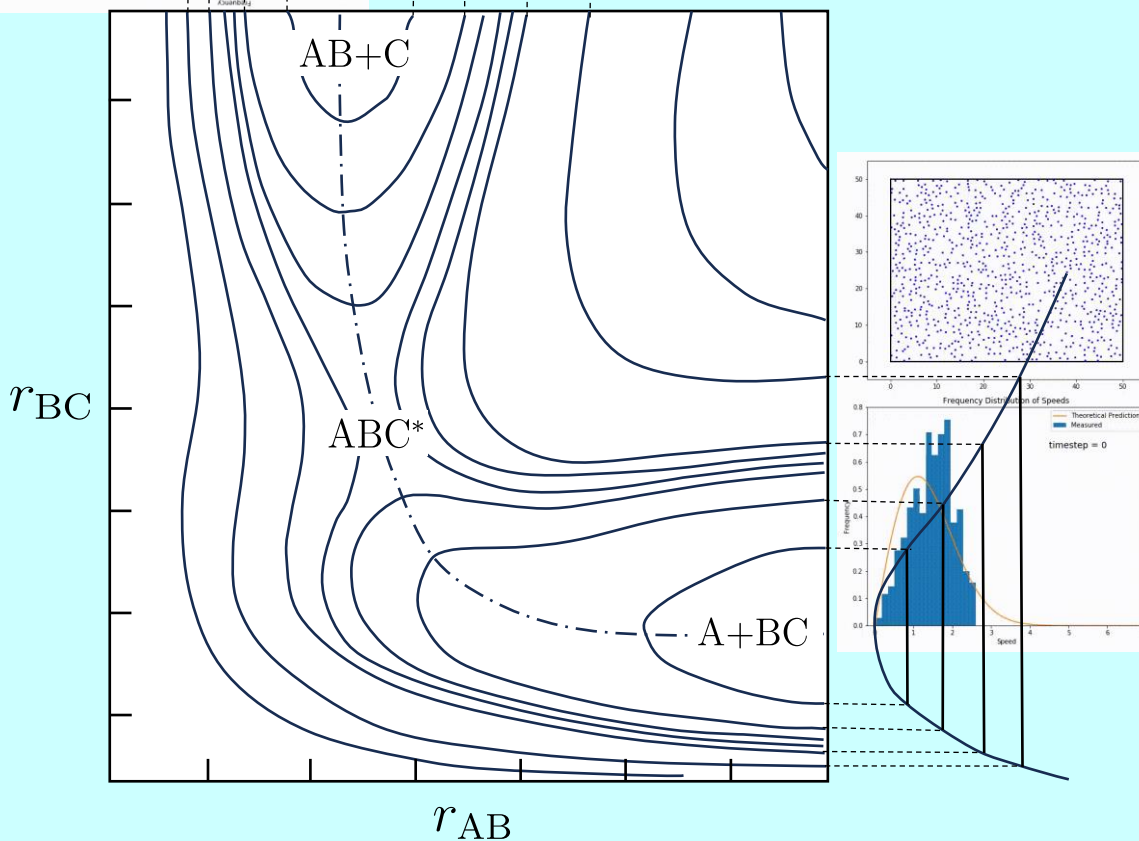
The gif is from Wikipedia (Boltzmann_distribution), Dswarts4, CC BY-SA 4.0

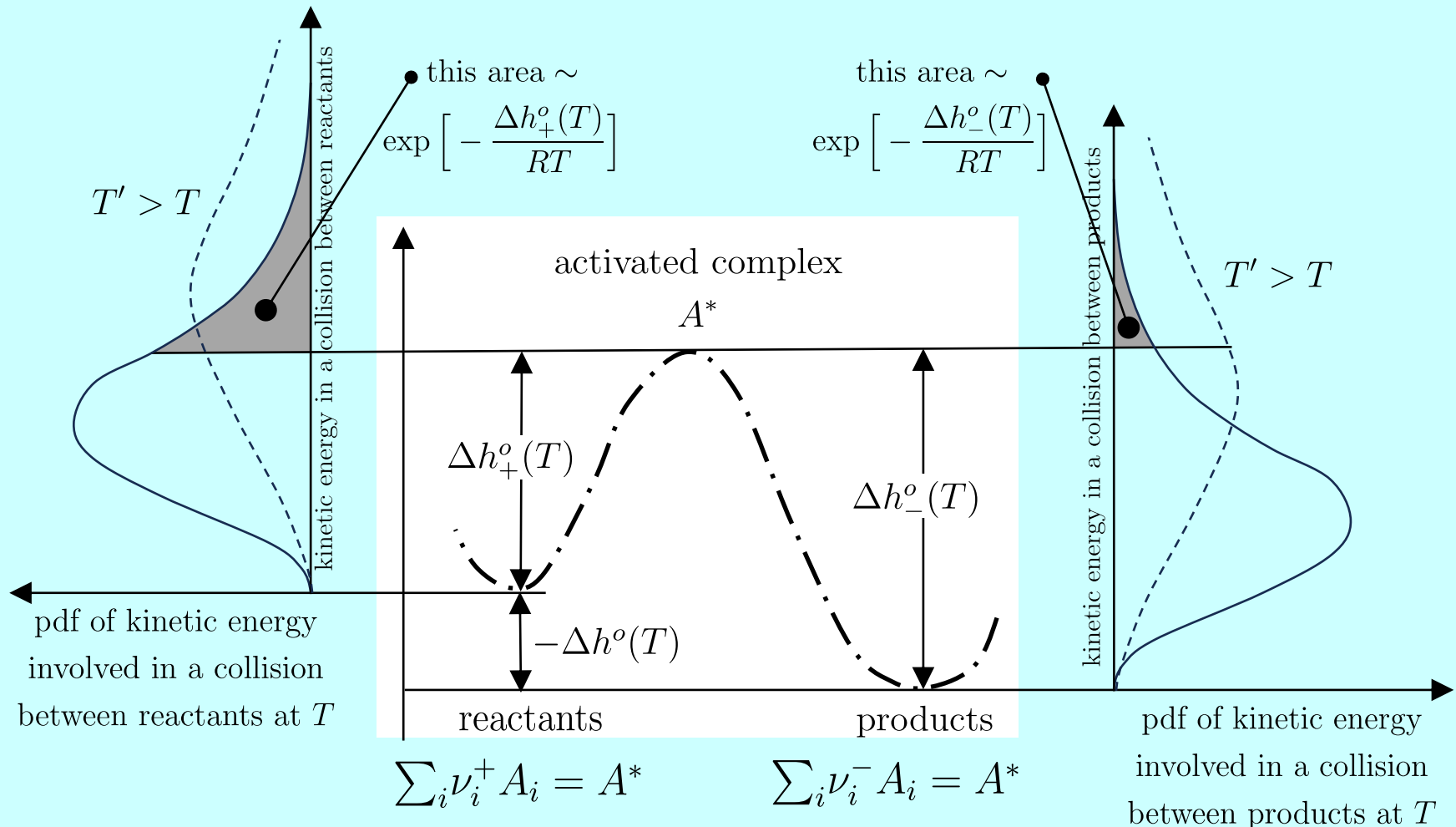# Arrhenius activation barrier

From kinetic theory of collisions and the Maxwell-Boltzmann distribution of velocities at stable equilibrium, the pdf at temperature T of a collision with kinetic energy greater than E_{kin} is

$$\int_{E_{\text{kin}}}^{\infty} \text{pdf}_T(E_{\text{kin}}) \, dE_{\text{kin}} \sim \exp\left[-\frac{E_{\text{kin}}}{RT}\right] \qquad \textbf{Arrhenius law}$$

this area $\sim$

$$\exp\left[-\frac{\Delta h_+^o(T)}{RT}\right]$$

this area $\sim$

$$\exp\left[-\frac{\Delta h_-^o(T)}{RT}\right]$$

$T' > T$

$T' > T$

kinetic energy in a collision between reactants

kinetic energy in a collision between products

activated complex

A^*

$\Delta h_+^o(T)$

$\Delta h_-^o(T)$

$-\Delta h^o(T)$

pdf of kinetic energy involved in a collision between reactants at T

reactants

products

pdf of kinetic energy involved in a collision between products at T

$$\sum_i \nu_i^+ A_i = A^*$$

$$\sum_i \nu_i^- A_i = A^*$$

Forward and backward reaction rates

model based on collision probabilities considerations

Forward half-reaction: $\sum_i \nu_i^+ A_i = A^*, \ \nu_i^+ > 0$

$\exp\left[-\dfrac{\Delta h_+^o(T)}{RT}\right]$ Arrhenius probability of a collision with overall $E_{\text{kin}} > \Delta h_+^o(T)$.

$A^+(T)$ Probability of decay of A^* towards the products.

$\prod_i y_i^{\nu_i^+}$ Probability that the collision involves the necessary molecules.

$\prod_i y_i^{\nu_i^+} = \dfrac{1}{[N]^{\nu^+}} \prod_i [N_i]^{\nu_i^+}$

Backward half-reaction: $\sum_i \nu_i^- A_i = A^*, \ \nu_i^- > 0$

$\exp\left[-\dfrac{\Delta h_+^o(T)}{RT}\right]$ Arrhenius probability of a collision with overall $E_{\text{kin}} > \Delta h_+^o(T)$.

$A^-(T)$ probability of decay of A^* towards the reactants.

$\prod_i y_i^{\nu_i^-}$ Probability that the collision involves the necessary molecules.

$\prod_i y_i^{\nu_i^-} = \dfrac{1}{[N]^{\nu^-}} \prod_i [N_i]^{\nu_i^-}$

$$\dot\epsilon^+ = \underbrace{\frac{A^+(T)}{[N]^{\nu^+}} \exp\left[-\frac{\Delta h_+^o(T)}{RT}\right]}_{k_o^+(T) \text{ forward rate constant}} \prod_i [N_i]^{\nu_i^+}$$

$$\dot\epsilon^- = \underbrace{\frac{A^-(T)}{[N]^{\nu^-}} \exp\left[-\frac{\Delta h_-^o(T)}{RT}\right]}_{k_o^-(T) \text{ backward rate constant}} \prod_i [N_i]^{\nu_i^-}$$

net reaction rate of $\sum_i \nu_i A_i = 0$ with $\nu_i = \nu_i^- - \nu_i^+$: $\dot\epsilon = \dot\epsilon^+ - \dot\epsilon^-$ $\dot n_i = \nu_i \dot\epsilon = (\nu_i^- - \nu_i^+)(\dot\epsilon^+ - \dot\epsilon^-)$

Detailed kinetic mechanism for the oxidation of hydrocarbons

$$k_\ell^+(T) = A_\ell^+ T^{b_\ell^+} \exp\left(-E_\ell^+/RT\right)$$

$$k_\ell^-(T) = k_\ell^+(T)/K_\ell^{co}(T)$$

Hydrogen: K=8 species, I=24 reactions

|	Reactions	A	b	E
1	O+O+M=O2+M	1.20E+17	-1	0
2	O+H+M=OH+M	5.00E+17	-1	0
3	H+H+M=H2+M	1.00E+18	-1	0
4	H+H+H2=H2+H2	9.00E+16	-0.6	0
5	H+H+H2O=H2+H2O	6.00E+19	-1.3	0
6	H+OH+M=H2O+M	2.20E+22	-2	0
7	H+O2+M=HO2+M	2.80E+18	-0.9	0
8	H+O2+O2=HO2+O2	2.08E+19	-1.2	0
9	H+O2+H2O=HO2+H2O	1.13E+19	-0.8	0
10	OH+OH+M=H2O2+M	7.40E+13	-0.4	0
11	O+H2=H+OH	3.87E+04	2.7	6260
12	O+HO2=OH+O2	2.00E+13	0	0
13	O+H2O2=OH+HO2	9.63E+06	2	4000
14	H+O2=O+OH	2.65E+16	-0.7	17041
15	H+HO2=O+H2O	3.97E+12	0	671
16	H+HO2=O2+H2	4.48E+13	0	1068
17	H+HO2=OH+OH	8.40E+13	0	635
18	H+H2O2=HO2+H2	1.21E+07	2	5200
19	H+H2O2=OH+H2O	1.00E+13	0	3600
20	OH+H2=H+H2O	2.16E+08	1.5	3430
21	OH+OH=O+H2O	3.57E+04	2.4	-2110
22	OH+HO2=O2+H2O	1.45E+13	0	-500
23	OH+H2O2=HO2+H2O	2.00E+12	0	427
24	HO2+HO2=O2+H2O2	1.30E+11	0	-1630
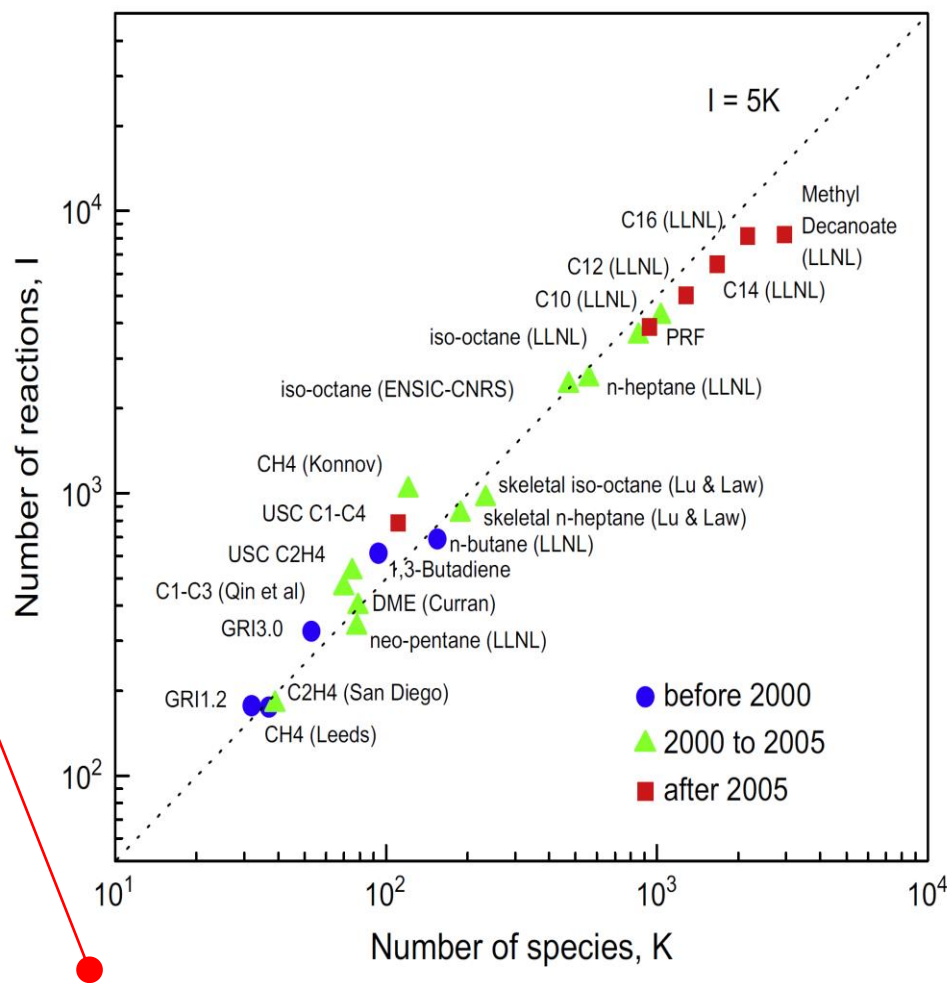
Fig. 10. Size of selected detailed and skeletal mechanisms for hydrocarbon fuels, together with the approximate years when the mechanisms were compiled.

Fig.10 in T. Lu and C.K. Law, Progress in Energy and Combustion Science 35, 192 (2009).

Principle of detailed balance and degree of disequilibrium

Recall: $\quad \dot{\epsilon}^+ = k_o^+(T) \prod_i [N_i]^{\nu_i^+} \, (> 0), \quad \dot{\epsilon}^- = k_o^-(T) \prod_i [N_i]^{\nu_i^-} \, (> 0), \quad \nu_i = \nu_i^- - \nu_i^+$

$$\prod_i [N_i]^{\nu_i} = K^c(T) \exp\left[-\frac{Y}{R}\right] \qquad K^c(T) = \left[\frac{p_o}{RT}\right]^\nu \exp\left[-\frac{\Delta g^o(T)}{RT}\right]$$

In general

$$\frac{\dot{\epsilon}^-}{\dot{\epsilon}^+} = \frac{k_o^-(T) \prod_i [N_i]^{\nu_i^-}}{k_o^+(T) \prod_i [N_i]^{\nu_i^+}} = \frac{k_o^-(T)}{k_o^+(T)} \prod_i [N_i]^{\nu_i} = \frac{k_o^-(T)}{k_o^+(T)} K^c(T) \exp\left[-\frac{Y}{R}\right]$$

This holds also at chemical equilibrium, where we have $Y = 0$ and $\dot{\epsilon}_o^- = \dot{\epsilon}_o^+$, therefore

$$1 = \frac{\dot{\epsilon}_o^-}{\dot{\epsilon}_o^+} = \frac{k_o^-(T) \prod_i [N_i]^{\nu_i^-}}{k_o^+(T) \prod_i [N_i]^{\nu_i^+}} = \frac{k_o^-(T)}{k_o^+(T)} \prod_i [N_i]^{\nu_i} = \frac{k_o^-(T)}{k_o^+(T)} K^c(T)$$

implying the following relations (the first is the **principle of detailed balance**)

$$\underbrace{k_o^-(T) = \frac{k_o^+(T)}{K^c(T)}}_{\substack{\text{backward rate constant from} \\ \text{forward rate constant and} \\ \text{equilibrium constant}}} \qquad \underbrace{\frac{\dot{\epsilon}^-}{\dot{\epsilon}^+} = \exp\left[-\frac{Y}{R}\right]}_{\text{fluctuation relation}} \qquad \underbrace{\text{DoD} \overset{\text{def}}{=} \frac{Y}{R} = \ln\frac{\dot{\epsilon}^+}{\dot{\epsilon}^-}}_{\substack{\text{degree of} \\ \text{disequilibrium}}}$$

Sign of the affinity, direction of reaction, and fluctuation relation

For a single mechanism, the rate of change of the entropy due to the chemical reaction is

$$\left.\frac{\partial S}{\partial t}\right|_{\text{chem}} = Y\dot{\epsilon} = (\dot{\epsilon}^+ - \dot{\epsilon}^-)Y = R(\dot{\epsilon}^+ - \dot{\epsilon}^-)\ln\frac{\dot{\epsilon}^+}{\dot{\epsilon}^-} \geq 0$$

for an isolated system, the entropy balance requires

$$\left.\frac{\partial S}{\partial t}\right|_{\text{chem}} = \dot{S}_{\text{irr}}$$

The sign of Y determines the net direction of the reaction. We may define the competing contributions to the entropy production of the forward and backward reaction, $\dot{S}^+ = Y\dot{\epsilon}^+$ and $\dot{S}^- = Y\dot{\epsilon}^-$, and write

$$\left.\frac{\partial S}{\partial t}\right|_{\text{chem}} = \dot{S}^+ - \dot{S}^-$$

The forward and backward rates, $\dot{\epsilon}^+$ and $\dot{\epsilon}^-$, are both positive by definition, and related by the fluctuation relation (recall that $Y = Y^+ - Y^-$)

$$\frac{\dot{S}^-}{\dot{S}^+} = \frac{\dot{\epsilon}^-}{\dot{\epsilon}^+} = \exp\left[-\frac{Y}{R}\right] = \exp\left[\frac{Y^- - Y^+}{R}\right] = \exp(-\text{DoD}) = \frac{\exp(\text{DoD}^-)}{\exp(\text{DoD}^+)}$$

Since both $\dot{S}^+$ and $\dot{S}^-$ have the same sign as Y, in order to have $\partial S/\partial t|_{\text{chem}} \geq 0$
for $Y > 0$ (i.e., $Y^+ > Y^-$), we need $\dot{\epsilon}^+ > \dot{\epsilon}^- > 0$, so that $\dot{S}^+ > \dot{S}^- > 0$;
for $Y < 0$, (i.e., $Y^- > Y^+$), we need $\dot{\epsilon}^- > \dot{\epsilon}^+ > 0$, so that $\dot{S}^- < \dot{S}^+ < 0$;
for $Y = 0$, (i.e., $Y^- = Y^+$), we need $\dot{\epsilon}^+ = \dot{\epsilon}^- > 0$, so that $\dot{S}^- = \dot{S}^+ = 0$.

Forward and backward reaction rates

model based on hypothetical half-equilibrium concentrations of the activated complex

Recall the nonequilibrium law of mass action (in terms of concentrations)

$$\prod_i [N_i]^{\nu_i} = K^c(T) \exp\left[-\frac{Y}{R}\right] \qquad \text{where } Y = -\frac{1}{T}\sum_i \nu_i \mu_i = Y^+ - Y^- \qquad \text{for reaction } \sum_i \nu_i A_i = 0$$

we may write it also for the half-reactions of formation of the activated complex A_* ($\nu_i = \nu_i^- - \nu_i^+$)

$$\frac{[N_*]}{\prod_i [N_i]^{\nu_i^\pm}} = K_\pm^c(T) \exp\left[-\frac{Y_\pm}{R}\right] \quad \text{where } Y_\pm = -\frac{1}{T}\left[\mu_* - \sum_i \nu_i^\pm \mu_i\right] \text{ for reactions } -\sum_i \nu_i^\pm A_i + A^* = 0$$

Denote by $[N_*]_\pm^{\text{eq}}$ the hypothetical concentrations that would obtain if $Y_\pm = 0$, respectively, i.e.,

$$[N_*]_\pm^{\text{eq}} = K_\pm^c(T) \prod_i [N_i]^{\nu_i^\pm} \qquad \text{therefore we can rewrite the above as } [N_*] = [N_*]_\pm^{\text{eq}} \exp\left[-\frac{Y_\pm}{R}\right]$$

$$\Rightarrow \quad \frac{[N_*]_-^{\text{eq}}}{[N_*]_+^{\text{eq}}} = \exp\left[-\frac{Y}{R}\right] \quad \text{or} \quad \boxed{\text{DoD} = \frac{Y}{R} = \ln\frac{[N_*]_+^{\text{eq}}}{[N_*]_-^{\text{eq}}}} \quad \left(\begin{array}{l}\text{at equil.} \\ (Y=0)\end{array} \ [N_*]_+^{\text{eq}}|_o = [N_*]_-^{\text{eq}}|_o = [N_*]_o\right)$$

Assume that the forward and backward reaction rates are proportional to the hypothetical equilibrium concentrations $[N_*]_\pm^{\text{eq}}$ of the activated complex

$$\dot{\epsilon}^\pm = \kappa_\pm [N_*]_\pm^{\text{eq}} \qquad \kappa_\pm = \text{ frequency of forward/backward decay of } A^*$$

$$\Rightarrow \quad \dot{\epsilon}^\pm = \underbrace{\kappa_\pm K_\pm^c(T)}_{k_o^\pm(T)} \prod_i [N_i]^{\nu_i^\pm} \qquad \frac{\dot{\epsilon}^-}{\dot{\epsilon}^+} = \frac{\kappa^-}{\kappa^+}\frac{[N_*]_-^{\text{eq}}}{[N_*]_+^{\text{eq}}} = \frac{\kappa^-}{\kappa^+}\exp\left[-Y/R\right]$$

This holds also at chemical equilibrium, where we have $Y = 0$ and $\dot{\epsilon}_o^- = \dot{\epsilon}_o^+$, therefore, the **principle of detailed balance** takes the form $\kappa^- = \kappa^+$, so that $\dot{\epsilon} = \kappa\left[K_+^c(T) - K_-^c(T)\right]$.

Partial shifting chemical equilibrium
assuming some reactions equilibrate much faster than the others

$$\frac{\partial S}{\partial t}\bigg|_{\text{chem}} = \sum_{j=1}^{\text{z}} \left(\frac{\partial S_{\boldsymbol{\epsilon}}^{\text{on}}}{\partial \epsilon_j}\right)_{U,V,\boldsymbol{n}_a,\boldsymbol{\nu}} \dot{\epsilon}_j = \sum_{j=1}^{\text{z}} Y_j\, \dot{\epsilon}_j = \boldsymbol{Y}\cdot\dot{\boldsymbol{\epsilon}}$$

Assume we can identify a subset of reactions that are much faster than the others

$$\frac{\partial S}{\partial t}\bigg|_{\text{chem}} = \sum_{j=1}^{\text{z}_{\text{slow}}} Y_j\, \dot{\epsilon}_j + \sum_{k=1}^{\text{z}_{\text{fast}}} Y_k\, \dot{\epsilon}_k = \boldsymbol{Y}_{\text{slow}}\cdot\dot{\boldsymbol{\epsilon}}^{\text{slow}} + \boldsymbol{Y}_{\text{fast}}\cdot\dot{\boldsymbol{\epsilon}}^{\text{fast}}$$

$$\boldsymbol{n}(t) = \underbrace{\boldsymbol{n}_a + \boldsymbol{\nu}_{\text{slow}}\cdot\boldsymbol{\epsilon}^{\text{slow}}(t)}_{\text{slowly shifting}} + \boldsymbol{\nu}_{\text{fast}}\cdot\boldsymbol{\epsilon}^{\text{fast}}(t)$$

Assume the z_{fast} fast reactions are at equilibrium, i.e., their z_{fast} reaction coordinates are

$$\boldsymbol{\epsilon}^{\text{fast}}(t) = \boldsymbol{\epsilon}_o^{\text{fast}}\left(U, V, \boldsymbol{n}_a + \boldsymbol{\nu}^{\text{slow}}\cdot\boldsymbol{\epsilon}^{\text{slow}}(t)\right)$$

where $\boldsymbol{\epsilon}_o^{\text{fast}}$ is obtained, at each time t, by the solution of the system of z_{fast} equilibrium conditions

$$\boldsymbol{Y}^{\text{fast}}\left(U, V, \boldsymbol{n}_a + \boldsymbol{\nu}^{\text{slow}}\cdot\boldsymbol{\epsilon}^{\text{slow}}(t) + \boldsymbol{\nu}_{\text{fast}}\cdot\boldsymbol{\epsilon}_o^{\text{fast}}\right) = 0$$

As a result, the affinities of the z_{slow} slow reactions

$$\boldsymbol{Y}^{\text{slow}} = \boldsymbol{Y}^{\text{slow}}\left(U, V, \boldsymbol{n}_a + \boldsymbol{\nu}^{\text{slow}}\cdot\boldsymbol{\epsilon}^{\text{slow}}(t) + \boldsymbol{\nu}_{\text{fast}}\cdot\boldsymbol{\epsilon}_o^{\text{fast}}\left(U, V, \boldsymbol{n}_a + \boldsymbol{\nu}^{\text{slow}}\cdot\boldsymbol{\epsilon}^{\text{slow}}(t)\right)\right)$$
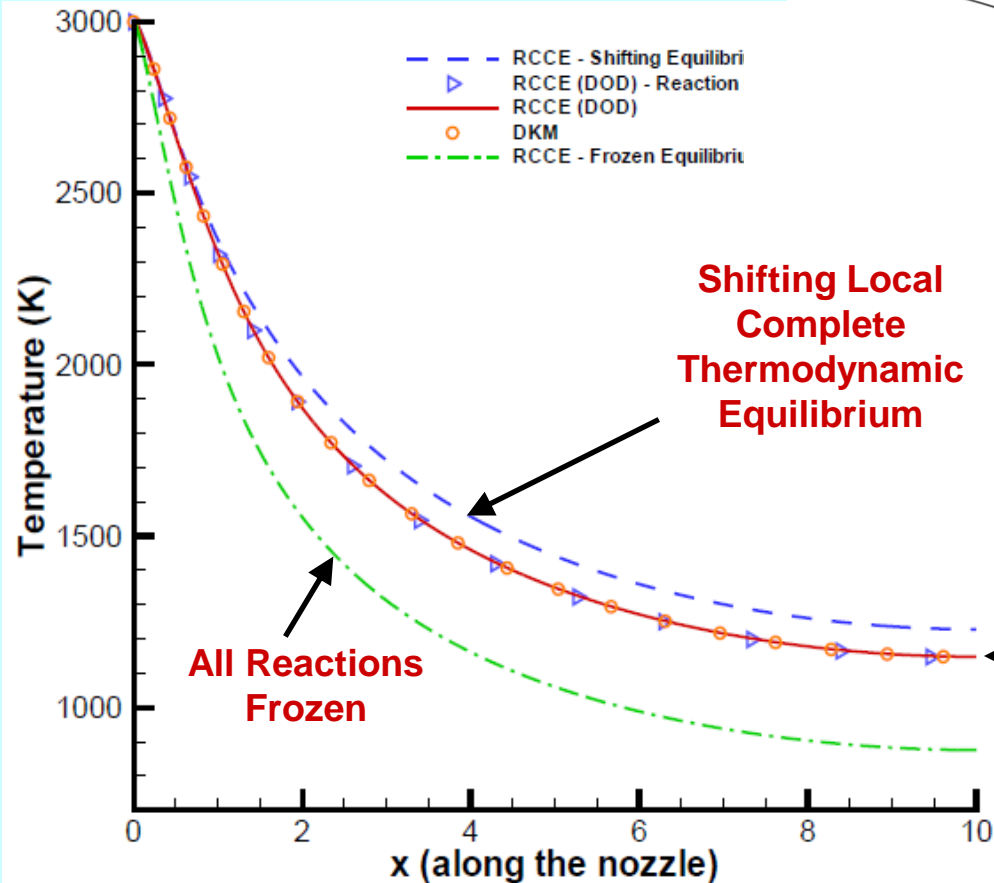
Nonequilibrium build up in rapid supersonic nozzle expansion

of high-temperature products of hydrogen oxy-combustion

Products of H_2-O_2 combustion enter nozzle at chemical equilibrium:

Ma =1
T = 3000 K
p = 2.5 MPa

Ma ~ 4
T ~ 1000 K
p ~ 10 kPa

Shifting Local Complete Thermodynamic Equilibrium

All Reactions Frozen

Full Detailed Kinetic Model (8 species, 24 reactions)
Rate Controlled Costrained Equilibrium Model (8 species, 2+2 constraints)

DoD build up in rapid supersonic nozzle expansion
of high-temperature products of hydrogen oxy-combustion

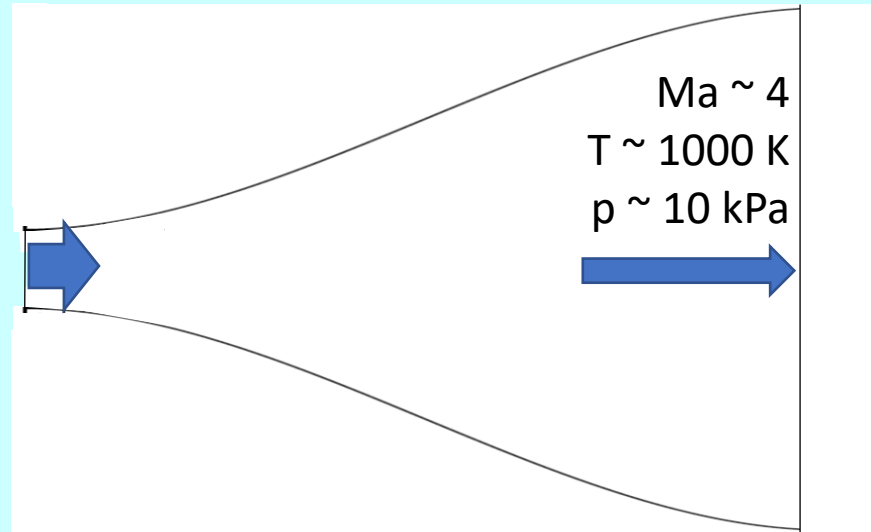Products of H_2-O_2 combustion enter nozzle at chemical equilibrium:

Short residence time (few ms).
Chemistry does not keep up.
Composition goes off equilibrium.
Degrees of disequilibrium build up.

Ma = 1
T = 3000 K
p = 2.5 MPa

Ma ~ 4
T ~ 1000 K
p ~ 10 kPa

2B: Two-body reactions

	M=0, FO-FV=0
11	O+H2=H+OH
13	O+H2O2=OH+HO2
14	H+O2=O+OH
18	H+H2O2=HO2+H2
20	OH+H2=H+H2O
21	OH+OH=O+H2O
23	OH+H2O2=HO2+H2O

	M=0, FO-FV=2
12	O+HO2=OH+O2
15	H+HO2=O+H2O
16	H+HO2=O2+H2
17	H+HO2=OH+OH
19	H+H2O2=OH+H2O
22	OH+HO2=O2+H2O
24	HO2+HO2=O2+H2O2

3B: Three-body reactions

	M=-1, FO-FV=0
7	H+O2+M=HO2+M
8	H+O2+O2=HO2+O2
9	H+O2+H2O=HO2+H2O
10	OH+OH+M=H2O2+M

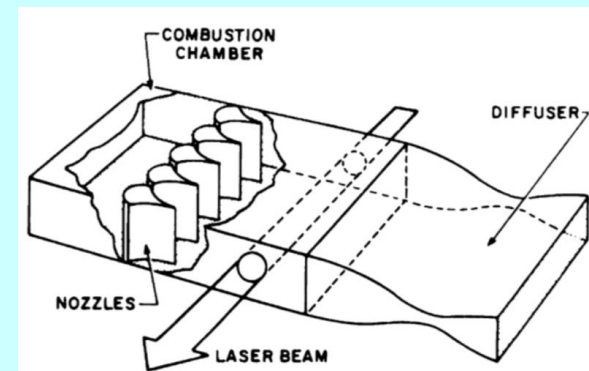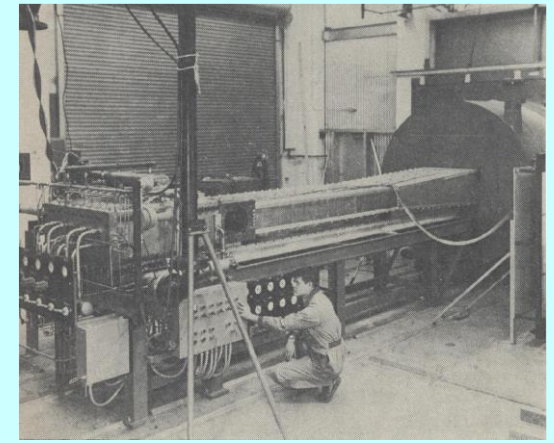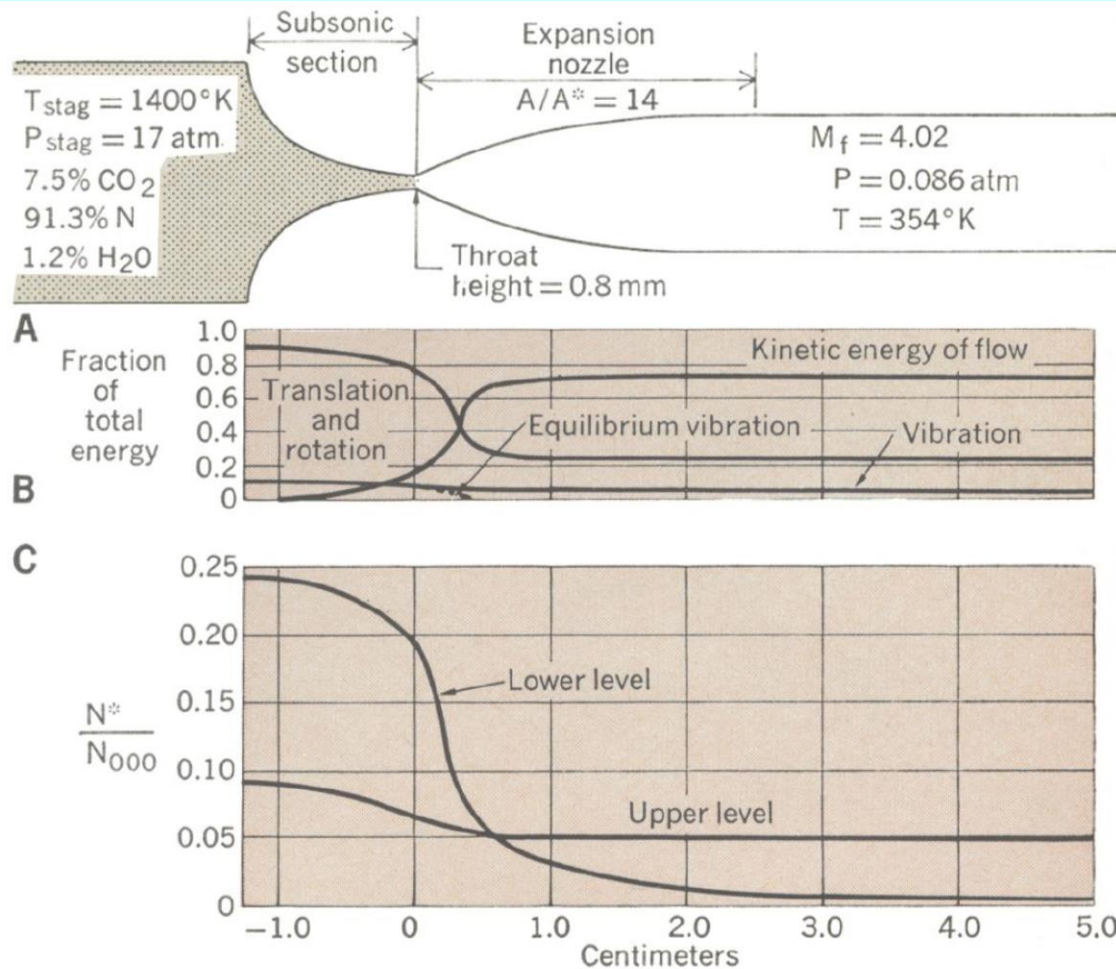|	M=-1, FO-FV=2
1	O+O+M=O2+M
2	O+H+M=OH+M
3	H+H+M=H2+M
4	H+H+H2=H2+H2
5	H+H+H2O=H2+H2O
6	H+OH+M=H2O+M

all DoD's = 0

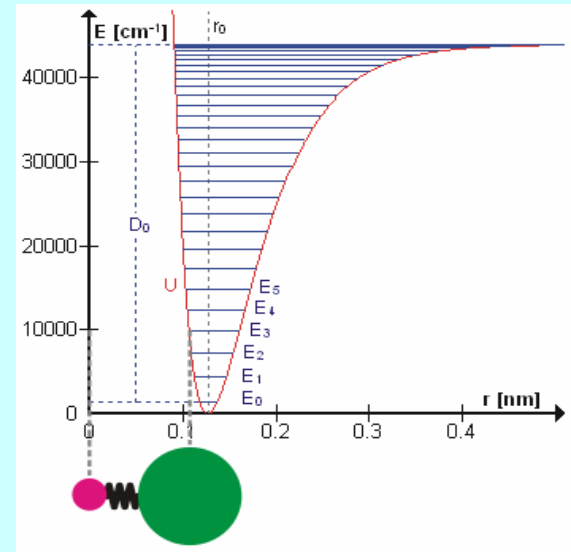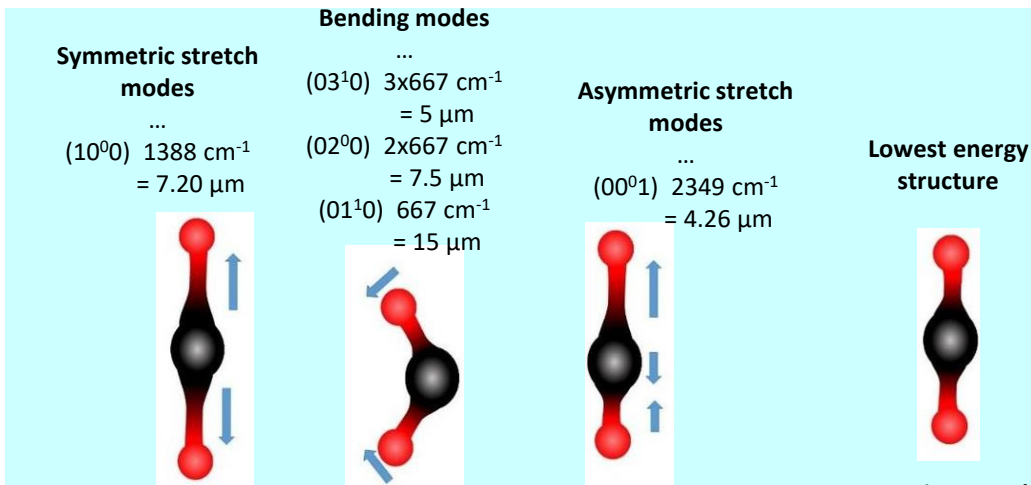**The composition is thrown out of equilibrium due to rapid expansion**
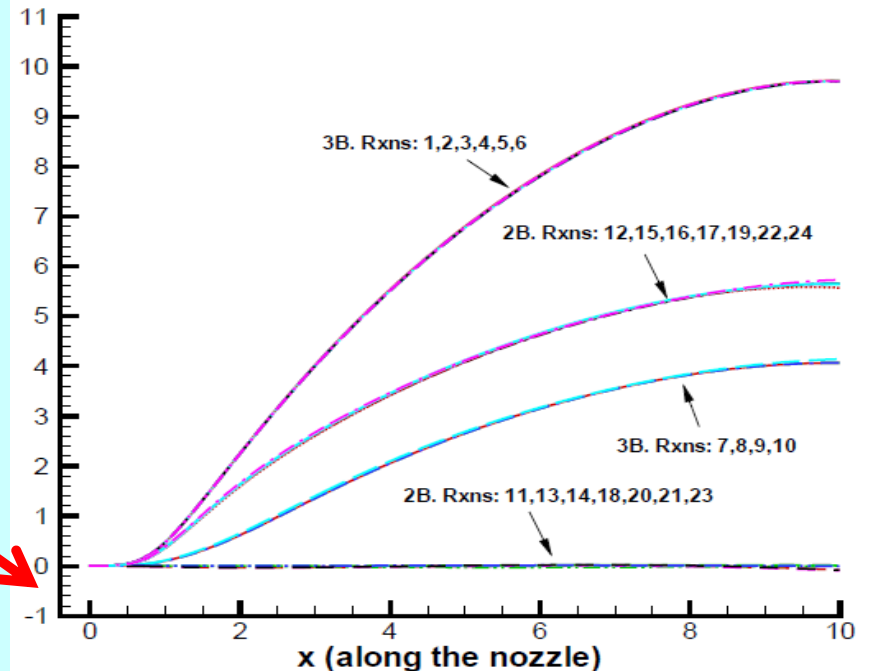
3B. Rxns: 1,2,3,4,5,6
2B. Rxns: 12,15,16,17,19,22,24
3B. Rxns: 7,8,9,10
2B. Rxns: 11,13,14,18,20,21,23

x (along the nozzle)

Nonequilibrium gasdynamic N_2-CO_2 infrared power laser

$T_{stag} = 1400°K$
$P_{stag} = 17$ atm.
7.5% CO_2
91.3% N
1.2% H_2O

Subsonic section

Expansion nozzle
$A/A^* = 14$

$M_f = 4.02$
$P = 0.086$ atm
$T = 354°K$

Throat height = 0.8 mm

A — Fraction of total energy

Kinetic energy of flow
Translation and rotation
Equilibrium vibration
Vibration

B

C — $\dfrac{N^*}{N_{000}}$

Lower level
Upper level

Centimeters

COMBUSTION CHAMBER
DIFFUSER
NOZZLES
LASER BEAM

Figures and text adapted from: E.T. Gerry, Gasdynamic Lasers, IEEE Spectrum, Vol.7, 51 (1970).
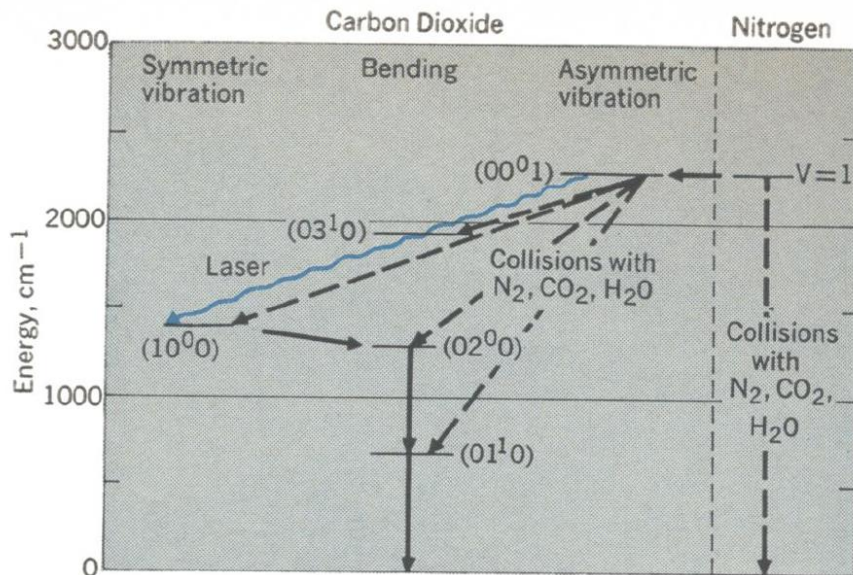
In the stagnation region, most of the energy is associated with the random translation and rotation of the gas molecules and 10 percent (or less) is associated with vibration. As the gas is expanded through the supersonic nozzle, the random translational and rotational energies are converted into the directed kinetic energy of flow. The vibrational energy, if it remained in equilibrium with the gas temperature, essentially would disappear downstream of the nozzle. Because of the rapid expansion, however, the excited vibrational energy levels take longer to equilibrate than the translational/rotational degrees of freedom, and so a "population inversion" obtains about 1 cm downstream of the throat and remains for about 1 m downstream. With inverted population, stimulated emission prevails on absorption, leading to amplification of the beam of coherent photons.

Vibrational levels of the CO2 molecule

Symmetric stretch modes
...
(10^00) 1388 cm^{-1}
= 7.20 µm

Bending modes
...
(03^10) 3x667 cm^{-1}
= 5 µm
(02^00) 2x667 cm^{-1}
= 7.5 µm
(01^10) 667 cm^{-1}
= 15 µm

Asymmetric stretch modes
...
(00^01) 2349 cm^{-1}
= 4.26 µm

Lowest energy structure

GIF by Darekk2 from Wikipedia

Lasing wavelength
(2349-1388) cm^{-1}
= 10.4 µm
(infrared)
(visible 3.8—7.4 µm)

FIGURE 2. Exchanges between energy levels in a CO₂-N₂ laser. Sequential numbers relate respectively to asymmetric-stretch, bending, and symmetric-stretch mode levels. Superscript accompanying bending mode indicates the plane of vibration. V = 1 denotes first excited vibrational state.

There are three mechanisms by which vibrational energy levels of the molecules interact with radiation:

PARTICLE DROPS DOWN. PHOTON IS EMITTED WITH ENERGY $h\nu = \varepsilon_2 - \varepsilon_1$. IT CAN BE EMITTED IN ANY DIRECTION	Spontaneous emission
INCOMING PHOTON OF FREQUENCY $\nu = (\varepsilon_2 - \varepsilon_1)/h$. PARTICLE DROPS DOWN. TWO PHOTONS OF EXACTLY SAME FREQUENCY, IN PHASE WITH AND IN SAME DIRECTION AS INCOMING PHOTON	Stimulated emission
INCOMING PHOTON OF FREQUENCY $\nu = (\varepsilon_2 - \varepsilon_1)/h$. PARTICLE MOVES UP	Absorption

Figures and text adapted from: E.T. Gerry, Gasdynamic Lasers, IEEE Spectrum, Vol.7, 51 (1970).

Nonequilibrium gasdynamic N_2-CO_2 infrared power laser
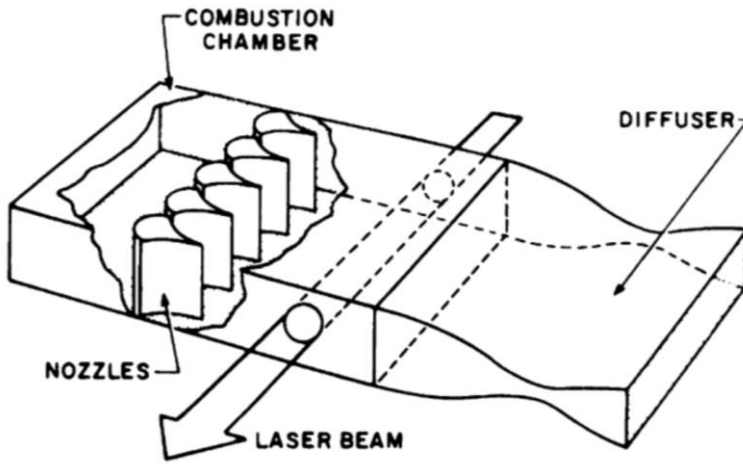
Gerry at AVCO Everett in 1970 reports a continuous output of 60kW. Nitrogen, a simple diatomic molecule, has only one vibrational mode. Energy can be lost from this mode by collisions with nitrogen, CO2, and H2O, returning the energy molecule excited directly to the ground state.

Carbon dioxide, being a linear triatomic molecule, has three basic modes of vibration: asymmetric stretch, which forms the upper laser level; symmetric stretch, which forms the lower laser level; and bending.
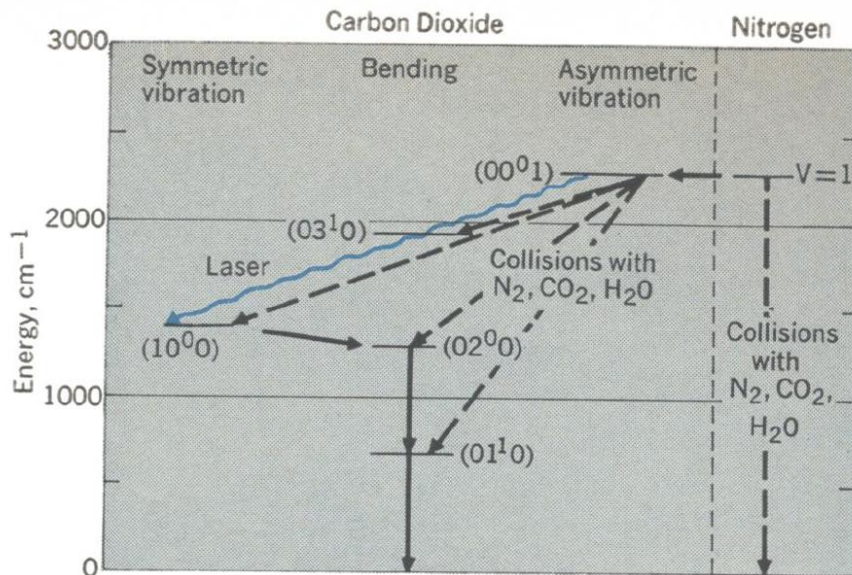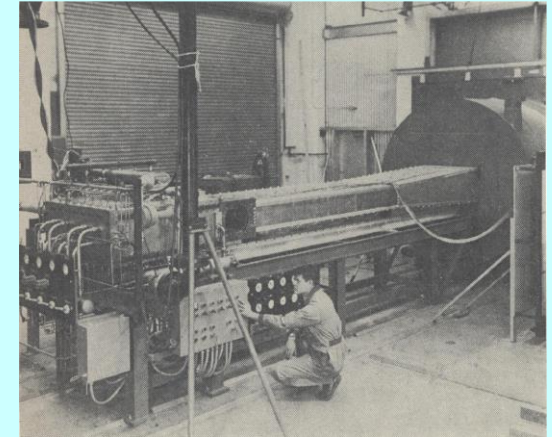
FIGURE 2. Exchanges between energy levels in a CO₂-N₂ laser. Sequential numbers relate respectively to asymmetric-stretch, bending, and symmetric-stretch mode levels. Superscript accompanying bending mode indicates the plane of vibration. V = 1 denotes first excited vibrational state.

There are three mechanisms by which vibrational energy levels of the molecules interact with radiation:

PHOTON IS EMITTED WITH ENERGY $h\nu = \varepsilon_2 - \varepsilon_1$. IT CAN BE EMITTED IN ANY DIRECTION	Spontaneous emission
INCOMING PHOTON OF FREQUENCY $\nu = (\varepsilon_2 - \varepsilon_1)/h$. TWO PHOTONS OF EXACTLY SAME FREQUENCY, IN PHASE WITH AND IN SAME DIRECTION AS INCOMING PHOTON	Stimulated emission
INCOMING PHOTON OF FREQUENCY $\nu = (\varepsilon_2 - \varepsilon_1)/h$	Absorption

Figures and text adapted from: E.T. Gerry, Gasdynamic Lasers, IEEE Spectrum, Vol.7, 51 (1970).

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Gif animation showing Boltzmann distribution courtesy of Dswartz4 on Wikipedia. License: CC BY-SA. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use.

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Image showing size of selected detailed and skeletal mechanisms for hydrocarbon fuels, together with the approximate years when the mechanisms were compiled courtesy Elsevier, Inc., https://www.sciencedirect.com. Used with permission.

Slides 19–21:

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2.43 Advanced Thermodynamics
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