Outline

	Date	Class #			Comb. Lecture	Problem Due
Nov	11	19	√	Concepts, Candle, Fireplace, Premixed, Diffusion	1	
	13	20	√	Heats of Formation, Heats of Reaction, Heat Capacities, Enthalpies	2	#1
	18	21	√	Stoichiometry, Equilibrium Constants	3	#2,#3
	20	22	√	Adiabatic Flame Temperature, Multi-Compo Equilibrium, NASA-Lewis Code	4	#4
	27			BYU Friday, **NO Class**		
	29			**Thanksgiving**		
Dec	2	25	√	Heterogeneous	5	#5
	4		→	NO_x Mec Soot	6	#6
	9	27		Turbulence, Explosions	7	#7
	11	28		ew	8	#8

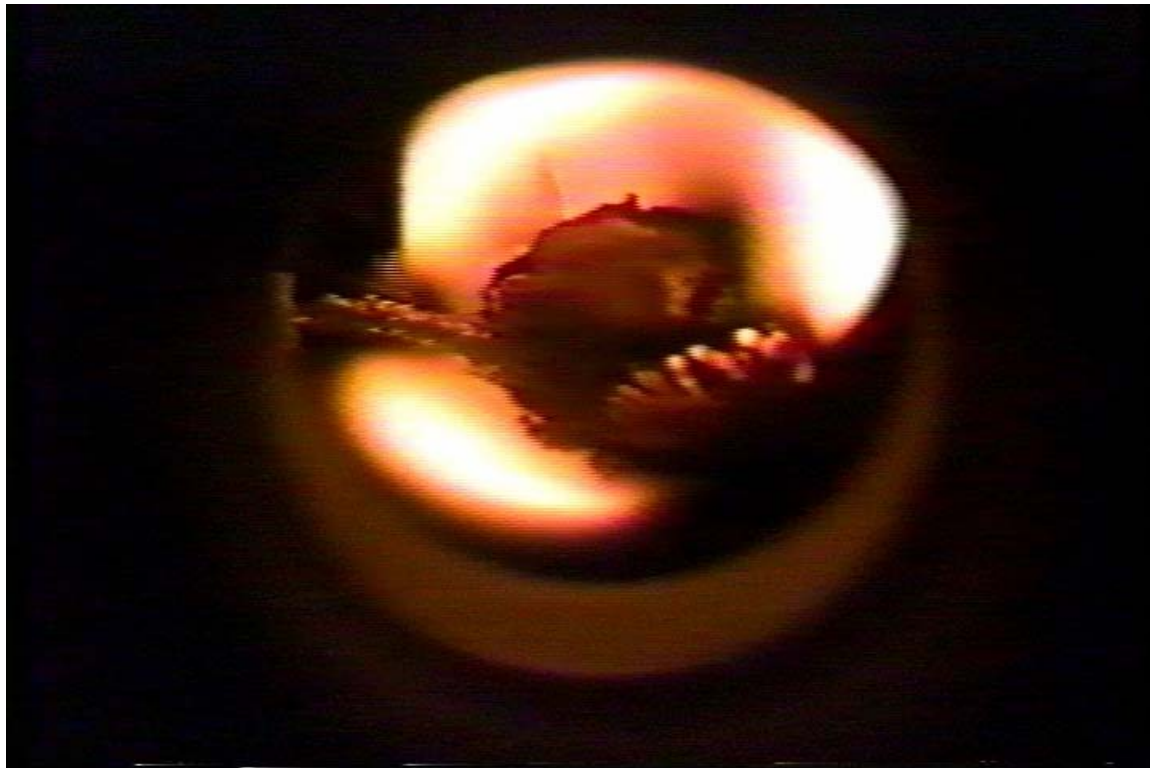**Only one more lecture class after today!**

Combustion Kinetics
Combustion Class 6

- ## Heterogeneous kinetics
  - ### Chemical reaction rate
  - ### Mass transfer rate

- ## Homogeneous kinetics
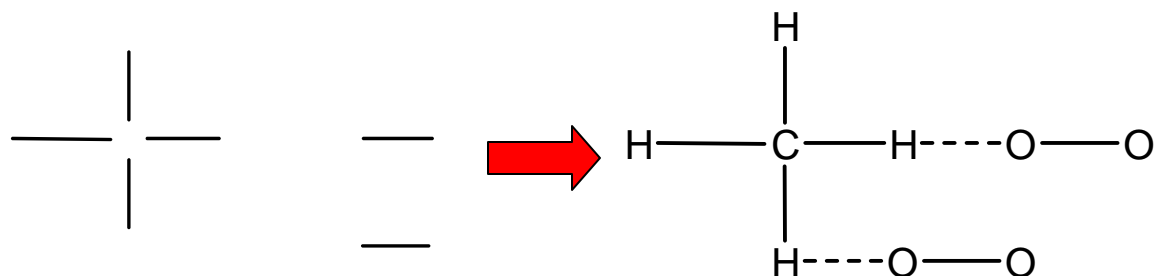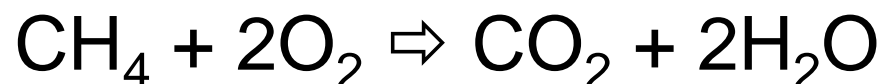 - ### Importance of radicals
  - ### Examples
  - ### NO_x

Heterogeneous Kinetics
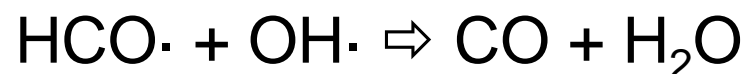
Board Discussion

Elementary Step Reactions

- How does the chemistry really happen?

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

??? Very unlikely!

More Realistic Chemistry

$CH_4 + OH\cdot \Rightarrow CH_3\cdot + H_2O$

$H_2O \Rightarrow OH\cdot + H\cdot$

$CH_3\cdot + O_2 \Rightarrow CH_3O\cdot + O\cdot$

$CH_3O\cdot \Rightarrow CH_2O + H\cdot$

$CH_2O + O\cdot \Rightarrow HCO\cdot + OH\cdot$

$HCO\cdot + OH\cdot \Rightarrow CO + H_2O$
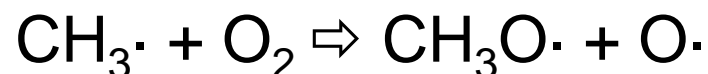
etc.....

Bottom Line:

- These <u>are</u> elementary steps
  - Chemistry happens!
- Lots of radical chemistry in flames
- High temperatures necessary to maintain radical pool
- This is why flames go out when cooled!

TABLE 2. The Westbrook and Dryer Comprehensive Mechanism for Methanol Oxidation

Reaction	log A	n	E_a	Reference[b]
2.1 $CH_3OH + M \rightarrow CH_3 + OH + M$	18.5	0	80.0	This study
2.2 $CH_3OH + O_2 \rightarrow CH_2OH + HO_2$	13.6	0	50.9	Aronowitz et al. (1978)
2.3 $CH_3OH + OH \rightarrow CH_2OH + H_2O$	12.6	0	2.0	This study
2.4 $CH_3OH + O \rightarrow CH_2OH + OH$	12.2	0	2.3	LeFevre et al. (1972)
2.5 $CH_3OH + H \rightarrow CH_2OH + H_2$	13.5	0	7.0	This study
2.6 $CH_3OH + H \rightarrow CH_3 + H_2O$	12.7	0	5.3	This study
2.7 $CH_3OH + CH_3 \rightarrow CH_2OH + CH_4$	11.3	0	9.8	Gray and Herod (1968)
2.8 $CH_3OH + HO_2 \rightarrow CH_2OH + H_2O_2$	12.8	0	19.4	Aronowitz et al. (1978)
2.9 $CH_2OH + M \rightarrow CH_2O + H + M$	13.4	0	29.0	This study
2.10 $CH_3OH + O_2 \rightarrow CH_2O + HO_2$	12.0	0	6.0	Aronowitz et al. (1978)
2.11 $CH_4 + M \rightarrow CH_3 + H + M$	17.1	0	88.4	Hartig et al. (1971)
2.12 $CH_4 + H \rightarrow CH_3 + H_2$	14.1	0	11.9	Baldwin et al. (1970a)
2.13 $CH_4 + OH \rightarrow CH_3 + H_2O$	3.5	3.08	2.0	Zellner and Steinert (1976)
2.14 $CH_4 + O \rightarrow CH_3 + OH$	13.2	0	9.2	Herron (1969)
2.15 $CH_4 + HO_2 \rightarrow CH_3 + H_2O_2$	13.3	0	18.0	Skinner et al. (1972)
2.16 $CH_3 + HO_2 \rightarrow CH_3O + OH$	13.2	0	0.0	Colket (1975)
2.17 $CH_3 + OH \rightarrow CH_2O + H_2$	12.6	0	0.0	Fenimore (1969)
2.18 $CH_3 + O \rightarrow CH_2O + H$	14.1	0	2.0	Peeters and Mahnen (1973)
2.19 $CH_3 + O_2 \rightarrow CH_2O + O$	13.4	0	29.0	Brabbs and Brokaw (1975)
2.20 $CH_2O + CH_3 \rightarrow CH_4 + HCO$	10.0	0.5	6.0	Tunder et al.
2.21 $CH_3 + HCO \rightarrow CH_4 + CO$	11.5	0.5	0.0	Tunder et al.
2.22 $CH_3 + HO_2 \rightarrow CH_4 + O_2$	12.0	0	0.4	Skinner et al. (1972)
2.23 $CH_3O + M \rightarrow CH_2O + H + M$	13.7	0	21.0	Brabbs and Brokaw (1975)
2.24 $CH_3O + O_2 \rightarrow CH_2O + HO_2$	12.0	0	6.0	Engleman (1976)
2.25 $CH_2O + M \rightarrow HCO + H + M$	16.7	0	72.0	Schecker and Jost (1969)
2.26 $CH_2O + OH \rightarrow HCO + H_2O$	14.7	0	6.3	Bowman (1975)
2.27 $CH_2O + H \rightarrow HCO + H_3$	12.6	0	3.8	Westenberg and deHaas (1972a)
2.28 $CH_2O + O \rightarrow HCO + OH$	13.7	0	4.6	Bowman (1975)
2.29 $CH_2O + HO_2 \rightarrow HCO + H_2O_2$	12.0	0	8.0	Lloyd (1974)
2.30 $HCO + OH \rightarrow CO + H_2O$	14.0	0	0.0	Bowman (1970)
2.31 $HCO + M \rightarrow H + CO + M$	14.2	0	19.0	Westbrook et al. (1977)
2.32 $HCO + H \rightarrow CO + H_2$	14.3	0	0.0	Niki et al. (1969)
2.33 $HCO + O \rightarrow CO + OH$	14.0	0	0.0	Westenberg and deHaas (1972b)
2.34 $HCO + HO_2 \rightarrow CH_2O + O_2$	14.0	0	3.0	Baldwin and Walker (1973)
2.35 $HCO + O_2 \rightarrow CO + HO_2$	12.5	0	7.0	Westbrook et al. (1977)
2.36 $CO + OH \rightarrow CO_2 + H$	7.1	1.3	-0.8	Baulch and Drysdale (1974)
2.37 $CO + HO_2 \rightarrow CO_2 + OH$	14.0	0	23.0	Baldwin et al. (1970b)
2.38 $CO + O + M \rightarrow CO_2 + M$	15.8	0	4.1	Simonaitis and Heicklen (1972)
2.39 $CO_2 + O \rightarrow CO + O_2$	12.4	0	43.8	Gardiner et al. (1971)
2.40 $H + O_2 \rightarrow O + OH$	14.3	0	16.8	Baulch et al. (1973a)
2.41 $H_2 + O \rightarrow H + OH$	10.3	1	8.9	Baulch et al. (1973b)
2.42 $H_2O + O \rightarrow OH + OH$	13.5	0	18.4	Baulch et al. (1973b)
2.43 $H_2O + H \rightarrow H_2 + OH$	14.0	0	20.3	Baulch et al. (1973b)

TABLE 2.   *(Continued)*

Reaction	log A	n	E_a	Reference[b]
2.44 $H_2O_2 + OH \rightarrow H_2O + HO_2$	13.0	0	1.8	Baulch et al. (1973b)
2.45 $H_2O + M \rightarrow H + OH + M$	16.3	0	105.1	Baulch et al. (1973b)
2.46 $H + O_2 + M \rightarrow HO_2 + M$	15.2	0	-1.0	Baulch et al. (1973b)
2.47 $HO_2 + O \rightarrow OH + O_2$	13.7	0	1.0	Lloyd (1974)
2.48 $HO_2 + H \rightarrow OH + OH$	14.4	0	1.9	Baulch et al. (1973b)
2.49 $HO_2 + H \rightarrow H_2 + O_2$	13.4	0	0.7	Baulch et al. (1973b)
2.50 $HO_2 + OH \rightarrow H_2O + O_2$	13.7	0	1.0	Lloyd (1974)
2.51 $H_2O_2 + O_2 \rightarrow HO_2 + HO_2$	13.6	0	42.6	Lloyd (1974)
2.52 $H_2O_2 + M \rightarrow OH + OH + M$	17.1	0	45.5	Baulch et al. (1973b)
2.53 $H_2O_2 + H \rightarrow HO_2 + H_2$	12.2	0	3.8	Baulch et al. (1973b)
2.54 $O + H + M \rightarrow OH + M$	16.0	0	0.0	Moretti (1965)
2.55 $O_2 + M \rightarrow O + O + M$	15.7	0	115.0	Jenkins et al. (1967)
2.56 $H_2 + M \rightarrow H + H + M$	14.3	0	96.0	Baulch et al. (1973b)
2.57 $C_2H_6 \rightarrow CH_3 + CH_3$	19.4	-1	88.3	Pacey (1973)
2.58 $C_2H_6 + CH_3 \rightarrow C_2H_5 + CH_4$	-0.3	4	8.3	Clark and Dove (1973)
2.59 $C_2H_6 + H \rightarrow C_2H_5 + H_2$	2.7	3.5	5.2	Clark and Dove (1973)
2.60 $C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	13.8	0	2.4	Greiner (1970)
2.61 $C_2H_6 + O \rightarrow C_2H_5 + OH$	13.4	0	6.4	Herron and Huie (1973)
2.62 $C_2H_5 \rightarrow C_2H_4 + H$	13.6	0	38.0	Lin and Back (1966)
2.63 $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	12.0	0	5.0	Cooke and Williams (1971)
2.64 $C_2H_5 + C_2H_3 \rightarrow C_2H_4 + C_2H_4$	17.5	0	35.6	Benson and Haugen (1967)
2.65 $C_2H_4 + O \rightarrow CH_3 + HCO$	13.0	0	1.1	David et al. (1972)
2.66 $C_2H_4 + M \rightarrow C_2H_3 + H + M$	17.6	0	98.2	Just et al. (1977)
2.67 $C_2H_4 + H \rightarrow C_2H_3 + H_2$	13.8	0	6.0	Benson and Haugen (1967)
2.68 $C_2H_4 + OH \rightarrow C_2H_3 + H_2O$	14.0	0	3.5	Baldwin et al. (1966)
2.69 $C_2H_4 + O \rightarrow CH_2O + CH_2$	13.4	0	5.0	Peeters and Mahnen (1973)
2.70 $C_2H_3 + M \rightarrow C_2H_2 + H + M$	16.5	0	40.5	Benson and Haugen (1967)
2.71 $C_2H_2 + M \rightarrow C_2H + H + M$	14.0	0	114.0	Jachimowski (1977)
2.72 $C_2H_2 + O_2 \rightarrow HCO + HCO$	12.6	0	28.0	Gardiner and Walker (1968)
2.73 $C_2H_2 + H \rightarrow C_2H + H_2$	14.3	0	19.0	Browne et al. (1969)
2.74 $C_2H_2 + OH \rightarrow C_2H + H_2O$	12.8	0	7.0	Vandooren and Van Tiggelen (1977)
2.75 $C_2H_2 + O \rightarrow C_2H + OH$	15.5	-0.6	17.0	Browne et al. (1969)
2.76 $C_2H_2 + O \rightarrow CH_2 + CO$	13.8	0	4.0	Vandooren and Van Tiggelen (1977)
2.77 $C_2H + O_2 \rightarrow HCO + CO$	13.0	0	7.0	Browne et al. (1969)
2.78 $C_2H + O \rightarrow CO + CH$	13.7	0	0.0	Browne et al. (1969)
2.79 $CH_2 + O_2 \rightarrow HCO + OH$	14.0	0	3.7	Benson and Haugen (1967)
2.80 $CH_2 + O \rightarrow CH + OH$	11.3	0.68	25.0	Mayer et al. (1967)
2.81 $CH_2 + H \rightarrow CH + H_2$	11.4	0.67	25.7	Mayer et al. (1967)
2.82 $CH_2 + OH \rightarrow CH + H_2O$	11.4	0.67	25.7	Peeters and Vinckier (1975)
2.83 $CH + O_2 \rightarrow CO + OH$	11.1	0.67	25.7	Peeters and Vinckier (1975)
2.84 $CH + O_2 \rightarrow HCO + O$	13.0	0	0.0	Jachimowski (1977)

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[a]Units are cm-mol-s-kcal. $k = AT^n \exp(-Ea/rT)$

[b]References refer to sources noted in the original article.

Detailed Premixed Flame Measurements
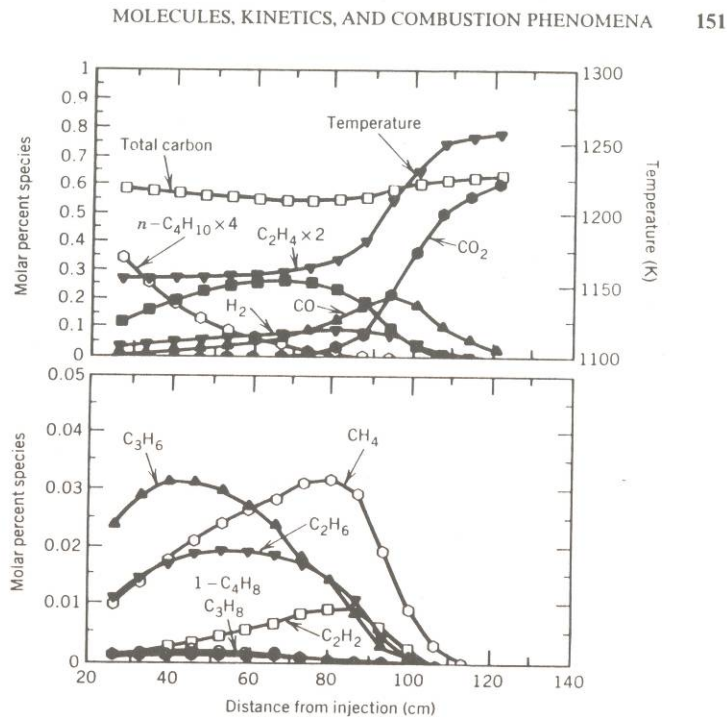
A. Propane/Air

B. Butane/Air

FIGURE 11. Species evolution for the reaction of *n*-butane and oxygen as a function of reaction distance. Data are from the Princeton Flow Reactor, for an initial equivalence ratio of 0.80, an initial reaction temperature of 1155 K, and atmospheric pressure. A distance of 1.0 cm corresponds to approximately 0.67 msec of reaction time. Figure from Ref. 54.
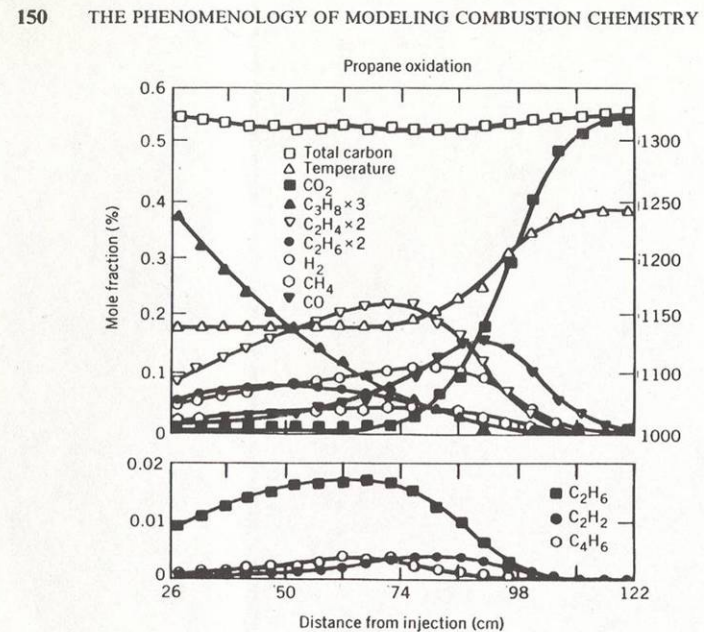
FIGURE 10. Species evolution for the reaction of propane and oxygen as a function of reaction distance. Data are from the Princeton Flow Reactor, for an initial equivalence ratio of 0.82, an initial reaction temperature of 1138 K, and atmospheric pressure. A distance of 1.0 cm corresponds to approximately 0.90 msec of reaction time. Figure from Ref. 53.

From F. L. Dryer, "The Phenomenology of Modeling Combustion Chemistry," in *Fossil Fuel Combustion: A Source Book*, edited by W. Bartok and A. F. Sarofim, John Wiley & Sons, New York (1991).

$$C_nH_{2(n+1)} + \frac{2(n+1)}{2}O_2 \rightarrow (n+1)H_2O + nCO \tag{67}$$

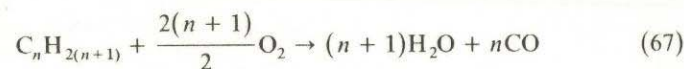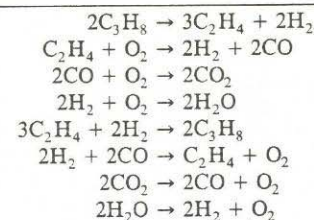$$CO + \frac{1}{2}O_2 = CO_2 \tag{68}$$

TABLE 7. Parameters for Two-Step Reaction Mechanism, Giving Best Agreement between Experimental and Computed Flammability Limits[a]

Fuel	A	E_a	a	b
CH_4	2.8×10^9	48.4	-0.3	1.3
CH_4	1.5×10^7	30.0	-0.3	1.3
C_2H_6	1.3×10^{12}	30.0	0.1	1.65
C_3H_8	1.0×10^{12}	30.0	0.1	1.65
C_4H_{10}	8.8×10^{11}	30.0	0.15	1.6
C_5H_{12}	7.8×10^{11}	30.0	0.25	1.5
C_6H_{14}	7.0×10^{11}	30.0	0.25	1.5
C_7H_{16}	6.3×10^{11}	30.0	0.25	1.5
C_8H_{18}	5.7×10^{11}	30.0	0.25	1.5
C_8H_{18}	9.6×10^{12}	40.0	0.25	1.5
C_9H_{20}	5.2×10^{11}	30.0	0.25	1.5
$C_{10}H_{22}$	4.7×10^{11}	30.0	0.25	1.5
CH_3OH	3.7×10^{12}	30.0	0.25	1.5
C_2H_5OH	1.8×10^{12}	30.0	0.15	1.6
C_6H_6	2.4×10^{11}	30.0	-0.1	1.85
C_7H_8	1.9×10^{11}	30.0	-0.1	1.85

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[a]Same units as in Table 6.

TABLE 8. Summary of the Modified Four-Step, Reversible Mechanism for Laminar Flames of Propane and Air

$$2C_3H_8 \rightarrow 3C_2H_4 + 2H_2$$
$$C_2H_4 + O_2 \rightarrow 2H_2 + 2CO$$
$$2CO + O_2 \rightarrow 2CO_2$$
$$2H_2 + O_2 \rightarrow 2H_2O$$
$$3C_2H_4 + 2H_2 \rightarrow 2C_3H_8$$
$$2H_2 + 2CO \rightarrow C_2H_4 + O_2$$
$$2CO_2 \rightarrow 2CO + O_2$$
$$2H_2O \rightarrow 2H_2 + O_2$$

With rate expressions:

$$R_1 = f_1(P)2.089 \times 10^{17} \exp(-49{,}600/RT)[C_3H_8]^{0.50}[O_2]^{1.07}[C_2H_4]^{0.40}$$

$$R_2 = f_2(P)2 \times 10^{13} \exp(-50{,}000/RT)[C_2H_4]^{0.90}[O_2]^{1.18}[C_3H_8]^{-0.37}$$

$$R_3 = S(\phi)1.5 \times 10^{13} \exp(-40{,}000/RT)[CO]^{1.0}[O_2]^{0.25}[H_2O]^{0.50}$$

$$R_4 = 3.311 \times 10^{13} \exp(-38{,}100/RT)[H_2]^{0.85}[O_2]^{1.42}[C_2H_4]^{-0.56}$$

$$R_5 = 4.920 \times 10^8 \exp(-49{,}600/RT)[C_3H_8]^{0.127}[O_2]^{1.07}[C_2H_4]^{0.40}$$

$$R_6 = 2.25 \times 10^9 \exp(-50{,}000/RT)[C_2H_4]^{0.528}[O_2]^{1.18}[C_3H_8]^{-0.37}$$

$$R_7 = 4.16 \times 10^{16}T^{-1/2}\exp(-106{,}950/RT)[CO_2]^{1.0}[O_2]^{-0.25}[H_2O]^{0.50}$$

$$R_8 = 6.12 \times 10^{15}T^{-1/2}\exp(-100{,}586/RT)[H_2]^{-0.153}[O_2]^{0.916}[C_2H_4]^{-0.563}[H_2O]^{1.0},$$

where

$$f_1(P) = 6.434P^{-0.8116}$$
$$f_2(P) = 1.115 - 1.125e^{-0.251}$$
$$S(\phi) = \min[1.0, 16.0\exp(-2.48\phi)]$$

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From F. L. Dryer, "The Phenomenology of Modeling Combustion Chemistry," in *Fossil Fuel Combustion: A Source Book*, edited by W. Bartok and A. F. Sarofim, John Wiley & Sons, New York (1991).

NO_x
(Nitrogen Oxides from Combustion)

A. Thermal NO_x

- $N_2 + O_2 \rightarrow 2NO$ (involves N, O, and OH radicals)
- Nitrogen and oxygen only, no other major species
- Dominant source of NO_x in gaseous hydrocarbon combustion (methane, etc.)

B. Fuel NO_x

- Nitrogen in fuel $\rightarrow$ NO, NO_2 and N_2O
- Example: pyridine combustion (⬡), coal combustion
- Dominant source of NO_x in coal combustion

C. Prompt NO_x

- CH or CH_2 + N_2 $\rightarrow$ HCN $\rightarrow$ NO, etc.
- Hard to quantify because radical concentrations are generally unknown
- Not usually a dominant source of NO_x in combustion

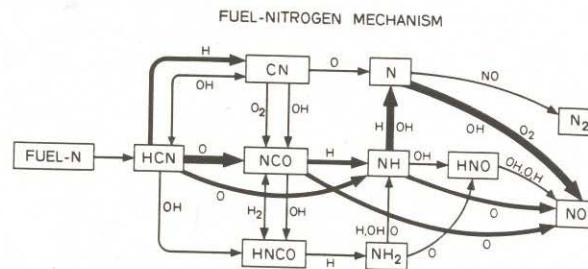242   CHEMISTRY OF GASEOUS POLLUTANT FORMATION AND DESTRUCTION

FIGURE 12. Schematic diagram of the principal reaction paths in the fuel nitrogen conversion process in flames.

FORMATION AND DESTRUCTION OF NITROGEN OXIDES IN FLAMES   233

TABLE 10. Rate Coefficients for Thermal NO Formation Reactions[a]

Reaction Number	Reaction	A	B	$C(K)$
18	$O + N_2 \rightarrow NO + N$	1.8(11)	0	38.4(3)
−19	$O + NO \rightarrow N + O_2$	3.8(6)	1.0	20.8(3)
−20	$H + NO \rightarrow OH + N$	2.6(11)	0	25.4(3)

[a]From Hanson and Salimian.[26] Units: kgmol, m³, K, sec; $k = AT^B \exp(-C/T)$.

3.1. Thermal NO Formation

The three principal reactions that comprise the thermal NO formation mechanism are

$$O + N_2 \rightleftarrows NO + N \tag{18}$$

$$N + O_2 \rightleftarrows NO + O \tag{19}$$

$$N + OH \rightleftarrows NO + H \tag{20}$$

The rate coefficients for both the forward and reverse reactions have been measured over a wide temperature range (Table 10).[26]

Invoking a steady-state approximation for the N-atom concentration[*] and assuming that reaction (9) is partially equilibrated, the NO formation rate due to the thermal mechanism may be expressed,

$$\frac{d(NO)}{dt} = 2k_{18}(O)(N_2)\frac{1 - (NO)^2/K(O_2)(N_2)}{1 + k_{-18}(NO)/[k_{19}(O_2) + k_{20}(OH)]} \tag{21}$$

where $K = (k_{18}/k_{-18})(k_{19}/k_{-19})$ = equilibrium constant for the reaction $N_2 + O_2 \rightleftarrows 2NO$. Calculation of the NO formation rate requires values of the local temperature and the local concentrations of O_2, N_2, O, and OH.
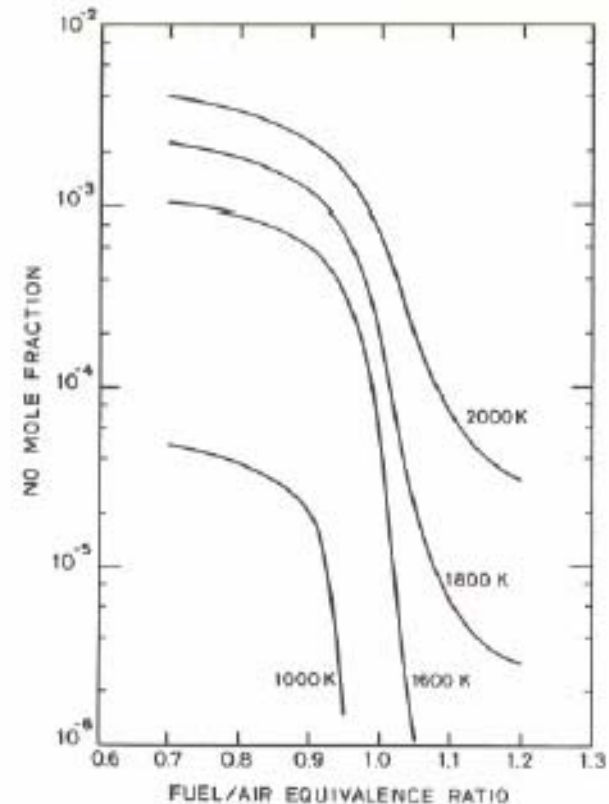

FIGURE 5. Equilibrium NO mole fractions for premixed methane-air combustion at a pressure of 1 atm.

From F. L. Dryer, "The Phenomenology of Modeling Combustion Chemistry," in *Fossil Fuel Combustion: A Source Book*, edited by W. Bartok and A. F. Sarofim, John Wiley & Sons, New York (1991).

FATE OF NITROGEN OXIDES IN THE ATMOSPHERE

$$O_2 + h\nu \rightarrow O + O$$

$$O + O_2 \xrightarrow{M} O_3$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2$$

$$\overline{O + O_3 \rightarrow O_2 + O_2}$$

+ O

Ozone Layer

Stratosphere

25 Km

ULTRAVIOLET SUNLIGHT ENERGY

PRODUCT O_2

NO_2

NO

R

O

RO

AIR (O_2)

O_3

AIR (O_2)

Troposphere

N_2O

$\tau \sim 100$ yrs

I R Radiation