AER 1304 Fundamentals of Combustion
Fall 2013

Instructor	Prof. Ömer L. Gülder Room 111, Institute for Aerospace Studies Phone: 416-667-7721, ogulder (at) utias.utoronto.ca
T.A.	Parsa Tamadonfar UTIAS Combustion & Propulsion Lab. Parsa.tamadonfar (at) utoronto.ca
Course Objectives	The main aim is to provide the required foundation for graduate students involved in research on any aspects of reacting flows, propulsion, and combustion. The main emphasis of the course is on the aerothermochemistry of the propulsion systems as well as on the fundamental principles of combustion. It also introduces the students to laser-based measurements in aerodynamics, fluid mechanics, and combustion.
Class Hours	Thursdays 14:00-17:00 at UTIAS Lecture Hall First meeting: Thursday September 19, 2013 at 14:00, Lecture Hall
Office Hours	I am in my office or at the Combustion Lab most of the time. My office door is open when I am in. If you wish, you can arrange an appointment. Electronic-communication is encouraged.
Class Members	I will update the information on the course webpage related to class rescheduling, assignments, and any other urgent matters. http://arrow.utias.utoronto.ca/~ogulder/AER1304.htm
Prerequisites	Undergraduate Thermodynamics, Fluid Mechanics, and Heat Transfer (or equivalent subjects with the consent of the instructor)
Grading	30% Midterm Test (November 07, 2013) 20% Assignments 50% Final Exam (December 05, 2013)
Assignments	Problem sets will be assigned periodically. It is highly recommended that you try to solve yourself the assigned problem sets.
Required Textbook	S. R. Turns, *An Introduction to Combustion*, 3rd Edition, McGraw Hill, 2011 (NOTE: 2nd Edition of the same book is acceptable).
Suggested Reading	1. I. Glassman and R. A. Yetter, *Combustion*, 4th Edition, Academic Press, 2008. 2. F. A. Williams, *Combustion Theory*, 2nd Edition,

Benjamin/Cummings, 1988.

3. N. Peters, *Turbulent Combustion*, Cambridge University Press, 2000.
4. J. Warnatz, U. Maas, and R. W. Dibble, *Combustion*, 2nd or later editions, Springer, 1999.
5. J. M. Beér, and N. A Chigier, *Combustion Aerodynamics*, Applied Science, 1972.

COURSE DESCRIPTION

This course starts with a review of chemical thermodynamics, statistical mechanics, equilibrium chemistry, chemical kinetics, and conservation equations. Then the following subjects are covered: chemical and dynamic structure of laminar premixed, diffusion, and partially premixed flames; turbulent premixed combustion; turbulent diffusive combustion in one and two-phase flows; aerodynamics and stabilization of flames; ignition, extinction and combustion instabilities; non-intrusive combustion diagnostics and flame spectroscopy.

TENTATIVE COURSE OUTLINE

I. Review and Background

1. Review of thermodynamics and statistical mechanics
2. Chemical kinetics of combustion
3. Conservation equations
4. Rankine-Hugoniot Relations

II. Laminar Flames

1. Premixed flames
2. Diffusion (non-premixed) flames
3. Partially premixed flames

III. Turbulent Combustion

1. Premixed flames
2. Diffusion flames
3. Partially premixed flames
4. Droplet and spray combustion
5. Flame stabilization

IV. Combustion Instabilities

V. Combustion Measurements

1. Flow field diagnostics
2. Temperature diagnostics
3. Chemical species diagnostics
4. Particle and spray diagnostics

Tentative Schedule

SUBJECT	Lecture Dates [hrs]	Chapter in Textbook	Comments
0. INTRODUCTION	Sept. 19 [1]		
1. REVIEW OF COMBUSTION THERMOCHEMISTRY [4]	Sept. 19 [2] Sept. 26 [1]	Ch#2 Lecture Notes	
2. REVIEW OF CHEMICAL KINETICS AND COMBUSTION CHEMISTRY [3]	Sept. 26 [2] Oct. 03 [1]	Ch#4,5	
3. TRANSPORT PHENOMENA [3]	Oct. 03 [2] Oct. 10 [1]	Ch#3,6	
4. PREMIXED COMBUSTION [4]	Oct. 10 [2] Oct. 17 [1]	Ch#8,(11)12 Lecture Notes	
5. NON-PREMIXED (DIFFUSION) FLAMES [5]	Oct. 17 [2] Oct. 24 [1]	Ch#9,(10)13	
6. DETONATIONS [3]	Oct. 24 [2] Oct. 31 [1]	Ch#16 Lecture Notes	
REVIEW AND TUTORIAL	Oct. 31 [2]		
♣ MIDTERM TEST ♣	Nov. 07 [2.5]		Subjects 1 to 4
7. COMBUSTION ENGINES	Nov. 14 [3]	Lecture Notes	
8. POLLUTANT FORMATION [3]	Nov. 21 [3]	Ch#15	
9. COMBUSTION MEASUREMENTS	Nov. 28 [3]	Lecture Notes	TENTATIVE
♣ FINAL EXAM ♣	Dec. 05 [3]		Subjects 1 to 8

What is Combustion?

Combustion is a key element of many of modern society's critical technologies. Combustion accounts for approximately 85 percent of the world's energy usage and is vital to our current way of life. Spacecraft and aircraft propulsion, electric power production, home heating, ground transportation, and materials processing all use combustion to convert chemical energy to thermal energy or propulsive force.

Examples of combustion applications:

- Gas turbines and jet engines
- Rocket propulsion
- Piston engines
- Guns and explosives
- Furnaces and boilers
- Flame synthesis of materials (fullerenes, nano-materials)
- Chemical processing (e.g. carbon black production)
- Forming of materials
- Fire hazards and safety

Combustion is a complex interaction of physical (fluid dynamics, heat and mass transfer), and chemical processes (thermodynamics, and chemical kinetics). Practical applications of the combustion phenomena also involve applied sciences such as aerodynamics, fuel technology, and mechanical engineering.

The transport of energy, mass, and momentum are the physical processes involved in combustion. The conduction of thermal energy, the diffusion of chemical species, and the flow of gases all follow from the release of chemical energy in the exothermic reaction. The subject areas most relevant to combustion in the fields of thermodynamics, transport phenomena, and chemical kinetics can be summarized as follows:

Thermodynamics:

- Stoichiometry
- Properties of gases and gas mixtures
- Heat of formation
- Heat of reaction
- Equilibrium
- Adiabatic flame temperature

Heat and Mass Transfer:

- Heat transfer by conduction
- Heat transfer by convection
- Heat transfer by radiation

- Mass transfer

Fluid Dynamics:

- Laminar flows
- Turbulence
- Effects of inertia and viscosity
- Combustion aerodynamics

Chemical Kinetics:

- Application of thermodynamics to a reacting system gives us the equilibrium composition of the combustion products and maximum temperature corresponding to this composition, i.e. the adiabatic flame temperature. However, thermodynamics alone is not capable of telling us whether a reactive system will reach equilibrium. If the time scales of chemical reactions involved in a combustion process are comparable to the time scales of physical processes (e.g. diffusion, fluid flow) taking place simultaneously, the system may never reach equilibrium. Then, we need the rate of chemical reactions involved in combustion.

Current Status of Combustion Science:

Despite vigorous scientific efforts for over a century, researchers still lack full understanding of many fundamental combustion processes.

Primary sources of the combustion research literature:

1. Combustion and Flame (journal)
2. Combustion Science and Technology (journal)
3. Combustion Theory and Modelling (journal)
4. Progress in Energy and Combustion Science (review journal)
5. Proceedings of the Combustion Institute (Biennial Combustion Symposia (International) proceedings).
6. Combustion, Explosions and Shock Waves (journal translated from Russian)

University of Toronto Library has electronic subscriptions to these combustion journals and they are available on-line.

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Fundamental Definitions

Chemical Reaction:

- exchange and/or rearrangement of atoms between colliding molecules

$$\underbrace{\mathrm{CO} + \mathrm{H_2O}} \rightarrow \underbrace{\mathrm{CO_2} + \mathrm{H_2}}$$

$$\text{Reactants} \rightarrow \text{Products}$$

- The atoms are conserved (C, H, O)
- On the other hand, molecules are not conserved.

$$\mathrm{H_2} + 0.5(\mathrm{O_2} + 3.76\mathrm{N_2}) \rightarrow \mathrm{H_2O} + 1.88\mathrm{N_2}$$

$$\text{Reactants} \rightarrow \text{Products}$$

Amount of substance or mole numbers (mol):

- 1 ***mol*** of a compound corresponds to $6.023 \cdot 10^{23}$ particles (atoms, molecules, or any chemical species).
- Avogadro's constant = $6.023 \cdot 10^{23}$
- ***Mole fraction*** χ_i of species i with mole number of N_i is

$$\chi_i = \frac{N_i}{\sum_{j=1}^{S} N_j}$$

- ***Mass fraction*** Y_i of species i with mass of m_i is

$$Y_i = \frac{m_i}{\sum_{j=1}^{S} m_j}$$

- ***Molar or Molecular Mass***, M_i (molecular weight is misleading and should not be used)
  - $M_{\mathrm{CH_4}} = 16 \;\; \mathrm{g/mol}$
  - $M_{\mathrm{H_2}} = 2 \;\; \mathrm{g/mol}$
  - $M_{\mathrm{O_2}} = 32 \;\; \mathrm{g/mol}$

- ***Mean molar mass***, $\overline{M}$, of a mixture of species denotes an average molar mass:

$$\overline{M} = \sum \chi_i M_i$$

- $S =$ number of species in the system

$$Y_i = \frac{M_i N_i}{\sum_{j=1}^{S} M_j N_j} = \frac{M_i \chi_i}{\sum_{j=1}^{S} M_j \chi_j}$$

$$\chi_i = \frac{Y_i}{M_i \overline{M}} = \frac{Y_i / M_i}{\sum_{j=1}^{S} Y_j / M_j}$$

For a system of volume, V:

- ***Mass density (density)***, $\rho = m/V$ (kg/m^3)
- ***Molar density (**concentration**)***, $c = N/V$ (kmol/m^3)
- Mean molar mass is given by:

$$\frac{\rho}{c} = \frac{m}{N} = \overline{M}$$

Chemical kinetics convention: concentrations c of chemical species are usually shown by species symbol in square brackets.

$$c_{\mathrm{CO_2}} = [\mathrm{CO_2}]$$

For most conditions involved in combustion, it is satisfactory to use the perfect gas equation of state for the gas phase.

$$PV = NR^oT$$

$$(\mathrm{Pa})(\mathrm{m}^3) = (\mathrm{mol})(\mathrm{J/molK})(\mathrm{K})$$

R^o = 8.314 J / mol K, universal gas constant

P = pressure, Pa

T = temperature, K

When the gas phase temperatures are near or less than the critical temperatures, or when pressures are near or above the critical pressures, the density or concentration is not correctly predicted by the perfect gas relationship. Real gas equations should be used.

- van der Waals
- Peng-Robinson

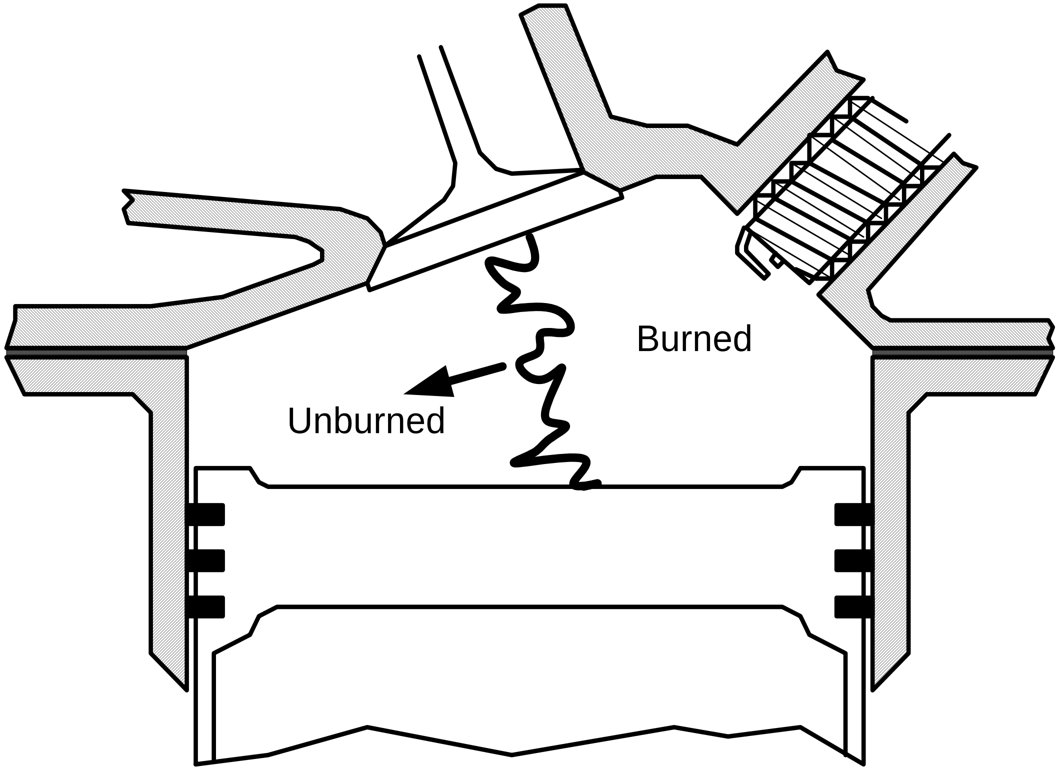
Basic Flame Types:

- Premixed Flames
    - Laminar
    - Turbulent
- Non-Premixed (Diffusion) Flames
    - Laminar
    - Turbulent
- Partially Premixed Flames
    - Laminar
    - Turbulent

♠ *triple flames, edge flames,...*

Laminar (Turbulent) Premixed Flames:

- Fuel (in gaseous form) and oxidizer are homogeneously mixed before the combustion event
- Flow is laminar (turbulent)
- Turbulent premixed flames:
  - combustion in gasoline engines
  - lean-premixed gas turbine combustion



- Cross-section of a gasoline engine combustion chamber.

Stoichiometry:

- A premixed flame is stoichiometric if the premixed reactants contain right amount of oxidizer to consume (burn) the fuel completely.
- If there is an excess of fuel: fuel-rich system
- If there is an excess of oxygen: fuel-lean system
- Standard air composition commonly used for combustion calculations:

$$\mathrm{O_2} + 3.762\mathrm{N_2}$$

Stoichiometry (cont'd):

$$\mathrm{C_3H_8} + 5(\mathrm{O_2} + 3.762\mathrm{N_2}) \rightarrow$$

$$4\mathrm{H_2O} + 3\mathrm{CO_2} + 18.81\mathrm{N_2}$$

- $(A/F)_{stoich}$=air-to-fuel ratio (mass)= (mass of air)/(mass of fuel)
- $(A/F)_{stoich}$=[5(32+3.762*28)]/(44) = 15.6
- $\Phi = (A/F)_{stoich}/(A/F)_{actual}$ = Fuel Equivalence Ratio

Stoichiometry (cont'd)::

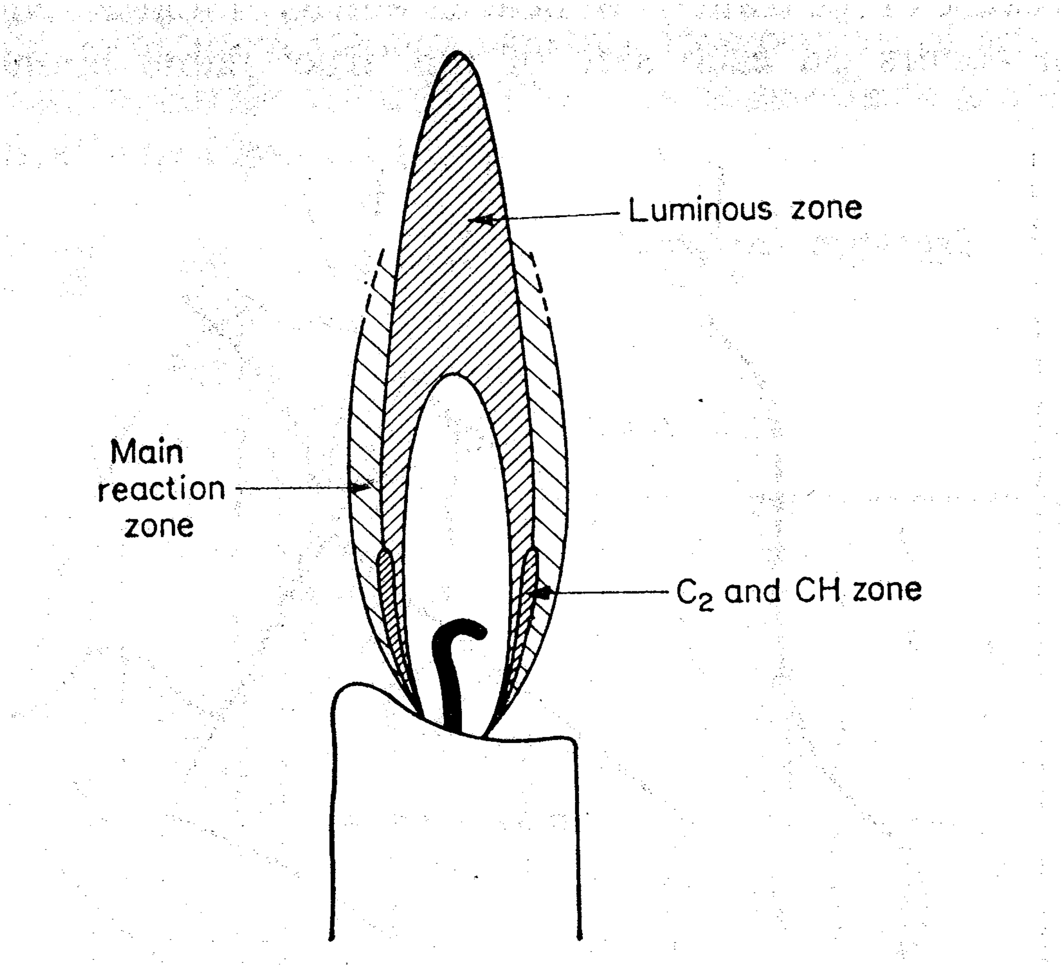
- $\Phi = 1$: stoichiometric combustion
- $\Phi < 1$: lean mixture, lean combustion
- $\Phi > 1$: rich mixture, rich combustion
- European convention (and to a certain extent Japanese) is to use Air equivalence ratio, λ:

$$\lambda = 1/\Phi$$

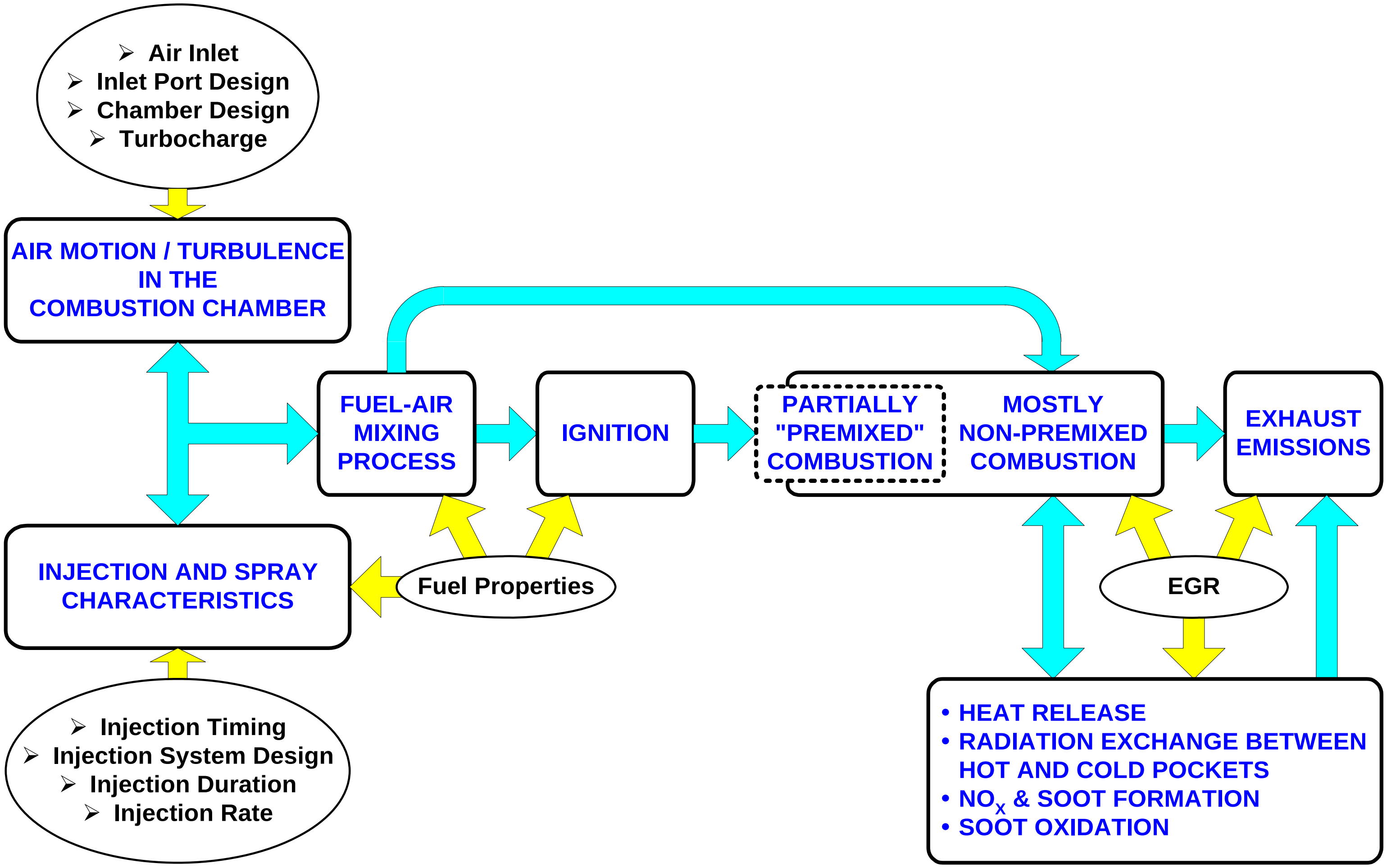
- In certain industries, excess air ratio, excess oxygen, and similar terminologies are also used.

Laminar (Turbulent) Non- Premixed Flames:

- Fuel (in gaseous form) and oxidizer are mixed/come in to contact during the combustion process
- A candle flame is a typical laminar non-premixed (diffusion) flame
- Turbulent non-premixed flames:
  - hydrogen rocket engine
  - current aero gas turbines
  - diesel engines



A candle flame.



- Air Inlet
- Inlet Port Design
- Chamber Design
- Turbocharge

AIR MOTION / TURBULENCE IN THE COMBUSTION CHAMBER

FUEL-AIR MIXING PROCESS

IGNITION

PARTIALLY "PREMIXED" COMBUSTION

MOSTLY NON-PREMIXED COMBUSTION

EXHAUST EMISSIONS

INJECTION AND SPRAY CHARACTERISTICS

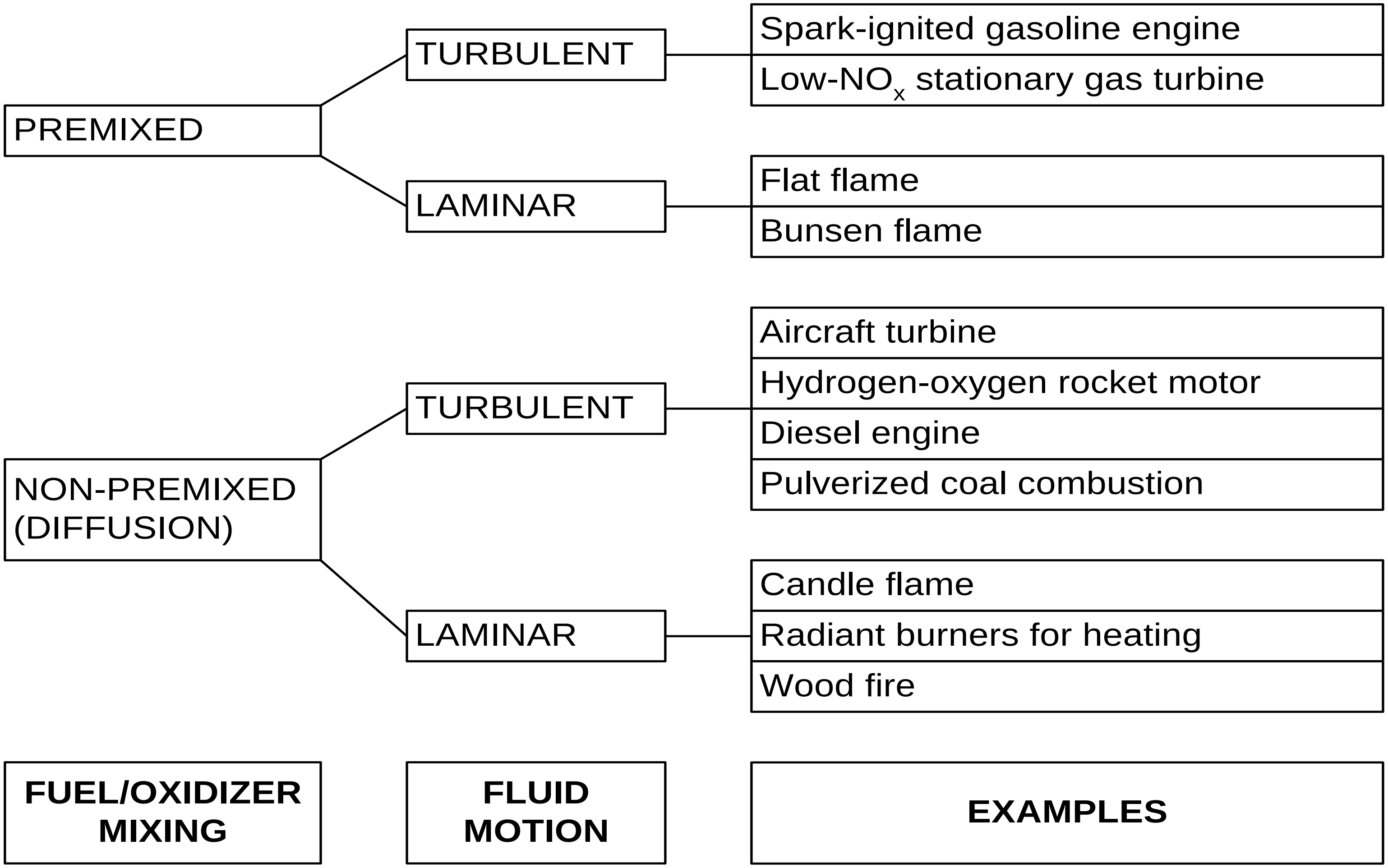
Fuel Properties

EGR

- Injection Timing
- Injection System Design
- Injection Duration
- Injection Rate

- **HEAT RELEASE**
- **RADIATION EXCHANGE BETWEEN HOT AND COLD POCKETS**
- **NO_X & SOOT FORMATION**
- **SOOT OXIDATION**

Processes in the diesel engine combustion.



FUEL/OXIDIZER MIXING	**FLUID MOTION**	**EXAMPLES**
PREMIXED	TURBULENT	Spark-ignited gasoline engine Low-NO_x stationary gas turbine
	LAMINAR	Flat flame Bunsen flame
NON-PREMIXED (DIFFUSION)	TURBULENT	Aircraft turbine Hydrogen-oxygen rocket motor Diesel engine Pulverized coal combustion
	LAMINAR	Candle flame Radiant burners for heating Wood fire

Examples of combustion systems.

1. Combustion & Thermochemistry

This section will cover the following concepts:

- Basic property relations for ideal gas and ideal gas mixtures.
- First law of thermodynamics.
- Enthalpy/heat of reaction; adiabatic flame temperature.
- Chemical equilibrium.

Review of Property Relations:

- ***Extensive Properties:*** depends on amount of substance considered. Usually denoted by capital letters. Examples are: V for volume, U for total internal energy, H for total enthalpy.

- ***Intensive Properties:*** expressed per unit amount of substance (mass or mole). Its numerical value is independent of the amount of substance present. Usually denoted with lower case letters. Examples are: specific volume v, specific enthalpy h, specific heat c_p.

- ***Intensive Properties (Cont'd):*** Important exceptions to this lower case conventions are temperature T and pressure P.

  Molar based properties will be denoted by an overbar, e.g., $\bar{h}$ for specific enthalpy per unit mole, J/mol.

  Extensive properties are related to the intensive ones by the amount of substance present:

$$V = m \cdot v (\text{or} \quad N \cdot \bar{v}) \tag{1.1}$$

$$H = m \cdot h (\text{or} \quad N \cdot \bar{h})$$

Equation of State:

- Provides the relationship among the pressure, temperature, and volume.
- Ideal-gas behaviour: intermolecular forces and volume of molecules are ignored.

$$PV = NR_uT \tag{1.2a}$$

$$PV = mRT \tag{1.2b}$$

$$Pv = RT \tag{1.2c}$$

$$P = \rho RT \tag{1.2d}$$

Equation of State (Cont'd):

- The specific gas constant R is related to the universal gas constant R_u (or R^o) by:

$$R = \frac{R_u}{MW} \tag{1.3}$$

  $R_u = 8314.7$ J/(kmol K)

  MW is the molecular weight (or, more precisely, molecular mass).

- Throughout this course, all gaseous species and gas mixtures will be assumed to be ideal.

Calorific Equations of State:

- Relates enthalpy and internal energy to pressure and temperature:

$$u = u(T, v) \tag{1.4a}$$

$$h = h(T, P) \tag{1.4a}$$

- By differentiating Eqns 1.4a and b:

$$\mathrm{d}u = \left(\frac{\partial u}{\partial T}\right)_v \mathrm{d}T + \left(\frac{\partial u}{\partial v}\right)_T \mathrm{d}v \tag{1.5a}$$

$$\mathrm{d}h = \left(\frac{\partial h}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial h}{\partial P}\right)_T \mathrm{d}P \tag{1.5b}$$

Calorific Equations of State (Cont'd):

- In Eqs 1.5a and b:

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \qquad (1.6a)$$

$$c_p = \left(\frac{\partial h}{\partial T}\right)_P \qquad (1.6b)$$

- For an ideal gas:
  $(\partial u/\partial v)_T = 0$ and
  $(\partial h/\partial P)_T = 0$

Calorific Equations of State (Cont'd):

- Integrating Eqs 1.5 and substitute in 1.6 provide

$$u(T) - u_{\mathrm{ref}} = \int_{T_{\mathrm{ref}}}^{T} c_v \mathrm{d}T \qquad (1.7a)$$

$$h(T) - h_{\mathrm{ref}} = \int_{T_{\mathrm{ref}}}^{T} c_p \mathrm{d}T \qquad (1.7b)$$

- We will define an appropriate reference state in a subsequent section.

Calorific Equations of State (Cont'd):

- For both real and ideal gases, the specific heats are *generally* functions of temperature.
- Internal energy of a molecule: translational, vibrational and rotational are temperature dependent.
- Monatomic species: only translational energy.
- Diatomic and triatomic: all three, i.e., translational, vibrational and rotational.
- In general, the more complex the molecule, the greater its molar specific heat.

Ideal Gas Mixtures:

- Mole fraction of species i:

$$\chi_i \equiv \frac{N_i}{\sum_j N_j} = N_i/N_{\mathrm{tot}} \qquad (1.8)$$

- Mass fraction of species i:

$$Y_i \equiv \frac{m_i}{\sum_j m_j} = m_i/m_{\mathrm{tot}} \qquad (1.9)$$

Ideal Gas Mixtures (Cont'd):

- By definition the sum of all the mole (and mass) fractions must be unity:

$$\sum_i \chi_i = 1 \quad \text{and} \quad \sum_i Y_i = 1 \qquad (1.10a\&b)$$

- Relations between χ and Y:

$$Y_i = \chi_i MW_i / MW_{\text{mix}} \qquad (1.11a)$$

$$\chi_i = Y_i MW_{\text{mix}} / MW_i \qquad (1.11b)$$

Ideal Gas Mixtures (Cont'd):

- Mixture molecular weight (mass):

$$MW_{\text{mix}} = \sum_i \chi_i MW_i \qquad (1.12a)$$

$$MW_{\text{mix}} = \frac{1}{\sum_i (Y_i / MW_i)} \qquad (1.12b)$$

- Total pressure is the sum of the partial pressures:

$$P = \sum_i P_i \qquad (1.13)$$

Ideal Gas Mixtures (Cont'd):

- Partial pressure of the ith species is the pressure of this species if it were isolated from the mixture.

$$P_i = \chi_i P \tag{1.14}$$

- For ideal gas mixtures:

$$h_{\text{mix}} = \sum_i Y_i h_i \tag{1.15a}$$

$$\bar{h}_{\text{mix}} = \sum_i \chi_i \bar{h}_i \tag{1.15b}$$

Ideal Gas Mixtures (Cont'd):

- Mixture entropies also is calculated as a weighted sum of the constituents:

$$s_{\mathrm{mix}}(T,P) = \sum_i Y_i s_i(T,P) \tag{1.16a}$$

$$\bar{s}_{\mathrm{mix}}(T,P) = \sum_i \chi_i \bar{s}_i(T,P) \tag{1.16a}$$

- Pure species entropies depend on the species partial pressures as implied in Eqs 1.16.

Ideal Gas Mixtures (Cont'd):

- If we take the standard state as 1 atm ($P_{\mathrm{ref}} = P^o = 1$ atm), then:

$$s_i(T, P_i) = s_i(T, P_{\mathrm{ref}}) - R \cdot \ln \frac{P_i}{P_{\mathrm{ref}}} \qquad (1.17a)$$

$$\bar{s}_i(T, P_i) = \bar{s}_i(T, P_{\mathrm{ref}}) - R_u \cdot \ln \frac{P_i}{P_{\mathrm{ref}}} \qquad (1.17b)$$

- Appendix A in the textbook lists entropies for several species.

Latent Heat (Enthalpy) of Vaporization:

- h_{fg} is the heat required in a $P = \text{const.}$ process to completely vaporize a unit mass of liquid at a given temperature:

$$h_{fg} \equiv h_{\text{vapor}}(T, P) - h_{\text{liquid}}(T, P) \qquad (1.18)$$

- Clausius-Clapeyron equation:

$$\frac{\mathrm{d}P_{\text{sat}}}{P_{\text{sat}}} = \frac{h_{fg}}{R} \frac{\mathrm{d}T}{T_{\text{sat}}^2} \qquad (1.19)$$

First Law of Thermodynamics:

First Law - Fixed Mass:

- Conservation of energy is the fundamental principle in the first law of thermodynamics. For a fixed mass system, energy conservation is expressed for a finite change between two states, 1 and 2, as:

$$\underbrace{{}_1Q_2}_{\substack{\text{Heat added}\\ \text{to the system}}} \quad - \quad \underbrace{{}_1W_2}_{\substack{\text{Work done}\\ \text{by the system}}} \quad = \quad \underbrace{\Delta E_{1-2}}_{\substack{\text{Change in total}\\ \text{energy of system}}} \qquad (1.20)$$

First Law - Fixed Mass (Cont'd):

- Both ${}_1Q_2$ and ${}_1W_2$ are path functions and occur only at the system boundaries. $\Delta E_{1-2} \equiv E_2 - E_1$ is the change in the total energy of the system, i.e.

$$E = m[\underbrace{u}_{\text{system internal energy}} + \underbrace{(1/2)v^2}_{\text{system kinetic energy}} + \underbrace{gz}_{\text{system potential energy}}] \qquad (2.21)$$

The sytem energy is a state variable and does not depend on the path taken.

First Law - Fixed Mass (Cont'd):

- We can write Eq 1.20 as a unit mass basis, or expressed to represent an instant in time:

$$ {}_1q_2 - {}_1w_2 = \Delta e_{1-2} = e_2 - e_1 \tag{1.22} $$

$$ \underbrace{\dot{Q}}_{\substack{\text{instantaneous}\\ \text{rate of heat}\\ \text{transferred}}} \quad - \quad \underbrace{\dot{W}}_{\substack{\text{instantaneous}\\ \text{rate of work}\\ \text{done}}} \quad = \quad \underbrace{\mathrm{d}E/\mathrm{d}t}_{\substack{\text{instantaneous}\\ \text{change of}\\ \text{system energy}}} \tag{1.23} $$

$$ \dot{q} - \dot{w} = \mathrm{d}e/\mathrm{d}t \tag{1.24} $$

First Law - Control Volume:

- Steady-state, steady-flow form of the first law:

$$\underbrace{\dot{Q}_{cv}}_{\substack{\text{Rate of heat}\\ \text{transferred from}\\ \text{surroundings}}} - \underbrace{\dot{W}_{cv}}_{\substack{\text{Rate of work}\\ \text{done by control}\\ \text{volume excluding}\\ \text{flow work}}} = \underbrace{\dot{m}e_{\mathrm{o}}}_{\substack{\text{Rate of energy}\\ \text{flow out of CV}}}$$

$$- \underbrace{\dot{m}e_{\mathrm{i}}}_{\substack{\text{Rate of energy}\\ \text{flow into CV}}} + \underbrace{\dot{m}(P_{\mathrm{o}}v_{\mathrm{o}} - P_{\mathrm{i}}v_{\mathrm{i}})}_{\substack{\text{Net rate of work}\\ \text{associated with}\\ \text{pressure forces}}} \qquad (1.25)$$

First Law - Control Volume (Cont'd):

- Main assumptions in the previuos equation:
  - The control volume is fixed relative to the coordinate system.
  - The properties of the fluid at each point within CV, or on the control surface, do not vary with time.
  - Fluid properties are uniform over inlet and outlet areas.
  - There is only one inlet and one outlet stream.

First Law - Control Volume (Cont'd):

- Specific energy e of the inlet and outlet stream consist of:

$$\underbrace{e}_{\substack{\text{Total}\\ \text{energy per}\\ \text{unit mass}}} = \underbrace{u}_{\substack{\text{Internal}\\ \text{energy per}\\ \text{unit mass}}} + \underbrace{(1/2)v^2}_{\substack{\text{Kinetic}\\ \text{energy per}\\ \text{unit mass}}} + \underbrace{gz}_{\substack{\text{Potential}\\ \text{energy per}\\ \text{unit mass}}} \tag{1.26}$$

$v =$ velocity where the stream crosses the CV

$z =$ elevation where stream crosses the CV

$g =$ gravitational acceleration

First Law - Control Volume (Cont'd):

- Enthalpy:

$$h \equiv u + Pv = u + P/\rho \qquad (1.27)$$

- Eqns 1.25-1.27 yield:

$$\dot{Q}_{cv} - \dot{W}_{cv} = \dot{m}[(h_\mathrm{o} - h_\mathrm{i}) + \frac{1}{2}(v_\mathrm{o}^2 - v_\mathrm{i}^2) + g(z_\mathrm{o} - z_\mathrm{i})] \qquad (1.28)$$

- On a mass-specific basis, Eqn 2.28 reads

$$q_{cv} - w_{cv} = (h_\mathrm{o} - h_\mathrm{i}) + (1/2)(v_\mathrm{o}^2 - v_\mathrm{i}^2) + g(z_\mathrm{o} - z_\mathrm{i}) \qquad (1.29)$$

Reactant and Product Mixtures:

Stoichiometry:

- The stoichiometric quantity of oxidizer is just that amount needed to completely burn a quantity of fuel. For a hydrocarbon fuel, C_xH_y, stoichiometric relation is

$$C_xH_y + a(O_2 + 3.76N_2) \rightarrow$$

$$xCO_2 + (y/2)H_2O + 3.76aN_2 \quad (1.30)$$

where

$$a = x + y/4 \qquad (1.31)$$

Stoichiometry (Cont'd):

- The stoichiometric air-fuel ratio is

$$(A/F)_{\text{stoic}} = \left(\frac{m_{\text{air}}}{m_{\text{fuel}}}\right) = \frac{4.76a}{1}\frac{MW_{\text{air}}}{MW_{\text{fuel}}} \quad (1.32)$$

- The equivalence ratio is defined as

$$\Phi = \frac{(A/F)_{\text{stoic}}}{(A/F)} = \frac{(F/A)}{(F/A)_{\text{stoic}}} \quad (1.33a)$$

Stoichiometry (Cont'd):

- $\Phi > 1$: Fuel-rich mixtures.
- $\Phi < 1$: Fuel-lean mixtures.
- $\Phi = 1$: Stoichiometric mixtures.
- % stoichiometric and % excess air;

$$\%\text{stoichiometric air} = 100\%/\Phi \qquad (1.33b)$$

$$\%\text{excess air} = [(1-\Phi)/\Phi]\cdot 100\% \qquad (1.33c)$$

Absolute (or Standardized) Enthalpy and Enthalpy of Formation:

- For any species, we can define an *absolute enthalpy* that is the sum of an *enthalpy of formation* and *sensible enthalpy change*:

$$\underbrace{\bar{h}_i(T)}_{\substack{\text{absolute enthalpy}\\ \text{at temperature T}}} = \underbrace{\bar{h}^o_{f,i}(T_{\text{ref}})}_{\substack{\text{enthalpy of}\\ \text{formation at}\\ \text{standard ref}\\ \text{state } (T_{\text{ref}},P^o)}} + \underbrace{\Delta\bar{h}_{s,i}(T_{\text{ref}})}_{\substack{\text{sensible enthalpy}\\ \text{change in going}\\ \text{from } T_{\text{ref}} \text{ to } T}} \tag{1.34}$$

where $\Delta\bar{h}_{s,i} \equiv \bar{h}_i(T) - \bar{h}^o_{f,i}(T_{\text{ref}})$

Absolute (or Standardized) Enthalpy (Cont'd):

- Define a standard reference state.

$$T_{\mathrm{ref}} = 298.15\mathrm{K}\ (25\ ^{o}\mathrm{C})$$

$$P_{\mathrm{ref}} = P^{o} = 1\mathrm{atm}\ (101.325\ \mathrm{kPa})$$

- Enthalpies of formation are zero for the elements in their naturally occuring state at the reference temperature and pressure.
- For example, at 25 °C and 1 atm, oxygen exists as diatomic molecules; then

$$(\bar{h}^{o}_{f,\mathrm{O}_2})_{298} = 0$$

Absolute (or Standardized) Enthalpy (Cont'd):

- To form oxygen atoms at the standard state requires breaking of a chemical bond.
- The bond dissociation energy of O_2 at standard state is $498,390$ kJ/kmol.
- Breaking of the bond creates two O atoms; therefore the *enthalpy of formation* of atomic oxygen is

$$(\bar{h}^o_{f,\mathrm{O}})_{298} = 249,195 \ \mathrm{kJ/kmol}$$

Enthalpy of Formation (Cont'd):

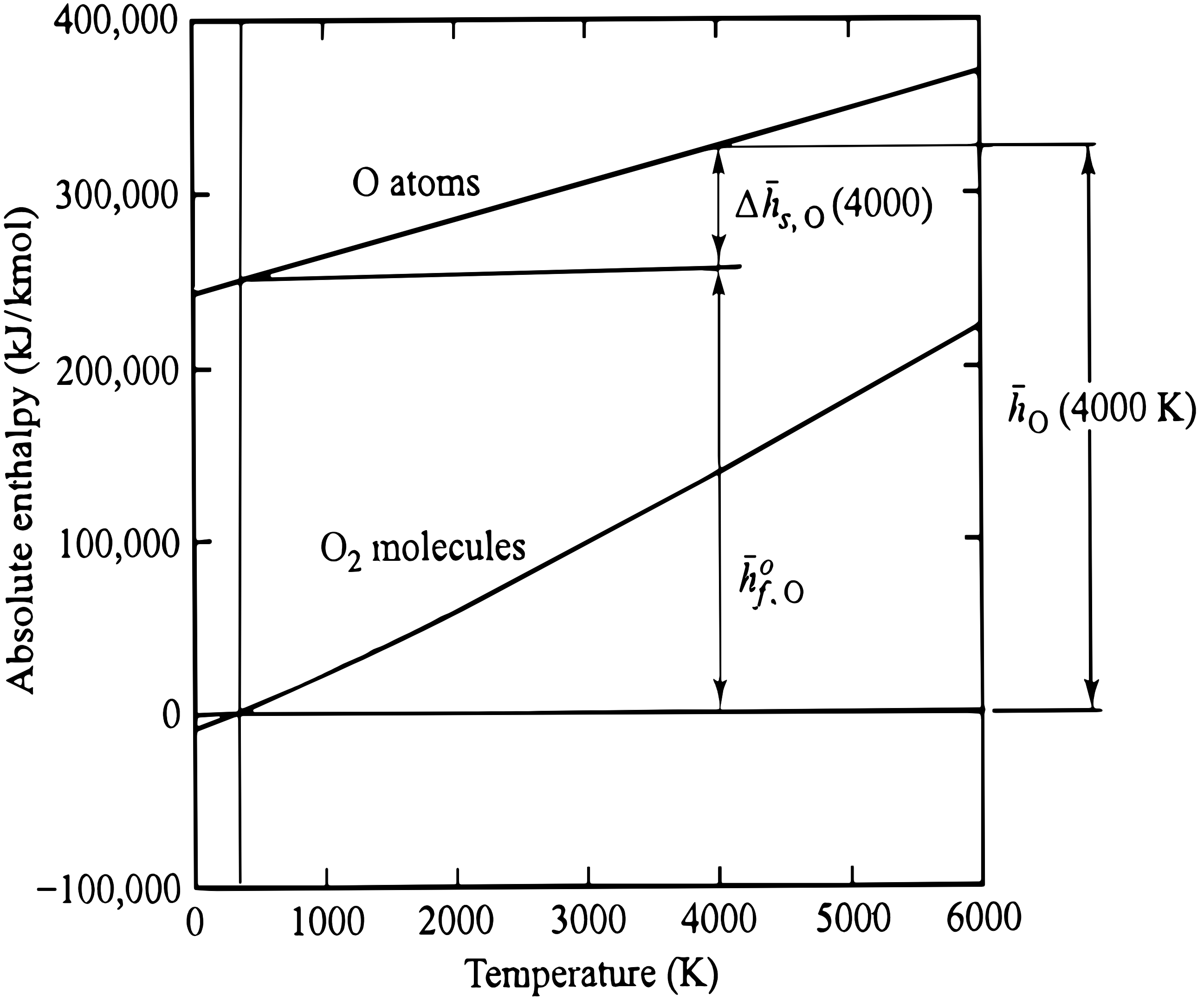
- Thus, enthalpies of formation is the net change in enthalpy associated with breaking the chemical bonds of the standard state elements and forming new bonds to create the compound of interest.
- Examples:

$$(\bar{h}^o_{f,\mathrm{N}_2})_{298} = 0$$

$$(\bar{h}^o_{f,\mathrm{H}_2})_{298} = 0$$

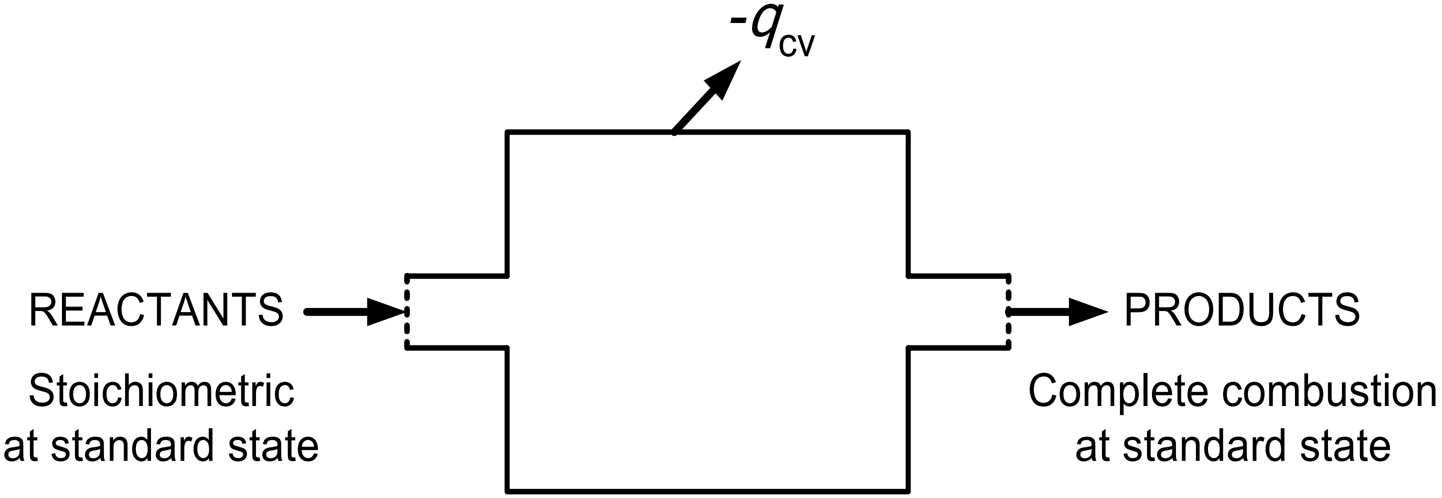
$$(\bar{h}^o_{f,\mathrm{N}})_{298} = 472,629 \text{ kJ/kmol}$$

$$(\bar{h}^o_{f,\mathrm{H}})_{298} = 217,977 \text{ kJ/kmol}$$



Abs. enthalpy, heat of formation, and sensible enthalpy

Enthalpy of Combustion and Heating Values



Steady-flow reactor

Enthalpy of Combustion and Heating Values (Cont'd)

- Reactants: stoichiometric mixture at standard state conditions.
- Products: complete combustion, and products are at standard state conditions.
- For products to exit at the same T as the reactants, heat must be removed.
- The amount of heat removed can be related to the reactant and product absolute enthalpies by applying the steady-flow form of the first law:

Enthalpy of Combustion and Heating Values (Cont'd):

From eqn 1.29:

$$q_{\rm cv} = h_{\rm o} - h_{\rm i} = h_{\rm prod} - h_{\rm reac} \qquad (1.35)$$

- The *enthalpy of reaction*, or the *enthalpy of combustion*, $\Delta h_{\rm R}$, is (per mass of mixture)

$$\Delta h_{\rm R} \equiv q_{\rm cv} = h_{\rm prod} - h_{\rm reac} \qquad (1.36a)$$

or, in terms of extensive properties

$$\Delta H_{\rm R} = H_{\rm prod} - H_{\rm reac} \qquad (1.36b)$$

Enthalpy of Combustion and Heating Values (Cont'd):

- Example:

- At standard state, the reactants enthalpy of a stoichiometric mixture of CH_4 and air, where 1 kmol of fuel reacts, is $-74,831$ kJ.
- At the same conditions, the combustion products have an absolute enthalpy of $-877,236$ kJ.

$$\begin{aligned}\Delta H_{\mathrm{R}} &= -877,236 - (-74,831) \\ &= -802,405\mathrm{kJ}\end{aligned}$$

Enthalpy of Combustion and Heating Values (Cont'd):

- This value can be adjusted to a per-mass-of-fuel basis:

$$\Delta h_{\mathrm{R}}\left(\frac{\mathrm{kJ}}{\mathrm{kg}_{\mathrm{fuel}}}\right) = \Delta H_{\mathrm{R}}/MW_{\mathrm{fuel}} \qquad (1.37)$$

- or

$$\begin{aligned}\Delta h_{\mathrm{R}}\left(\frac{\mathrm{kJ}}{\mathrm{kg}_{\mathrm{fuel}}}\right) &= (-802,405/16.043) \\ &= -50,016\end{aligned}$$

Enthalpy of Combustion and Heating Values (Cont'd):

- For a per-unit-mass-of-mixture basis:

$$\Delta h_{\mathrm{R}}\left(\frac{\mathrm{kJ}}{\mathrm{kg_{mix}}}\right) = \Delta h_{\mathrm{R}}\left(\frac{\mathrm{kJ}}{\mathrm{kg_{fuel}}}\right)\frac{m_{\mathrm{fuel}}}{m_{\mathrm{mix}}} \qquad (1.38)$$

where

$$\frac{m_{\mathrm{fuel}}}{m_{\mathrm{mix}}} = \frac{m_{\mathrm{fuel}}}{m_{\mathrm{air}} + m_{\mathrm{fuel}}} = \frac{1}{(A/F) + 1} \qquad (1.39)$$

$$\begin{aligned}\Delta h_{\mathrm{R}}(\mathrm{kJ/kg_{mix}}) &= -50,016/(17.11 + 1)\\ &= -2761.8\end{aligned}$$

Enthalpy of Combustion and Heating Values (Cont'd):

- Enthalpy of combustion depends on temperature chosen for its evaluation since enthalpies of reactants and products are temperature dependent.
- The *heat of combustion*, Δh_c (known also as the *heating value* or *calorific value*), is numerically equal to the enthalpy of combustion, but with opposite sign.
- HHV: *higher heating value* ($H_2O\rightarrow$ liquid)
- LHV: *lower heating value* ($H_2O\rightarrow$ vapor)

Adiabatic Flame Temperatures:

- We will differentiate between two adiabatic flame temperatures:
  - constant-pressure combustion
  - constant-volume combustion
- Constant-Pressure: If a fuel-air mixture burns adiabatically at constant pressure, absolute enthalpy of reactants at the initial state (say, $T_1 = 298$ K, $P = 1$ atm) equals absolute enthalpy of the products at final state ($T = T_{\rm ad}$, $P = 1$ atm).

Constant Pressure T_{ad} *(Cont'd):*

- Definition of the constant-pressure adiabatic flame temperature is

$$H_{\mathrm{reac}}(T_{\mathrm{i}}, P) = H_{\mathrm{prod}}(T_{\mathrm{ad}}, P) \qquad (1.40a)$$

or, on a per-mass-of-mixture basis,

$$h_{\mathrm{reac}}(T_{\mathrm{i}}, P) = h_{\mathrm{prod}}(T_{\mathrm{ad}}, P) \qquad (1.40b)$$

- Conceptually, adiabatic flame temperature is simple, however, evaluating this quantity requires knowledge of the composition of the combustion products.

Constant Volume* T_{ad}*:

- When we are dealing with constant-pressure combustion systems, such as gas turbine combustors and rocket engines, the appropriate approach would involve constant-pressure T_{ad}.
- When we are dealing with constant-volume combustion systems, such as enclosed explosions or Otto-cycle (idealized thermodynamic cycle for gasoline engine combustion) analysis, the appropriate approach would involve constant-volume T_{ad}.

Constant Volume T_{ad} *(Cont'd):*

- Definition:

$$U_{\mathrm{reac}}(T_{\mathrm{init}}, P_{\mathrm{init}}) = U_{\mathrm{prod}}(T_{\mathrm{ad}}, P_{\mathrm{f}}) \qquad (1.41)$$

  where U is the absolute (or standardized) internal energy of the mixture.

- Most thermodynamic property compilations and calculations provide H (or h) rather than U (or u). So we consider the fact that:

$$H = U + PV$$

Constant Volume T_{ad} *(Cont'd):*

- Eqn 1.41:

$$H_{\mathrm{reac}} - H_{\mathrm{prod}} - V(P_{\mathrm{init}} - P_{\mathrm{f}}) = 0 \qquad (1.42)$$

- If we apply the ideal-gas law;

$$P_{\mathrm{init}}V = \sum_{\mathrm{reac}} N_i R_u T_{\mathrm{init}} = N_{\mathrm{reac}} R_u T_{\mathrm{init}}$$

$$P_{\mathrm{f}}V = \sum_{\mathrm{prod}} N_i R_u T_{\mathrm{ad}} = N_{\mathrm{prod}} R_u T_{\mathrm{ad}}$$

Constant Volume T_{ad} ***(Cont'd):***

- Substituting in Eqn 1.42

$$H_{\mathrm{reac}} - H_{\mathrm{prod}} - R_u(N_{\mathrm{reac}}T_{\mathrm{init}} - N_{\mathrm{prod}}T_{\mathrm{ad}}) = 0 \tag{1.43}$$

Since

$$m_{\mathrm{mix}}/N_{\mathrm{reac}} \equiv MW_{\mathrm{reac}}$$

$$m_{\mathrm{mix}}/N_{\mathrm{prod}} \equiv MW_{\mathrm{prod}}$$

$$h_{\mathrm{reac}} - h_{\mathrm{prod}} - R_u\left(\frac{T_{\mathrm{init}}}{MW_{\mathrm{reac}}} - \frac{T_{\mathrm{ad}}}{MW_{\mathrm{prod}}}\right) = 0 \tag{1.44}$$

Chemical Equilibrium:

- Products of combustion are not a simple mixture of ideal products.
- We used ideal products approach to determine stoichiometry.
- Ideal combustion products for a hydrocarbon fuel:
  - $\Phi = 1$: CO_2, H_2O, N_2
  - $\Phi < 1$: CO_2, H_2O, N_2, O_2
  - $\Phi > 1$: CO_2, H_2O, N_2, CO, H_2

- Real combustion products of a hydrocarbon fuel may include:
  - CO_2, H_2O, N_2, O_2, H_2, OH, CO, H, O, N, NO, ...
- Major species, i.e.,

  CO_2, H_2O, N_2, O_2, H_2, CO,

  dissociate into a host of minor species, i.e.,

  H, N, O, OH, NO.
- Our objective here is to calculate the mole fraction of all product species.

Second-Law Considerations:

- Second-Law of Thermodynamics → Concept of chemical equilibrium.
- Consider a V =const., adiabatic reaction vessel in which a fixed mass of reactants form products.
- As reaction proceeds, T and P rise until a final equilibrium condition is reached.
- This final state is not governed solely by first-law considerations, but requires invoking the second-law.

Second-Law Considerations (Cont'd):

- Consider the following combustion reaction:

$$\mathrm{CO} + 0.5\mathrm{O}_2 \rightarrow \mathrm{CO}_2 \tag{1.45}$$

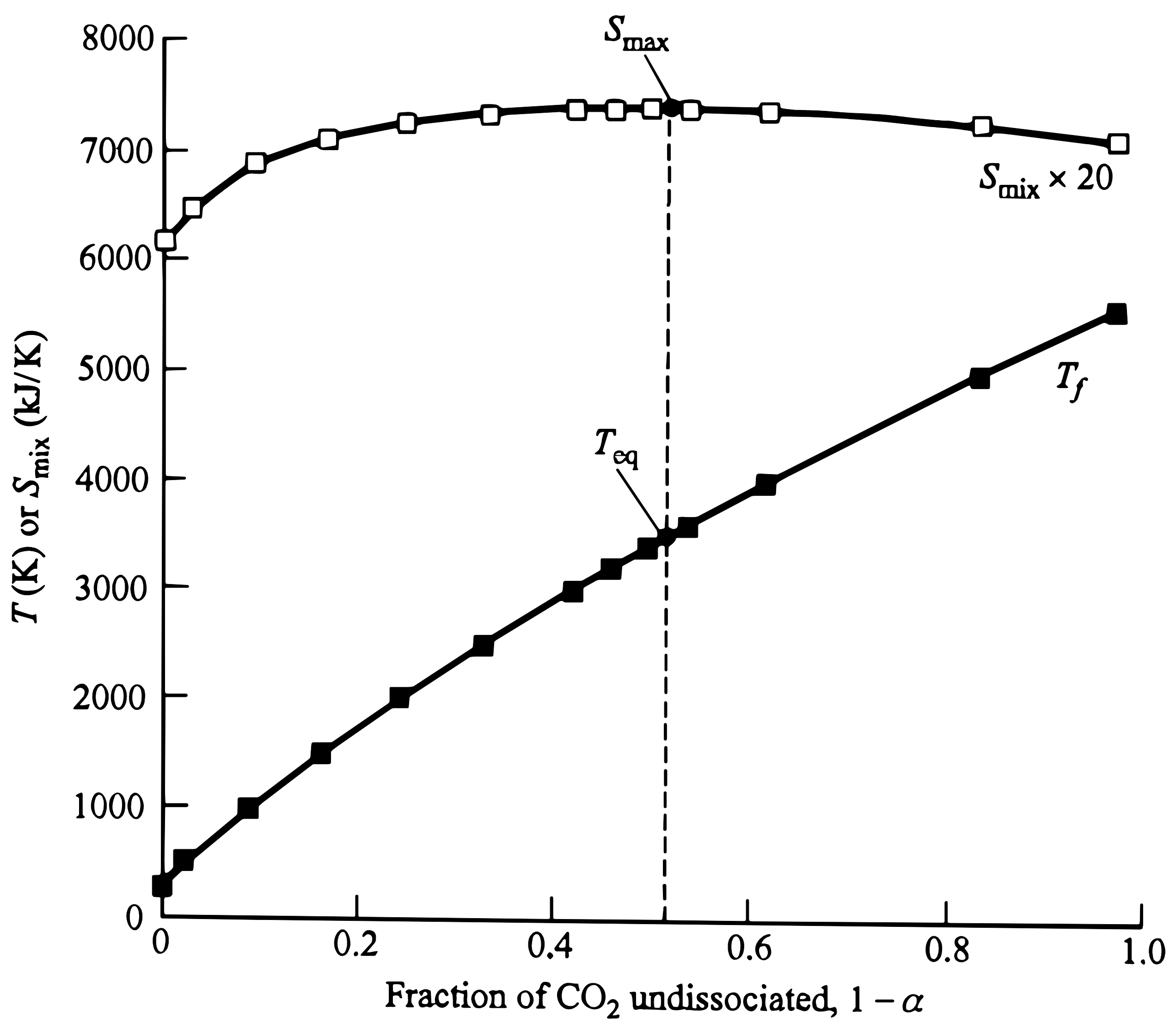
- If the final T is high enough, CO_2 will dissociate. Assuming products are CO_2, CO, and O_2

$$\Big[\mathrm{CO} + 0.5\mathrm{O}_2\Big]_{\substack{\text{cold}\\ \text{reactants}}} \rightarrow$$

$$\Big[(1-\alpha)\mathrm{CO}_2 + \alpha\mathrm{CO} + (\alpha/2)\mathrm{O}_2\Big]_{\substack{\text{hot}\\ \text{products}}} \tag{1.46}$$

Second-Law Considerations (Cont'd):

- $\alpha =$ fraction of CO_2 dissociated.
- It is possible to calculate the adiabatic flame temperature as a function of α using Eqn 1.42.
- $\alpha = 1$: no heat release; T, P, and χ_i remain unchanged.
- $\alpha = 0$: maximum possible heat release; P and T would be the highest possible allowed by the first-law.
- Variation of temperature with α:



Chemical equilibrium for a fixed mass system.

Second-Law Considerations (Cont'd):

- Let's see what constraints second-law imposes on this system
- Entropy of the mixture:

$$S_{\text{mix}}(T_f, P) = \sum_{i=1}^{3} N_i \bar{s}_i(T_f, P_i)$$

$$= (1-\alpha)\bar{s}_{\text{CO}_2} + \alpha\bar{s}_{\text{CO}} + (\alpha/2)\bar{s}_{\text{O}_2} \qquad (1.47)$$

$$\bar{s}_i = \bar{s}_i^o(T_{\text{ref}}) + \int_{T_{\text{ref}}}^{T_f} \bar{c}_{p,i}\frac{\mathrm{d}T}{T} - R_u \ln\frac{P_i}{P^o} \qquad (1.48)$$

Second-Law Considerations (Cont'd):

- If we plot mixture entropy versus α, we see that entropy reaches maximum at about $\alpha = 0.5$.
- For our choice of conditions, the second law requires that entropy change internal to the system

$$\mathrm{d}S \geq 0 \tag{1.49}$$

- χ_i will shift toward the point of maximum entropy when approaching from both sides.
- Once maximum entropy is reached, no change in χ_i is allowed.

Second-Law Considerations (Cont'd):

- Then, formally the condition for equilibrium is:

$$(\mathrm{d}S)_{U,V,m} = 0 \tag{1.50}$$

- If we fix the internal energy, U, volume, V, and mass, m, of an isolated system, application of the
  - first law (Eqn 1.41),
  - second law (Eqn 1.49) and
  - equation of state (Eqn 1.2)

  define the equilibrium T, P, and χ_i.

Gibbs Function:

- For an isolated system of fixed volume, mass, and energy system, the maximum entropy approach demonstrates the role of second law.
- In most typical sysytems, however, the equilibrium χ_i are required for a given T, P, and Φ.
- For such cases, the *Gibbs free energy*, G replaces entropy as the important thermodynamic property.
- Gibbs free energy is defined as:

$$G \equiv H - TS \tag{1.51}$$

Gibbs Function (Cont'd):

- Second law in terms of G:

$$(\mathrm{d}G)_{T,P,m} \leq 0 \tag{1.52}$$

- which states that Gibbs function always decreases for a spontaneous, isothermal, isobaric change of a fixed-mass system.
- This allows us to calculate equilibrium χ_i at a given P, and T.
- At equilibrium:

$$(\mathrm{d}G)_{T,P,m} = 0 \tag{1.53}$$

Gibbs Function (Cont'd):

- For a mixture of ideal gases, the Gibbs function of the ith species

$$\bar{g}_{i,T} = \bar{g}^o_{i,T} + R_u T \ln(P_i/P^o) \tag{1.54}$$

$\bar{g}^o_{i,T}$ is Gibbs function at standard-state pressure, $P_i = P^o$.

- In reacting systems, *Gibbs function of formation* is

$$\bar{g}^o_{f,i}(T) \equiv \bar{g}^o_i(T) - \sum_j \nu'_j \bar{g}^o_j(T) \tag{1.55}$$

Gibbs Function (Cont'd):

- ν_j' are the stoichiometric coefficients of the elements required to form one mole of the compound of interest.
- $\nu_{\mathrm{O_2}}' = 0.5$ and $\nu_{\mathrm{C}}' = 1$ for forming one mole of CO from O_2 and C.
- Similar to enthalpies, $\bar{g}_{f,i}^{o}(T)$ of the naturally occuring elemets are assigned values of zero at the reference state.

Gibbs Function (Cont'd):

- Gibbs function for a mixture of ideal gases

$$G_{\mathrm{mix}} = \sum N_i \bar{g}^o_{i,T} = \sum N_i [\bar{g}^o_{i,T} + R_u T \ln(P_i/P^o)] \qquad (1.56)$$

- For a fixed T and P, the equilibrium condition becomes

$$\mathrm{d}G_{\mathrm{mix}} = 0 \qquad (1.57)$$

or

$$\sum \mathrm{d}N_i [\bar{g}^o_{i,T} + R_u T \ln(P_i/P^o)] + \sum N_i \mathrm{d}[\bar{g}^o_{i,T} + R_u T \ln(P_i/P^o)] = 0 \qquad (1.58)$$

Gibbs Function (Cont'd):

- Second term in the last equation is zero, because $\mathrm{d}(\ln P_i) = \mathrm{d}P_i/P_i$ and $\sum \mathrm{d}P_i = 0$ and total pressure is constant. Then,

$$\mathrm{d}G_{\mathrm{mix}} = 0 = \sum \mathrm{d}N_i[\bar{g}^o_{i,T} + R_u T \ln(P_i/P^o)] \tag{1.59}$$

- For a general system, where

$$a\mathrm{A} + b\mathrm{B} + ... \Leftrightarrow e\mathrm{E} + f\mathrm{F} + ... \tag{1.60}$$

Gibbs Function (Cont'd):

- The change in the number of each species is proportional to its stoichiometric coefficient,

$$\begin{aligned} \mathrm{d}N_A &= -\kappa a \\ \mathrm{d}N_B &= -\kappa b \\ . &= . \\ \mathrm{d}N_E &= +\kappa e \\ \mathrm{d}N_F &= +\kappa f \\ . &= . \end{aligned} \tag{1.61}$$

Gibbs Function (Cont'd):

substitute Eqn 1.61 into 1.59 and eliminate κ

$$\begin{aligned} &- a[\bar{g}^o_{A,T} + R_u T \ln(P_A/P^o)] \\ &- b[\bar{g}^o_{B,T} + R_u T \ln(P_B/P^o)] - .. \\ &+ e[\bar{g}^o_{E,T} + R_u T \ln(P_E/P^o)] \\ &+ f[\bar{g}^o_{F,T} + R_u T \ln(P_F/P^o)] + .. = 0 \end{aligned} \qquad (1.62)$$

or $$-(e\bar{g}^o_{E,T} + f\bar{g}^o_{F,T} + .. - a\bar{g}^o_{A,T} - b\bar{g}^o_{B,T} - ..)$$

$$= R_u T \ln \frac{(P_E/P^o)^e \cdot (P_F/P^o)^f \cdot ..}{(P_A/P^o)^a \cdot (P_B/P^o)^b \cdot ..} \qquad (1.63)$$

Gibbs Function (Cont'd):

Left hand side of Eqn 1.63 is the *standard-state Gibbs function change*:

$$\Delta G^o_T = (e\bar{g}^o_{E,T} + f\bar{g}^o_{F,T} + .. - a\bar{g}^o_{A,T} - b\bar{g}^o_{B,T} - ..) \tag{1.64a}$$

$$\Delta G^o_T \equiv (e\bar{g}^o_{f,E} + f\bar{g}^o_{f,F} + .. - a\bar{g}^o_{f,A} - b\bar{g}^o_{f,B} - ..)_T \tag{1.64b}$$

- Argument of the natural logarithm in Eqn 1.63 is defined as the *equilibrium constant* K_p

$$K_p = \frac{(P_E/P^o)^e \cdot (P_F/P^o)^f \cdot ..}{(P_A/P^o)^a \cdot (P_B/P^o)^b \cdot ..} \tag{1.65}$$

Gibbs Function (Cont'd):

Then we have:

$$\Delta G_T^o = -R_u T \ln K_p \qquad (1.66a)$$

$$K_p = \exp[-\Delta G_T^o/(R_u T)] \qquad (1.66b)$$

- Eqns 1.65 and 1.66 give a qualitative indication of whether a particular reaction favors products or reactants at equilibrium:

Reactants: If $\Delta G_T^o > 0 \Rightarrow \ln K_p < 0 \Rightarrow K_p < 1$

Products: If $\Delta G_T^o < 0 \Rightarrow \ln K_p > 0 \Rightarrow K_p > 1$

Gibbs Function (Cont'd):

- Similar physical insight can be obtained by considering the definition of ΔG_T^o in etrms of enthalpy and entropy changes:

  $$\Delta G_T^o = \Delta H^o - T \Delta S^o$$

  which can be substituted into Eqn 1.66b

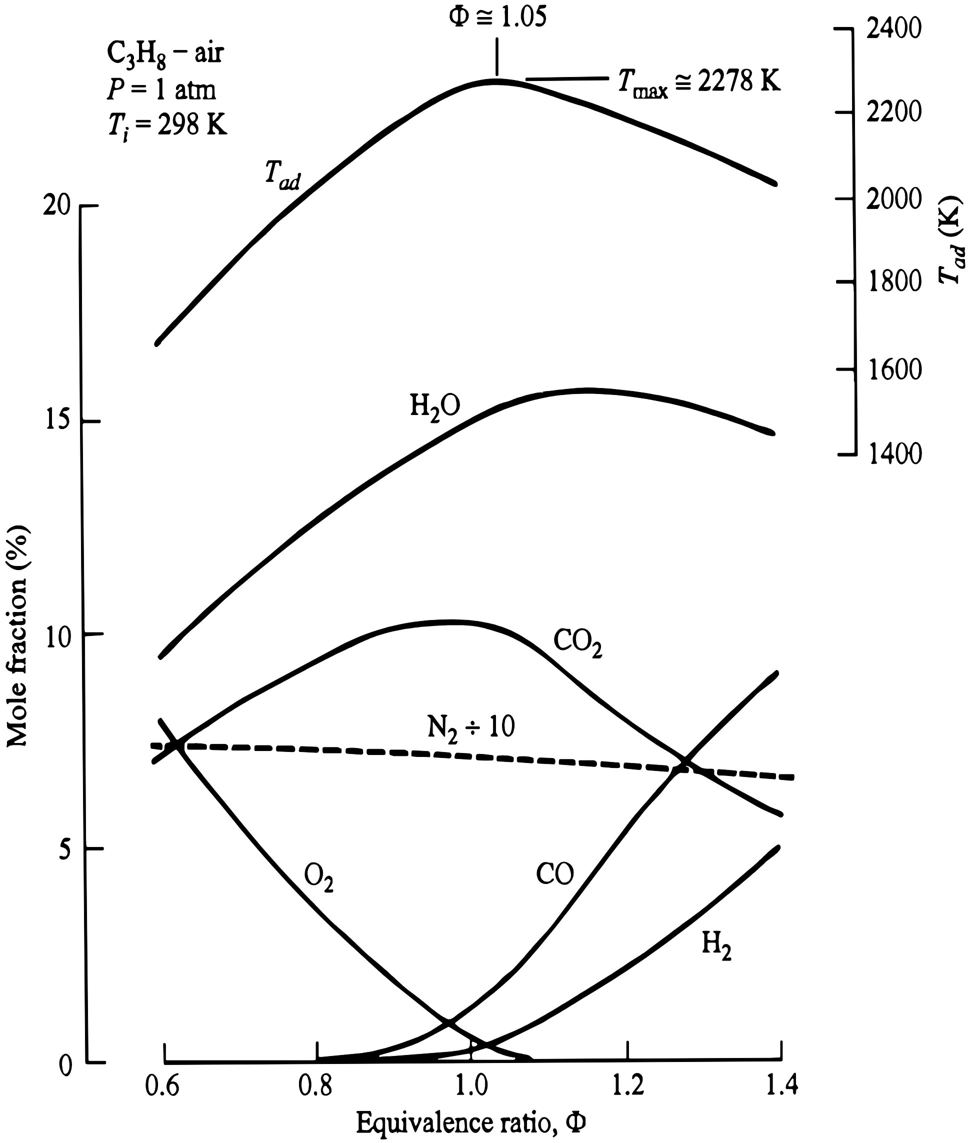
  $$K_p = \exp[-\Delta H^o/(R_u T)] \cdot \exp(\Delta S^o / R_u)$$

  - For $K_p > 1$, which favors products, ΔH^o should be negative (exothermic reaction). Also positive changes in entropy lead to $K_p > 1$

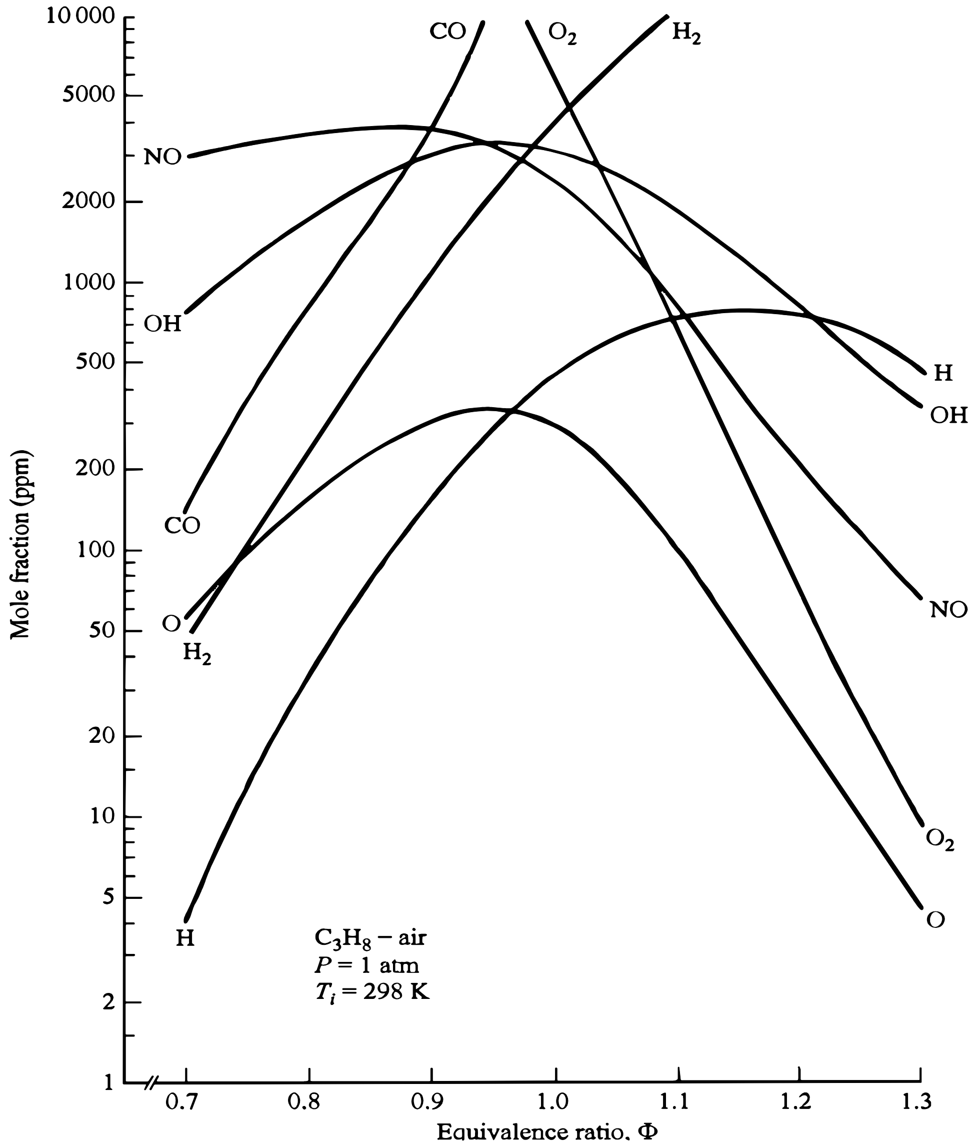
Equilibrium Products of Combustion:

Full Equilibrium:

- Calculate the adiabatic flame temperature and detailed composition of the products of combustion:
  - Eqn 1.40 (or 1.41) (1st law)
  - Eqn 1.66 (Gibbs funct.-Equilibrium const.)
  - Apropriate atom conservation constants
- Constant pressure combustion of Propane, C_3H_8, with air, assuming that the products are CO_2, CO, H_2O, H_2, H, OH, O_2, O, NO, N_2, and N:



T_{ad} and major species distribution.



Minor species distribution of propane-air combustion.

Water-Gas Equilibrium:

- Develop simple relations to calculate ideal products of combustion (no dissociation producing minor species) for lean and rich conditions:
- We employ a single equilibrium reaction (water-gas shift reaction):

  $$\mathrm{CO} + \mathrm{H_2O} \Leftrightarrow \mathrm{CO_2} + \mathrm{H_2}$$

  to account for simultaneous presence of CO and $\mathrm{H_2}$, considered as the incomplete combustion products.

Water-Gas Equilibrium (Cont'd):

- Combustion of an arbitrary hydrocarbon is considered:

$$C_xH_y + a(O_2 + 3.76N_2) \rightarrow$$

$$bCO_2 + cCO + dH_2O + eH_2 + fO_2 + 3.76aN_2 \qquad (1.67a)$$

For $\Phi \leq 1$ becomes:

$$C_xH_y + a(O_2 + 3.76N_2) \rightarrow$$

$$bCO_2 + dH_2O + fO_2 + 3.76aN_2 \qquad (1.67b)$$

Water-Gas Equilibrium (Cont'd):

For rich conditions, $\Phi > 1$:

$$C_xH_y + a(O_2 + 3.76N_2) \rightarrow$$

$$bCO_2 + cCO + dH_2O + eH_2 + 3.76aN_2 \quad (1.67c)$$

Note that a can be related to Φ:

$$a = \frac{x + y/4}{\Phi} \qquad (1.68)$$

So for a given fuel and Φ, a is a known quantity.

Water-Gas Equilibrium (Cont'd):

For $\Phi \leq 1$, c and e are zero:

$$\begin{aligned} b &= x \\ d &= y/2 \\ f &= [(1-\Phi)/\Phi](x+y/4) \end{aligned} \tag{1.69}$$

Total number of moles of products:

$$N_{\mathrm{TOT}} = x + y/2 + \left(\frac{x+y/4}{\Phi}\right)(1-\Phi+3.76) \tag{1.70}$$

Water-Gas Equilibrium (Cont'd):

For $\Phi \leq 1$ mole fraction of products:

$$\begin{aligned}
\chi_{\mathrm{CO_2}} &= x/N_{\mathrm{TOT}} \\
\chi_{\mathrm{CO}} &= 0 \\
\chi_{\mathrm{H_2O}} &= (y/2)/N_{\mathrm{TOT}} \\
\chi_{\mathrm{H_2}} &= 0 \\
\chi_{\mathrm{O_2}} &= [(1-\Phi)/\Phi](x+y/4)/N_{\mathrm{TOT}} \\
\chi_{\mathrm{N_2}} &= 3.76(x+y/4)/(\Phi N_{\mathrm{TOT}})
\end{aligned} \tag{1.71}$$

Water-Gas Equilibrium (Cont'd):

For $\Phi > 1$ no oxygen appears, $f = 0$. To calculate the remaining constants, we use the three atomic balances (C, H, and O) and water-gas shift equilibrium:

$$K_P = \frac{(P_{\mathrm{CO_2}}/P^o) \cdot (P_{\mathrm{H_2}}/P^o)}{(P_{\mathrm{CO}}/P^o) \cdot (P_{\mathrm{H_2O}}/P^o)} = \frac{b \cdot e}{c \cdot d} \tag{1.72}$$

$$\begin{aligned} c &= x - b \\ d &= 2a - b - x \\ e &= -2a + b + x + y/2 \end{aligned} \tag{1.73}$$

Water-Gas Equilibrium (Cont'd):

Combining Eqn 1.73 with 1.72 yields a quadratic equation in b. Its solution is (negative root selected to yield positive values of b):

$$
\begin{aligned}
b = & \frac{2a(K_p - 1) + x + y/2}{2(K_p - 1)} \\
& - \frac{1}{2(K_p - 1)}\{[2a(K)p - 1) + x + y/2]^2 \\
& - 4K_p(K_p - 1)(2ax - x^2)\}^{1/2}
\end{aligned} \tag{1.74}
$$

Water-Gas Equilibrium (Cont'd):

For $\Phi > 1$ mole fraction of products:

$$N_{\mathrm{TOT}} = b + c + d + e + 3.76a = x + y/2 + 3.76a \tag{1.75}$$

$$\begin{aligned}
\chi_{\mathrm{CO_2}} &= b/N_{\mathrm{TOT}} \\
\chi_{\mathrm{CO}} &= (x - b)/N_{\mathrm{TOT}} \\
\chi_{\mathrm{H_2O}} &= (2a - b - x)/N_{\mathrm{TOT}} \\
\chi_{\mathrm{H_2}} &= (-2a + b + x + y/2)/N_{\mathrm{TOT}} \\
\chi_{\mathrm{O_2}} &= 0 \\
\chi_{\mathrm{N_2}} &= 3.76a/N_{\mathrm{TOT}}
\end{aligned} \tag{1.76}$$

2. Chemical Kinetics

Introduction:

- Thermodynamic laws allow determination of the equilibrium state of a chemical reaction system.
- If one assumes that the chemical reactions are fast compared to the other transport processes like
    - diffusion,
    - heat conduction, and
    - flow,
- then, thermodynamics describe the system locally.

Introduction (Cont'd):

- In most combustion cases, however, chemical reactions occur on time scales comparable with that of the flow and the molecular transport processes.
- Then, information is needed about the rate of chemical reactions.
- Chemical reaction rates control pollutant formation, ignition, and flame extinction in most combustion processes.

Global & Elementary Reactions

- An *elementary* reaction is one that occurs on a molecular level exactly in the way which is described by the reaction equation.

$$OH + H_2 \rightarrow H_2O + H$$

- The equation above is an elementary reaction. On the contrary, the following is not an elementary reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$

- Above reaction is *global* or *overall* reaction.

- A general *global reaction mechanism* involving overall reaction of a moles of oxidizer with one mole of fuel to form b moles of products:

$$\mathrm{F} + a\mathrm{Ox} \rightarrow b\mathrm{Pr} \tag{2.1}$$

- Experimental observations yield the rate at which fuel is consumed as

$$\frac{\mathrm{d}[\mathrm{F}]}{\mathrm{d}t} = -k_G(T)[\mathrm{F}]^n[\mathrm{Ox}]^m \tag{2.2}$$

- $[\mathrm{X}]$ denotes molar concentration of X, e.g. kmol/m^3.
- $k_G(T)$ is the global rate coefficient.
- n and m relate to the *reaction order*.
- According to Eqn 2.2, reaction is
  - nth order with respect to fuel,
  - mth order with respect to oxidant, and
  - $(m+n)$th order overall.
- m and n are determined from experimental data and are not necessarily integers.

- Use of global reactions to express chemistry is usually a *black box* approach and has limited use in combustion.
- It does not provide a basis for understanding what is actually happening.
- Let's consider the following global reaction:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{2.3}$$

- It implies that two moles of hydrogen molecule react with one mole of oxygen to form one mole of water, which is not strictly true.

- In reality many sequential processes occur that involve several *intermediate species*. Following *elementary reactions*, among others, are important in conversion of H_2 and O_2 to water:

$$\mathrm{H_2 + O_2 \rightarrow HO_2 + H} \tag{2.4}$$

$$\mathrm{H + O_2 \rightarrow OH + O} \tag{2.5}$$

$$\mathrm{OH + H_2 \rightarrow H_2O + H} \tag{2.6}$$

$$\mathrm{H + O_2 + M \rightarrow HO_2 + M} \tag{2.7}$$

- *Radicals* or *free radicals* or *reactive species* are reactive molecules, or atoms, that have unpaired electrons.
- To have a complete picture of the combustion of H_2 with O_2, more than 20 elementary reactions can be considered.
- *Reaction mechanism* is the collection of elementary reactions to describe the overall reaction.
- Reaction mechanisms may involve a few steps or as many as several hundred (even thousands).
- (State-of-the-art).

Elementary Reaction Rates

- Using the concept of elementary reactions has many advantages.
- Reaction order is constant and can be experimentally determined.
- *molecularity of the reaction*: number of species that form the reaction complex.
  - Unimolecular
  - Bimolecular
  - Trimolecular / Termolecular

Bimolecular Reactions & Collision Theory

- Most combustion related elementary reactions are bimolecular:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D} \tag{2.8}$$

- The rate at which the reaction proceeds is

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{bimolec}}[\mathrm{A}][\mathrm{B}] \tag{2.9}$$

- $k_{\mathrm{bimolec}} \propto f(T)$ and has a theoretical basis, unlike k_G, rate coefficient of a global reaction.

- Collision theory for bimolecular reactions has several shortcomings.
- Approach is important for historical reasons and may provide a simple way to visualize bimolecular reactions.
- Uses the concepts of wall collision frequency, mean molecular speed, and mean free path.
- The simpler approach is to consider a single molecule of diameter σ travelling at constant speed v and experiencing collisions with identical, but stationary molecules.

- If the distance travelled (mean free path) between colisions is large, then moving molecule sweeps out a cylindrical volume of $v\pi\sigma^2\Delta t$.
- For random distribution of stationary molecules with number density n/V, number of collisions

$$Z \equiv \frac{\text{collisions}}{\text{per unit time}} = (n/V)v\pi\sigma^2 \qquad (2.10)$$

- For Maxwellian velocity distribution for all molecules

$$Z_c = \sqrt{2}(n/V)\pi\sigma^2\bar{v} \qquad (2.11)$$

- Eqn.2.11 applies to identical molecules. For different molecules, we can use $\sigma_{\mathrm{A}} + \sigma_{\mathrm{B}} \equiv 2\sigma_{\mathrm{AB}}$

$$Z_c = \sqrt{2}(n_{\mathrm{B}}/V)\pi\sigma_{\mathrm{AB}}^2\bar{v}_{\mathrm{A}} \tag{2.12}$$

  which expresses frequency of collisions of a single A molecule with all B molecules.

- For all A molecules

$$Z_{\mathrm{AB}}/V = (n_{\mathrm{A}}/V)(n_{\mathrm{B}}/V)\pi\sigma_{\mathrm{AB}}^2(\bar{v}_{\mathrm{A}}^2 + \bar{v}_{\mathrm{B}}^2)^{1/2} \tag{2.13}$$

If we express mean molecular speed in terms of temperature,

$$Z_{\mathrm{AB}}/V = (n_{\mathrm{A}}/V)(n_{\mathrm{B}}/V)\pi\sigma_{\mathrm{AB}}^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \tag{2.14}$$

k_B = Boltzmann constant.

$\mu = (m_{\mathrm{A}}m_{\mathrm{B}})/(m_{\mathrm{A}}+m_{\mathrm{B}})$ = reduced mass.

T = absolute temperature.

- We can relate Z_{AB}/V to reaction rates

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \left[\begin{array}{c}\text{No. of collisons}\\ \text{A and B molecules}\\ \text{per unit volume}\\ \text{per unit time}\end{array}\right] \cdot \left[\begin{array}{c}\text{Probability that}\\ \text{a collision}\\ \text{leads to}\\ \text{reaction}\end{array}\right]$$

$$\cdot \left[\frac{\text{kmol of A}}{\text{No. of molecules of A}}\right] \qquad (2.15a)$$

or

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = (Z_{\mathrm{AB}}/V)\mathcal{P}N_{AV}^{-1} \qquad (2.15b)$$

- The probability that a collision will lead to a reaction can be expressed as a product of two factors:
  - an energy factor

    $$\exp\left[-E_A/(R_u T)\right]$$

    which expresses the fraction of collisions that occur with an energy above the *activation energy*
  - a geometrical or *steric factor* p, that takes into account the geometry of collisions between A and B.

- With substitutions $n_{\mathrm{A}}/V = [A]N_{AV}$ and $n_{\mathrm{B}}/V = [B]N_{AV}$, Eqn.2.15b becomes

$$-\frac{\mathrm{d[A]}}{\mathrm{d}t} = pN_{AV}\sigma^2_{\mathrm{AB}}\Big[\frac{8\pi k_B T}{\mu}\Big]^{1/2} \cdot \exp\left[-E_A/(R_u T)\right]\mathrm{[A][B]} \tag{2.16}$$

- Comparing Eqn. 2.16 with 2.9

$$k(T) = pN_{AV}\sigma^2_{\mathrm{AB}}\Big[\frac{8\pi k_B T}{\mu}\Big]^{1/2} \exp\Big[\frac{-E_A}{R_u T}\Big] \tag{2.17}$$

- Collision theory is not capable of providing any means to determine E_A or p.
- More advanced theories do allow calculation of $k(T)$ from first principles to a limited extent.
- If the temperature range of interest is not too large, k_{bimolec} can be expressed by the semi-empirical *Arrhenius* form

$$k(T) = A \exp\left[\frac{-E_A}{R_u T}\right] \tag{2.18}$$

where A is a constant termed *pre-exponential factor* or *frequency factor*.

- Most of the time the experimental values for rate coefficients in Arrhenius form expressed as

$$k(T) = AT^b \exp\left[\frac{-E_A}{R_u T}\right] \tag{2.19}$$

  where A, b, and E_A are three empirical constants.

- The standard method for obtaining E_A is to graph experimental rate constant data versus inverse of temperature, i.e. $\log k$ vs $1/T$. The slope gives E_A/R_u.

Unimolecular Reactions:

- Involves single species

$$\mathrm{A} \rightarrow \mathrm{B} \tag{2.20}$$

$$\mathrm{A} \rightarrow \mathrm{B} + \mathrm{C} \tag{2.21}$$

- Examples: $O_2 \rightarrow O + O$; $H_2 \rightarrow H + H$.
- First order at high pressures

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{uni}}[\mathrm{A}] \tag{2.22}$$

- At low pressures, the reaction rate may also depend a third molecule that may exist within the reaction volume

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k[\mathrm{A}][\mathrm{M}] \tag{2.23}$$

Termolecular Reactions:

$$\mathrm{A} + \mathrm{B} + \mathrm{M} \rightarrow \mathrm{C} + \mathrm{M} \tag{2.24}$$

- Termolecular reactions are third order

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{ter}}[\mathrm{A}][\mathrm{B}][\mathrm{M}] \tag{2.25}$$

Multistep Mechanisms

Net Production Rates

- Consider some of the reactions in H_2-O_2 system

$$H_2 + O_2 \underset{k_{r1}}{\overset{k_{f1}}{\rightleftharpoons}} HO_2 + H \qquad (R.1)$$

$$H + O_2 \underset{k_{r2}}{\overset{k_{f2}}{\rightleftharpoons}} OH + O \qquad (R.2)$$

$$OH + H_2 \underset{k_{r3}}{\overset{k_{f3}}{\rightleftharpoons}} H_2O + H \qquad (R.3)$$

$$H + O_2 + M \underset{k_{r4}}{\overset{k_{f4}}{\rightleftharpoons}} HO_2 + M \qquad (R.4)$$

- The net production rate of any species, say X, involved is the sum of all of the individual elementary rates producing X minus all of the rates destroying X.
- Net production rate of O_2 is then,

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} =& k_{r1}[\mathrm{HO_2}][\mathrm{H}] + k_{r2}[\mathrm{OH}][\mathrm{O}] \\ &+ k_{r4}[\mathrm{HO_2}][\mathrm{M}] - k_{f1}[\mathrm{H_2}][\mathrm{O_2}] \\ &- k_{f2}[\mathrm{H}][\mathrm{O_2}] - k_{f4}[\mathrm{H}][\mathrm{O_2}][\mathrm{M}]\end{aligned} \qquad (2.26)$$

- Net production rate for H atoms:

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} =& k_{f1}[\mathrm{H_2}][\mathrm{O_2}] + k_{r2}[\mathrm{OH}][\mathrm{O}] \\ & + k_{f3}[\mathrm{OH}][\mathrm{H_2}] + k_{r4}[\mathrm{HO_2}][\mathrm{M}] \\ & - k_{r1}[\mathrm{HO_2}][\mathrm{H}] - k_{f2}[\mathrm{H}][\mathrm{O_2}] \\ & - k_{r3}[\mathrm{H_2O}][\mathrm{H}] - k_{f4}[\mathrm{H}][\mathrm{O_2}][\mathrm{M}]\end{aligned} \tag{2.27}$$

$$\begin{aligned}\frac{\mathrm{d}[X_i](t)}{\mathrm{d}t} &= f_i\{[X_1](t), [X_2](t), ...[X_n](t)\} \\ [X_i](0) &= [X_i]_0\end{aligned} \tag{2.28}$$

Compact Notation:

- Since mechanisms may involve many elementary steps and many species, a generalized compact notation has been developed for the mechanism and the individual species production rates.
- For the mechanism,

$$\sum_{j=1}^{N} \nu'_{ji} X_j \rightleftharpoons \sum_{j=1}^{N} \nu''_{ji} X_j \quad \text{for } i = 1, 2, ...L \quad (2.29)$$

where ν'_{ji} and ν''_{ji} are stoichiometric coefficients of reactants and products, respectively.

N		L	
j	Species	i	Reaction
1	O_2	1	R.1
2	H_2	2	R.2
3	H_2O	3	R.3
4	HO_2	4	R.4
5	O		
6	H		
7	OH		
8	M		

- Stoichiometric coefficient matrices:

$$\nu'_{ji} = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \end{bmatrix} \qquad (2.30a)$$

$$\nu''_{ji} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \end{bmatrix} \qquad (2.30b)$$

- Net production rate of each species in a multistep mechanism:

$$\mathrm{d}[X_j]/\mathrm{d}t \equiv \dot{\omega}_j = \sum_{i=1}^{L} \nu_{ji} q_i \quad \text{for} \quad j = 1, 2, ...N \tag{2.31}$$

where

$$\nu_{ji} = (\nu''_{ji} - \nu'_{ji}) \tag{2.32}$$

$$q_i = k_{fi} \prod_{j=1}^{N} [X_j]^{\nu'_{ji}} - k_{ri} \prod_{j=1}^{N} [X_j]^{\nu''_{ji}} \tag{2.33}$$

- For example, $q_i (= q_1)$ for reaction R.1 is

$$\begin{aligned} q_i = & k_{f1} [\mathrm{O_2}]^1 [\mathrm{H_2}]^1 [\mathrm{H_2O}]^0 \\ & [\mathrm{HO_2}]^0 [\mathrm{O}]^0 [\mathrm{H}]^0 [\mathrm{OH}]^0 [\mathrm{M}]^0 \\ & - k_{r1} [\mathrm{O_2}]^0 [\mathrm{H_2}]^0 [\mathrm{H_2O}]^0 \\ & [\mathrm{HO_2}]^1 [\mathrm{O}]^0 [\mathrm{H}]^1 [\mathrm{OH}]^0 [\mathrm{M}]^0 \\ & = k_{f1} [\mathrm{O_2}][\mathrm{H_2}] - k_{r1} [\mathrm{HO_2}][\mathrm{H}] \end{aligned} \tag{2.34}$$

- Writing similar expressions for $i = 2, 3,$ and 4 and summing completes the total rate expression for $\dot{\omega}_j$.

Rate Coefficients and Equilibrium Constants:

- At equilibrium forward and reverse reaction rates must be equal.

$$\mathrm{A} + \mathrm{B} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{C} + \mathrm{D} \tag{2.35}$$

- Formation rate of species A:

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_f[\mathrm{A}][\mathrm{B}] + k_r[\mathrm{C}][\mathrm{D}] \tag{2.36}$$

- For equilibrium, time rate of change of [A] must be zero. Same goes for B, C, and D.

- Then, Eqn. 2.36

$$0 = -k_f[\mathrm{A}][\mathrm{B}] + k_r[\mathrm{C}][\mathrm{D}] \tag{2.37}$$

arranging

$$\frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]} = \frac{k_f(T)}{k_r(T)} \tag{2.38}$$

- Previously we have defined equilibrium constant as,

$$K_p = \frac{(P_{\mathrm{C}}/P^o)^c(P_{\mathrm{D}}/P^o)^d \ldots}{(P_{\mathrm{A}}/P^o)^a(P_{\mathrm{B}}/P^o)^b \ldots} \tag{2.39}$$

- Since molar concentrations are related to mol fractions and partial pressures as,

$$[X_i] = \chi_i P/(R_u T) = P_i/(R_u T) \tag{2.40}$$

we can define an equlibrium constant based on molar concentrations, K_c and relate it to K_p,

$$K_p = K_c (R_u T/P^o)^{c+d+\ldots-a-b\ldots} \tag{2.41a}$$

or

$$K_P = K_c (R_u T/P^o)^{\Sigma\nu'' - \Sigma\nu'} \tag{2.41b}$$

where, K_c is defined as,

$$K_c = \frac{[\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}}...}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}...} = \frac{\prod\limits_{\mathrm{prod}} [X_i]^{\nu_i''}}{\prod\limits_{\mathrm{react}} [X_i]^{\nu_i'}} \qquad (2.42)$$

- So that,

$$\frac{k_f(T)}{k_r(T)} = K_c(T) \qquad (2.43)$$

- For bimolecular reactions $K_c = K_p$.

Steady-State Approximation

- Analysis of reactive systems can be simplified by applying steady-state approximation to the reactive species or radicals.
- Steady-state approximation is justified when the reaction forming the intermediate species is slow, while the reaction destroying the intermediate species is very fast.
- As a result the concentration of the radical is small in comparison with those of the reactants and products.

- Example (Zeldovich mechanism for NO formation):

$$O + N_2 \xrightarrow{k_1} NO + N$$

$$N + O_2 \xrightarrow{k_2} NO + O$$

  First reaction is slow (rate limiting); while second is fast.

- Net production rate of N atoms,

$$\frac{\mathrm{d}[N]}{\mathrm{d}t} = k_1[O][N_2] - k_2[N][O_2] \qquad (2.44)$$

- After a rapid transient allowing buildup of N, $\mathrm{d[N]}/\mathrm{d}t$ approaches zero.

$$0 = k_1[\mathrm{O}][\mathrm{N_2}] - k_2[\mathrm{N}]_{\mathrm{ss}}[\mathrm{O_2}] \tag{2.45}$$

$$[\mathrm{N}]_{\mathrm{ss}} = \frac{k_1[\mathrm{O}][\mathrm{N_2}]}{k_2[\mathrm{O_2}]} \tag{2.46}$$

- Time rate of change of $[\mathrm{N}]_{\mathrm{ss}}$ is

$$\frac{\mathrm{d}[\mathrm{N}]_{\mathrm{ss}}}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{k_1[\mathrm{O}][\mathrm{N_2}]}{k_2[\mathrm{O_2}]}\right] \tag{2.47}$$

Mechanism for Unimolecular Reactions

- Let's consider a three-step mechanism:

$$A + M \xrightarrow{k_{\mathrm{e}}} A^* + M \tag{2.48a}$$

$$A^* + M \xrightarrow{k_{\mathrm{de}}} A + M \tag{2.48b}$$

$$A^* \xrightarrow{k_{\mathrm{unim}}} \text{products} \tag{2.48c}$$

- In step 1: kinetic energy transferred to A from M; A has increased internal vibrational and rotational energies and becomes an *energized* A molecule, A^*.

- Two possible scenarios for A^*:
  - A^* may collide with another molecule and goes back to A (2.48b)
  - A^* may decompose into products (2.48c)
- The rate at which products are formed:

$$\frac{\mathrm{d}[\text{products}]}{\mathrm{d}t} = k_{\text{unim}}[\mathrm{A}^*] \tag{2.49}$$

- Net production rate of A^*:

$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = k_{\mathrm{e}}[\mathrm{A}][\mathrm{M}] - k_{\mathrm{de}}[\mathrm{A}^*][\mathrm{M}] - k_{\text{unim}}[\mathrm{A}^*] \tag{2.50}$$

- Steady-state approximation for A*, i.e. $\mathrm{d}[\mathrm{A}^*]/\mathrm{d}t = 0$,

$$[\mathrm{A}^*] = \frac{k_\mathrm{e}[\mathrm{A}][\mathrm{M}]}{k_\mathrm{de}[\mathrm{M}] + k_\mathrm{unim}} \tag{2.51}$$

- Substitute Eqn.2.51 into 2.49,

$$\frac{\mathrm{d}[\mathrm{products}]}{\mathrm{d}t} = \frac{k_\mathrm{e}[\mathrm{A}][\mathrm{M}]}{(k_\mathrm{de}/k_\mathrm{unim})[\mathrm{M}] + 1} \tag{2.52}$$

- Another form of writing the overall rate of production of *products* for the overall reaction:

$$\mathrm{A} \xrightarrow{k_{\mathrm{app}}} \text{products} \tag{2.53}$$

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{\text{products}}{\mathrm{d}t} = k_{\mathrm{app}}[\mathrm{A}] \tag{2.54}$$

k_{app} is an apparent unimolecular rate coef.

- Equating Eqns.2.52 and 2.54 yields

$$k_{\mathrm{app}} = \frac{k_{\mathrm{e}}[\mathrm{M}]}{(k_{\mathrm{de}}/k_{\mathrm{unim}})[\mathrm{M}] + 1} \tag{2.55}$$

- Eqn.2.55 lets us to explain pressure dependence of unimolecular reactions:

- At high enough pressures $(k_{\mathrm{de}}[\mathrm{M}]/k_{\mathrm{unim}}) >> 1$ because [M] increases as the pressure is increased; then

$$k_{\mathrm{app}}(P \to \infty) = k_{\mathrm{unim}} k_{\mathrm{e}} / k_{\mathrm{de}} \tag{2.56}$$

- At low enough pressures $(k_{\mathrm{de}}[\mathrm{M}]/k_{\mathrm{unim}}) << 1$, then

$$k_{\mathrm{app}}(P \to 0) = k_{\mathrm{e}}[\mathrm{M}] \tag{2.57}$$

Chain and Chain-Branching Reactions:

- *Chain reactions* produce one or more radical species that subsequently react to produce another radical(s).
- To learn some of the features of chain reactions, we consider a hypothetical chain mechanism, which is globally represented as

$$\mathrm{A_2 + B_2 \longrightarrow 2AB}$$

- *Chain initiation*:

$$\mathrm{A_2 + M \xrightarrow{k_1} A + A + M} \qquad \text{(C.1)}$$

- *Chain-propagating reactions* involving free radicals A and B:

$$A + B_2 \xrightarrow{k_2} AB + B \tag{C.2}$$

$$B + A_2 \xrightarrow{k_3} AB + A \tag{C.3}$$

- *Chain-terminating reaction* is

$$A + B + M \xrightarrow{k_4} AB + M \tag{C.4}$$

where AB is the stable product.

- Concentrations of A and B are small throughout the course of reaction, so is AB at initial stages; thus we ignore reverse reactions and determine reaction rates for stable species as:

$$\frac{\mathrm{d}[\mathrm{A}_2]}{\mathrm{d}t} = -k_1[\mathrm{A}_2][\mathrm{M}] - k_3[\mathrm{A}_2][\mathrm{B}] \tag{2.58}$$

$$\frac{\mathrm{d}[\mathrm{B}_2]}{\mathrm{d}t} = -k_2[\mathrm{B}_2][\mathrm{A}] \tag{2.59}$$

$$\frac{\mathrm{d}[\mathrm{AB}]}{\mathrm{d}t} = k_2[\mathrm{A}][\mathrm{B}_2] + k_3[\mathrm{B}][\mathrm{A}_2] + k_4[\mathrm{A}][\mathrm{B}][\mathrm{M}] \tag{2.60}$$

- If we use the steady-state approximation for free radicals A and B:

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = 2k_1[\mathrm{A_2}][\mathrm{M}] - k_2[\mathrm{A}][\mathrm{B_2}] + k_3[\mathrm{B}][\mathrm{A_2}] - k_4[\mathrm{A}][\mathrm{B}][\mathrm{M}] = 0 \tag{2.61}$$

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = k_2[\mathrm{A}][\mathrm{B_2}] - k_3[\mathrm{B}][\mathrm{A_2}] - k_4[\mathrm{A}][\mathrm{B}][\mathrm{M}] = 0 \tag{2.62}$$

- Simultaneous solution of Eqns. 2.61 and 2.62 for A:

$$[\mathrm{A}] = \frac{k_1}{2k_2}\frac{[\mathrm{M}][\mathrm{A}_2]}{[\mathrm{B}_2]} + \frac{k_3}{k_4}\frac{[\mathrm{A}_2]}{[\mathrm{M}]} \cdot \left\{ \left[1 + \left(\frac{k_1 k_4}{2k_2 k_3}\frac{[\mathrm{M}]^2}{[\mathrm{B}_2]} \right)^2 \right]^{1/2} - 1 \right\} \tag{2.63}$$

- A similar expression can be written for [B].
- With the steady-state values for [A] and [B],

$$\mathrm{d}[\mathrm{A}_2]/\mathrm{d}t, \quad \mathrm{d}[\mathrm{B}_2]/\mathrm{d}t, \quad \text{and} \quad \mathrm{d}[\mathrm{AB}]/\mathrm{d}t$$

can be found for initial values of $[\mathrm{A}_2]$ and $[\mathrm{B}_2]$.

- If we consider the simplest of the three, $d[B_2]/dt$:

$$\frac{d[B_2]}{dt} = -\frac{k_1}{2}[A_2][M] - \frac{k_2 k_3}{k_4}\frac{[A_2][B_2]}{[M]} \left\{ \left[1 + \left(\frac{k_1 k_4}{2 k_2 k_3} \frac{[M]^2}{[B_2]} \right)^2 \right]^{1/2} - 1 \right\} \tag{2.64}$$

- The last two Eqns can be further simplified:

$$k_1 k_4 [M]^2 / (2 k_2 k_3 [B_2]) << 1$$

since k_2 and k_3 must be much larger than k_1 and k_4 for steady-state approximation to apply.

- Eqns. 2.63 and 2.64 can be approximated as:

$$[\mathrm{A}] \approx \frac{k_1}{2k_2}\frac{[\mathrm{M}][\mathrm{A_2}]}{[\mathrm{B_2}]} + \frac{k_1^2 k_4}{8k_2^2 k_3}\frac{[\mathrm{M}]^3[\mathrm{A_2}]}{[\mathrm{B_2}]^2} \qquad (2.65)$$

$$\frac{\mathrm{d}[\mathrm{B_2}]}{\mathrm{d}t} \approx -\frac{k_1}{2}[\mathrm{A_2}][\mathrm{M}] - \frac{k_1^2 k_4}{4k_2 k_3}\frac{[\mathrm{M}]^3[\mathrm{A_2}]}{[\mathrm{B_2}]} \qquad (2.66)$$

- First term in both Eqns. dominates at low pressures.

- Concentration of A depends on the ratio k_1/k_2.
- Rate at which B_2 dissapears is governed by k_1.
- Increasing k_2 and k_3 increases radical concentration, but has no effect on production rate of products.
- [A] and [B] are directly proportional to P.
- Reaction rates of major species scale with pressure squared.
  - provided that second terms in Eqns.2.65 and 2.66 remain small.

- At high pressures, the second terms in Eqns. 2.65 and 2.66 become important (they increase with pressure faster than the first terms do).
- So, k_4 has some influence at high pressures, although it does not have much influence on radical concentrations or overall reaction rate at lower pressures.
- *Chain-branching reactions* involve the formation of two radical species from a reaction that consumes only one radical.

$$\mathrm{O} + \mathrm{H_2O} \longrightarrow \mathrm{OH} + \mathrm{OH}$$

Chemical Time Scales:

- Magnitude of chemical times relative to convective or mixing times is of importance in combustion.
- *Unimolecular reactions*

$$\mathrm{A} \xrightarrow{k_{\mathrm{app}}} \text{products} \tag{2.53}$$

$$-\frac{\mathrm{d[A]}}{\mathrm{d}t} = \frac{\text{products}}{\mathrm{d}t} = k_{\mathrm{app}}[\mathrm{A}] \tag{2.54}$$

- Integrating at constant T for $[\mathrm{A}](t=0)=[\mathrm{A}]_0$,

$$[\mathrm{A}](t) = [\mathrm{A}]_0 \exp\left[-k_{\mathrm{app}} t\right] \tag{2.67}$$

- Characteristic chemical time can be defined as the time required for the concentration of A to fall from its initial value to a value equal to $1/e$ times the initial value,

$$\frac{[\mathrm{A}](\tau_{\mathrm{chem}})}{[\mathrm{A}]_0} = 1/e \tag{2.68}$$

- Combining Eqns. 2.67 and 2.68 yields,

$$1/e = \exp\left[-k_{\mathrm{app}}\tau_{\mathrm{chem}}\right) \tag{2.69}$$

or

$$\tau_{\mathrm{chem}} = 1/k_{\mathrm{app}} \tag{2.70}$$

- *Bimolecular Reactions*

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_{\mathrm{bimolec}}} \mathrm{C} + \mathrm{D} \tag{2.8}$$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{bimolec}}[\mathrm{A}][\mathrm{B}] \tag{2.9}$$

- For this single reaction [A] and [B] are related by stoichiometry. Any change in [A] has a corresponding change in [B],

$$x \equiv [\mathrm{A}]_0 - [\mathrm{A}] = [\mathrm{B}]_0 - [\mathrm{B}] \tag{2.71}$$

$$[\mathrm{B}] = [\mathrm{A}] + [\mathrm{B}]_0 - [\mathrm{A}]_0 \tag{2.72}$$

- Substituting Eqn.4.71 into 4.9 and integrating,

$$\frac{[\mathrm{A}](t)}{[\mathrm{B}](t)} = \frac{[\mathrm{A}]_0}{[\mathrm{B}]_0} \exp\{([\mathrm{A}]_0 - [\mathrm{B}]_0) k_{\mathrm{bimolec}} t\} \tag{2.73}$$

- Substitute Eqn.2.72 into 2.73, and set:

$$[\mathrm{A}]/[\mathrm{A}]_0 = 1/e \quad \text{when} \quad t = \tau_{\mathrm{chem}}$$

gives

$$\tau_{\mathrm{chem}} = \frac{\ln\left[e + (1-e)([\mathrm{A}]_0/[\mathrm{B}]_0)\right]}{([\mathrm{B}]_0 - [\mathrm{A}]_0)k_{\mathrm{bimolec}}} \tag{2.74}$$

- If $[\mathrm{B}]_0 >> [\mathrm{A}]_0$,

$$\tau_{\mathrm{chem}} = \frac{1}{[\mathrm{B}]_0 k_{\mathrm{bimolec}}} \tag{2.75}$$

- *Termolecular Reactions*

$$\mathrm{A} + \mathrm{B} + \mathrm{M} \xrightarrow{k_{\mathrm{ter}}} \mathrm{C} + \mathrm{M} \tag{2.24}$$

- For a simple system at constant T, [M] is constant

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = (-k_{\mathrm{ter}}[\mathrm{M}])[\mathrm{A}][\mathrm{B}] \tag{2.9}$$

  where $(-k_{\mathrm{ter}}[\mathrm{M}])$ plays the same role as k_{bimolec} does for a bimolecular reaction.

- Then, the characteristic time for termolecular reactions is,

$$\tau_{\text{chem}} = \frac{\ln\left[e + (1-e)([\mathrm{A}]_0/[\mathrm{B}]_0)\right]}{([\mathrm{B}]_0 - [\mathrm{A}]_0)k_{\text{ter}}[\mathrm{M}]} \qquad (2.77)$$

And, when $[\mathrm{B}]_0 >> [\mathrm{A}]_0$,

$$\tau_{\text{chem}} = \frac{1}{[\mathrm{B}]_0(k_{\text{ter}}[\mathrm{M}])} \qquad (2.78)$$

3. Combustion Chemistry

- For many kinetically controlled systems, the number of elementary reaction steps is so large that simple analytical solutions are not possible.
- Most of the time, a large number of chemical species are involved.
- Even in combustion of simple hydrocarbons, number of species involved is quite high.
- To illustrate how the fundamental principles of chemical kinetics apply to real-world problems, we will consider some examples.

Hydrogen-Oxygen Reaction

The reaction between hydrogen and oxygen is a good example of a multicomponent kinetic system. To describe the sysytem properly, we should consider eight major species and at least 16 reactions.

- The overall reaction is:

  $$2H_2 + O_2 \rightarrow 2H_2O$$

  This reaction is exothermic; but mixtures of gaseous hydrogen and oxygen are quite stable at atmospheric conditions. Any conceivable direct reaction between the two gases is zero.

- The reaction half-time at atmospheric conditions has been estimated to be much larger than the age of the universe.
- If the reaction is initiated by some free-radical species, then the reaction proceeds very rapidly and violently.
- The radicals are typically H and O atoms produced from the dissociation of H_2 and O_2, respectively.
- We will consider a simplified mechanism that represents the gross features of $H_2 + O_2$ at low P.

- Initiation

$$H_2 \xrightarrow{k_o} 2H \qquad (H.0a)$$

$$O_2 \xrightarrow{k_o} 2O \qquad (H.0b)$$

- Chain branching

$$O_2 + H \xrightarrow{k_2} OH + O \qquad (H.2)$$

$$H_2 + O \xrightarrow{k_3} OH + H \qquad (H.3)$$

- Chain propagation

$$H_2 + OH \xrightarrow{k_1} H_2O + H \qquad \text{(H.1)}$$

- Chain termination

$$H + \text{wall} \xrightarrow{k_4} (1/2)H_2 \qquad \text{(H.4)}$$

$$H + O_2 + M \xrightarrow{k_5} HO_2 + M \qquad \text{(H.5)}$$

- Initiation step is the dissociation of some amount of molecular species by a spark, flame, electric discharge, or some other means.

- Bond energies:

  O = O : 5.1 eV

  H – H : 4.5 eV

  O – H : 4.4 eV

- Reaction (2) is endothermic by 0.7 eV (about 70 kJ/mol) and progresses slowly.
- Reactions (3) and (1) are endothermic by 0.1 eV, and these reactions are relatively fast.
- The OH and O radicals are therefore rapidly consumed, and the principal chain carrier is H atoms.

- We will find the rate equation for the free-radical density n^*, which is taken to be the same as that for [H] atoms:

$$\frac{\mathrm{d}n^*}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t}$$

$$= k_o[\mathrm{H}_2] - k_2[\mathrm{H}][\mathrm{O}_2] + k_3[\mathrm{O}][\mathrm{H}_2] + k_1[\mathrm{OH}][\mathrm{H}_2]$$
$$-k_4[\mathrm{H}] - k_5[\mathrm{H}][\mathrm{O}_2][\mathrm{M}] \qquad (3.1)$$

- For other free-radical species:

$$\frac{\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t} = k_2[\mathrm{H}][\mathrm{O}_2] + k_3[\mathrm{O}][\mathrm{H}_2] - k_1[\mathrm{OH}][\mathrm{H}_2] \qquad (3.2)$$

$$\frac{\mathrm{d[O]}}{\mathrm{d}t} = k_o[\mathrm{O_2}] + k_2[\mathrm{H}][\mathrm{O_2}] - k_3[\mathrm{O}][\mathrm{H_2}] \qquad (3.3)$$

- Since [O] and [OH] are both much lower than [H], we can assume that both of these species are at steady-state:

$$\frac{\mathrm{d[OH]}}{\mathrm{d}t} = \frac{\mathrm{d[O]}}{\mathrm{d}t} = 0 \qquad (3.4)$$

that yields

$$[\mathrm{O}]_{\mathrm{ss}} = \frac{k_o[\mathrm{O_2}] + k_2[\mathrm{H}][\mathrm{O_2}]}{k_3[\mathrm{H_2}]} \qquad (3.5)$$

and for [OH],

$$[\mathrm{OH}]_{\mathrm{ss}} = \frac{k_2[\mathrm{H}][\mathrm{O}_2] + k_3[\mathrm{O}][\mathrm{H}_2]}{k_1[\mathrm{H}_2]} \qquad (3.6)$$

Substituting for $[\mathrm{O}]_{\mathrm{ss}}$

$$[\mathrm{OH}]_{\mathrm{ss}} = \frac{2k_2[\mathrm{H}][\mathrm{O}_2] + k_o[\mathrm{O}_2]}{k_1[\mathrm{H}_2]} \qquad (3.7)$$

- We substitute the steady-state values of [OH] and [O] radicals in the rate equation for free-radical density

$$\frac{\mathrm{d}n^*}{\mathrm{d}t} = k_o[\mathrm{H_2}] - k_2[\mathrm{H}][\mathrm{O_2}] + k_3\frac{k_2[\mathrm{H}][\mathrm{O_2}] + k_o[\mathrm{O_2}]}{k_3[\mathrm{H_2}]}[\mathrm{H_2}]$$

$$+k_1[\mathrm{H_2}]\frac{2k_2[\mathrm{H}][\mathrm{O_2}] + k_o[\mathrm{O_2}]}{k_1[\mathrm{H_2}]} - k_4[\mathrm{H}] - k_5[\mathrm{H}][\mathrm{O_2}][\mathrm{M}]$$

$$= \underbrace{k_o([\mathrm{H_2}] + 2[\mathrm{O_2}])}_{w_o} + (\underbrace{2k_2[\mathrm{O_2}]}_{f} - \underbrace{k_4 - k_5[\mathrm{O_2}][\mathrm{M}]}_{g})n^* \tag{3.8}$$

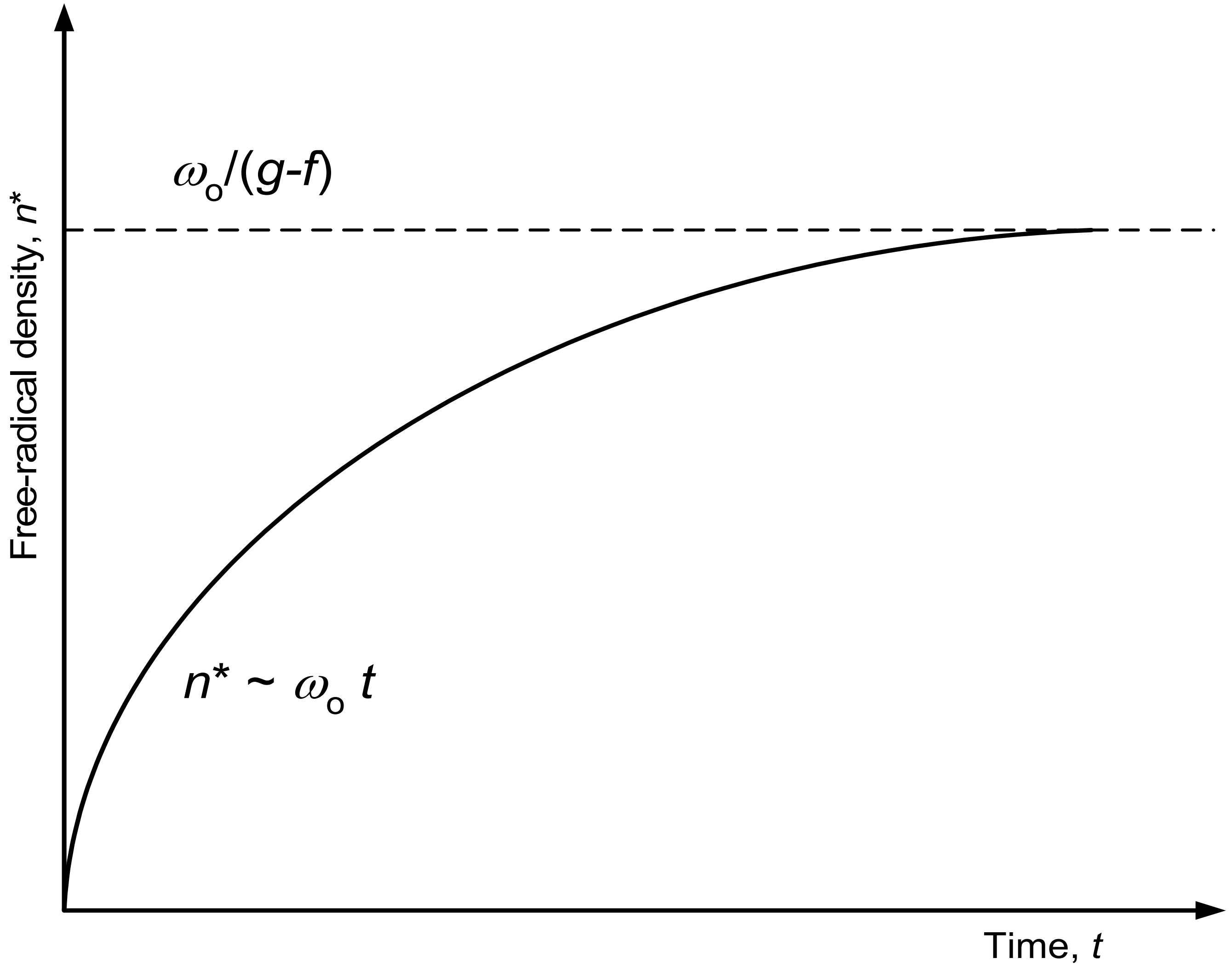
so that

$$\frac{\mathrm{d}n^*}{\mathrm{d}t} = w_o + (f - g)n^* \tag{3.9}$$

- f: chain branching
- g: chain termination
- Two classes of solutions are possible:
  1. $g > f$: termination exceeds branching
  2. $g < f$: branching exceeds termination
- Solution 1 implies that

$$k_4 > (2k_2 - k_5[\mathrm{M}])[\mathrm{O}_2] \qquad (3.10)$$

so that $g > f$ is assured at sufficiently low O_2 pressures.


$\omega_o/(g\text{-}f)$
Free-radical density, n^*
$n^* \sim \omega_o\, t$
Time, t

- The solution is then

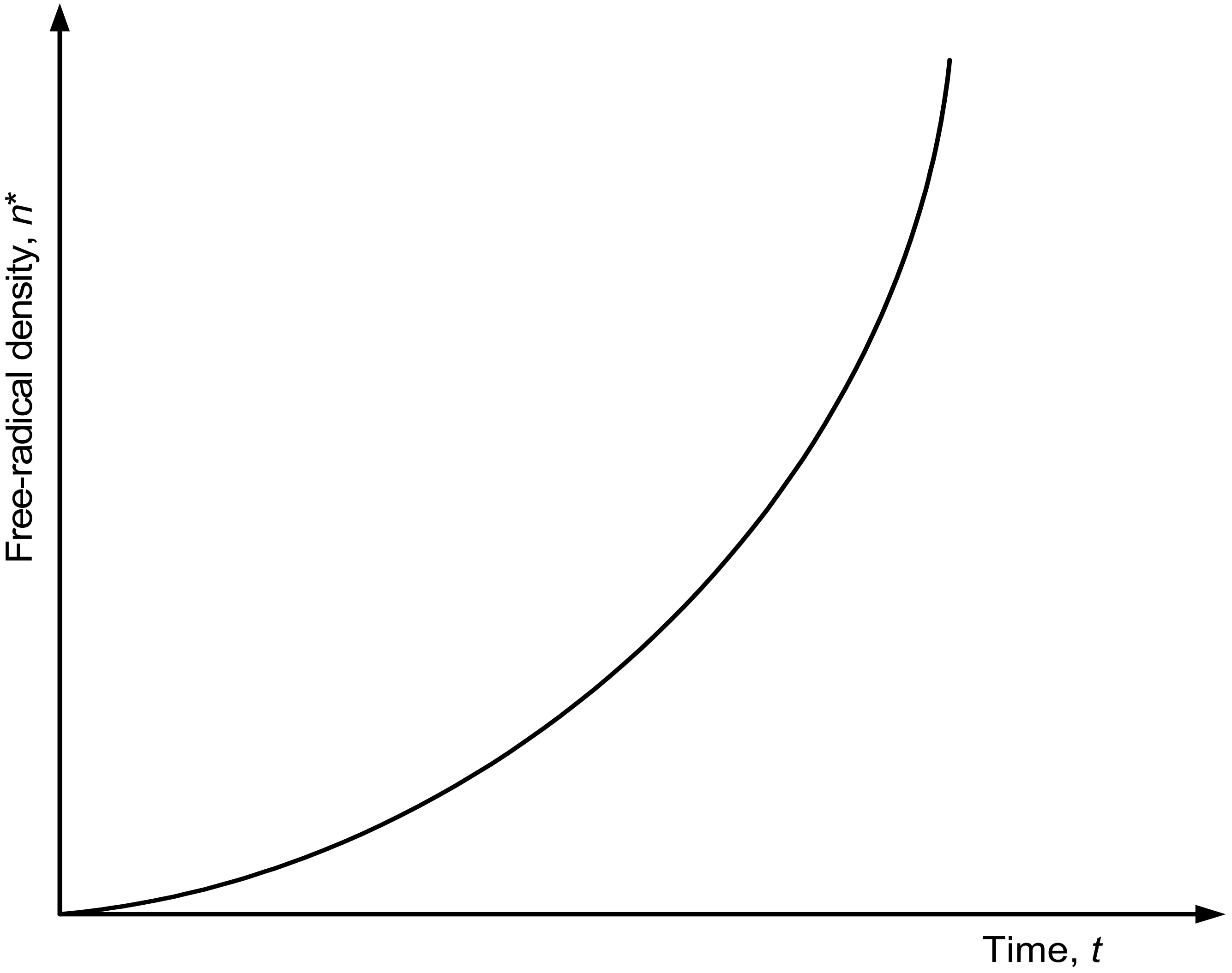
$$n^* = \frac{w_o}{g-f}\{1 - e^{-(g-f)t}\} \tag{3.11}$$

- At short times, n^* increases almost linearly with slope $\sim w_o t$ and reaches a steady-state value of

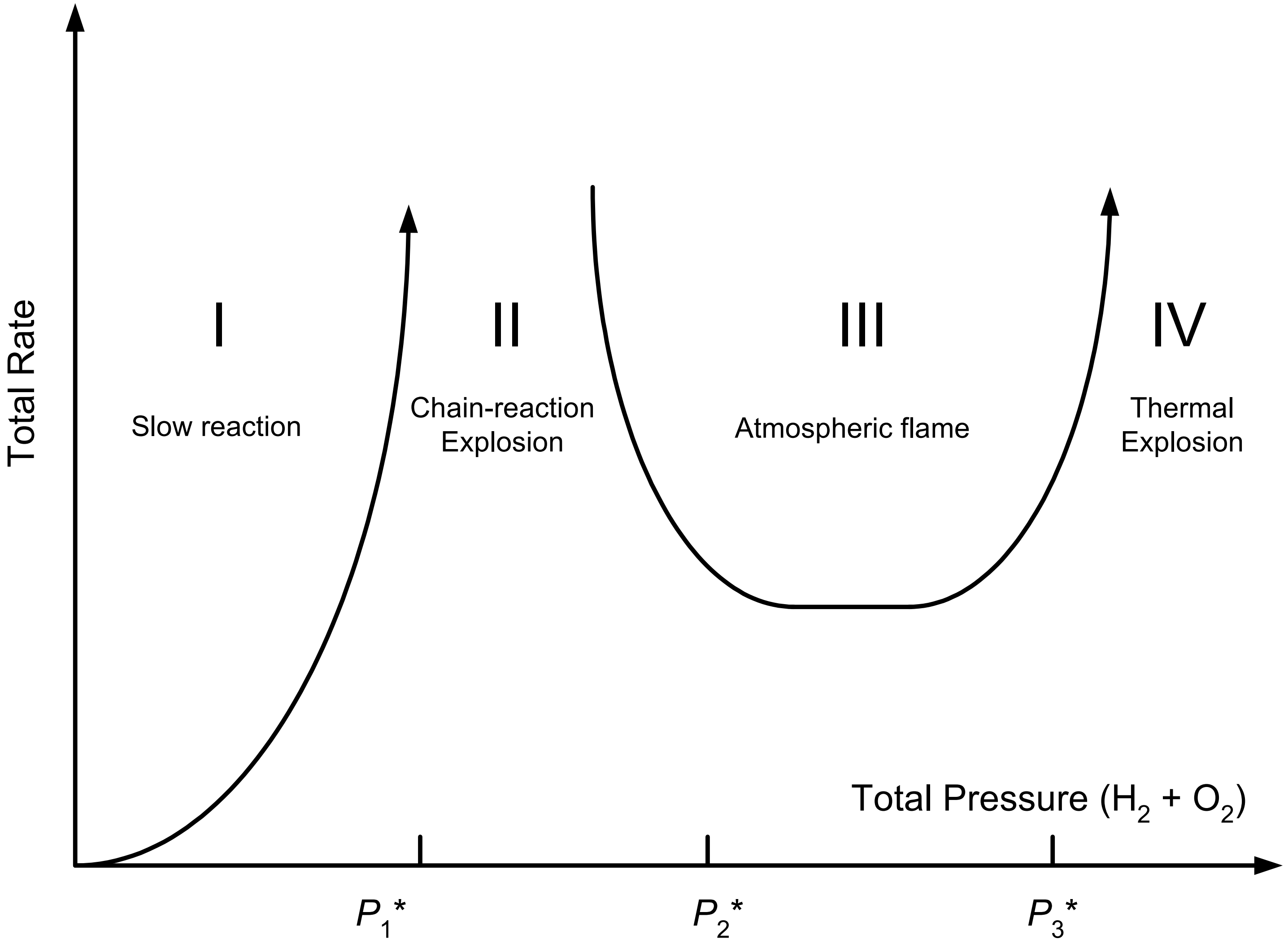
$$n^*_{ss} = w_o/(g-f) \tag{3.12}$$

- At higher O_2 pressures $g < f$, then

$$n^* = \frac{w_o}{f-g}\{e^{(f-g)t} - 1\} \tag{3.13}$$


Free-radical density, n^*
Time, t

- In this case, the free-radical concentration increases exponentially, and, since the overall rate depends on the radical concentration, the reaction velocity increases rapidly. This is usually termed as an explosion.
- The hydrogen-oxygen reaction behaves quite differently in different pressure regimes.
- It is possible to construct an explosion boundary for the hydrogen-oxygen reaction as a function of temperature and pressure.


Total Rate
I
Slow reaction
II
Chain-reaction Explosion
III
Atmospheric flame
IV
Thermal Explosion
Total Pressure (H_2 + O_2)
P_1*
P_2*
P_3*

- *Region I:* The reaction is wall-recombination limited, and proceeds to a steady-state.
- *Region II:* f begins to exceed g, the branched-chain reaction takes over and explosion ensues.
- *Region III:* As the pressure is further increased, the explosion is quenched and another regime of steady-state is encountered.

  In III, kinetics are dominated by relatively unreactive HO_2 (hydroperoxyl) radicals. Other reactions, in addition to those we considered above, are important and include the following:

$$2HO_2 \longrightarrow H_2O_2 + O_2 \tag{H.6}$$

$$H_2 + HO_2 \longrightarrow H_2O_2 + H \tag{H.7}$$

$$H + HO_2 \longrightarrow 2OH \tag{H.8}$$

$$H + HO_2 \longrightarrow H_2 + O_2 \tag{H.9}$$

$$H + HO_2 \longrightarrow H_2O + O \tag{H.10}$$

$$H_2O_2 + M \longrightarrow 2OH + M \tag{H.11}$$

$$H_2O_2 + H \longrightarrow H_2O + OH \tag{H.12}$$

$$H_2O_2 + H \longrightarrow H_2 + O_2 \tag{H.13}$$

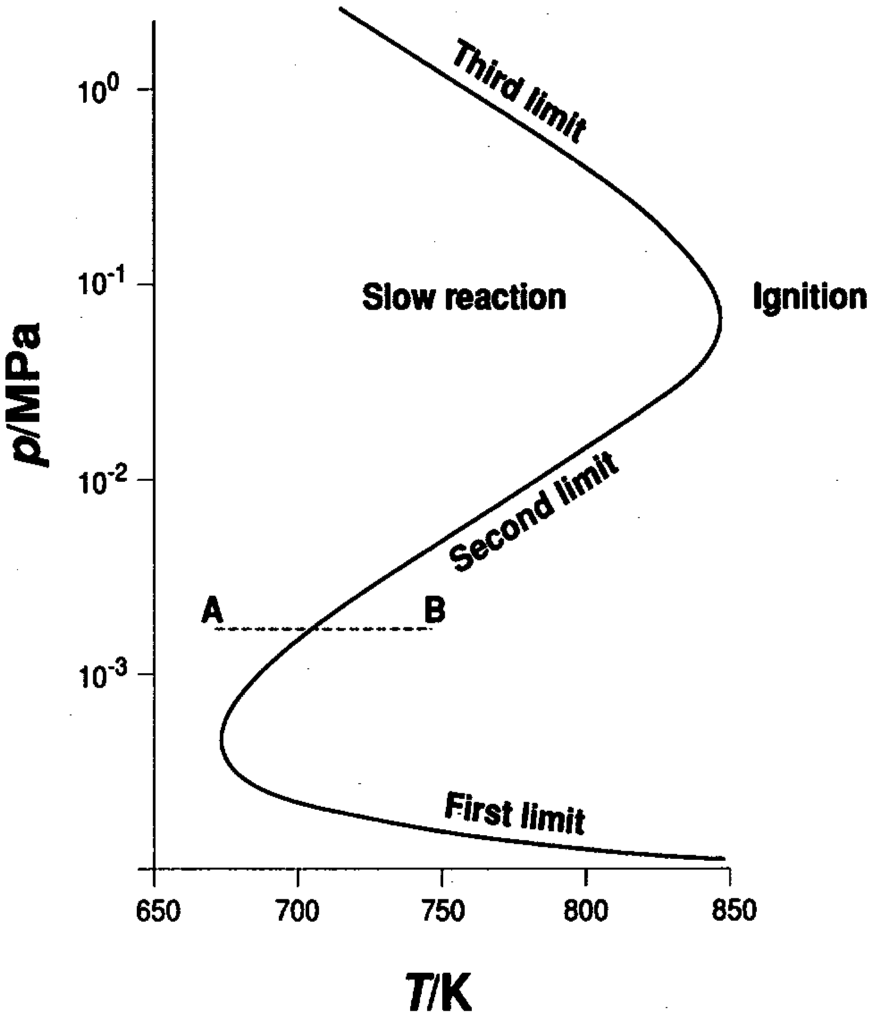
$$H_2O_2 + OH \longrightarrow H_2O + HO_2 \tag{H.14}$$

$$H + OH + M \longrightarrow H_2O + M \tag{H.15}$$

$$H + H + M \longrightarrow H_2 + M \tag{H.16}$$

- *Region IV:* At a still high pressure, the amount of heat liberated in the exothermic steps of the mechanism becomes larger than can be dissipated by conduction and other thermal transport processes, and the temperature rises. This, in turn increases the rates of initiation and provides heat for endothermic chain-branching reactions leading to more heat release, resulting in a thermal explosion.

- Experimentally observed $(P - T)$ boundaries of the H_2-O_2 reaction in a closed vessel is shown below.


Third limit
Slow reaction
Ignition
Second limit
First limit
A
B
10^0
10^{-1}
10^{-2}
10^{-3}
p/MPa
650
700
750
800
850
T/K

Carbon Monoxide Oxidation

- Oxidation of CO is important in hydrocarbon combustion.
- From a *very simplistic* point-of-view, hydrocarbon combustion (related to C content) can be characterized as a two-step process:
  - breakdown of fuel to CO.
  - oxidation of CO to CO_2.
- CO oxidation is extremely slow in the absence of small amounts of H_2 or H_2O.

- If the H_2O is the primary hydrogen-containing species, the CO oxidation can be described by:

$$CO + O_2 \longrightarrow CO_2 + O \qquad (CO.1)$$

$$O + H_2O \longrightarrow OH + OH \qquad (CO.2)$$

$$CO + OH \longrightarrow CO_2 + H \qquad (CO.3)$$

$$H + O_2 \longrightarrow OH + O \qquad (CO.4)$$

- (CO.1) is slow; not much contribution to CO_2 formation, but chain inititation reaction.
- (CO.3) is the actual CO oxidation step; also chain-propagation step producing H atoms.

- (CO.2) and (CO.4) are chain-branching reactions producing OH, and OH and H, respectively.
- (CO.3) reaction is the key step in CO oxidation.

- If H_2 is present, then following steps are involved:

$$O + H_2 \longrightarrow OH + H \qquad (CO.5)$$

$$OH + H_2 \longrightarrow H_2O + H \qquad (CO.6)$$

$$CO + HO_2 \longrightarrow CO_2 + OH \qquad (CO.7)$$

- In the presence of H_2, the entire H_2-O_2 reaction system should be included to describe CO oxidation.

Oxidation of Higher Paraffins

General Scheme:

- Alkanes=Paraffins: saturated, straight chain or branched-chain, single-bonded hydrocarbons.
- General formula: C_nH_{2n+2}.
- Generic oxidation discussion will be for $n > 2$.
- Methane (and ethane) display some unique characteristics not common with higher alkanes.
- Overview of the key points of alkane oxidation.

- Three sequential processes:
  1. Fuel is attacked by O and H; breaks down to H_2 and olefins (double-bonded straight hydrocarbons). H_2 oxidizes to H_2O.
  2. Unsaturated olefins form CO and H_2. Almost all H_2 converts to water.
  3. CO burns to CO_2 releasing almost all of the heat associated with combustion:

$$\mathrm{CO} + \mathrm{OH} \longrightarrow \mathrm{CO_2} + \mathrm{H} \qquad (\mathrm{CO.3})$$

- These three processes can be further detailed as (with the example of propane, C_3H_8):

Step#1. A C-C bond is broken in the original fuel molecule. A C-C bond is weaker than an H-C bond.

$$C_3H_8 + M \longrightarrow C_2H_5 + CH_3 + M \qquad (P.1)$$

Step#2. Two resulting hydrocarbon radicals break down further to olefins: H-*atom abstraction*.

$$C_2H_5 + M \longrightarrow C_2H_4 + H + M \qquad (P.2a)$$

$$CH_3 + M \longrightarrow CH_2 + H + M \qquad (P.2b)$$

Step#3. H atoms from Step#2 starts a radical pool:

$$H + O_2 \longrightarrow O + OH \qquad (P.3)$$

Step#4. With the development of a radical pool, attack on the fuel molecule intensifies.

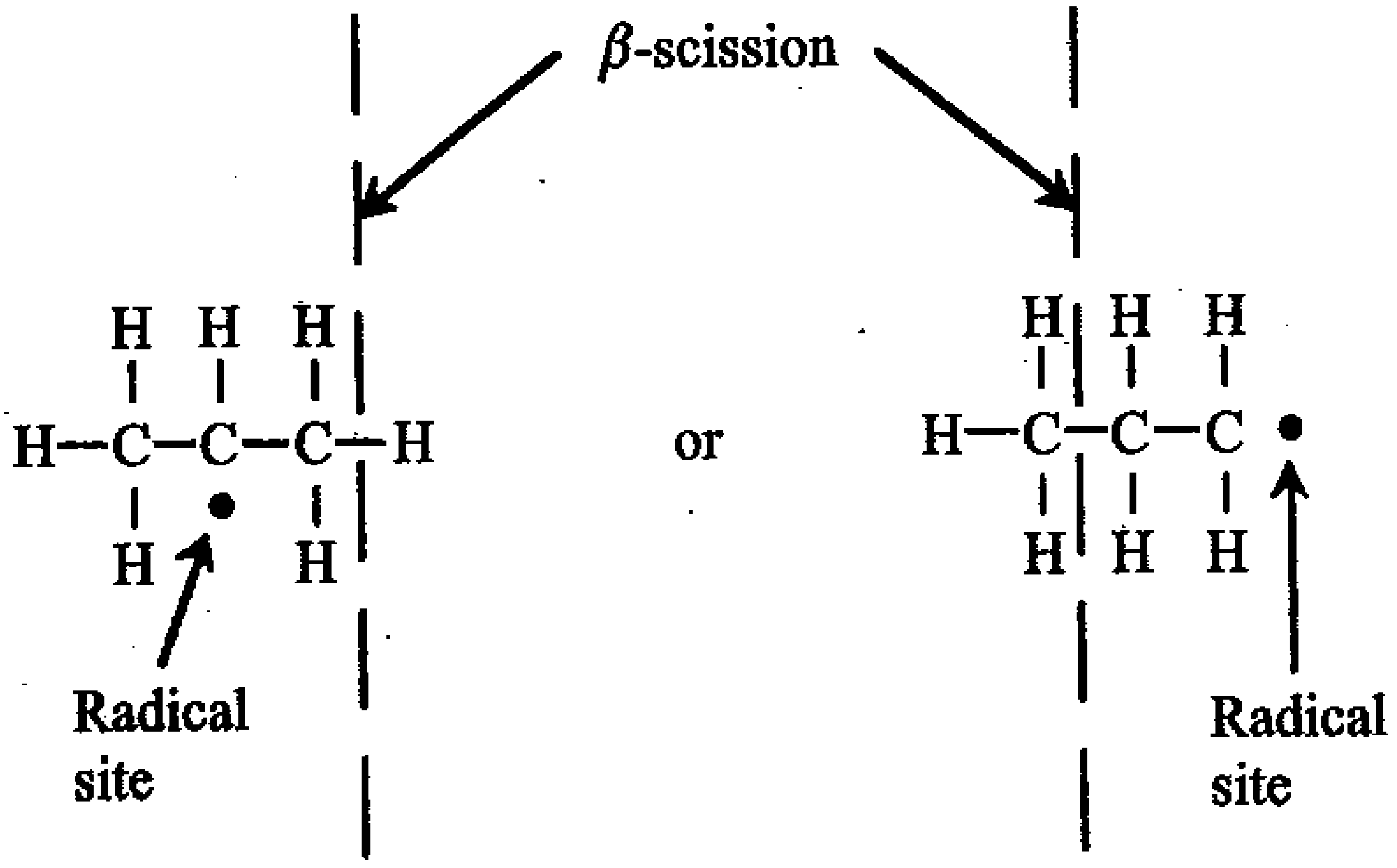
$$C_3H_8 + OH \longrightarrow C_3H_7 + H_2O \quad (P.4a)$$
$$C_3H_8 + H \longrightarrow C_3H_7 + H_2 \quad (P.4b)$$
$$C_3H_8 + O \longrightarrow C_3H_7 + OH \quad (P.4c)$$

Step#5. Hydrocarbon radicals decay to olefins and H atoms via H-atom abstraction.

$$C_3H_7 + M \longrightarrow C_3H_6 + H + M \qquad (P.5)$$

This process obeys the *β-scission rule*, which states that C-C or C-H bond broken will be the one that is one place removed from the radical site.

$$C_3H_7 + M \begin{array}{l} \nearrow \quad C_3H_6 + H + M \\ \\ \searrow \quad C_2H_4 + CH_3 + M \end{array} \qquad (P.6)$$



Isopropyl radical

n-Propyl radical

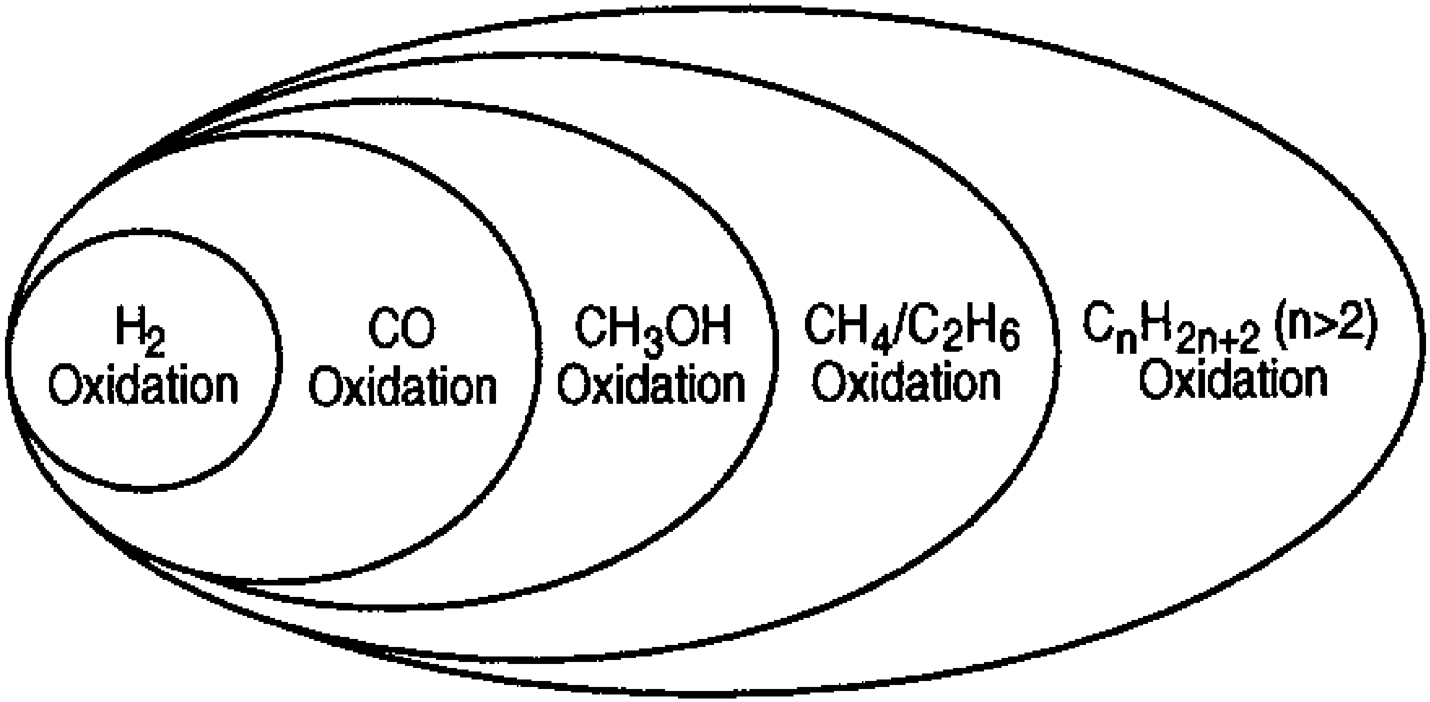
Step#6. Oxidation of olefins created in Steps#2 and 5 by O that produces formyl radicals (HCO) and formaldehyde (H_2CO).

$$C_3H_6 + O \longrightarrow C_2H_5 + HCO \qquad (P.7a)$$

$$C_3H_6 + O \longrightarrow C_2H_4 + H_2CO \qquad (P.7b)$$

Step#7. Methyl radicals (CH_3), formaldeydhe (H_2CO), and methylene (CH_2) oxidize.

Step#8. Carbon monoxide oxidizes following the CO mechanism discussed previously.



Hierarchy in the reaction mechanism describing alkane combustion.

Global Mechanisms:

- Global models do not capture all the features of hydrocarbon combustion, but they may be useful in simple engineering approximations as long as their limitations are recognized.
- A single-step expression:

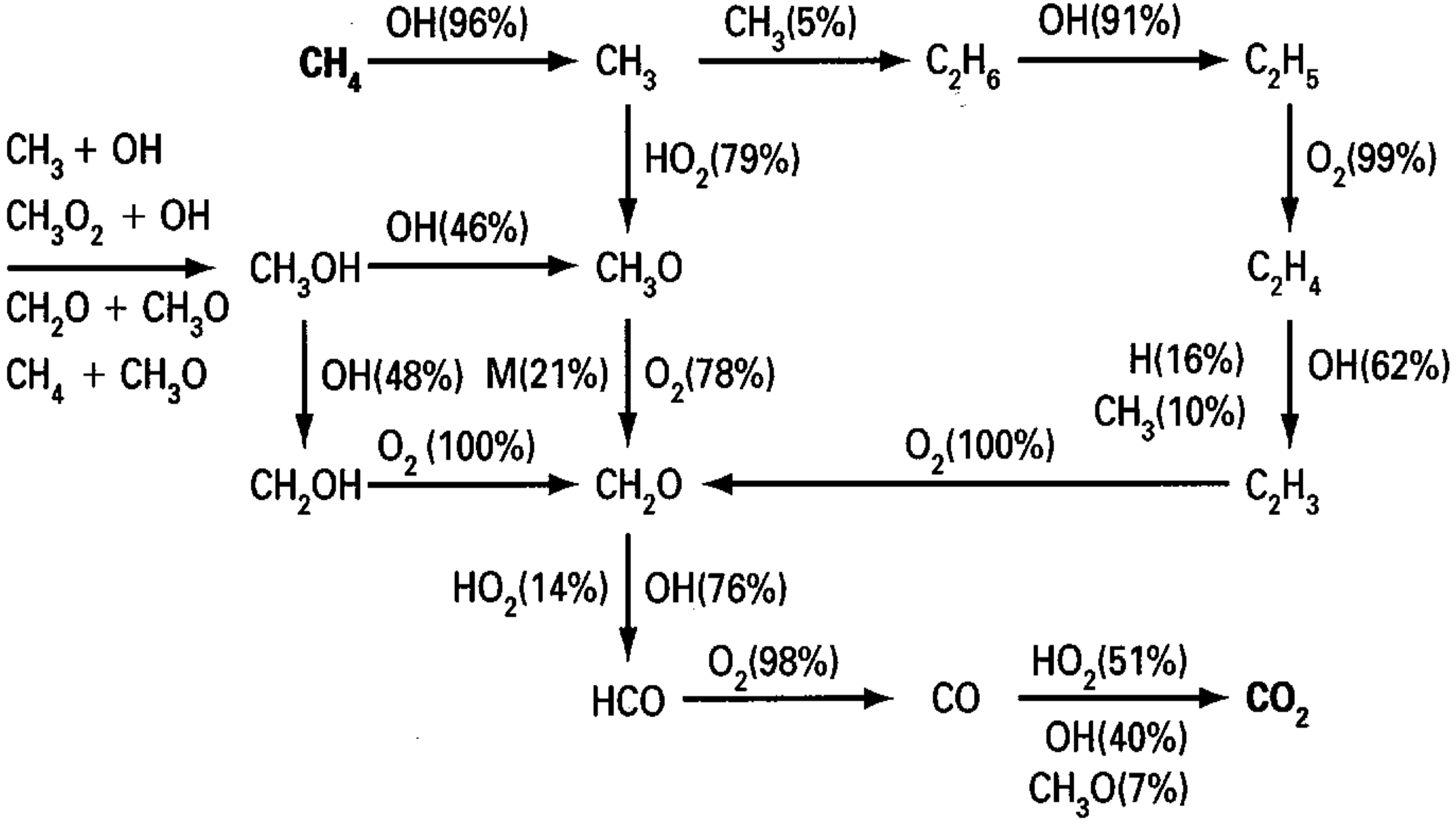
$$\mathrm{C}_x\mathrm{H}_y + (x + y/4)\mathrm{O}_2 \xrightarrow{k_G} x\mathrm{CO}_2 + (y/2)\mathrm{H}_2\mathrm{O} \tag{G.1}$$

$$\frac{\mathrm{d}[\mathrm{C}_x\mathrm{H}_y]}{\mathrm{d}t} = -A\exp\left[-E_a/(R_uT)\right][\mathrm{C}_x\mathrm{H}_y]^m[\mathrm{O}_2]^n \tag{G.2}$$

- A multi-step global mechanism:

$$\begin{aligned} C_nH_{2n+2} &\rightarrow (n/2)C_2H_4 + H_2 && \text{(M.1)} \\ C_2H_4 + O_2 &\rightarrow 2CO + 2H_2 && \text{(M.2)} \\ CO + (1/2)O_2 &\rightarrow CO_2 && \text{(M.3)} \\ H_2 + (1/2)O_2 &\rightarrow H_2O && \text{(M.4)} \end{aligned}$$

which assumes that the intermediate hydrocarbon is ethylene (C_2H_4).



Methane oxidation mechanism

Nitrogen Oxide Kinetics

- Combustion products contain NO at levels of several hundred to several thousand parts per million (ppm) and NO_2 levels in tens of ppm.
- In the atmosphere, in the presence of ultraviolet sunlight, an equilibrium is established:

$$NO_2 + O_2 \overset{h\nu}{\rightleftharpoons} NO + \underbrace{O_3}_{\text{ozone}}$$

- Presence of certain hydrocarbons (e.g., unburned hydrocarbons from combustion, methane from various sources) slowly unbalances the above reaction.
- NO contributes to destruction of ozone in stratosphere.
- NO contributes to production of ground level ozone.
- NO is involved in photochemical smog and haze.

The main sources of nitrogen oxide, NO_x, emissions from combustion are:

- *Thermal* NO: oxidation of molecular nitrogen in the postflame zone.
- *Prompt* NO: formation of NO in the flame zone (*Fenimore* mechanism).
- N_2O-*intermediate* mechanism.
- *Fuel* NO: oxidation of nitrogen-containing compounds in the fuel.

Relative importance of these three are dependent on the operating conditions and fuel. In most practical combustion devices the thermal NO is the main source.

- The basic mechanism for thermal NO production is given by six reactions known as *extended Zeldovich mechanism*:

$$O + N_2 \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} NO + N \qquad (N.1)$$

$$N + O_2 \underset{k_{2r}}{\overset{k_{2f}}{\rightleftharpoons}} NO + O \qquad (N.2)$$

$$N + OH \underset{k_{3r}}{\overset{k_{3f}}{\rightleftharpoons}} NO + H \qquad (N.3)$$

- The contribution of reaction 3 is small for lean mixtures, but for rich mixtures it should be considered. Forward reaction 1 controls the system, but it is slow at low temperatures (high activation energy). Thus it is effective in post-flame zone where temperature is high and the time is available.
- Concentrations of 1000 to 4000 ppm are typically observed in uncontrolled combustion systems.
- From reactions 1-3, the rate of formation of thermal NO can be calculated:

$$\frac{\mathrm{d}[\mathrm{NO}]}{\mathrm{d}t} = k_{1f}[\mathrm{O}][\mathrm{N}_2] - k_{1r}[\mathrm{NO}][\mathrm{N}] + k_{2f}[\mathrm{N}][\mathrm{O}_2]$$

$$-k_{2r}[\mathrm{NO}][\mathrm{O}] + k_{3f}[\mathrm{N}][\mathrm{OH}] - k_{3r}[\mathrm{NO}][\mathrm{H}] \qquad (3.14)$$

- To calculate the NO formation rate, we need the concentrations of O, N, OH, and H.
- In detailed calculations, these are computed using detailed kinetic mechanisms for the fuel used.
- For very approximate calculations, these may be assumed to be in chemical equilibrium.

- At moderately high temperatures N does not stay at thermodynamic equilibrium. A better approximation could be to assume N to be at steady-state.
- From reactions 1-3, we have

$$\frac{\mathrm{d[N]}}{\mathrm{d}t} = k_{1f}[\mathrm{O}][\mathrm{N_2}] - k_{1r}[\mathrm{NO}][\mathrm{N}] - k_{2f}[\mathrm{N}][\mathrm{O_2}]$$

$$+k_{2r}[\mathrm{NO}][\mathrm{O}] - k_{3f}[\mathrm{N}][\mathrm{OH}] + k_{3r}[\mathrm{NO}][\mathrm{H}] = 0$$

$$[\mathrm{N}]_{\mathrm{ss}} = \frac{k_{1f}[\mathrm{O}][\mathrm{N_2}] + k_{2r}[\mathrm{NO}][\mathrm{O}] + k_{3r}[\mathrm{NO}][\mathrm{H}]}{k_{1r}[\mathrm{NO}] + k_{2f}[\mathrm{O_2}] + k_{3f}[\mathrm{OH}]} \tag{3.15}$$

- The reaction rate constants, in [m^3/ kmol s], for 1-3 are as follows:

$$\begin{aligned} k_{1f} &= 1.8 \cdot 10^{11} \exp\left(-38,370/T\right) \\ k_{1r} &= 3.8 \cdot 10^{10} \exp\left(-425/T\right) \\ k_{2f} &= 1.8 \cdot 10^{7} T \exp\left(-4680/T\right) \\ k_{2r} &= 3.8 \cdot 10^{6} T \exp\left(-20,820/T\right) \\ k_{3f} &= 7.1 \cdot 10^{10} \exp\left(-450/T\right) \\ k_{3r} &= 1.7 \cdot 10^{11} \exp\left(-24,560/T\right) \end{aligned} \tag{5.16}$$

- N_2O-*intermediate mechanism* is important in very-lean combustion ($\Phi < 0.8$). This mechanism can be represented by:

$$O + N_2 + M \rightleftharpoons N_2O + M \qquad (N.4)$$

$$H + N_2O \rightleftharpoons NO + NH \qquad (N.5)$$

$$O + N_2O \rightleftharpoons NO + NO \qquad (N.6)$$

- This mechanism is important in NO control strategies in lean-premixed gas turbine combustion applications.

- It has been shown that some NO is rapidly produced in the flame zone long before there would be time to form NO by the thermal mechanism. This is also known as the *Fenimore mechanism*:
  - The general scheme is that hydrocarbon radicals form CN and HCN

$$CH + N_2 \rightleftharpoons HCN + N \qquad (N.7)$$

$$C + N_2 \rightleftharpoons CN + N \qquad (N.8)$$

- The conversion of hydrogen cyanide, HCN, to form NO is as follows

$$\mathrm{HCN} + \mathrm{O} \rightleftharpoons \mathrm{NCO} + \mathrm{H} \tag{N.9}$$

$$\mathrm{NCO} + \mathrm{H} \rightleftharpoons \mathrm{NH} + \mathrm{CO} \tag{N.10}$$

$$\mathrm{NH} + \mathrm{H} \rightleftharpoons \mathrm{N} + \mathrm{H_2} \tag{N.11}$$

$$\mathrm{N} + \mathrm{OH} \rightleftharpoons \mathrm{NO} + \mathrm{H} \tag{N.3}$$

- For equivalence ratios higher than 1.2, chemistry becomes more complex and it couples with the thermal mechanism.

4. Introduction to Heat & Mass Transfer

This section will cover the following concepts:

- A rudimentary introduction to mass transfer.
- Mass transfer from a molecular point of view.
- Fundamental similarity of heat and mass transfer.
- Application of mass transfer concepts:
    - Evaporation of a liquid layer
    - Evaporation of a liquid droplet

Mass Transfer:

Mass-Transfer Rate Laws:

- *Fick's Law of Diffusion:* Describes, in its basic form, the rate at which two gas species diffuse through each other.
- For one-dimensional binary diffusion:

$$\underbrace{\dot{m}''_{\mathrm{A}}}_{\substack{\text{mass flow of A}\\ \text{per unit area}}} = \underbrace{Y_{\mathrm{A}}(\dot{m}''_{\mathrm{A}} + \dot{m}''_{\mathrm{B}})}_{\substack{\text{mass flow of A}\\ \text{associated with bulk}\\ \text{flow per unit area}}} - \underbrace{\rho \mathcal{D}_{\mathrm{AB}} \frac{\mathrm{d}Y_{\mathrm{A}}}{\mathrm{d}x}}_{\substack{\text{mass flow of A}\\ \text{associated with}\\ \text{molecular diffusion}}} \tag{4.1}$$

- A is transported by two means: (a) bulk motion of the fluid, and (b) molecular diffusion.
- *Mass flux* is defined as the mass flowrate of species A per unit area perpendicular to the flow:

$$\dot{m}''_{\mathrm{A}} = \dot{m}_{\mathrm{A}}/A \tag{4.2}$$

  $\dot{m}''_{\mathrm{A}}$ has the units kg/(s m^2).
- The *binary diffusivity*, or the *molecular diffusion coefficient*, $\mathcal{D}_{\mathrm{AB}}$ is a property of the mixture and has units of m^2/s.

- In the absence of diffusion:

$$\begin{aligned} \dot{m}''_{\mathrm{A}} &= Y_{\mathrm{A}}(\dot{m}''_{\mathrm{A}} + \dot{m}''_{\mathrm{B}}) = Y_{\mathrm{A}}\dot{m}'' \\ &\equiv \text{Bulk flux of species A} \end{aligned} \tag{4.3a}$$

where $\dot{m}''$ is the mixture mass flux.

- The diffusional flux adds an additional component to the flux of A:

$$-\rho\mathcal{D}_{\mathrm{AB}}\frac{\mathrm{d}Y_{\mathrm{A}}}{\mathrm{d}x} \equiv \text{Diffusional flux of A}, \dot{m}''_{\mathrm{A,diff}} \tag{4.3b}$$

- Note that the negative sign causes the flux to be postive in the x-direction when the concentration gradient is negative.

- Analogy between the diffusion of heat (conduction) and molecular diffusion.

- *Fourier's law of heat conduction*:

$$\dot{Q}''_x = -k\frac{\mathrm{d}T}{\mathrm{d}x} \tag{4.4}$$

- Both expressions indicate a flux ($\dot{m}''_{\mathrm{A,diff}}$ or $\dot{Q}''_x$) being proportional to the gradient of a scalar quantity $[(\mathrm{d}Y_{\mathrm{A}}/\mathrm{d}x)$ or $(\mathrm{d}T/\mathrm{d}x)]$.

- A more general form of Eqn 4.1:

$$\overrightarrow{\dot{m}''_{\mathrm{A}}} = Y_{\mathrm{A}}(\overrightarrow{\dot{m}''_{\mathrm{A}}} + \overrightarrow{\dot{m}''_{\mathrm{B}}}) - \rho \mathcal{D}_{\mathrm{AB}} \nabla Y_{\mathrm{A}} \qquad (4.5)$$

symbols with over arrows represent vector quantities. Molar form of Eqn 4.5

$$\overrightarrow{\dot{N}''_{\mathrm{A}}} = \chi_{\mathrm{A}}(\overrightarrow{\dot{N}''_{\mathrm{A}}} + \overrightarrow{\dot{N}''_{\mathrm{B}}}) - c \mathcal{D}_{\mathrm{AB}} \nabla \chi_{\mathrm{A}} \qquad (4.6)$$

where $\dot{N}''_{\mathrm{A}}$, (kmol/(s m^2), is the molar flux of species A; χ_{A} is mole fraction, and c is the molar concentration, kmol/m^3.

- Meanings of bulk flow and diffusional flux can be better explained if we consider that:

$$\underbrace{\dot{m}''}_{\substack{\text{mixture}\\ \text{mass flux}}} = \underbrace{\dot{m}''_{\mathrm{A}}}_{\substack{\text{species A}\\ \text{mass flux}}} + \underbrace{\dot{m}''_{\mathrm{B}}}_{\substack{\text{species B}\\ \text{mass flux}}} \qquad (4.7)$$

- If we substitute for individual species fluxes from Eqn 4.1 into 4.7:

$$\dot{m}'' = Y_{\mathrm{A}}\dot{m}'' - \rho\mathcal{D}_{\mathrm{AB}}\frac{\mathrm{d}Y_{\mathrm{A}}}{\mathrm{d}x} + Y_{\mathrm{B}}\dot{m}'' - \rho\mathcal{D}_{\mathrm{BA}}\frac{\mathrm{d}Y_{\mathrm{B}}}{\mathrm{d}x} \qquad (4.8a)$$

- Or:

$$\dot{m}'' = (Y_\mathrm{A} + Y_\mathrm{B})\dot{m}'' - \rho\mathcal{D}_\mathrm{AB}\frac{\mathrm{d}Y_\mathrm{A}}{\mathrm{d}x} - \rho\mathcal{D}_\mathrm{BA}\frac{\mathrm{d}Y_\mathrm{B}}{\mathrm{d}x} \tag{4.8b}$$

- For a binary mixture, $Y_\mathrm{A} + Y_\mathrm{B} = 1$; then:

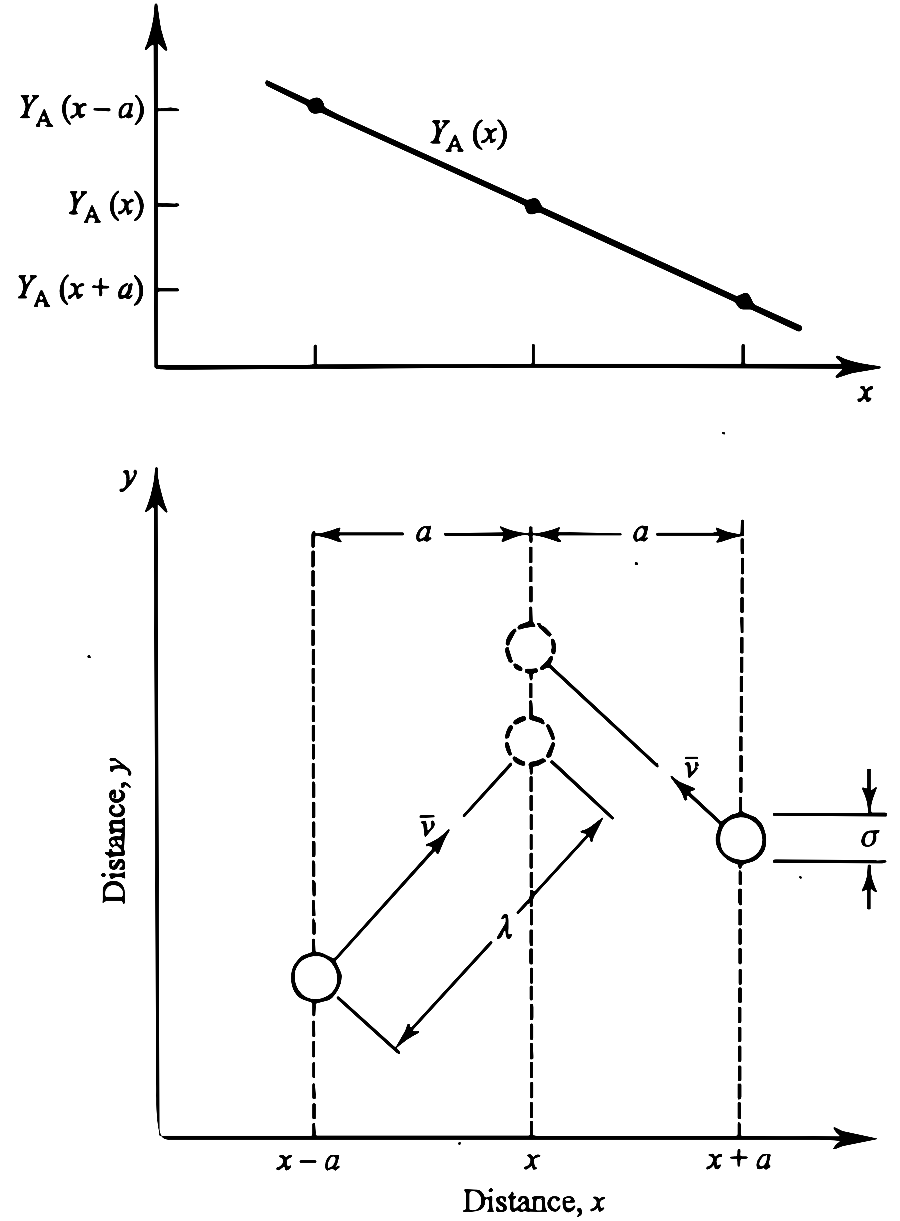
$$-\underbrace{\rho\mathcal{D}_\mathrm{AB}\frac{\mathrm{d}Y_\mathrm{A}}{\mathrm{d}x}}_{\substack{\text{diffusional flux}\\\text{of species A}}} - \underbrace{\rho\mathcal{D}_\mathrm{BA}\frac{\mathrm{d}Y_\mathrm{B}}{\mathrm{d}x}}_{\substack{\text{diffusional flux}\\\text{of species B}}} = 0 \tag{4.9}$$

- In general $\sum \dot{m}_i'' = 0$

- Some cautionary remarks:
  - We are assuming a binary gas and the diffusion is a result of concentration gradients only (ordinary diffusion).
  - Gradients of temperature and pressure can produce species diffusion.
  - *Soret effect*: species diffusion as a result of temperature gradient.
  - In most combustion systems, these effects are small and can be neglected.

Molecular Basis of Diffusion:

- We apply some concepts from the kinetic theory of gases.
  - Consider a stationary (no bulk flow) plane layer of a binary gas mixture consisting of rigid, non-attracting molecules.
  - Molecular masses of A and B are identical.
  - A concentration (mass-fraction) gradient exists in x-direction, and is sufficiently small that over smaller distances the gradient can be assumed to be linear.


$Y_A(x-a)$
$Y_A(x)$
$Y_A(x+a)$
$Y_A(x)$
x
y
a
a
$\bar{v}$
$\bar{v}$
λ
σ
Distance, y
$x-a$
x
$x+a$
Distance, x

- Average molecular properties from kinetic theory of gases:

$$\bar{v} \equiv \substack{\text{Mean speed} \\ \text{of species A} \\ \text{molecules}} = \left(\frac{8k_B T}{\pi m_{\mathrm{A}}}\right)^{1/2} \qquad (4.10a)$$

$$Z''_{\mathrm{A}} \equiv \substack{\text{Wall collision} \\ \text{frequency of A} \\ \text{molecules per unit area}} = \frac{1}{4}\left(\frac{n_{\mathrm{A}}}{V}\right)\bar{v} \qquad (4.10b)$$

$$\lambda \equiv \text{Mean free path} = \frac{1}{\sqrt{2}\pi(n_{\mathrm{tot}}/V)\sigma^2} \qquad (4.10c)$$

$$a \equiv \substack{\text{Average perpendicular distance} \\ \text{from plane of last collision to} \\ \text{plane where next collision occurs}} = \frac{2}{3}\lambda \qquad (4.10d)$$

where

- k_B: Boltzmann's constant.
- m_A: mass of a single A molecule.
- (n_A/V): number of A molecules per unit volume.
- (n_tot/V): total number of molecules per unit volume.
- σ: diameter of both A and B molecules.

- Net flux of A molecules at the x-plane:

$$\dot{m}''_\mathrm{A} = \dot{m}''_{\mathrm{A},(+)x-\mathrm{dir}} - \dot{m}''_{\mathrm{A},(-)x-\mathrm{dir}} \qquad (4.11)$$

- In terms of collision frequency, Eqn 4.11 becomes

$$\underbrace{\dot{m}''_{\mathrm{A}}}_{\substack{\text{Net mass}\\ \text{flux of}\\ \text{species A}}} = \underbrace{(Z''_{\mathrm{A}})_{x-a}}_{\substack{\text{Number of A}\\ \text{crossing plane x}\\ \text{originating from}\\ \text{plane at (x}-\text{a)}}} m_{\mathrm{A}} - \underbrace{(Z''_{\mathrm{A}})_{x+a}}_{\substack{\text{Number of A}\\ \text{crossing plane x}\\ \text{originating from}\\ \text{plane at (x+a)}}} m_{\mathrm{A}} \tag{4.12}$$

- Since $\rho \equiv m_{\mathrm{tot}}/V_{\mathrm{tot}}$, then we can relate Z''_{A} to mass fraction, Y_{A} (from Eqn 4.10b)

$$Z''_{\mathrm{A}} m_{\mathrm{A}} = \frac{1}{4}\frac{n_{\mathrm{A}} m_{\mathrm{A}}}{m_{\mathrm{tot}}}\rho\bar{v} = \frac{1}{4} Y_{\mathrm{A}} \rho \bar{v} \tag{4.13}$$

- Substituting Eqn 4.13 into 4.12

$$\dot{m}''_{\mathrm{A}} = \frac{1}{4}\rho\bar{v}(Y_{\mathrm{A},x-a} - Y_{\mathrm{A},x+a}) \qquad (4.14)$$

- With linear concentration assumption

$$\begin{aligned} \frac{\mathrm{d}Y}{\mathrm{d}x} &= \frac{Y_{\mathrm{A},x-a} - Y_{\mathrm{A},x+a}}{2a} \\ &= \frac{Y_{\mathrm{A},x-a} - Y_{\mathrm{A},x+a}}{4\lambda/3} \end{aligned} \qquad (4.15)$$

- From the last two equations, we get

$$\dot{m}''_{\mathrm{A}} = -\rho \frac{\bar{v}\lambda}{3} \frac{\mathrm{d}Y_{\mathrm{A}}}{\mathrm{d}x} \tag{4.16}$$

- Comparing Eqn. 3.16 with Eqn. 3.3b, $\mathcal{D}_{\mathrm{AB}}$ is

$$\mathcal{D}_{\mathrm{AB}} = \bar{v}\lambda/3 \tag{4.17}$$

- Substituting for $\bar{v}$ and λ, along with ideal-gas equation of state, $PV = nk_B T$

$$\mathcal{D}_{\mathrm{AB}} = \frac{2}{3}\left(\frac{k_B^3 T}{\pi^3 m_{\mathrm{A}}}\right)^{1/2} \frac{T}{\sigma^2 P} \tag{4.18a}$$

or

$$\mathcal{D}_{\mathrm{AB}} \propto T^{3/2} P^{-1} \qquad (4.18b)$$

- Diffusivity strongly depends on temperature and is inversely proportional to pressure.
- Mass flux of species A, however, depends on $\rho\mathcal{D}_{\mathrm{AB}}$, which then gives:

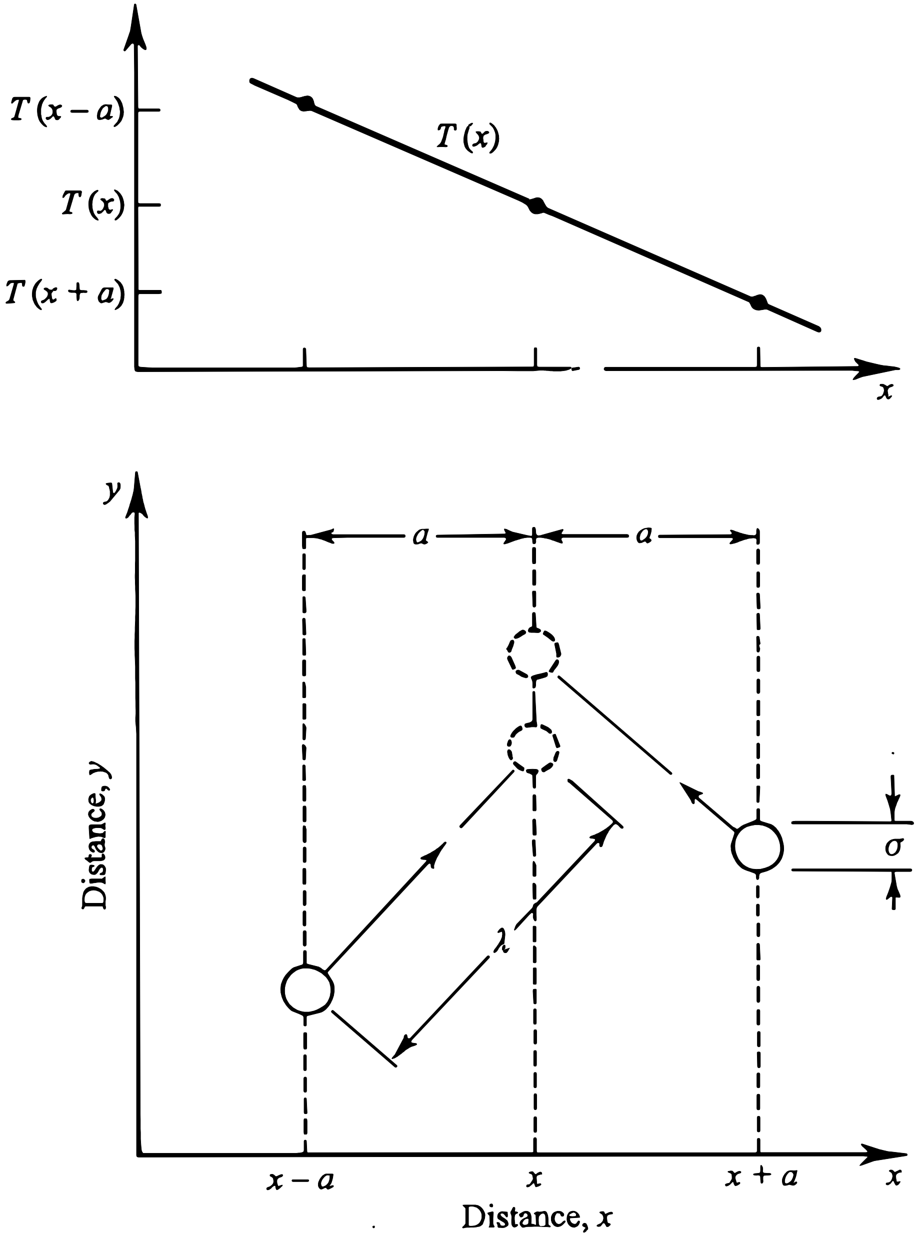
$$\rho\mathcal{D}_{\mathrm{AB}} \propto T^{1/2} P^{0} = T^{1/2} \qquad (4.18c)$$

- In some practical/simple combustion calculations, the weak temperature dependence is neglected and $\rho\mathcal{D}$ is treated as a constant.

Comparison with Heat Conduction:

- We apply the same kinetic theory concepts to the transport of energy.
- Same assumptions as in the molecular diffusion case.
- $\bar{v}$ and λ have the same definitions.
- Molecular collision frequency is now based on the total number density of molecules, n_{tot}/V,

$$Z'' = \substack{\text{Average wall collision} \\ \text{frequency per unit area}} = \frac{1}{4}\left(\frac{n_{\mathrm{tot}}}{V}\right)\bar{v} \qquad (4.19)$$


T (x − a)
T (x)
T (x + a)
T (x)
x
y
a
a
σ
λ
Distance, y
x − a
x
x + a
x
Distance, x

- In the no-interaction-at-a-distance hard-sphere model of the gas, the only energy storage mode is molecular translational (kinetic) energy.
- Energy balance at the x-plane;

$$\begin{array}{c}\text{Net energy flow}\\ \text{in } x\text{-direction}\end{array} = \begin{array}{c}\text{kinetic energy flux}\\ \text{with molecules}\\ \text{from } x-a \text{ to } x\end{array} - \begin{array}{c}\text{kinetic energy flux}\\ \text{with molecules}\\ \text{from } x+a \text{ to } x\end{array}$$

$$\dot{Q}''_x = Z''(ke)_{x-a} - Z''(ke)_{x+a} \qquad (4.20)$$

- ke is given by

$$ke = \frac{1}{2}m\bar{v}^2 = \frac{3}{2}k_BT \qquad (4.21)$$

heat flux can be related to temperature as

$$\dot{Q}''_x = \frac{3}{2}k_B Z''(T_{x-a} - T_{x+a}) \tag{4.22}$$

- The temperature gradient

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{T_{x+a} - T_{x-a}}{2a} \tag{4.23}$$

- Eqn. 4.23 into 3.22, and definitions of Z'' and a

$$\dot{Q}''_x = -\frac{1}{2}k_B\left(\frac{n}{V}\right)\bar{v}\lambda\frac{\mathrm{d}T}{\mathrm{d}x} \tag{4.24}$$

Comparing to Eqn. 4.4, k is

$$k = \frac{1}{2} k_B \left(\frac{n}{V} \right) \bar{v} \lambda \tag{4.25}$$

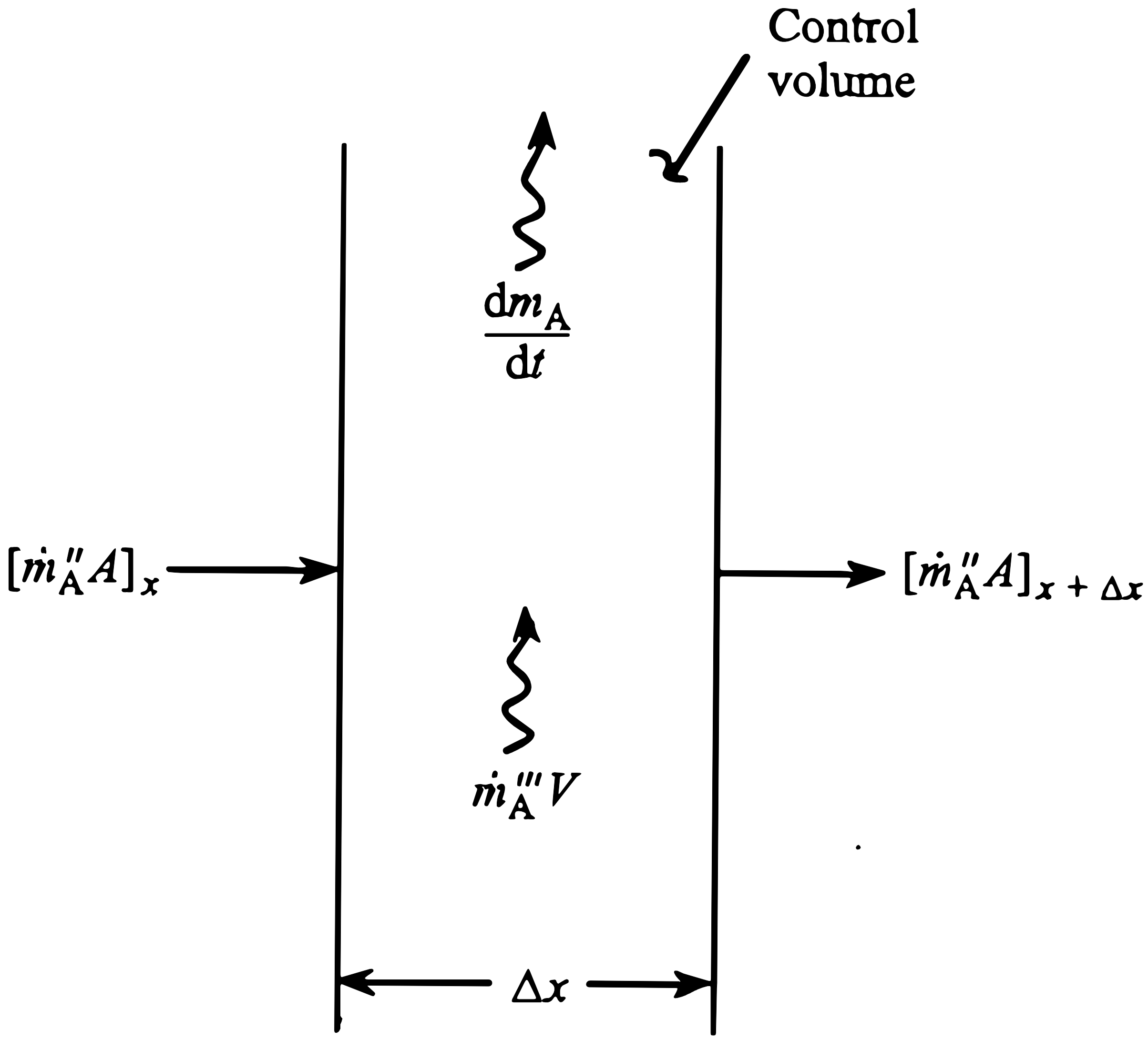
- In terms of T and molecular size,

$$k = \left(\frac{k_B^3}{\pi^3 m \sigma^4} \right)^{1/2} T^{1/2} \tag{4.26}$$

- Dependence of k on T (similar to $\rho\mathcal{D}$)

$$k \propto T^{1/2} \tag{4.27}$$

  - Note: For real gases T dependency is larger.


Control volume
$\frac{dm_A}{dt}$
$[\dot{m}''_A A]_x$
$[\dot{m}''_A A]_{x+\Delta x}$
$\dot{m}'''_A V$
Δx

Species Conservation:

- One-dimensional control volume
- Species A flows into and out of the control volume as a result of the combined action of bulk flow and diffusion.
- Within the control volume, species A may be created or destroyed as a result of chemical reaction.
- The net rate of increase in the mass of A within the control volume relates to the mass fluxes and reaction rate as follows:

$$\underbrace{\frac{\mathrm{d}m_{\mathrm{A},cv}}{\mathrm{d}t}}_{\substack{\text{Rate of increase}\\ \text{of mass A}\\ \text{within CV}}} = \underbrace{[\dot{m}''_{\mathrm{A}}A]_x}_{\substack{\text{Mass flow}\\ \text{of A into}\\ \text{CV}}} - \underbrace{[\dot{m}''_{\mathrm{A}}A]_{x+\Delta x}}_{\substack{\text{Mass flow}\\ \text{of A out}\\ \text{of the CV}}} + \underbrace{\dot{m}'''_{\mathrm{A}}V}_{\substack{\text{Mass prod.}\\ \text{rate of A}\\ \text{by reaction}}} \quad (4.28)$$

- where
  - $\dot{m}'''_{\mathrm{A}}$ is the mass production rate of species A per unit volume.
  - $\dot{m}''_{\mathrm{A}}$ is defined by Eqn. 4.1.

- Within the control volume $m_{\mathrm{A},cv} = Y_\mathrm{A} m_{cv} = Y_\mathrm{A}\rho V_{cv}$, and the volume $V_{cv} = A \cdot \Delta x$; Eqn. 4.28

$$A\Delta x \frac{\partial(\rho Y_\mathrm{A})}{\partial t} = A\left[Y_\mathrm{A}\dot{m}'' - \rho\mathcal{D}_\mathrm{AB}\frac{\partial Y_\mathrm{A}}{\partial x}\right]_x \qquad A\left[Y_\mathrm{A}\dot{m}'' - \rho\mathcal{D}_\mathrm{AB}\frac{\partial Y_\mathrm{A}}{\partial x}\right]_{x+\Delta x} + \dot{m}_\mathrm{A}''' A\Delta x \tag{4.29}$$

- Dividing by $A\Delta x$ and taking limit as $\Delta x \to 0$,

$$\frac{\partial(\rho Y_\mathrm{A})}{\partial t} = -\frac{\partial}{\partial x}\left[Y_\mathrm{A}\dot{m}'' - \rho\mathcal{D}_\mathrm{AB}\frac{\partial Y_\mathrm{A}}{\partial x}\right] + \dot{m}_\mathrm{A}''' \tag{4.30}$$

- For the steady-flow,

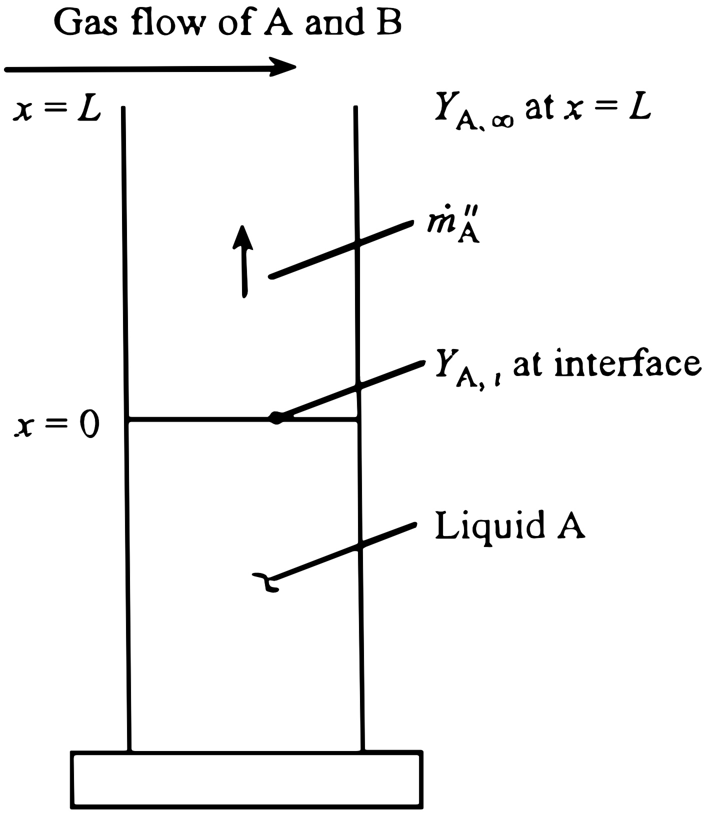
$$\dot{m}_{\mathrm{A}}''' - \frac{\mathrm{d}}{\mathrm{d}x}\left[Y_{\mathrm{A}}\dot{m}'' - \rho\mathcal{D}_{\mathrm{AB}}\frac{\mathrm{d}Y_{\mathrm{A}}}{\mathrm{d}x}\right] = 0 \qquad (4.31)$$

- Eqn. 4.31 is the steady-flow, one-dimensional form of species conservation for a binary gas mixture. For a multidimensional case, Eqn. 4.31 can be generalized as

$$\underbrace{\dot{m}_{\mathrm{A}}'''}_{\substack{\text{Net rate of}\\ \text{species A production}\\ \text{by chemical reaction}}} - \underbrace{\nabla\cdot\overrightarrow{\dot{m}_{\mathrm{A}}''}}_{\substack{\text{Net flow of species}\\ \text{A out of}\\ \text{control volume}}} = 0 \qquad (4.32)$$

Some Applications of Mass Transfer:

The Stefan Problem:



- Assumptions:
  - Liquid A in the cylinder maintained at a fixed height.
  - Steady-state
  - [A] in the flowing gas is less than [A] at the liquid-vapour interface.
  - B is insoluble in liquid A
- Overall conservation of mass:

$$\dot{m}''(x) = \text{constant} = \dot{m}''_{\mathrm{A}} + \dot{m}''_{\mathrm{B}} \tag{4.33}$$

Since $\dot{m}''_{\mathrm{B}} = 0$, then

$$\dot{m}''_{\mathrm{A}} = \dot{m}''(x) = \text{constant} \tag{4.34}$$

Then, Eqn. 3.1 now becomes

$$\dot{m}''_{\mathrm{A}} = Y_{\mathrm{A}}\dot{m}''_{\mathrm{A}} - \rho\mathcal{D}_{\mathrm{AB}}\frac{\mathrm{d}Y_{\mathrm{A}}}{\mathrm{d}x} \tag{4.35}$$

Rearranging and separating variables

$$-\frac{\dot{m}''_{\mathrm{A}}}{\rho\mathcal{D}_{\mathrm{AB}}}\mathrm{d}x = \frac{\mathrm{d}Y_{\mathrm{A}}}{1 - Y_{\mathrm{A}}} \tag{4.36}$$

Assuming $\rho\mathcal{D}_{\mathrm{AB}}$ to be constant, integrate Eqn. 4.36

$$-\frac{\dot{m}''_{\mathrm{A}}}{\rho\mathcal{D}_{\mathrm{AB}}}x = -\ln[1 - Y_{\mathrm{A}}] + C \tag{4.37}$$

With the boundary condition

$$Y_{\mathrm{A}}(x = 0) = Y_{\mathrm{A},i} \tag{4.38}$$

We can eliminate C; then

$$Y_{\mathrm{A}}(x) = 1 - (1 - Y_{\mathrm{A},i})\exp\left[\frac{\dot{m}''_{\mathrm{A}}x}{\rho\mathcal{D}_{\mathrm{AB}}}\right] \tag{4.39}$$

- The mass flux of A, $\dot{m}''_{\mathrm{A}}$, can be found by letting

$$Y_{\mathrm{A}}(x = L) = Y_{\mathrm{A},\infty}$$

  Then, Eqn. 4.39 reads

$$\dot{m}''_{\mathrm{A}} = \frac{\rho \mathcal{D}_{\mathrm{AB}}}{L} \ln\left[\frac{1 - Y_{\mathrm{A},\infty}}{1 - Y_{\mathrm{A},i}}\right] \qquad (4.40)$$

- Mass flux is proportional to $\rho\mathcal{D}$, and inversely proportional to L.

Liquid-Vapour Interface:

- *Saturation pressure*

$$P_{\mathrm{A},i} = P_{\mathrm{sat}}(T_{\mathrm{liq},i}) \tag{4.41}$$

- Partial pressure can be related to mole fraction and mass fraction

$$Y_{\mathrm{A},i} = \frac{P_{\mathrm{sat}}(T_{\mathrm{liq},i})}{P} \frac{MW_{\mathrm{A}}}{MW_{\mathrm{mix},i}} \tag{4.42}$$

  - To find $Y_{\mathrm{A},i}$ we need to know the interface temperature.

- *In crossing the liquid-vapour boundary, we maintain continuity of temperature*

$$T_{\mathrm{liq},i}(x = 0^-) = T_{\mathrm{vap},i}(x = 0^+) = T(0) \quad (4.43)$$

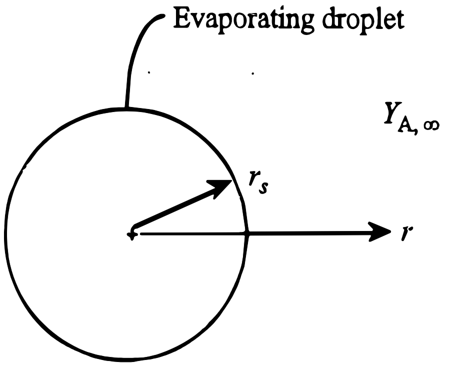
and energy is conserved at the interface. Heat is transferred from gas to liquid, $\dot{Q}_{g-i}$. Some of this heats the liquid, $\dot{Q}_{i-l}$, while the remainder causes phase change.

$$\dot{Q}_{g-i} - \dot{Q}_{i-l} = \dot{m}(h_{\mathrm{vap}} - h_{\mathrm{liq}}) = \dot{m}h_{\mathrm{fg}} \quad (4.44)$$

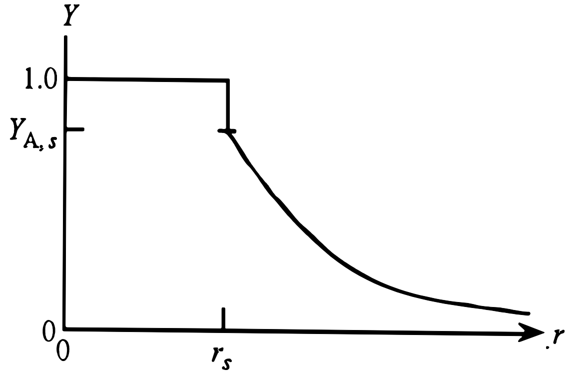
or

$$\dot{Q}_{\mathrm{net}} = \dot{m}h_{\mathrm{fg}} \quad (4.45)$$

Droplet Evaporation:



(a)



(b)

- Assumptions:

- The evaporation process is quasi-steady.
- The droplet temperature is uniform, and the temperature is assumed to be some fixed value below the boiling point of the liquid.
- The mass fraction of vapour at the droplet surface is determined by liquid-vapour equilibrium at the droplet temperature.
- We assume constant physical properties, e.g., $\rho\mathcal{D}$.

Evaporation Rate:

- Same approach as the Stefan problem; except change in coordinate sysytem.
- Overall mass conservation:

$$\dot{m}(r) = \text{constant} = 4\pi r^2 \dot{m}'' \tag{4.46}$$

- Species conservation for the droplet vapour:

$$\dot{m}''_{\mathrm{A}} = Y_{\mathrm{A}} \dot{m}''_{\mathrm{A}} - \rho \mathcal{D}_{\mathrm{AB}} \frac{\mathrm{d}Y_{\mathrm{A}}}{\mathrm{d}r} \tag{4.47}$$

- Substitute Eqn. 4.46 into 4.47 and solve for $\dot{m}$,

$$\dot{m} = -4\pi r^2 \frac{\rho \mathcal{D}_{\mathrm{AB}}}{1 - Y_{\mathrm{A}}} \frac{\mathrm{d}Y_{\mathrm{A}}}{\mathrm{d}r} \tag{4.48}$$

- Integrating and applying the boundary condition

$$Y_{\mathrm{A}}(r = r_s) = Y_{\mathrm{A},s} \tag{4.49}$$

  - yields

$$Y_{\mathrm{A}}(r) = 1 - \frac{(1 - Y_{\mathrm{A},s}) \exp\left[-\dot{m}/(4\pi\rho\mathcal{D}_{\mathrm{AB}} r)\right)}{\exp\left[-\dot{m}/(4\pi\rho\mathcal{D}_{\mathrm{AB}} r_s)\right]} \tag{4.50}$$

- Evaporation rate can be determined from Eqn. 4.50 by letting $Y_{\mathrm{A}} = Y_{\mathrm{A},\infty}$ for $r \rightarrow \infty$:

$$\dot{m} = 4\pi r_s \rho \mathcal{D}_{\mathrm{AB}} \ln \left[\frac{(1 - Y_{\mathrm{A},\infty})}{(1 - Y_{\mathrm{A},s})} \right] \qquad (4.51)$$

- In Eqn. 4.51, we can define the dimensionless *transfer number*, B_Y,

$$1 + B_Y \equiv \frac{1 - Y_{\mathrm{A},\infty}}{1 - Y_{\mathrm{A},s}} \qquad (4.52a)$$

or

$$B_Y = \frac{Y_{\mathrm{A},s} - Y_{\mathrm{A},\infty}}{1 - Y_{\mathrm{A},s}} \tag{4.52b}$$

- Then the evaporation rate is

$$\dot{m} = 4\pi r_s \rho \mathcal{D}_{\mathrm{AB}} \ln\left(1 + B_Y\right) \tag{4.53}$$

- Droplet Mass Conservation:

$$\frac{\mathrm{d}m_d}{\mathrm{d}t} = -\dot{m} \tag{4.54}$$

where m_d is given by

$$m_d = \rho_l V = \rho_l \pi D^3/6 \tag{4.55}$$

where $D = 2r_s$, and V is the volume of the droplet.

- Substituting Eqns 4.55 and 4.53 into 4.54 and differentiating

$$\frac{\mathrm{d}D}{\mathrm{d}t} = -\frac{4\rho\mathcal{D}_{\mathrm{AB}}}{\rho_l D}\ln\left(1 + B_Y\right) \tag{4.56}$$

- Eqn 4.56 is more commonly expressed in term of D^2 rather than D,

$$\frac{\mathrm{d}D^2}{\mathrm{d}t} = -\frac{8\rho\mathcal{D}_{\mathrm{AB}}}{\rho_l}\ln\left(1 + B_Y\right) \tag{4.57}$$

- Equation 4.57 tells us that time derivative of the square of the droplet diameter is constant. D^2 varies with t with a slope equal to RHS of Eqn.4.57. This slope is defined as *evaporation constant* K:

$$K = \frac{8\rho\mathcal{D}_{\mathrm{AB}}}{\rho_l}\ln\left(1 + B_Y\right) \tag{4.58}$$

- Droplet evaporation time can be calculated from:

$$\int_{D_o^2}^{0} \mathrm{d}D^2 = -\int_{0}^{t_d} K\mathrm{d}t \tag{4.59}$$

which yields

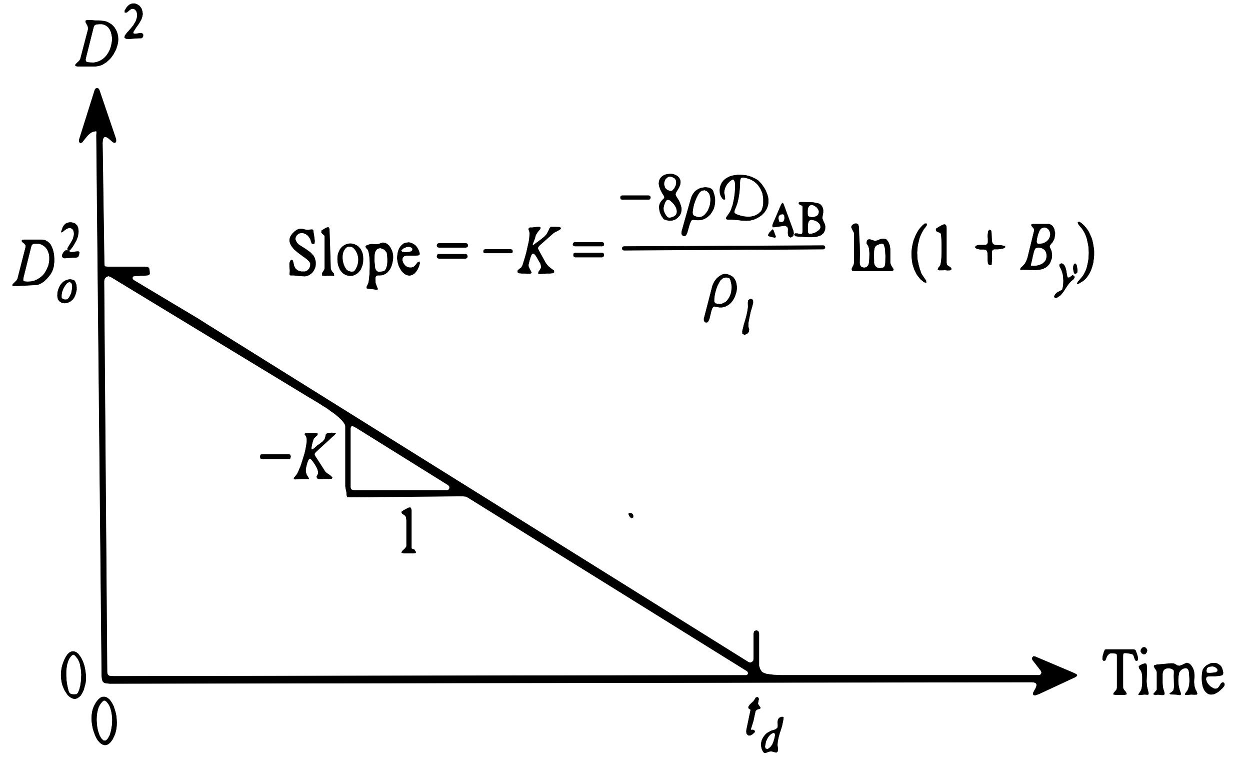
$$t_d = D_o^2/K \tag{4.60}$$

- We can change the limits to get a more general relationship to provide a general expression for the variation of D with time:

$$D^2(t) = D_o^2 - Kt \tag{4.61}$$

- Eq. 4.61 is referred to as the D^2 *law* for droplet evaporation.

D^2 law for droplet evaporation:



5. Coupling of Chemical Kinetics & Thermodynamics

Objectives of this section:

- Thermodynamics: Initial and final states are considered:
  - Adiabatic flame temperature
  - Equilibrium composition of products
  - No knowledge of chemical rate processes required

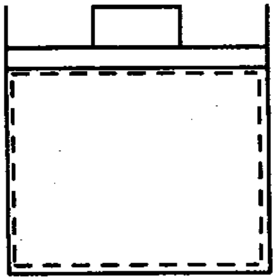
Objectives of this section (Cont'd):

- In this section aim is to couple thermodynamics with chemical rate processes.
- Follow the system temperature and the various species concentrations as functions of time as the system moves from reactants to products.
- Systems chosen to demonsrate the basic concepts will be simple with bold assumptions.
- Interrelationship among thermodynamics, chemical kinetics, and fluid mechanics.

Objectives of this section (Cont’d):

- We will consider four type of idealized reactors:
    1. Constant-pressure fixed-mass reactor
    2. Constant-volume fixed-mass reactor
    3. Well-stirred reactor
    4. Plug-flow reactor
- In first three we assume that systems are perfectly mixed and homogeneous in composition.
- In the 4th, perfect mixedness in radial direction; mixing and diffusion ignored in axial direction.

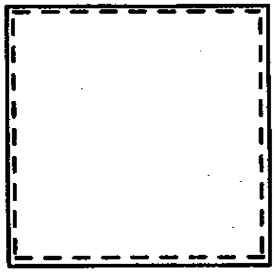
(a)
Constant-pressure fixed-mass reactor



$T = T(t)$
$[X_i] = [X_i](t)$
$V = V(t)$

Perfectly-mixed, homogeneous reaction

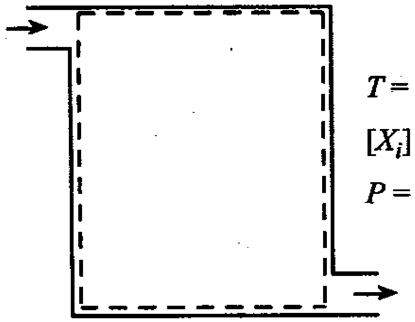
(b)
Constant-volume fixed-mass reactor



$T = T(t)$
$[X_i] = [X_i](t)$
$P = P(t)$

Perfectly-mixed, homogeneous reaction

(c)
Well-stirred reactor



T = constant
$[X_i]$ = constant
P = constant

Steady-state, steady-flow, perfectly mixed

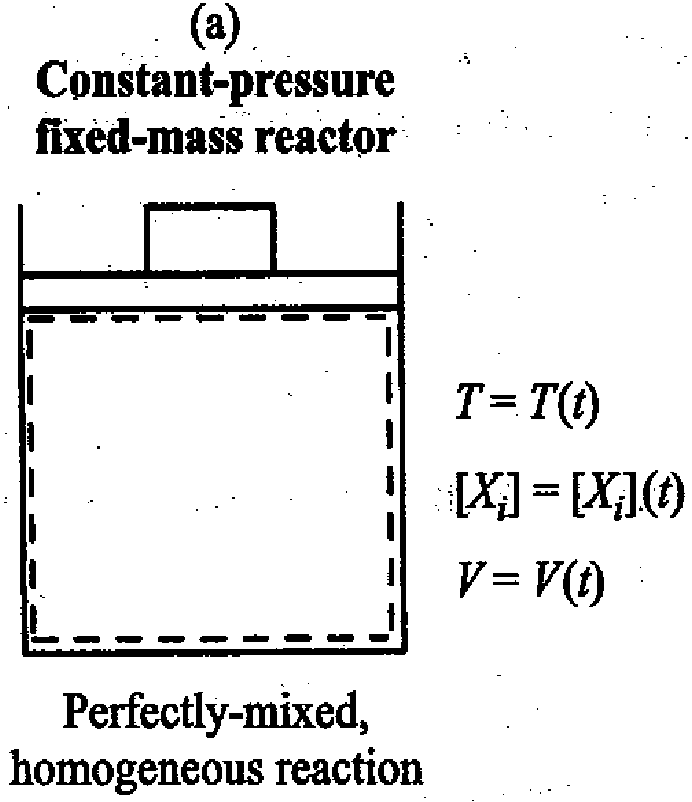
(d)
Plug-flow reactor

$T = T(x)$
$[X_i] = [X_i](x)$
$P = P(x)$
$\mathbf{V} = v_x(x)$

Steady-state, steady-flow, no axial mixing

Constant-Pressure Fixed Mass Reactor:

Application of Conservation Laws:



- Reactants react at each and every location within the volume at the same time.
- No temperature or composition gradients within the mixture.
- Single temperature and a set of species concentrations are sufficient to describe the evolution of the system.
- For combustion reactions, both temperature and volume will increase with time.
- There may be heat transfer through the reaction vessel walls.

- Conservation of energy for fixed-mass system:

$$\dot{Q} - \dot{W} = m\frac{\mathrm{d}u}{\mathrm{d}t} \tag{5.1}$$

  where $\dot{Q}$ is the heat transfer rate, and $\dot{W}$ is the work done.

- Using definition of enthalpy $h \equiv u + Pv$, and differentiating gives

$$\frac{\mathrm{d}u}{\mathrm{d}t} = \frac{\mathrm{d}h}{\mathrm{d}t} - P\frac{\mathrm{d}v}{\mathrm{d}t} \tag{5.2}$$

- Assuming only work is the $P - \mathrm{d}v$ work at the piston,

$$\frac{\dot{W}}{m} = P\frac{\mathrm{d}v}{\mathrm{d}t} \tag{5.3}$$

- Substitute Eqns.5.2 and 5.3 into 5.1,

$$\frac{\dot{Q}}{m} = \frac{\mathrm{d}h}{\mathrm{d}t} \tag{5.4}$$

- System enthalpy in terms of composition,

$$h = \frac{H}{m} = \Big[\sum_{i=1}^{N} N_i \bar{h}_i\Big]/m \tag{5.5}$$

- Differentiation of Eqn.5.5 gives

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{1}{m}\Big[\sum_i \Big(\bar{h}_i \frac{\mathrm{d}N_i}{\mathrm{d}t}\Big) + \sum_i \Big(N_i \frac{\mathrm{d}\bar{h}_i}{\mathrm{d}t}\Big)\Big] \quad (5.6)$$

- Ideal gas behaviour, i.e. $\bar{h}_i = f(T)$ only,

$$\frac{\mathrm{d}\bar{h}_i}{\mathrm{d}t} = \frac{\partial \bar{h}_i}{\partial T}\frac{\mathrm{d}T}{\mathrm{d}t} = \bar{c}_{p,i}\frac{\mathrm{d}T}{\mathrm{d}t} \quad (5.7)$$

where $\bar{c}_{p,i}$ is the molar specific heat at constant pressure.

- Eqn.5.7 provides the link to system temperature.
- Link to system composition:

$$N_i = V[X_i] \tag{5.8}$$

- Link to chemical dynamics:

$$\frac{\mathrm{d}N_i}{\mathrm{d}t} \equiv V\dot{\omega}_i \tag{5.9}$$

where $\dot{\omega}_i$ is the net production rate of species i (Eqns.2.31-2.34).

- Substitute Eqns.5.7-5.9 into 5.6, we get

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{(\dot{Q}/V) - \sum_i (\bar{h}_i \dot{\omega}_i)}{\sum_i ([X_i]\bar{c}_{p,i})} \tag{5.10}$$

where we use the calorific equation of state

$$\bar{h}_i = \bar{h}^o_{f,i} + \int_{T_{\mathrm{ref}}}^{T} \bar{c}_{p,i} \mathrm{d}T \tag{5.11}$$

- Volume is obtained by

$$V = \frac{m}{\sum_i([X_i]MW_i)} \tag{5.12}$$

- $[X_i]$ change with time as a result of both chemical reactions and changing volume:

$$\frac{\mathrm{d}[X_i]}{\mathrm{d}t} = \frac{\mathrm{d}(N_i/V)}{\mathrm{d}t} = \frac{1}{V}\frac{\mathrm{d}N_i}{\mathrm{d}t} - N_i\frac{1}{V^2}\frac{\mathrm{d}V}{\mathrm{d}t} \tag{5.13a}$$

or

$$\frac{\mathrm{d}[X_i]}{\mathrm{d}t} = \dot{\omega}_i - [X_i]\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}t} \tag{5.13b}$$

- The ideal gas law,

$$PV = \sum_i N_i R_u T \qquad (5.14a)$$

differentiating for $P =$constant, and rearranging

$$\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{1}{\sum_i N_i}\sum_i \frac{\mathrm{d}N_i}{\mathrm{d}t} + \frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}t} \qquad (5.14b)$$

- Substitute Eqn.5.9 into 5.14b, and then substitute the result into Eqn.5.13b:

the rate of change of the species concentrations:

$$\frac{\mathrm{d}[X_i]}{\mathrm{d}t} = \dot{\omega}_i - [X_i]\left[\frac{\sum \dot{\omega}_i}{\sum_j [X_j]} + \frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}t}\right] \qquad (5.15)$$

- In summary, the problem is to find the solution to the following set of differential equations:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = f([X_i], T) \qquad (5.16a)$$

$$\frac{\mathrm{d}[X_i]}{\mathrm{d}t} = f([X_i], T) \qquad i = 1, 2, ...N \qquad (5.16b)$$

subject to following initial conditions:

$$T(t = 0) = T_0 \tag{5.17a}$$

$$[X_i](t = 0) = [X_i]_0 \tag{5.17b}$$

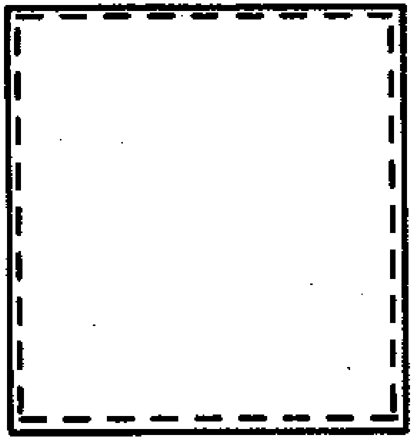
- Functional forms of Eqns. 5.17a and 5.17b are obtained from Eqns. 5.10 and 5.15. Eqn.5.11 gives enthalpy and Eqn.5.12 gives volume.
- Most of the time there is no analytical solution. Numerical integration can be done using an integration routine capable of handling stiff equations.

Constant-Volume Fixed Mass Reactor:

Application of Conservation Laws:

(b)

Constant-volume fixed-mass reactor



$T = T(t)$

$[X_i] = [X_i](t)$

$P = P(t)$

Perfectly-mixed, homogeneous reaction

- Application of energy conservation to the constant-volume fixed mass reactor is similar to constant-pressure case; only exception is $\dot{W} = 0$ for $V =$constant:

$$\frac{\mathrm{d}u}{\mathrm{d}t} = \frac{\dot{Q}}{m} \tag{5.18}$$

- Noting that u now plays the same role as h in our analysis for $P =$constant, expressions equivalent to Eqns.5.5-5.7 can be developed and substituted in Eqn.5.18. This will give, after rearrangement,

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{(\dot{Q}/V) - \sum_i (\bar{u}_i \dot{\omega}_i)}{\sum_i ([X_i]\bar{c}_{v,i})} \tag{5.19}$$

Since $\bar{u}_i = \bar{h}_i - R_u T$ and $\bar{c}_{v,i} = \bar{c}_{p,i} - R_u$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{(\dot{Q}/V) + R_u T \sum_i \dot{\omega}_i - \sum_i (\bar{h}_i \dot{\omega}_i)}{\sum_i ([X_i]\bar{c}_{p,i} - R_u)} \tag{5.20}$$

- $\mathrm{d}P/\mathrm{d}t$ is important in $V =$const. problems.

- to get $\mathrm{d}P/\mathrm{d}t$, we differentiate the ideal gas law:

$$PV = \sum_i N_i R_u T \tag{5.21}$$

$$V\frac{\mathrm{d}P}{\mathrm{d}t} = R_u T \frac{\mathrm{d}\sum_i N_i}{\mathrm{d}t} + R_u \sum_i N_i \frac{\mathrm{d}T}{\mathrm{d}t} \tag{5.22}$$

$$P = \sum_i [X_i] R_u T \tag{5.23}$$

$$V\frac{\mathrm{d}P}{\mathrm{d}t} = R_u T \sum_i \dot{\omega}_i + R_u \sum_i [X_i] \frac{\mathrm{d}T}{\mathrm{d}t} \tag{5.24}$$

- Eqn.5.20 can be integrated simultaneously with $\dot{\omega}_i$ to determine $T(t)$ and $[X_i](t)$,

$$\frac{\mathrm{d}T}{\mathrm{d}t} = f([X_i], T) \tag{5.25a}$$

$$\frac{\mathrm{d}[X_i]}{\mathrm{d}t} = f([X_i], T) \qquad i = 1, 2, ...N \tag{5.25b}$$

subject to following initial conditions:

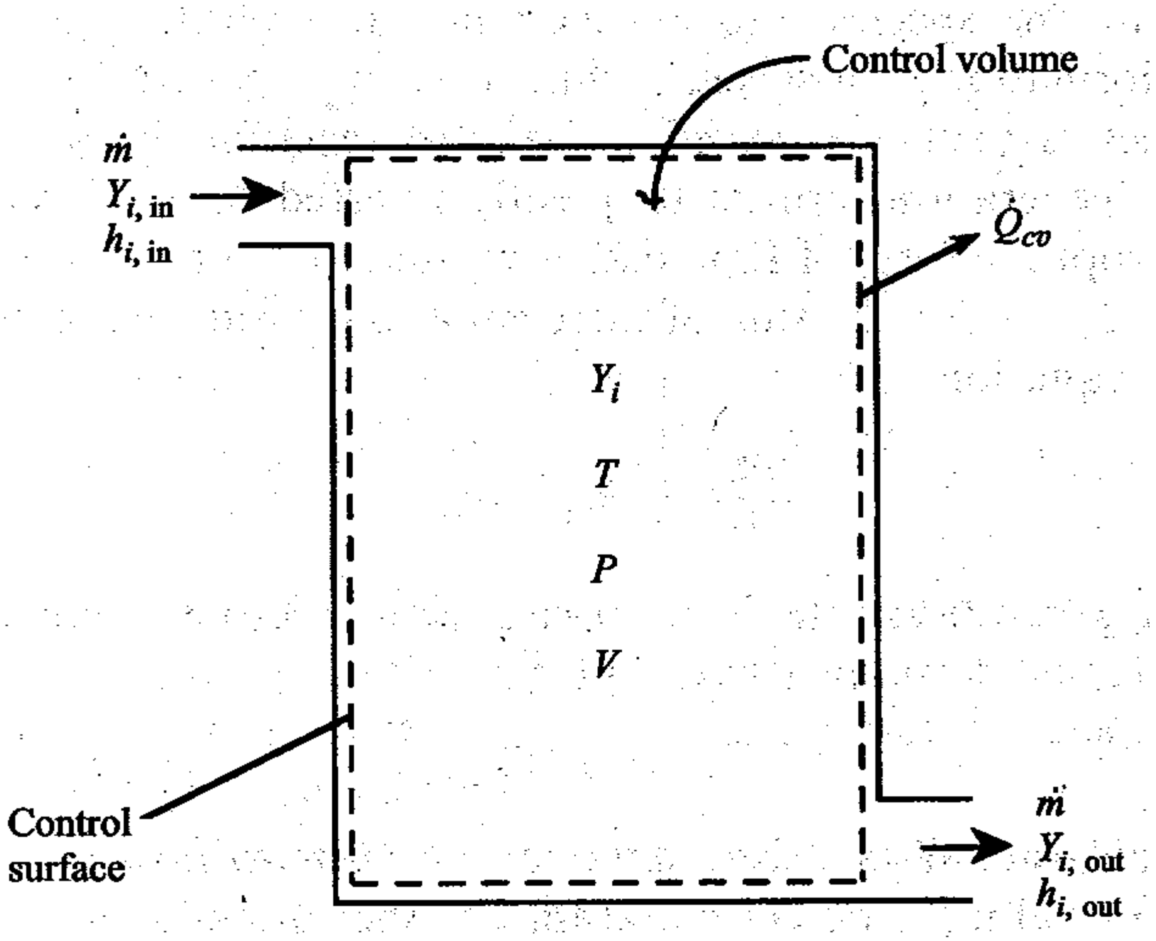
$$T(t = 0) = T_0 \tag{5.26a}$$

$$[X_i](t = 0) = [X_i]_0 \tag{5.26b}$$

Well-Stirred Reactor:

- Also called "perfectly-stirred reactor". Ideal reactor with perfect mixing achieved inside the control volume.
- Experimentally used for:
  - flame stability,
  - pollutant formation, and
  - obtaining global reaction parameters.
- "Longwell reactor".
- "Zeldovich reactor".

Well-Stirred Reactor:



Application of Conservation Laws:

- Mass conservation of arbitrary species i,

$$\underbrace{\frac{\mathrm{d}m_{i,\mathrm{cv}}}{\mathrm{d}t}}_{\substack{\text{Rate at which}\\ \text{mass of } i\\ \text{accumulates}\\ \text{within c.v.}}} = \underbrace{\dot{m}_i'''V}_{\substack{\text{Rate at which}\\ \text{mass of } i\\ \text{is generated}\\ \text{within c.v.}}} + \underbrace{\dot{m}_{i,\mathrm{in}}}_{\substack{\text{Mass flow}\\ \text{of } i\\ \text{into c.v.}}} - \underbrace{\dot{m}_{i,\mathrm{out}}}_{\substack{\text{Mass flow}\\ \text{of } i\\ \text{out of c.v.}}} \tag{5.27}$$

- $\dot{m}_i'''V$ is the source term: generation/destruction of species by chemical reactions through transformation of one species into another.

- We note that,

$$\frac{\mathrm{d}m_{\mathrm{cv}}}{\mathrm{d}t} = \dot{m}_{\mathrm{in}} - \dot{m}_{\mathrm{out}} \tag{5.28}$$

$\dot{m}_i'''$ is related to $\dot{\omega}_i$ by,

$$\dot{m}_i''' = \dot{\omega}_i MW_i \tag{5.29}$$

Ignoring any diffusional flux,

$$\dot{m}_i = \dot{m} Y_i \tag{5.30}$$

- If we apply Eqn.5.27 to the well-stirred reactor, time derivative on LHS dissapears for steady-state. With Eqns.5.29 and 5.30, Eqn.5.27 becomes,

$$\dot{\omega}_i MW_i V + \dot{m}(Y_{i,\text{in}} - Y_{i,\text{out}}) = 0 \quad \text{for } i = 1, 2, ...N \tag{5.31}$$

- Further, $Y_{i,\text{out}} = Y_{i,\text{cv}}$ and species production rate,

$$\dot{\omega}_i = f([X_i]_{\text{cv}}, T) = f([X_i]_{\text{out}}, T) \tag{5.32}$$

where

$$Y_i = \Big([X_i] MW_i\Big) / \Big(\sum_{j=1}^{N} [X_j] MW_j\Big) \tag{5.33}$$

- Eqn.5.31 can be written for N species to provide N equations with $N+1$ unknowns (assuming that $\dot{m}$ and V are known); additional equation comes from an energy balance.
- Steady-state, steady-flow energy conservation equation for well-stirred reactor,

$$\dot{Q} = \dot{m}(h_{\text{out}} - h_{\text{in}}) \tag{5.34}$$

in which we neglect any changes in kinetic and potential energies.

- In terms of individual species, Eqn.5.34 becomes

$$\dot{Q} = \dot{m}\left[\sum_{i=1}^{N} Y_{i,\mathrm{out}} h_i(T) - \sum_{i=1}^{N} Y_{i,\mathrm{in}} h_i(T_{\mathrm{in}})\right] \tag{5.35}$$

$$h_i(T) = h^o_{f,i} + \int_{T_{\mathrm{ref}}}^{T} c_{p,i}\mathrm{d}T \tag{5.36}$$

- Finding T and $Y_{i,\mathrm{out}}$ is similar to equilibrium flame T calculations; but the composition is constrained by chemical kinetics.

- Most of the time a mean *residence time* is defined for well-stirred reactors,

$$t_{\mathrm{R}} = \rho V / \dot{m} \tag{5.37}$$

where the mixture density is,

$$\rho = P \cdot MW_{\mathrm{mix}} / (R_u T) \tag{5.38}$$

- The equations describing the well-stirred reactor are a set of non-linear algebraic equations, rather than a system of ordinary differential equations.

Plug-Flow Reactor:

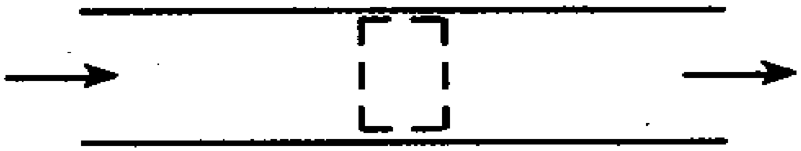
Assumptions:

- Steady-state, steady-flow.
- No mixing in axial direction; molecular/turbulent mass diffusion in flow direction is negligible.
- Uniform properties in the direction perpendicular to the flow; 1-D flow.
- Ideal frictionless flow; presure and velocity can be related by Euler equation.
- Ideal-gas behaviour.

Plug-Flow Reactor:

(d)

Plug-flow reactor



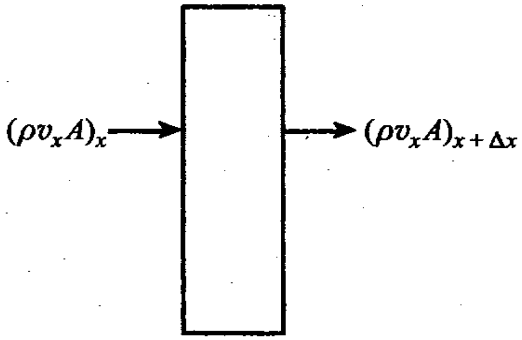
$$T = T(x)$$

$$[X_i] = [X_i](x)$$

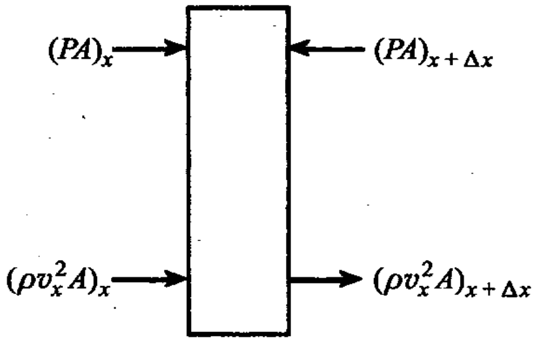
$$P = P(x)$$

$$\mathbf{V} = v_x(x)$$

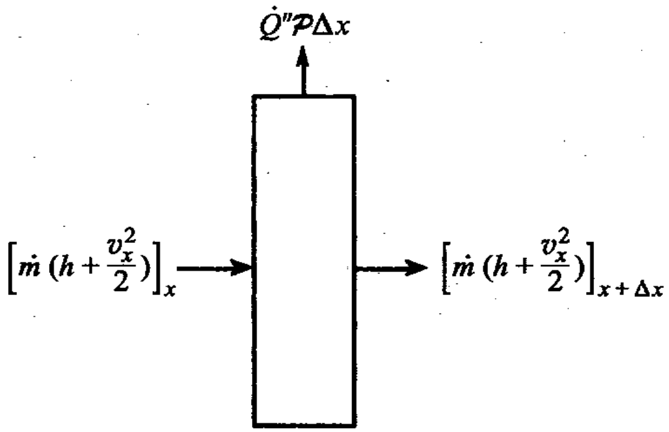
Steady-state,
steady-flow,
no axial mixing



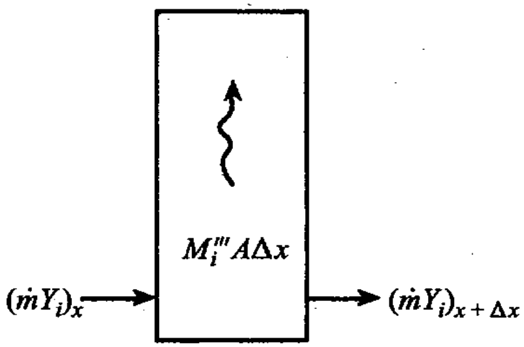
Mass



x-Momentum



Energy



Species

Application of Conservation Laws:

- The goal is to develop a system of 1st order ODEs whose solution describes the reactor flow properties as functions of axial distance, x.
- $6+2N$ equations and unkowns/functions.
- Number of unknowns can be reduced by N noting that $\dot{\omega}_i$ can be expressed in terms of Y_i.
- Known quantities: $\dot{m}$, k_i, $A(x)$, and $\dot{Q}''(x)$.
- $\dot{Q}''(x)$ may be calculated from a given wall temperature distribution.

Source of Equations	**Number of Equations**	**Variables or Derivatives Involved**
Fundamental conservation principles: mass, x-momentum, energy, species	$3+N$	$\frac{d\rho}{dx}, \frac{dv_x}{dx}, \frac{dP}{dx}, \frac{dh}{dx}, \frac{dY_i}{dx} (i=1,2,\ldots,N), \dot{\omega}_i (i=1,2,\ldots,N)$
Mass action laws	N	$\dot{\omega}_i\ (i=1,2,\ldots,N)$
Equation of state	1	$\frac{d\rho}{dx}, \frac{dP}{dx}, \frac{dT}{dx}, \frac{dMW_{\text{mix}}}{dx}$
Calorific equation of state	1	$\frac{dh}{dx}, \frac{dT}{dx}, \frac{dY_i}{dx}\ (i=1,2,\ldots,N)$
Definition of mixture molecular weight	1	$\frac{dMW_{\text{mix}}}{dx}, \frac{dY_i}{dx}\ (i=1,2,\ldots,N)$

- Mass conservation:

$$\frac{\mathrm{d}(\rho v_x A)}{\mathrm{d}x} = 0 \tag{5.39}$$

- x-Momentum conservation:

$$\frac{\mathrm{d}P}{\mathrm{d}x} + \rho v_x \frac{\mathrm{d}v_x}{\mathrm{d}x} = 0 \tag{5.40}$$

- Energy conservation:

$$\frac{\mathrm{d}(h + v_x^2/2)}{\mathrm{d}x} + \frac{\dot{Q}\mathcal{P}}{\dot{m}} = 0 \tag{5.41}$$

v_x is axial velocity; $\mathcal{P}$ is local perimeter.

- Species conservation:

$$\frac{\mathrm{d}Y_i}{\mathrm{d}x} - \frac{\dot{\omega}_i MW_i}{\rho v_x} = 0 \tag{5.42}$$

- Eqns.5.39 and 5.41 can be rearranged to give,

$$\frac{1}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}x} + \frac{1}{v_x}\frac{\mathrm{d}v_x}{\mathrm{d}x} + \frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}x} = 0 \tag{5.43}$$

$$\frac{\mathrm{d}h}{\mathrm{d}x} + v_x\frac{\mathrm{d}v_x}{\mathrm{d}x} + \frac{\dot{Q}''\mathcal{P}}{\dot{m}} = 0 \tag{5.44}$$

- Using the ideal-gas calorific equation,

$$h = h(T, Y_i) \tag{5.45}$$

$\mathrm{d}h/\mathrm{d}x$ and $\mathrm{d}T/\mathrm{d}x$ can be related,

$$\frac{\mathrm{d}h}{\mathrm{d}x} = c_p \frac{\mathrm{d}T}{\mathrm{d}x} + \sum_{i=1}^{N} h_i \frac{\mathrm{d}Y_i}{\mathrm{d}x} \tag{5.46}$$

- To complete the mathematical description of plug-flow reactor, we differentiate ideal-gas equation,

$$P = \rho R_u T/(MW_{\mathrm{mix}}) \tag{5.47}$$

to yield

$$\frac{1}{\rho}\frac{\mathrm{d}P}{\mathrm{d}x} = \frac{1}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}x} + \frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}x} - \frac{1}{MW_{\mathrm{mix}}}\frac{\mathrm{d}MW_{\mathrm{mix}}}{\mathrm{d}x} \tag{5.48}$$

where

$$MW_{\mathrm{mix}} = \left[\sum_{i=1}^{N} Y_i/(MW_i)\right]^{-1} \tag{5.49}$$

$$\frac{\mathrm{d}MW_{\mathrm{mix}}}{\mathrm{d}x} = -MW_{\mathrm{mix}}^2 \sum_{i=1}^{N} \frac{1}{MW_i}\frac{\mathrm{d}Y_i}{\mathrm{d}x} \tag{5.50}$$

- Number of equations can be reduced by eliminating some of the derivatives by substitution. If we retain the derivatives $\mathrm{d}T/\mathrm{d}x$, $\mathrm{d}\rho/\mathrm{d}x$, and $\mathrm{d}Y_i/\mathrm{d}x$, we get the following system of ODEs,

$$\frac{\mathrm{d}\rho}{\mathrm{d}x} = \frac{\mathcal{A}+\mathcal{B}}{P + \left(1 + \frac{v_x^2}{c_p T}\right) - \rho v_x^2} \tag{5.51}$$

$$\mathcal{A} = \left(1 - \frac{R_u}{c_p MW_{\mathrm{mix}}}\right)\rho^2 v_x^2 \left(\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}x}\right)$$

$$\mathcal{B} = \frac{\rho R_u}{v_x c_p MW_{\mathrm{mix}}} \sum_{i=1}^{N} MW_i \dot{\omega}_i \left(h_i - \frac{MW_{\mathrm{mix}}}{MW_i} c_p T\right)$$

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{v_x^2}{\rho c_p}\frac{\mathrm{d}\rho}{\mathrm{d}x} + \frac{v_x^2}{c_p}\left(\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}x}\right) - \frac{1}{v_x \rho c_p}\sum_{i=1}^{N} h_i \dot{\omega}_i MW_i \qquad (5.52)$$

$$\frac{\mathrm{d}Y_i}{\mathrm{d}x} = \frac{\dot{\omega}_i MW_i}{\rho v_x} \qquad (5.53)$$

Note that in Eqn.5.52, $\dot{Q}''$ has been set to zero for simplicity.

- A residence time can be defined, which adds one more equation,

$$\frac{\mathrm{d}t_{\mathrm{R}}}{\mathrm{d}x} = \frac{1}{v_x} \tag{5.54}$$

- Initial conditions to solve Eqns.5.51-5.64 are

$$T(0) = T_o \tag{5.55a}$$

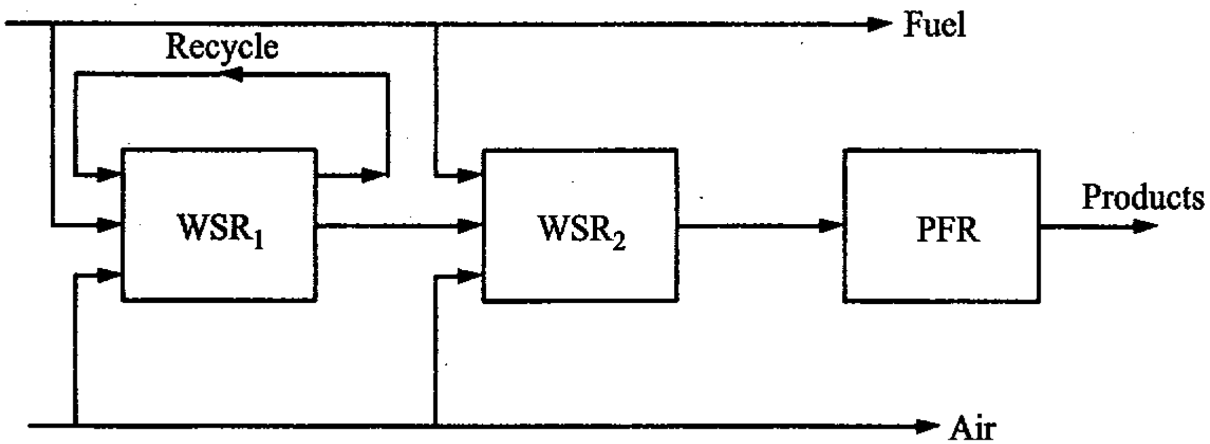
$$\rho(0) = \rho_o \tag{5,55b}$$

$$Y_i(0) = Y_{io} \quad i = 1, 2, ...N \tag{5.55c}$$

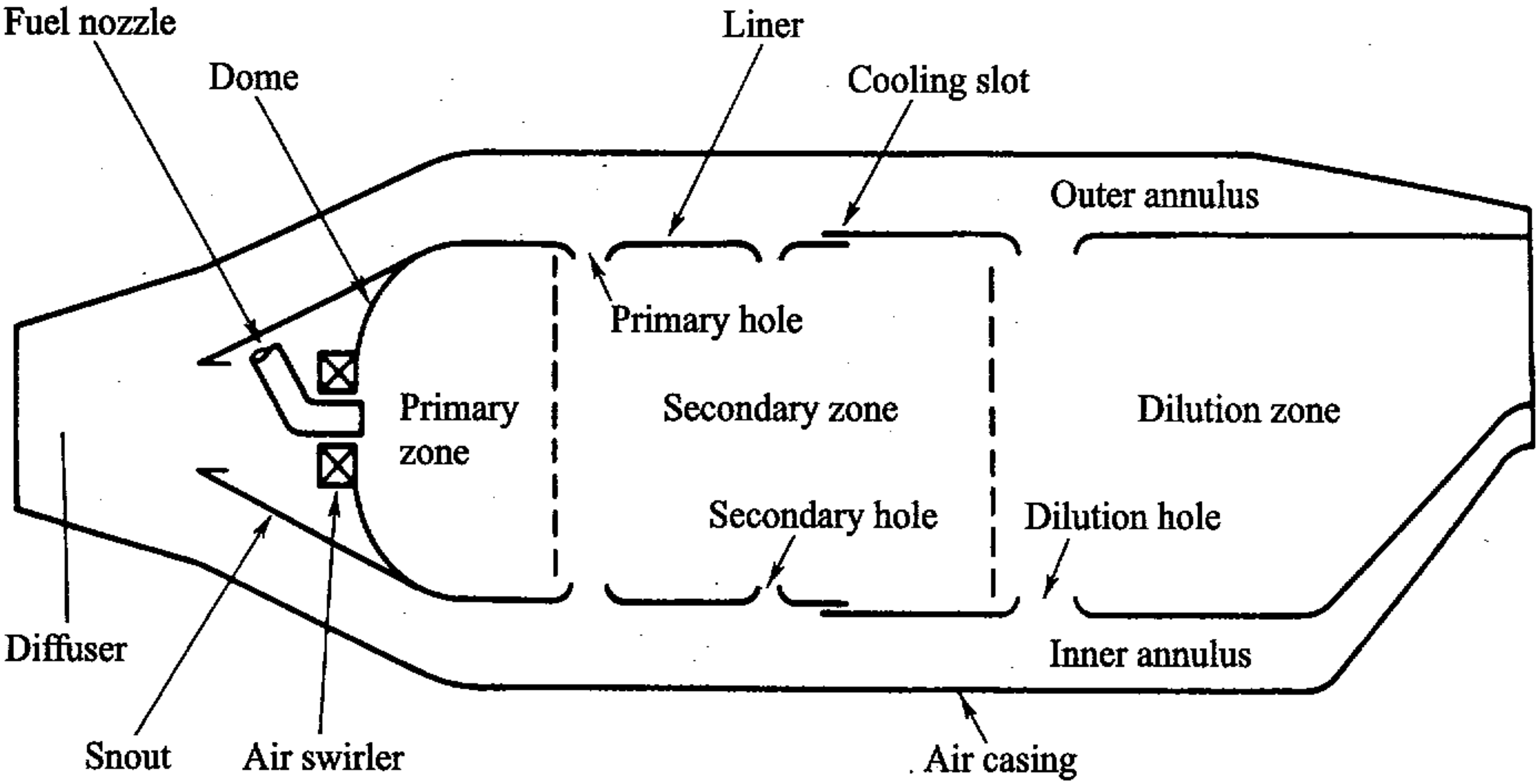
$$t_{\mathrm{R}}(0) = 0. \tag{5.55d}$$

Applications to Combustion System Modelling:

- Combinations of well-stirred and plug-flow reactors can be used to approximate more complex combustion systems.



Schematic of annular gas turbine combustor



- Gas turbine combustor is modelled as two well-stirred reactors and a plug-flow reactor.
  - WSR_1: primary zone with recirculation of combustion products.
  - WSR_2: secondary zone.
  - PFR: dilution zone.
- Reactor modelling approaches are often used as complementary tools to more sophisticated finite-element or finite-difference numerical models of combustion chambers.

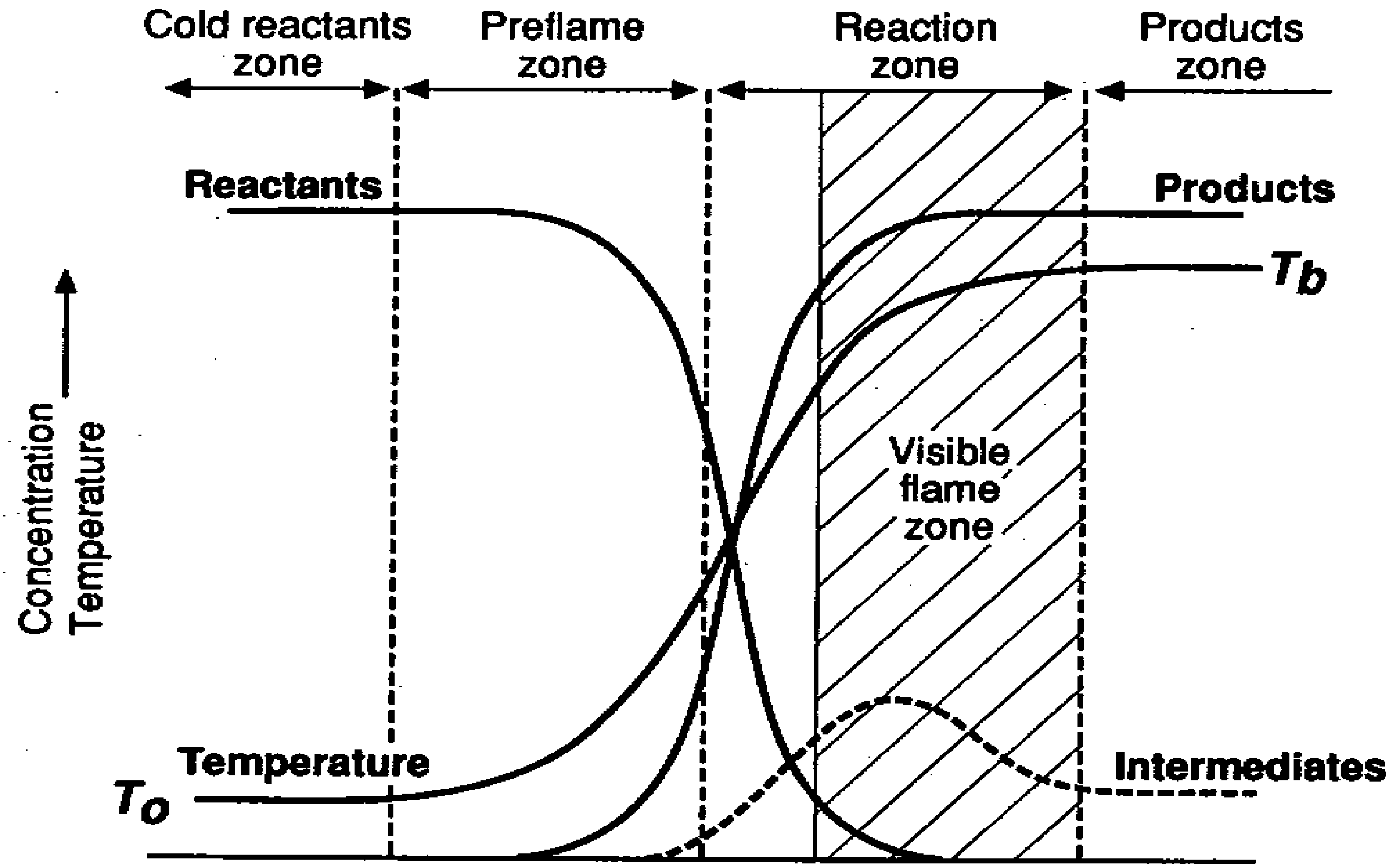
6. Laminar Premixed Flames

- A *premixed flame* is self-sustaining propagation of a localized combustion zone at subsonic velocities.
- We use the term *deflagration* in gasdynamics to define a premixed flame travelling at subsonic velocities.
- Consider a premixed flammable mixture in a long tube, open at both ends, ignited from one end. A combustion wave will travel down the tube starting from the ignition point.

- A flame is caused by a self-propagating exothermic reaction which is accompanied by a reaction zone.
- It will propagate through a stationary gas mixture at a characteristic velocity (*burning velocity*).
- For most hydrocarbon-air stoichiometric mixtures, this velocity is about 0.4 to 0.6 m/s.
- For hydrogen-air mixtures, this velocity is several meters per second.
- The velocity of this wave is controlled by the diffusion of heat and active radicals.

- For a flame burning in a mixture of gases of known pressure and composition, two characteristic properties may be defined and measured, the burning velocity and the flame temperature.
- Flame temperature can be predicted from thermodynamic data, if we invoke the assumption of chemical equilibrium.
- Various flame theories attempt to predict the laminar flame progation from physical and chemical properties; however, a closed form solution which is universal and accurate has not been possible.

- Historically, there have been two approaches to formulating the laminar flame propagation in premixed gases:
  1. Thermal propagation: the mixture is heated by conduction to the point where the rate of reaction is sufficiently rapid to become self-propagating.
  2. Diffusional propagation: diffusion of active species, such as atoms and radicals, from the reaction zone or the burned gas into the unreacted mixture causes reaction to occur.
- Reality: diffusion of heat and active radicals.


Cold reactants zone
Preflame zone
Reaction zone
Products zone
Reactants
Products
T_b
Concentration Temperature
Visible flame zone
Temperature
T_o
Intermediates

Simplified Analysis:

- Objective is to find a simple analytical expression for the laminar flame speed.

Assumptions:

- 1-D, constant area, steady-flow.
- Kinetic/potential energies, viscous effects, thermal radiation are all neglected.
- Pressure is assumed constant across the flame.
- Diffusion of heat and mass are governed by Fourier's and Fick's laws, respectively.

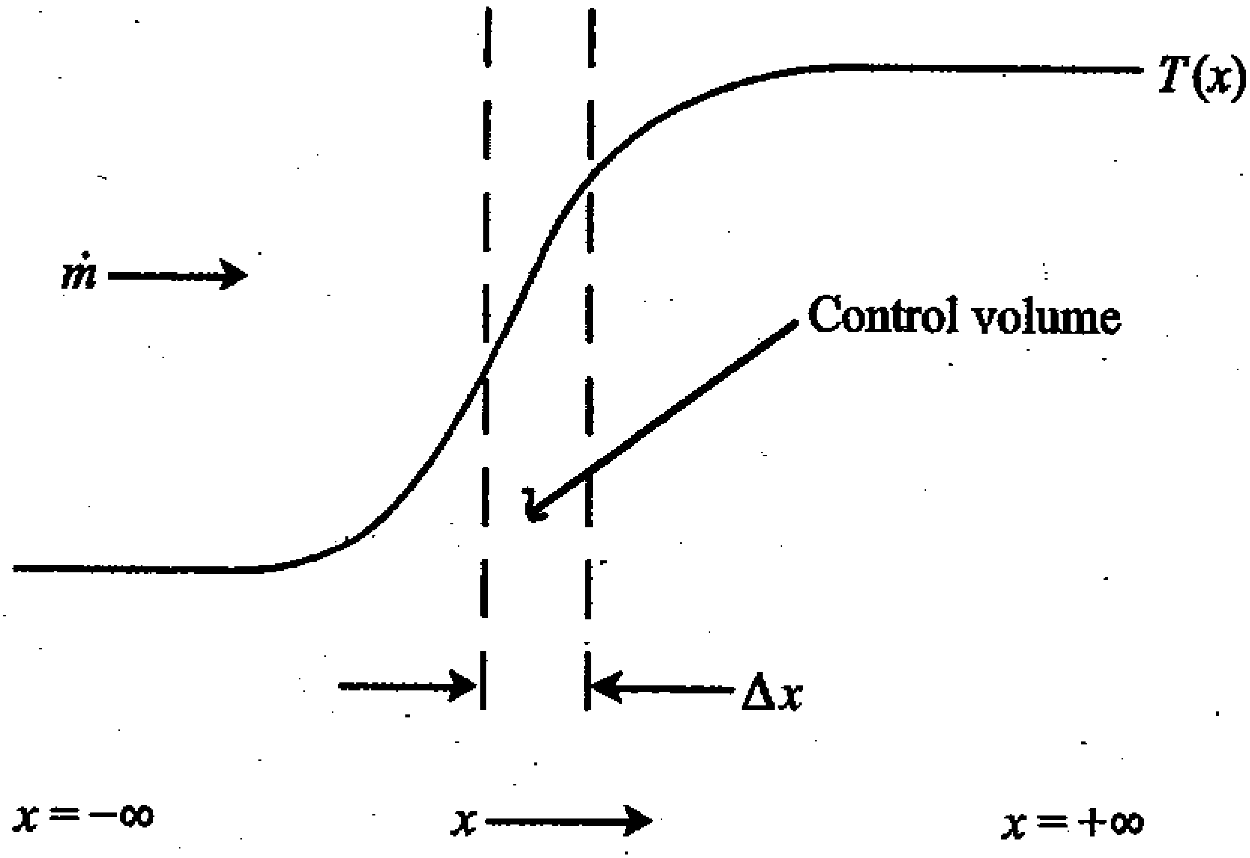
Assumptions (Cont'd):

- The Lewis number is unity,

$$\mathrm{Le} \equiv \frac{\alpha}{\mathcal{D}} = \frac{k}{\rho c_p \mathcal{D}} \tag{6.3}$$

  which means $k/c_p = \rho\mathcal{D}$ that simplifies the energy equation.

- Individual c_p values are all equal and constant.
- Single-step exothermic reaction describes combustion.
- $\Phi \leq 1$ so that the fuel is completely consumed.


$T(x)$
$\dot{m}$
Control volume
Δx
$x = -\infty$
x
$x = +\infty$

Conservation Laws:

- Mass conservation:

$$\frac{\mathrm{d}(\rho v_x)}{\mathrm{d}x} = 0 \qquad \text{(Turns – 7.4a)}$$

or

$$\dot{m}'' = \rho v_x = \text{constant} \qquad \text{(Turns – 7.4b)}$$

- Species conservation:

$$\frac{\mathrm{d}\dot{m}_i''}{\mathrm{d}x} = \dot{m}_i''' \qquad \text{(Turns – 7.9)}$$

With the application of Fick's diffusion law,

$$\frac{\mathrm{d}\left[\dot{m}''Y_i - \rho\mathcal{D}\frac{\mathrm{d}Y_i}{\mathrm{d}x}\right]}{\mathrm{d}x} = \dot{m}_i''' \qquad (\mathrm{Turns} - 7.8)$$

- For single-step reaction,

$$1\ \mathrm{kg\ fuel} + \nu\ \mathrm{kg\ oxidizer} \rightarrow (\nu + 1)\ \mathrm{kg\ products} \qquad (6.4)$$

$$\dot{m}_{\mathrm{F}}''' = \frac{1}{\nu}\dot{m}_{\mathrm{Ox}}''' = -\frac{1}{\nu+1}\dot{m}_{\mathrm{Pr}}''' \qquad (6.5)$$

- We can write Eqn.7.8 (Turns) for each species:
  - *Fuel:*

$$\dot{m}''\frac{\mathrm{d}Y_{\mathrm{F}}}{\mathrm{d}x}-\frac{\mathrm{d}\left(\rho\mathcal{D}\frac{\mathrm{d}Y_{\mathrm{F}}}{\mathrm{d}x}\right)}{\mathrm{d}x}=\dot{m}_{\mathrm{F}}''' \qquad (6.6a)$$

  - *Oxidizer:*

$$\dot{m}''\frac{\mathrm{d}Y_{\mathrm{Ox}}}{\mathrm{d}x}-\frac{\mathrm{d}\left(\rho\mathcal{D}\frac{\mathrm{d}Y_{\mathrm{Ox}}}{\mathrm{d}x}\right)}{\mathrm{d}x}=\nu\dot{m}_{\mathrm{F}}''' \qquad (6.6b)$$

- *Products:*

$$\dot{m}''\frac{\mathrm{d}Y_{\mathrm{Pr}}}{\mathrm{d}x} - \frac{\mathrm{d}\left(\rho\mathcal{D}\frac{\mathrm{d}Y_{\mathrm{Pr}}}{\mathrm{d}x}\right)}{\mathrm{d}x} = -(\nu+1)\dot{m}'''_{\mathrm{F}} \tag{6.6c}$$

- Energy Conservation:

$$\dot{m}''c_p\frac{\mathrm{d}T}{\mathrm{d}x} - \frac{\mathrm{d}}{\mathrm{d}x}\left[(\rho\mathcal{D}c_p)\frac{\mathrm{d}T}{\mathrm{d}x}\right] = -\sum h^o_{f,i}\dot{m}'''_i \tag{6.7a}$$

RHS of Eqn.6.7a can be written as,

$$-\sum h^o_{f,i}\dot{m}'''_i = -[h^o_{f,\mathrm{F}}\dot{m}'''_\mathrm{F} + h^o_{f,\mathrm{Ox}}\nu\dot{m}'''_\mathrm{F}$$
$$-h^o_{f,\mathrm{Pr}}(\nu+1)\dot{m}'''_\mathrm{F}]$$

or

$$-\sum h^o_{f,i}\dot{m}'''_i = -\dot{m}'''_\mathrm{F}\Delta h_c$$

where Δh_c is the heat of combustion,

$$\Delta h_c \equiv h^o_{f,\mathrm{F}} + \nu h^o_{f,\mathrm{Ox}} - (\nu+1)h^o_{f,\mathrm{Pr}}$$

- If we set $\rho\mathcal{D}c_p = k$, then Eqn.6.7a becomes,

$$\dot{m}''\frac{\mathrm{d}T}{\mathrm{d}x} - \frac{1}{c_p}\frac{\mathrm{d}\left(k\frac{\mathrm{d}T}{\mathrm{d}x}\right)}{\mathrm{d}x} = -\frac{\dot{m}_{\mathrm{F}}'''\Delta h_c}{c_p} \qquad (6.7b)$$

- The objective here is to find an expression for the laminar flame speed, which is related to the mass flux, $\dot{m}''$, by,

$$\dot{m}'' = \rho_u S_L \qquad (6.8)$$

- The approach is to assume a temperature profile that satisfies the boundary conditions, then integrate Eqn.6.7b.

- Boundary Conditions:
  - Upstream:

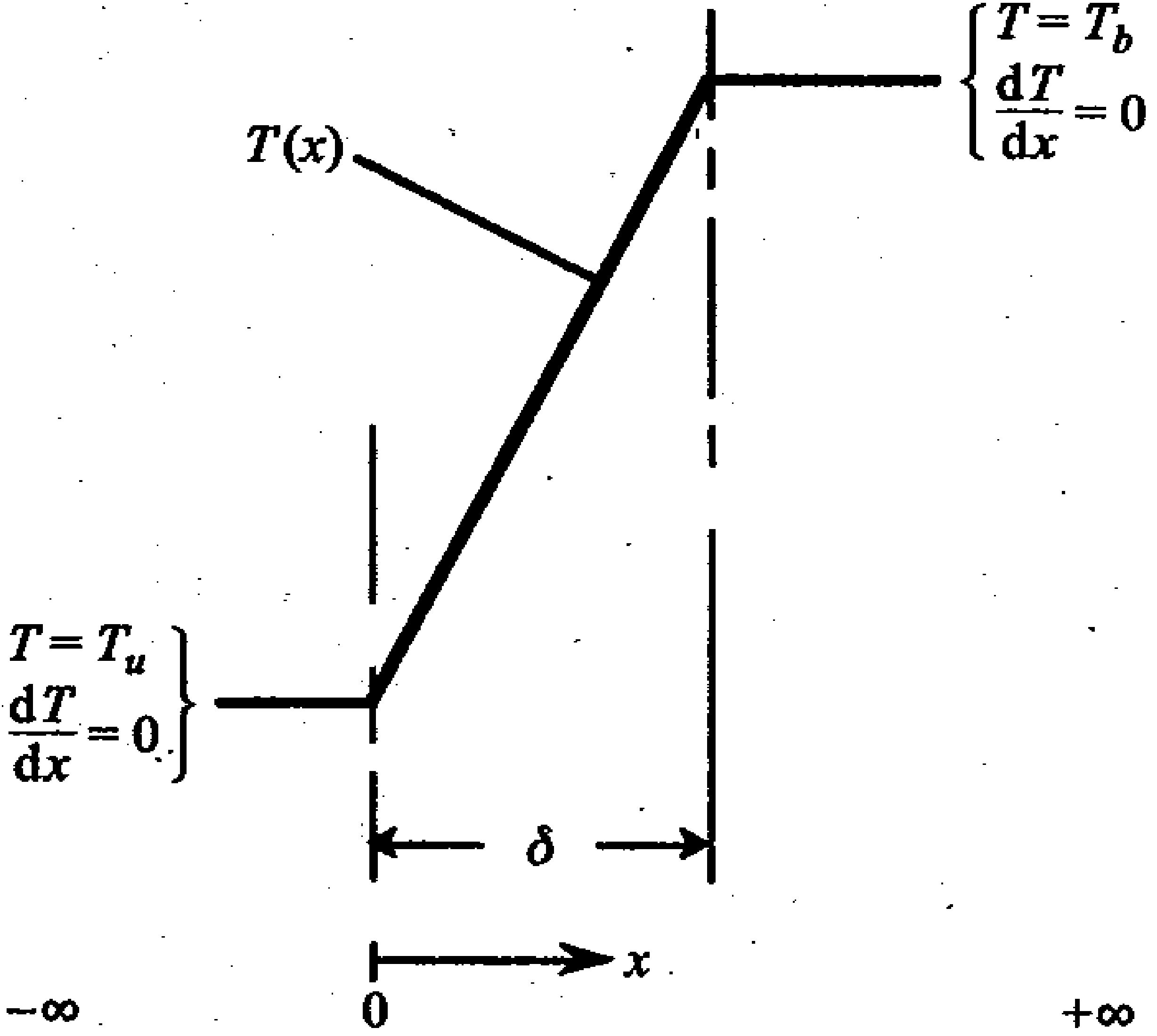
$$T(x \to -\infty) = T_u \qquad (6.9a)$$

$$\frac{\mathrm{d}T}{\mathrm{d}x}(\to -\infty) = 0 \qquad (6.9b)$$

  - Downstream:

$$T(x \to +\infty) = T_b \qquad (6.9c)$$

$$\frac{\mathrm{d}T}{\mathrm{d}x}(\to +\infty) = 0 \qquad (6.9d)$$


$T = T_b$
$\frac{dT}{dx} = 0$
$T(x)$
$T = T_u$
$\frac{dT}{dx} = 0$
δ
x
$-\infty$
0
$+\infty$

- We assume a simple linear temperature profile that extends from T_u to T_b over the distance of δ.
- Integrating Eqn.6.7b over x, subject to boundary conditions above,

$$\dot{m}''\Big[T\Big]_{T_u}^{T_b} - \frac{k}{c_p}\Big[\frac{\mathrm{d}T}{\mathrm{d}x}\Big]_0^0 = -\frac{\Delta h_c}{c_p}\int_{-\infty}^{\infty} \dot{m}_{\mathrm{F}}'''\mathrm{d}x \tag{6.10}$$

$$\dot{m}''(T_b - T_u) = -\frac{\Delta h_c}{c_p}\int_{-\infty}^{\infty} \dot{m}_{\mathrm{F}}'''\mathrm{d}x \tag{6.11}$$

- Limits of reaction rate integral can be switched to temperature from space coordinate, since $\dot{m}'''_{\mathrm{F}}$ is nonzero between T_u and T_b over the interval δ,

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{T_b - T_u}{\delta} \quad \text{or} \quad \mathrm{d}x = \frac{\delta}{T_b - T_u}\mathrm{d}T \qquad (6.12)$$

\- then Eqn,6.11 becomes,

$$\dot{m}''(T_b - T_u) = -\frac{\Delta h_c}{c_p}\frac{\delta}{(T_b - T_u)}\int_{T_u}^{T_b} \dot{m}'''_{\mathrm{F}}\mathrm{d}T \qquad (6.13)$$

- If we define the average reaction rate as,

$$\bar{\dot{m}}_{\mathrm{F}}''' \equiv \frac{1}{(T_b - T_u)} \int_{T_u}^{T_b} \dot{m}_{\mathrm{F}}''' \mathrm{d}T \tag{6.14}$$

\- We obtain,

$$\dot{m}''(T_b - T_u) = -\frac{\Delta h_c}{c_p} \delta \bar{\dot{m}}_{\mathrm{F}}''' \tag{6.15}$$

- In Eqn.6.15, we have two unknowns, $\dot{m}''$ and δ; we need a second equation to complete the solution.

- If we assume that the reaction rate is much smaller within the first half of δ, i.e., between $x = -\infty$ and $x = \delta/2$, we can reevaluate Eqn.6.10 from $x = -\infty$ to $x = \delta/2$. Noting that at $x = \delta/2$,

$$T = \frac{T_b + T_u}{2} \tag{6.16}$$

  - and

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{T_b - T_u}{\delta} \tag{6.12}$$

- Eqn.6.10, then becomes,

$$\dot{m}''\delta/2 - k/c_p = 0 \tag{6.17}$$

- Simultaneous solution of Eqns.6.15 and 6.17 gives,

$$\dot{m}'' = \left[2\frac{k}{c_p^2}\frac{(-\Delta h_c)}{(T_b - T_u)}\bar{\dot{m}}'''_{\mathrm{F}}\right]^{1/2} \tag{6.18}$$

  - and

$$\delta = 2k/(c_p\dot{m}'') \tag{6.19}$$

- Applying the definitions $S_L \equiv \dot{m}''/\rho_u$, $\alpha \equiv k/(\rho_u c_p)$, and recognizing that $\Delta h_c = (\nu + 1)c_p(T_b - T_u)$, we get,

$$S_L = \left[-2\alpha(\nu + 1)\frac{\bar{\dot{m}}'''_{\mathrm{F}}}{\rho_u}\right]^{1/2} \tag{6.20}$$

$$\delta = \left[\frac{-2\rho_u\alpha}{(\nu + 1)\bar{\dot{m}}'''_{\mathrm{F}}}\right]^{1/2} \tag{6.21a}$$

  - or

$$\delta = 2\alpha/S_L \tag{6.21b}$$

Factors Influencing Flame Velocity and Thickness

- From Eqns.6.20 and 6.21, we can infer temperature dependencies of S_L and δ. First we consider the following approximate temperature scalings,

$$\alpha \propto T_u \bar{T}^{0.75} P^{-1} \tag{6.27}$$

$$\bar{\dot{m}}_{\mathrm{F}}'''/\rho_u \propto T_u T_b^{-n} P^{n-1} \exp\left[-E_A/(R_u T_b)\right] \tag{6.28}$$

where n is the overall reaction order, and

$$\bar{T} \equiv 0.5(T_b + T_u)$$

- Combining the above scalings yields,

$$S_L \propto \bar{T}^{0.375} T_u T_b^{-\frac{n}{2}} \exp\left[\frac{-E_A}{2R_u T_b}\right] P^{\frac{n-2}{2}} \quad (6.29)$$

$$\delta \propto \bar{T}^{0.375} T_b^{\frac{n}{2}} \exp\left[\frac{E_A}{2R_u T_b}\right] P^{-\frac{n}{2}} \quad (6.30)$$

- Strong dependence on T:
  - on both T_u and T_b.
- Flame thickness is inversely proportional to S_L.
- For $n \approx 2$, S_L is independent of P!

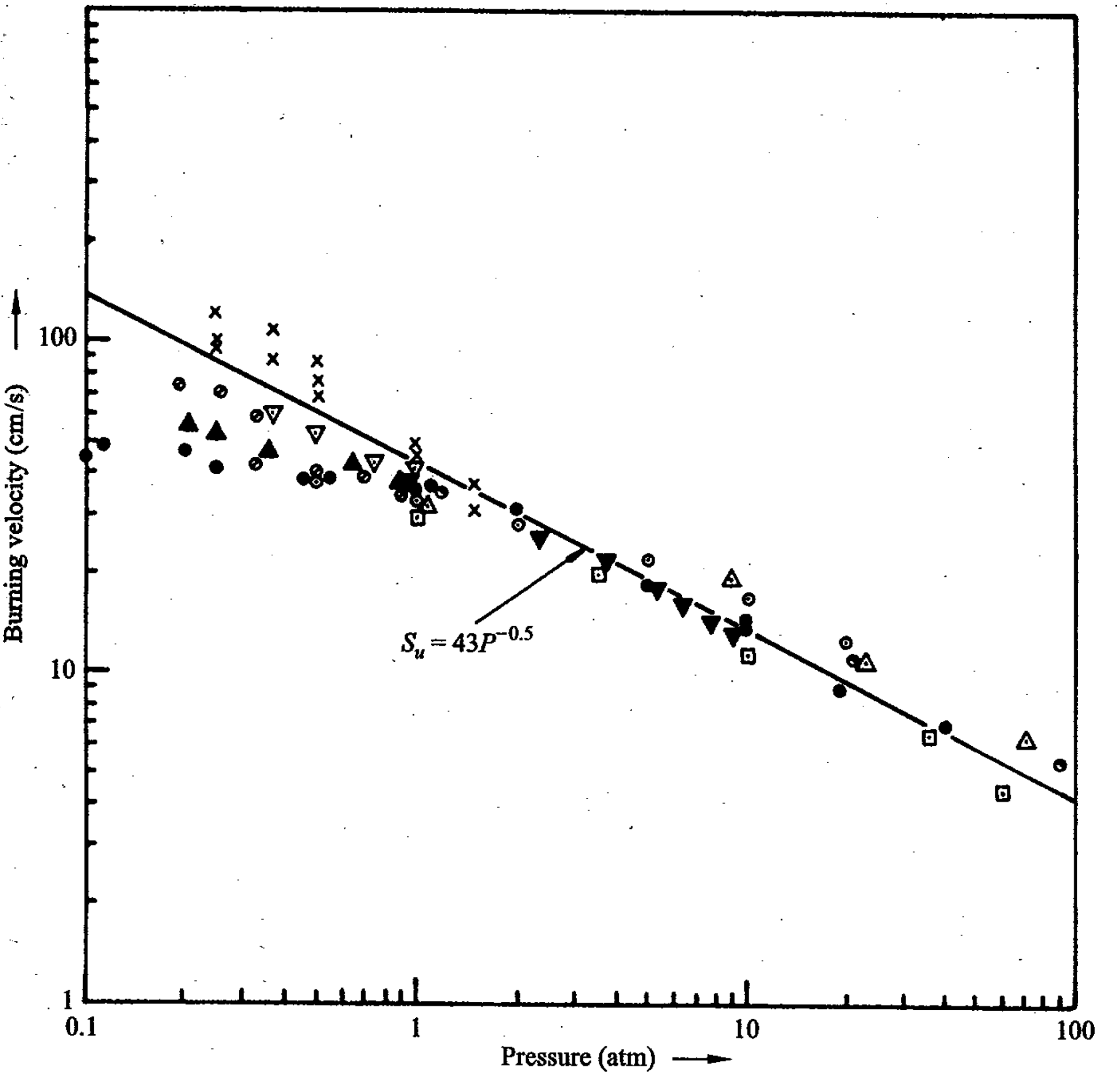
- Empirical correlation for stoichiometric methane-air mixtures:
  - Temperature:

$$S_L(\mathrm{cm/s}) = 10+3.71\cdot 10^{-4}[T_u(\mathrm{K})]^2 \quad (6.31)$$

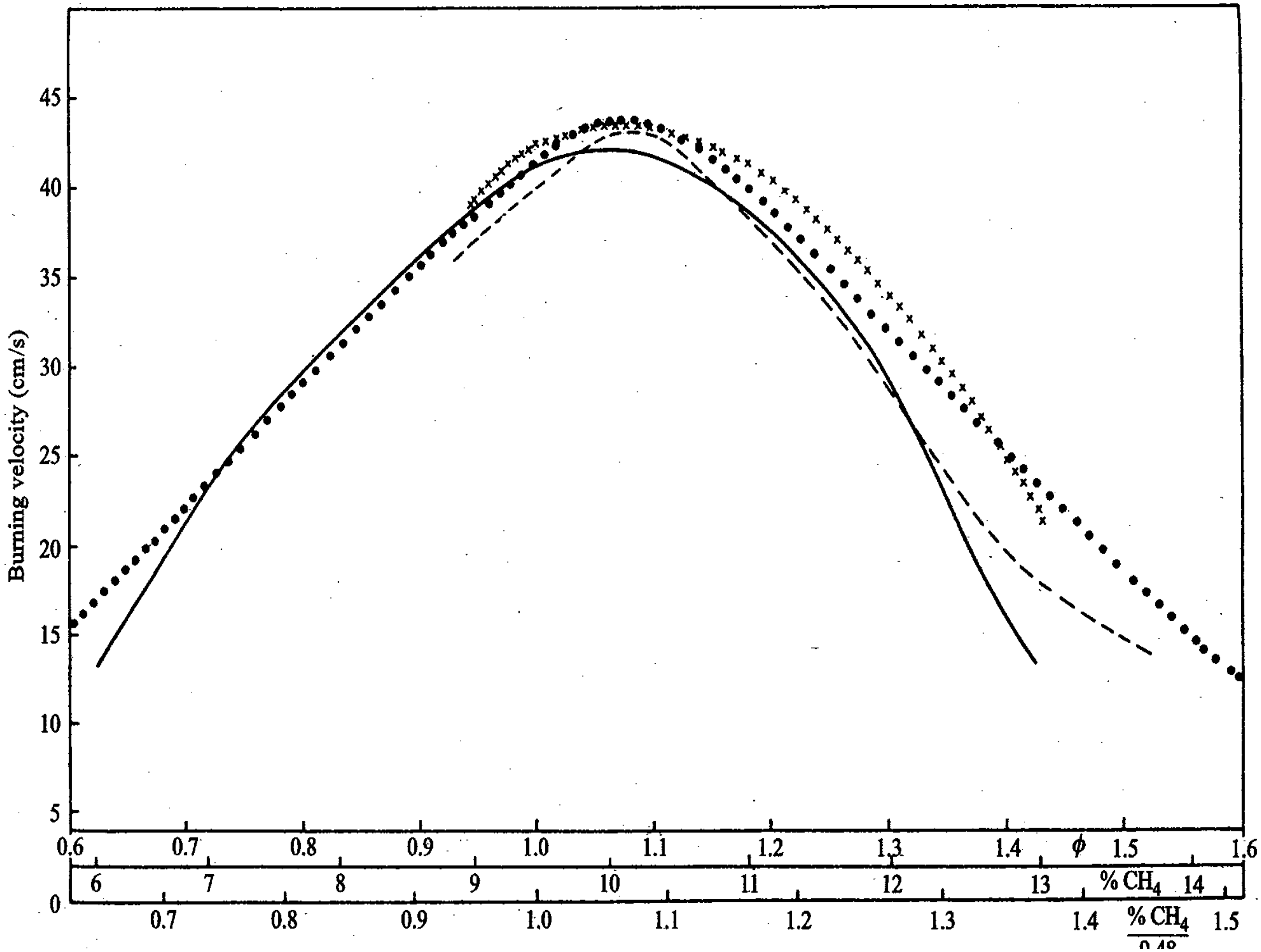
  - Pressure:

$$S_L(\mathrm{cm/s}) = 43\cdot[P(\mathrm{atm})]^{-0.5} \quad (6.32)$$

- Our simplified analysis captures the effect of T, but not the effect of P.



100
10
1
0.1
1
10
100
Burning velocity (cm/s)
Pressure (atm)
$S_u = 43P^{-0.5}$


Burning velocity (cm/s)
45
40
35
30
25
20
15
10
5
0
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
ϕ
1.5
1.6
6
7
8
9
10
11
12
13
% CH$_4$
14
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
% CH$_4$ / 0.48
1.5

Flame Speed Corelations:

$$S_L = S_{L,\mathrm{ref}} \left(\frac{T_u}{T_{u,\mathrm{ref}}} \right)^{\gamma} \left(\frac{P}{P_{\mathrm{ref}}} \right)^{\beta} (1 - 2.1 Y_{\mathrm{dil}}) \quad (6.33)$$

for $T_u \geq 350$ K. $T_{u,\mathrm{ref}} = 298$ K, and $P_{\mathrm{ref}} = 1$ atm.

$$S_{L,\mathrm{ref}} = B_M + B_2(\Phi - \Phi_M)^2$$

$$\gamma = 2.18 - 0.8(\Phi - 1)$$

$$\beta = -0.16 + 0.22(\Phi - 1)$$

Quenching, Flammability, and Ignition:

- Steady process: premixed flame propagation.
- Transient processes:
  - flame quenching (extinction)
  - ignition
- A flame can be extinguished by:
  - thermal effects (heat loss)*
  - chemical suppression
  - aerodynamic effects

Quenching by a Cold Wall:

- Premixed flames get extinguished upon entering sufficiently small passageways.
- If the passageway is large enough flame will propagate through it.
- *Quenching distance*: critical diameter of a tube or critical distance between two flat plates through which a flame will not propagate.
- *Flashback*: propagation of the flame back towards upstream of the burner.

- Flashback will happen if the reactant flow rate sustaining a laminar premixed flame is significantly reduced or shut-off and the passageways upstream of the flame are larger than the quenching distances.
- Quenching distances are determined experimentally:
  - Tube burners for quenching diameters.
  - High aspect ratio slot burners (rectangular) for qunching distances between two parellel flat plates.

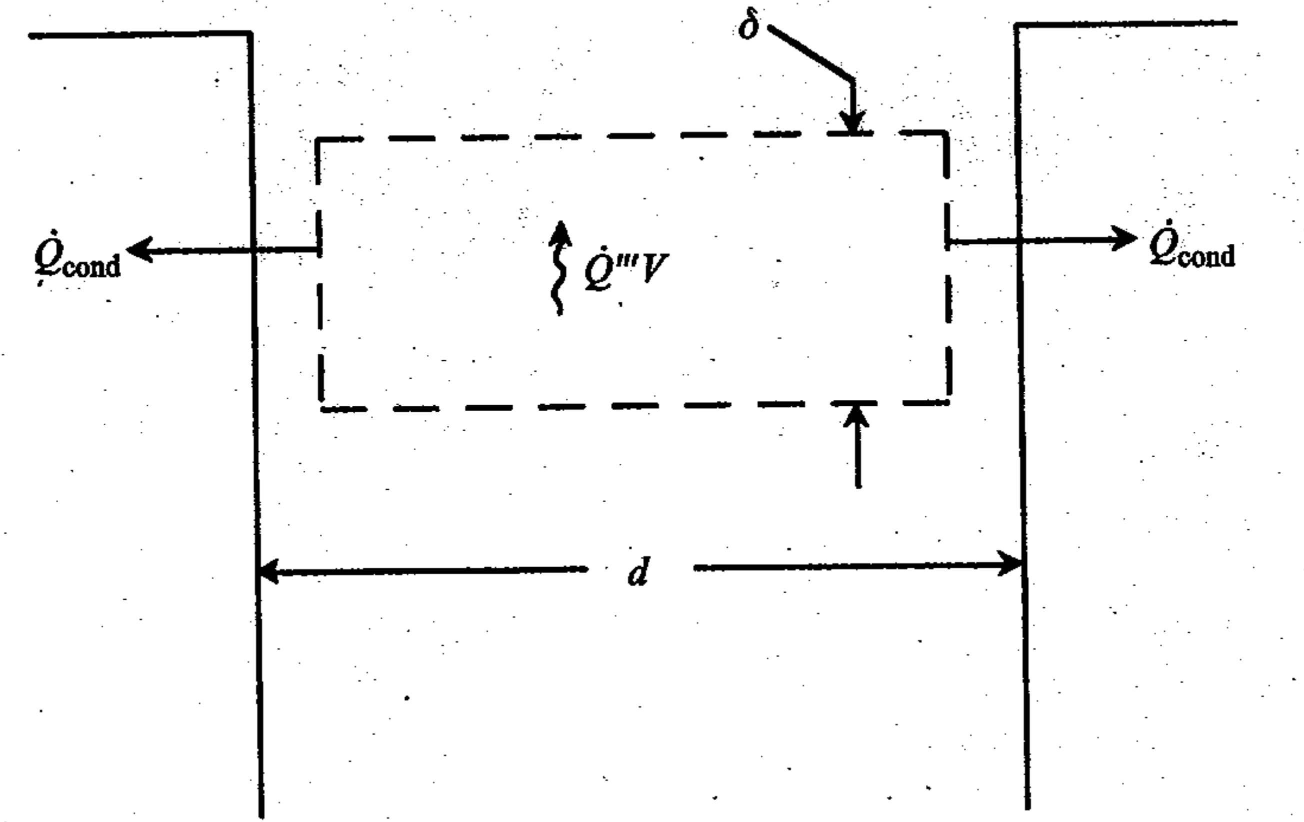
Ignition and Quenching Criteria:

I – Ignition will occur only if enough energy is added to the gas to heat a slab about as thick as a steady propagating laminar flame to the adiabatic flame temperature.

II – The rate of liberation of heat by chemical reactions inside the slab must approximately balance the rate of heat loss from the slab by thermal conduction.

- Using these two criteria, we can develop a simple anlysis of quenching.

A Simple Quenching Analysis:



- Energy balance: Equate heat produced by chemical reactions to heat loss by conduction to walls:

$$\dot{Q}'''V = \dot{Q}_{\text{cond,tot}} \tag{6.34}$$

- Volumetric heat release rate $\dot{Q}'''$ is related to $\bar{\dot{m}}_{\text{F}}'''$,

$$\dot{Q}''' = -\bar{\dot{m}}_{\text{F}}'''\Delta h_c \tag{6.35}$$

where

$$\bar{\dot{m}}_{\text{F}}''' \equiv \frac{1}{(T_b - T_u)} \int_{T_u}^{T_b} \dot{m}_{\text{F}}''' \mathrm{d}T \tag{6.14}$$

- Heat loss by conduction from the slab to the wall: Fourier's law:

$$\dot{Q}_{\text{cond}} = -kA\frac{\mathrm{d}T}{\mathrm{d}x}\bigg|_{T_w} \tag{6.36}$$

where both temperature gradient, $\mathrm{d}T/\mathrm{d}x$, and k are evaluated at gas temperatures at the wall.

$$A = 2\delta L$$

where L is the slot width.

- The temperature gradient $\mathrm{d}T/\mathrm{d}x$ is not straightforward to evaluate. A lower bound would be:

$$\frac{(T_b - T_w)}{(d/2)}$$

where a linear distribution from centerline to the wall is assumed. $\mathrm{d}T/\mathrm{d}x$ is likely to be greater than this, so we introduce a constatnt b defined as

$$\left|\frac{\mathrm{d}T}{\mathrm{d}x}\right| \equiv \frac{(T_b - T_w)}{(d/b)} \qquad (6.37)$$

where $b > 2$.

- Using Eqns.6.35 - 6.37 in quenching criterion, Eqn.6.34, gives

$$(-\bar{\dot{m}}_{\mathrm{F}}'''\Delta h_c)(\delta d L) = k(2\delta L)\frac{(T_b - T_w)}{(d/b)} \quad (6.38a)$$

or

$$d^2 = \frac{2kb(T_b - T_w)}{-\bar{\dot{m}}_{\mathrm{F}}'''\Delta h_c} \quad (6.38b)$$

- Eqn.6.38b can be simplified by assuming $T_w = T_u$ and using the following relationships:

$$S_L = \left[-2\alpha(\nu+1)\frac{\bar{\dot{m}}_{\mathrm{F}}'''}{\rho_u} \right]^{1/2} \tag{6.20}$$

and

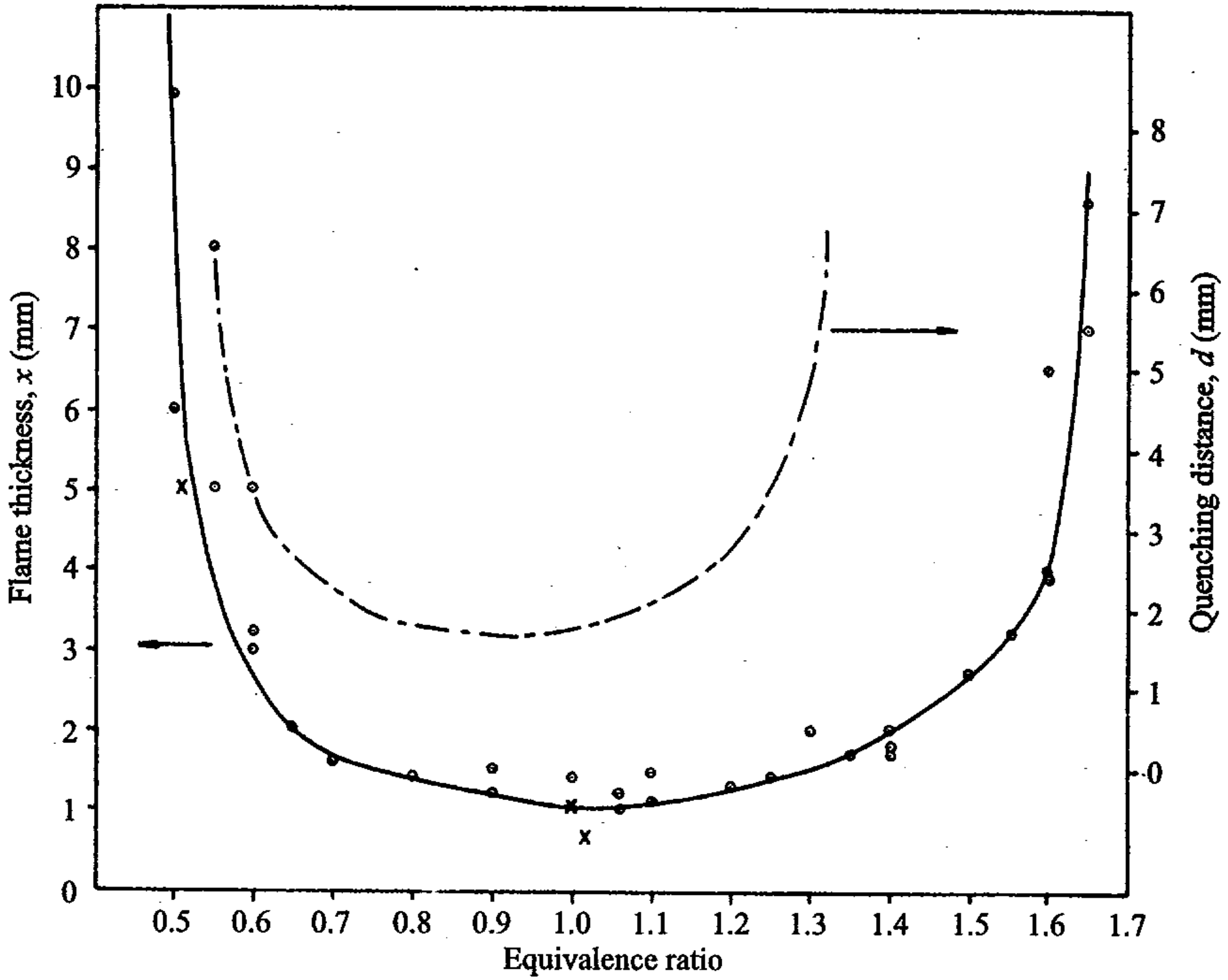
$$\Delta h_c = (\nu+1)c_p(T_b - T_u)$$

Then, Eqn.6.38b reads

$$d = 2\sqrt{b}\,\alpha/S_L \tag{6.39a}$$

or

$$d = \sqrt{b}\,\delta \tag{6.39b}$$



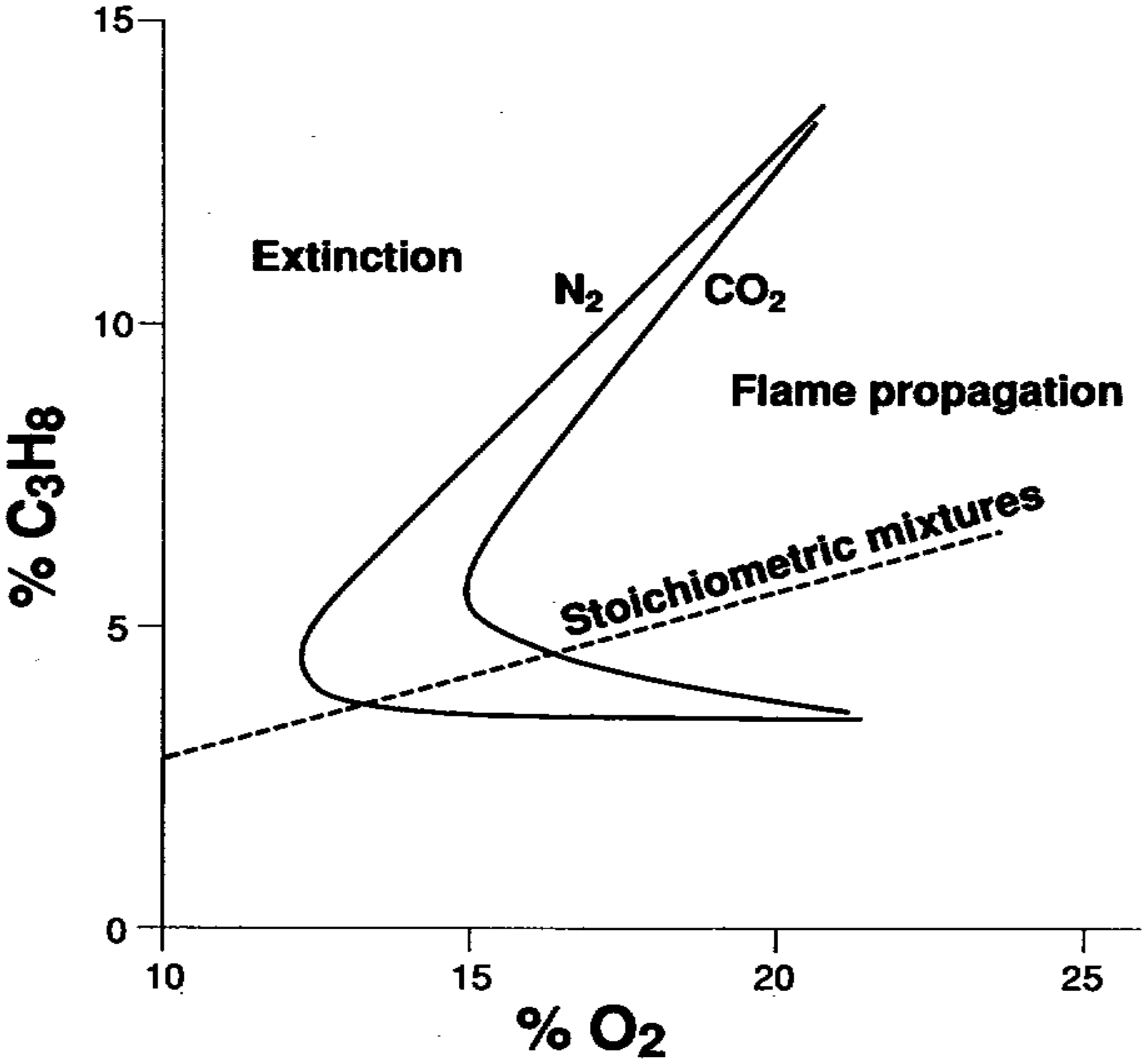
Flame thickness, x (mm)
Quenching distance, d (mm)
Equivalence ratio
0
1
2
3
4
5
6
7
8
9
10
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7

Flammability Limits:

- A premixed laminar flame will propagate only within a range of mixture strengths:
  - Lower limit (*lean limit*) of flammability, $\Phi < 1$.
  - Upper limit (*rich limit*) of flammability, $\Phi > 1$.
- Flammability limits are frequently quoted as percent of fuel by volume in the mixture, or as a percentage of the stoichiometric fuel requirement.

- It is ascertained whether or not a flame initiated at the bottom of a vertical tube propagates the length of the tube.
- Flammability limits must be measured under conditions which are not influenced by quenching effects, that is the reaction tube must be of suitably larger diameter.
- The ignition source must be of sufficeint energy to guarantee ignition, otherwise the property under investigation would be that of the limiting ignition energy and not of flammability.

- There are enormous variations between fuels.
- The flammability range in air:
  - For acetylene is 2.5-80% by vol.
  - For propane the range is 2.2-9.5%.
- In some systems the limit seem to correlate with a minimum flame temperature (about 1400 K for methane).
- The existence of flammability limits is predicted by theories of flame propagation provided the heat loss from the burned gas is included.

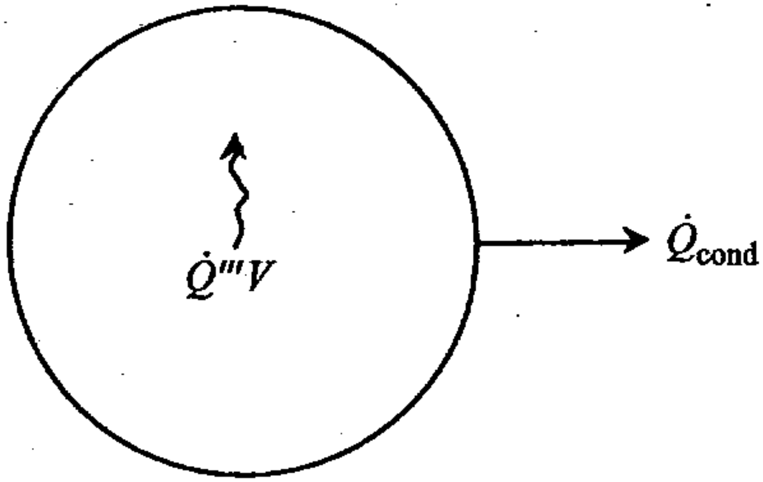

15
10
5
0
10
15
20
25
% C_3H_8
% O_2
Extinction
N_2
CO_2
Flame propagation
Stoichiometric mixtures

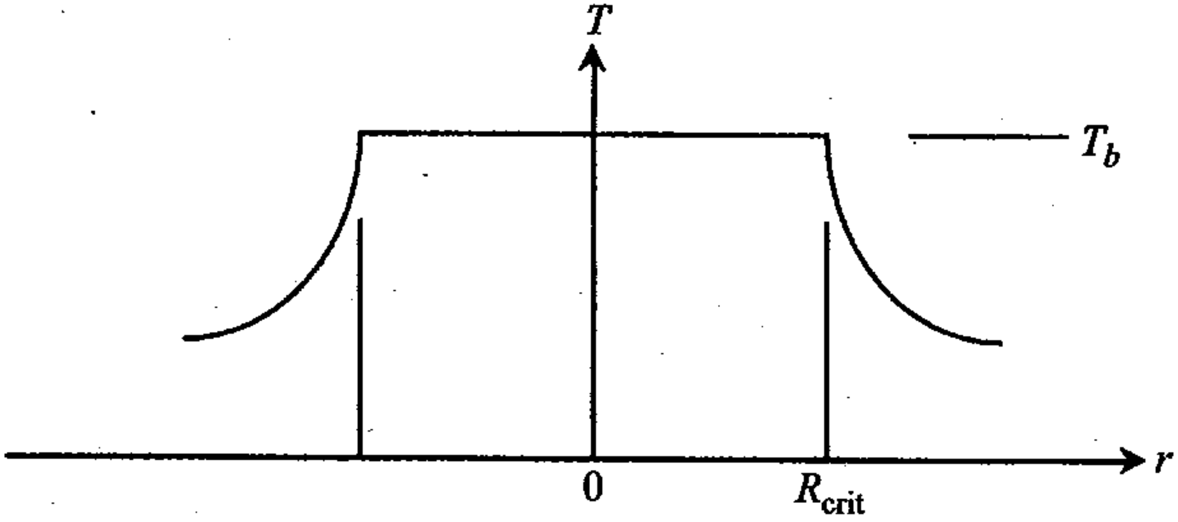
Ignition:

- Our focus will be on *minimum ignition energy*.
- We limit our discussion to ignition of a premixed gas by a spark.
- Spark ignition is used in:
  - Gas turbine engines
  - Gasoline engines (spark-ignition engines)
  - Industrial, commercial, and residential burners
- Ignition energy and its dependence on T and P.

Simplified Ignition Analysis:

- We use the second criterion of ignition and quenching.
- Define a critical gas volume radius such that a flame will not propagate if the actual radius is smaller than the critical value.
- The following step is to assume that the *minimum ignition energy* to be supplied by the spark is the energy required to heat the critical gas volume from its initial state to the flame temperature.


$\dot{Q}'''V$
$\dot{Q}_{\mathrm{cond}}$


T
T_b
r
0
R_{crit}

- Equate rate of heat liberated by reaction to rate of heat loss to the cold gas by conduction to determine the critical radius:

$$\dot{Q}'''V = \dot{Q}_{\mathrm{cond}} \tag{6.40}$$

$$\frac{-\bar{\dot{m}}'''_{\mathrm{F}}\Delta h_c 4\pi R_{\mathrm{crit}}^3}{3} = -k4\pi R_{\mathrm{crit}}^2 \frac{\mathrm{d}T}{\mathrm{d}r}\bigg|_{R_{\mathrm{crit}}} \tag{6.41}$$

- $(\mathrm{d}T/\mathrm{d}r)_{\mathrm{crit}}$ can be obtained from the temperature distribution in $(R_{\mathrm{crit}} \leq r \leq \infty)$

$$\left.\frac{\mathrm{d}T}{\mathrm{d}r}\right|_{R_{\mathrm{crit}}} = -\frac{(T_b - T_u)}{R_{\mathrm{crit}}} \tag{6.42}$$

- Substitute Eqn.6.42 into 6.41

$$R_{\mathrm{crit}}^2 = \frac{3k(T_b - T_u)}{-\bar{\dot{m}}_{\mathrm{F}}^{\prime\prime\prime}\Delta h_c} \tag{6.43}$$

- Using Eqn.6.20, we can express $\bar{\dot{m}}_{\mathrm{F}}^{\prime\prime\prime}$ in terms of S_L or δ.

- In addition, we have $\Delta h_c = (\nu + 1) c_p (T_b - T_u)$, then Eqn.6.43 becomes

$$R_{\text{crit}} = \sqrt{6}\,\frac{\alpha}{S_L} \tag{6.44a}$$

where $\alpha = k/(\rho c_p)$. In terms of δ, R_{crit} is,

$$R_{\text{crit}} = (\sqrt{6}/2)\delta \tag{6.44b}$$

- It should be noted that $\sqrt{6}/2$ is just an order of magnitude, and should not be taken as a precise constant. Therefore, the critical radius is a few times larger than the flame thickness.

- Assuming the energy added by the spark heats the critical volume to the burned-gas temperature,

$$E_{\text{ign}} = m_{\text{crit}} c_p (T_b - T_u) \tag{6.45}$$

where $m_{\text{crit}} = \rho_b 4\pi R_{\text{crit}}^3/3$, then

$$E_{\text{ign}} = 61.6 \rho_b c_p (T_b - T_u)(\alpha/S_L)^3 \tag{6.46}$$

Eliminating ρ_b using ideal gas law,

$$E_{\text{ign}} = 61.6 P \left(\frac{c_p}{R_b}\right) \left(\frac{T_b - T_u}{T_b}\right) \left(\frac{\alpha}{S_L}\right)^3 \tag{6.47}$$

Pressure and Temperature Dependencies:

- From Eqn.6.47, we can assess the P dependency of ignition energy.

- From Eqn.6.27

$$\alpha \propto T_u \bar{T}^{0.75} P^{-1} \tag{6.27}$$

- From Eqn.6.29 (with $n \approx 2$)

$$S_L \propto \bar{T}^{0.375} T_u T_b^{-\frac{n}{2}} \exp\left[\frac{-E_A}{2R_u T_b}\right] P^{\frac{n-2}{2}} \tag{6.29}$$

- The combined effects from S_L and α yield

$$E_{\mathrm{ign}} \propto P^{-2} \tag{6.48a}$$

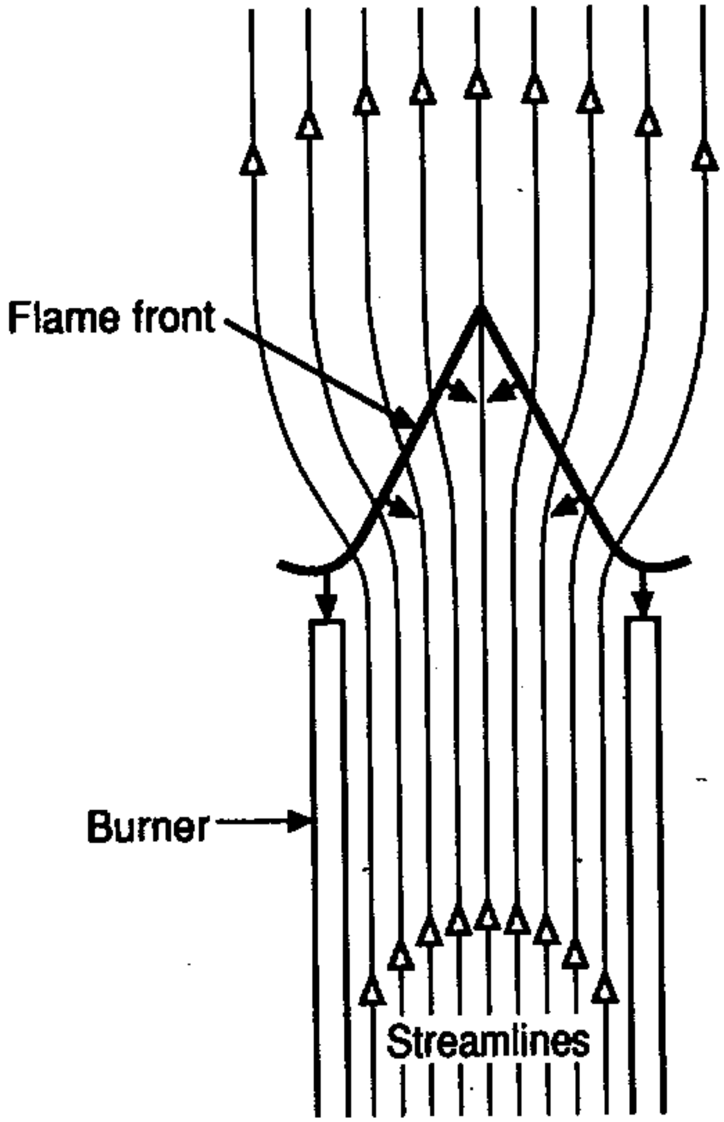
which agrees extremely well with the experimental results.

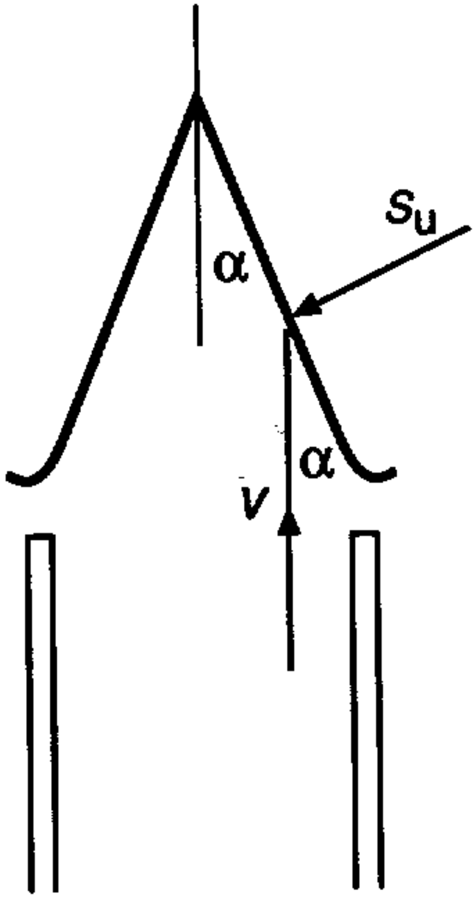
- As T_u is increased the minimum ignition energy decreases.

$$E_{\mathrm{ign}} \propto T_u^{-x} \tag{6.48b}$$

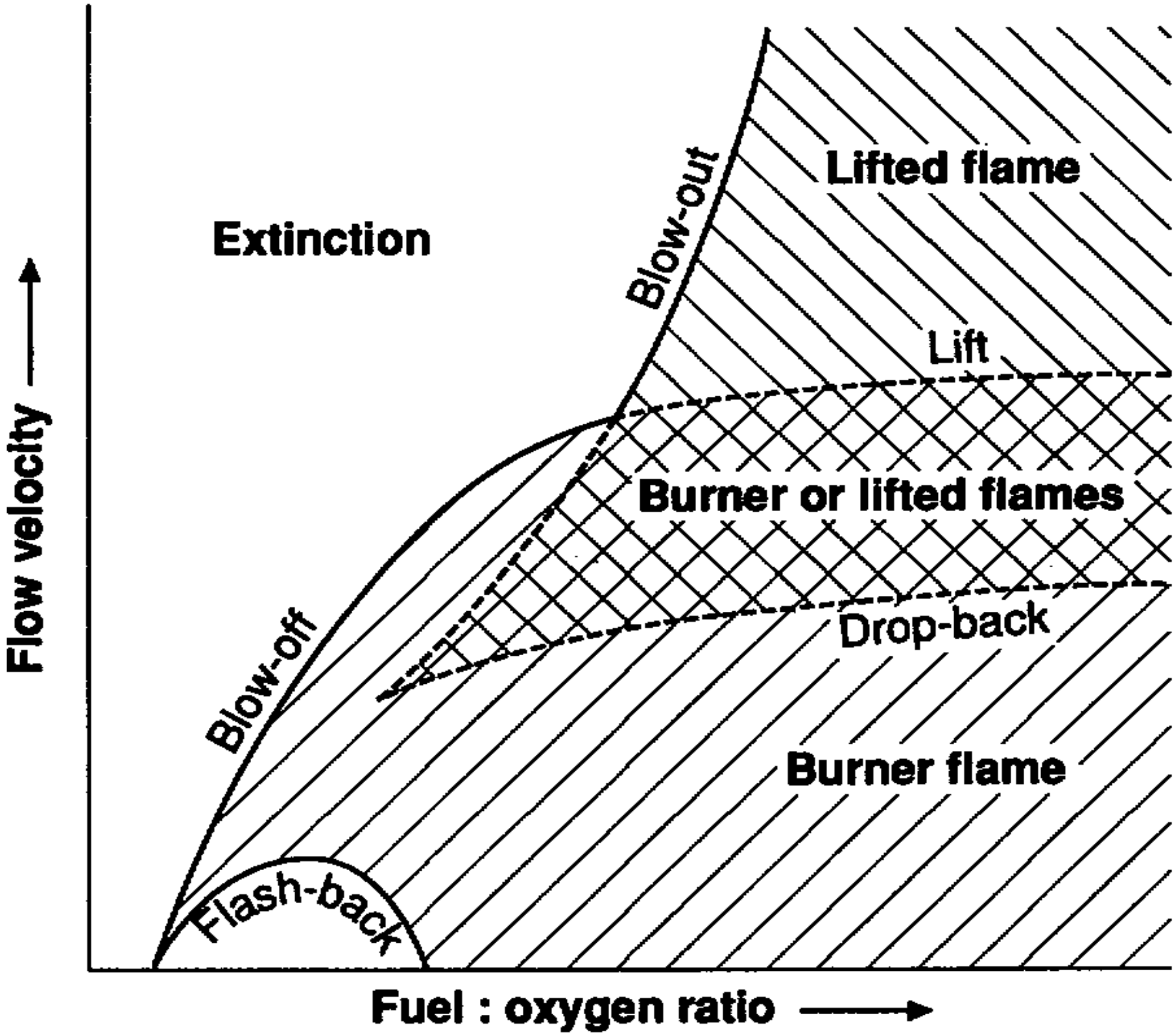
Flame Stabilization:

- Important design criteria: avoid *flashback* and *liftoff*.
- In flashback, flame enters and propagates through the burner upstream without quenching.
- In liftoff, flame is not attached to the burner, but stabilized at a distance from it.
- Flashback: safety hazard.
- Liftoff: issues related to incomplete burning, ignition problems, control of the flame position.


Flame front
Burner
Streamlines


s_u
α
α
v

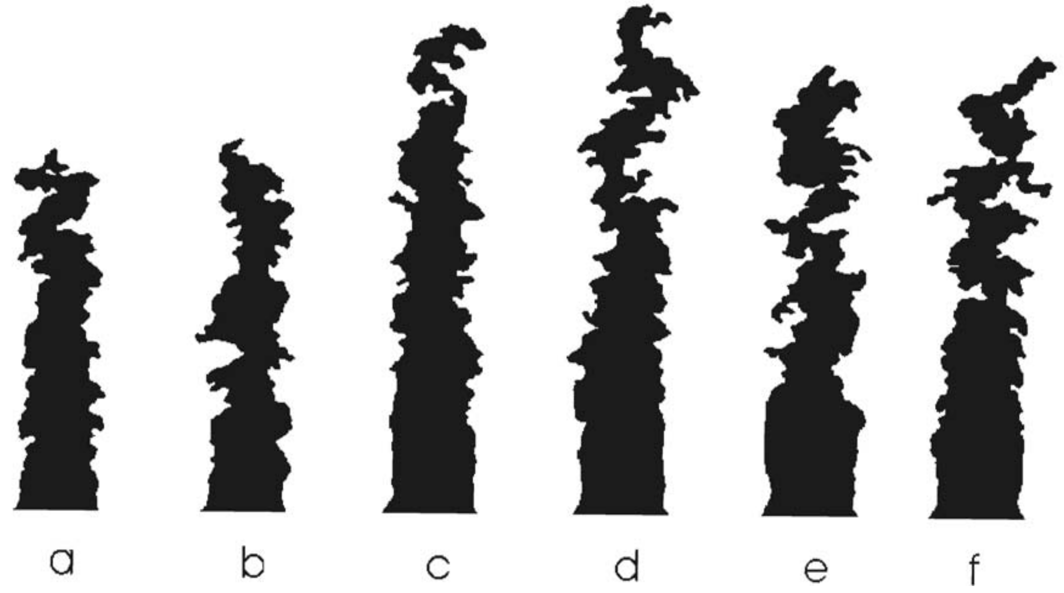
- Both flashback and liftoff are related to matching the local laminar flame speed to the local flow velocity.
- A flame can be stabilized on the burner only between certain flow velocity limits.
- If the gas velocity is progressively reduced, a point will be reached eventually at which the burning velocity exceeds the gas velocity somewhere across the burner.
  - At this point, flame will propagate back down the burner.

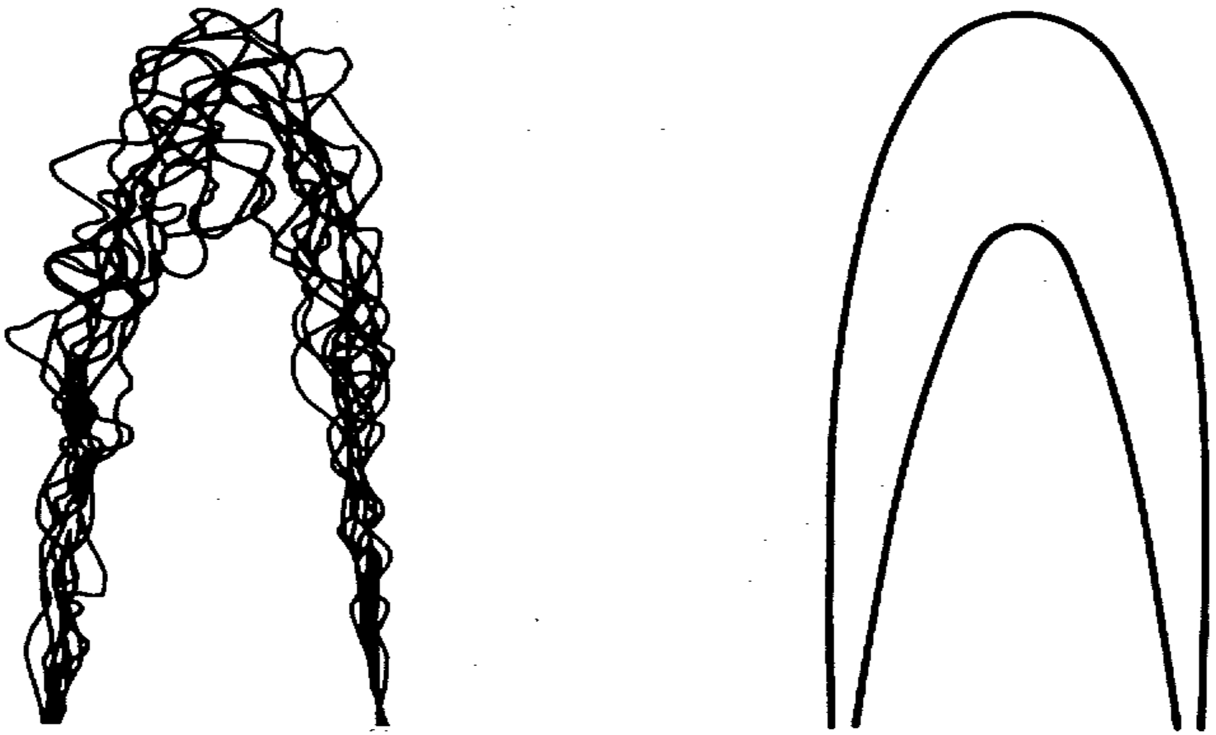

Extinction
Lifted flame
Blow-out
Lift
Burner or lifted flames
Blow-off
Drop-back
Burner flame
Flash-back
Flow velocity
Fuel : oxygen ratio

7. Turbulent Premixed Flames

- ***Background:***

- Structure of turbulent premixed flames;





- Instantaneous flame fronts (left) and turbulent flame brush envelope (right).

- Definitions:

- Laminar flame thickness:

$$\delta_L \sim \alpha/S_L = D/S_L = \nu/S_L \tag{1}$$

- Above equality implies that we assumed,

  Schmidt Number: Sc = ν/D = 1

  Lewis Number: Le = α/D = 1

  Prandtl Number: Pr = ν/α = 1

- Turbulent Reynolds number

$$\mathrm{Re}_\Lambda = \frac{u'\Lambda}{\nu} \tag{2}$$

  where Λ is the integral length scale of turbulence.

- Turbulent Damköhler number: ratio of characteristic flow time, τ_{flow}, to the characteristic chemical time, τ_c.

$$\mathrm{Da} = \frac{\tau_{flow}}{\tau_c} \tag{3}$$

- Characteristic flow time: $\tau_{flow} = \Lambda/u'$
- Characteristic chemical time: $\tau_c = \delta_L/S_L$
- Then Damköhler number is:

$$\mathrm{Da} = \frac{S_L \Lambda}{u' \delta_L} \tag{3a}$$

- Turbulence length scales:

  λ: Taylor microscale

  η: Kolmogorov length scale

- Karlovitz number:

$$\mathrm{Ka} = \left(\frac{\Lambda}{\eta}\right)^2 = \frac{\delta_L u'}{S_L \lambda} \tag{4}$$

- Turbulent Reynolds number based on λ:

$$\mathrm{Re}_\lambda = u'\lambda/\nu \tag{5}$$

- Turbulent Reynolds number based on η:

$$\mathrm{Re}_\eta = u'\eta/\nu \tag{6}$$

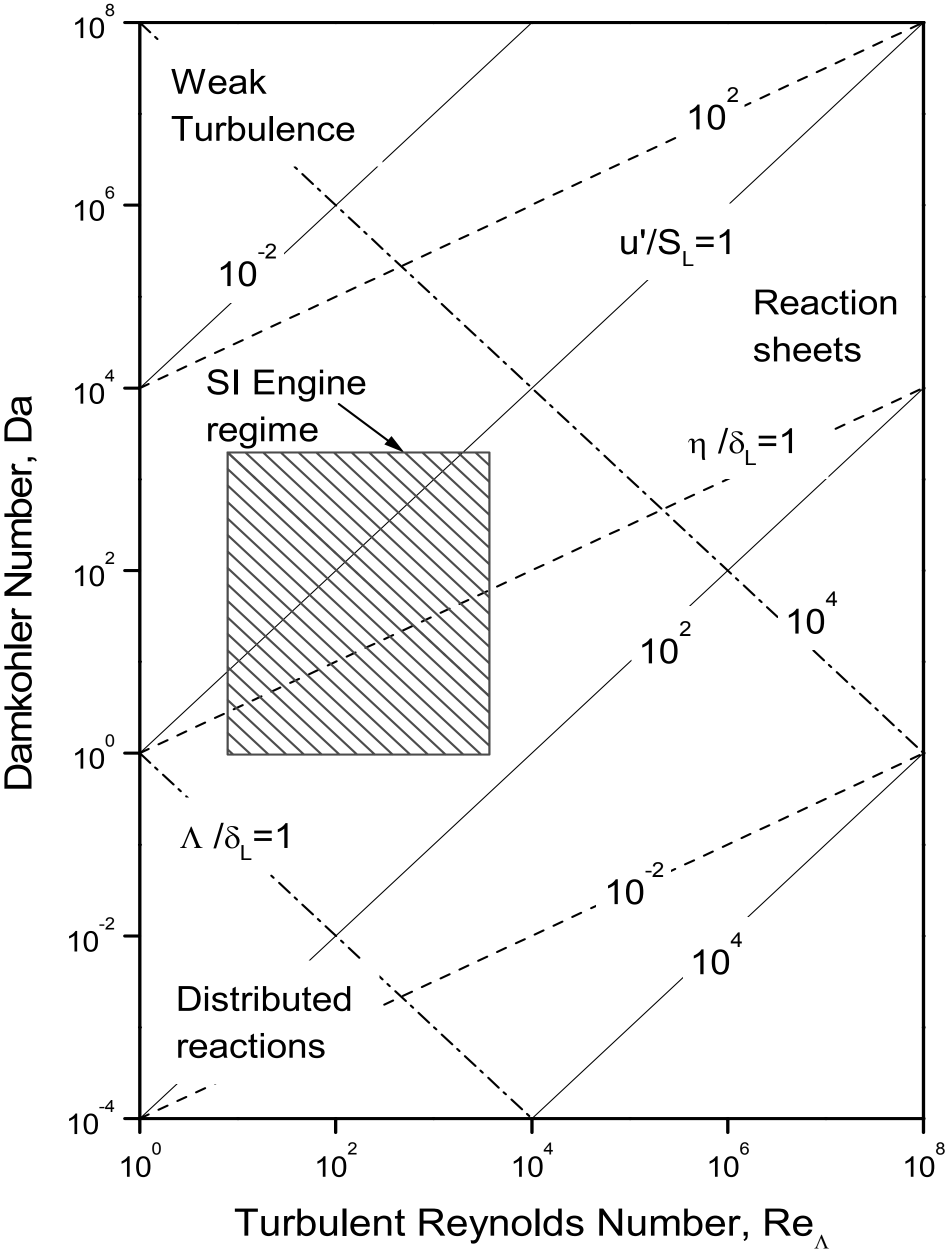
$$\mathrm{Re}_\Lambda \approx \mathrm{Re}_\lambda^2 \approx \mathrm{Re}_\eta^4 \tag{7}$$

- ***Turbulent Burning Velocity:***

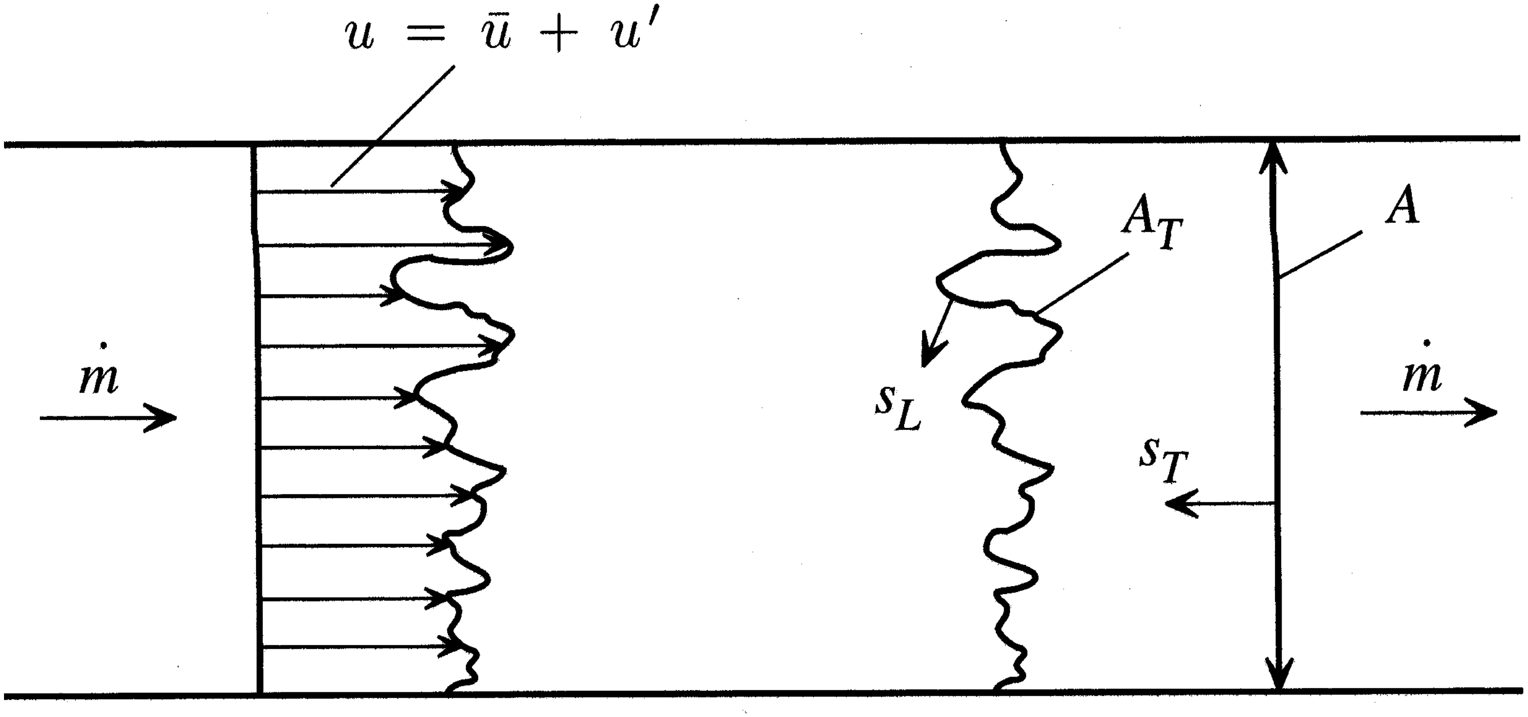
- One of the most important unresolved problems in premixed turbulent combustion is the determination of the turbulent burning velocity.

- Above statement assumes that *turbulent burning velocity* is a well-defined quantity that only depends on local mean properties.

- However, there is no consensus in literature whether the turbulent burning velocity is a characteristic quantity that can be defined unambigously for different geometries.


Weak Turbulence
Reaction sheets
SI Engine regime
Distributed reactions
u'/S_L=1
η /δ_L=1
Λ /δ_L=1
10^-2
10^2
10^4
10^2
10^-2
10^4
Damkohler Number, Da
Turbulent Reynolds Number, Re_Λ
10^8
10^6
10^4
10^2
10^0
10^-2
10^-4
10^0
10^2
10^4
10^6
10^8

- Turbulent premixed flame propagation was first investigated by Damköhler (1940).
- He identified two limiting cases based on the magnitude of the scale of turbulence as compared to the thickness of the laminar premixed flame.
- For large scale turbulence, Damköhler assumed that the interaction between a turbulent premixed flame (wrinkled flame) front and the turbulent flame front is purely kinematic.



Laminar flame structure.

- Damköhler equated the mass flux $\dot{m}$ through the instantaneous turbulent flame surface area A_T with the mass flux through the cross-sectional area A_o. He used S_L for mass flux through A_T, and S_T for mass flux through A.

$$\dot{m} = \rho_u S_L A_T = \rho_u S_T A_o \tag{8}$$

$$\frac{S_T}{S_L} = \frac{A_T}{A_o} \tag{9}$$

- Using geometric approximations, Damköhler proposed that (for large-scale, small-intensity turbulence),

$$\frac{A_T}{A_o} = 1 + \frac{u'}{S_L} \tag{10}$$

In view of Eq.2,

$$\frac{S_T}{S_L} = 1 + \frac{u'}{S_L} \tag{11}$$

  - u', turbulent fluctuating velocity in the unburned gas.

- Using similar geometric arguments, Schelkin showed that:

$$\frac{S_T}{S_L} = \left[1 + \left(\frac{2u'}{S_L}\right)^2\right]^{1/2} \tag{12}$$

- Relationship proposed by Klimov:

$$\frac{S_T}{S_L} = 3.5\left(\frac{u'}{S_L}\right)^{0.7} \tag{13}$$

- Clavin &Williams:

$$\frac{S_T}{S_L} = \left\{ 0.5 \left[1 + \left(1 + 8 \frac{u'^2}{S_L^2} \right)^{1/2} \right] \right\}^{1/2} \qquad (14)$$

- Gülder:

$$\frac{S_T}{S_L} = 1 + 0.62 \left(\frac{u'}{S_L} \right)^{1/2} \mathrm{Re}_{\Lambda}^{1/4} \qquad (15)$$

- For small-scale and high-intensity turbulence, Damköhler argued that turbulence only modifies the transport between the reaction zone and the unburned gas.

$$S_T/S_L \sim (D_T/D)^{1/2} \tag{16}$$

Since $D_T \propto u'\Lambda$ and $D \propto S_L\delta_L$

- Then we have,

$$\frac{S_T}{S_L} \sim \left(\frac{u'\Lambda}{S_L\delta_L}\right)^{1/2} \tag{17}$$

- For small-scale high-intensity turbulence conditions (usually called as distributed reaction regime), there are not many formulations available. In this regime, turbulent mixing is rapid as compared to the chemistry.

- For the distributed reaction regime the following semi-empirical model has been proposed, Gülder (1990):

$$\frac{S_T}{S_L} = 6.4 \left(\frac{S_L}{u'} \right)^{3/4} \tag{18}$$

State-of-the-art:

- Definition of turbulent burning velocity is not uniform/universal.
- Experimental data scatter is significant between different experimental rigs.
- Numerical simulation:
    - Flamelet model/assumption
    - Turbulent burning closure
    - Direct numerical simulation

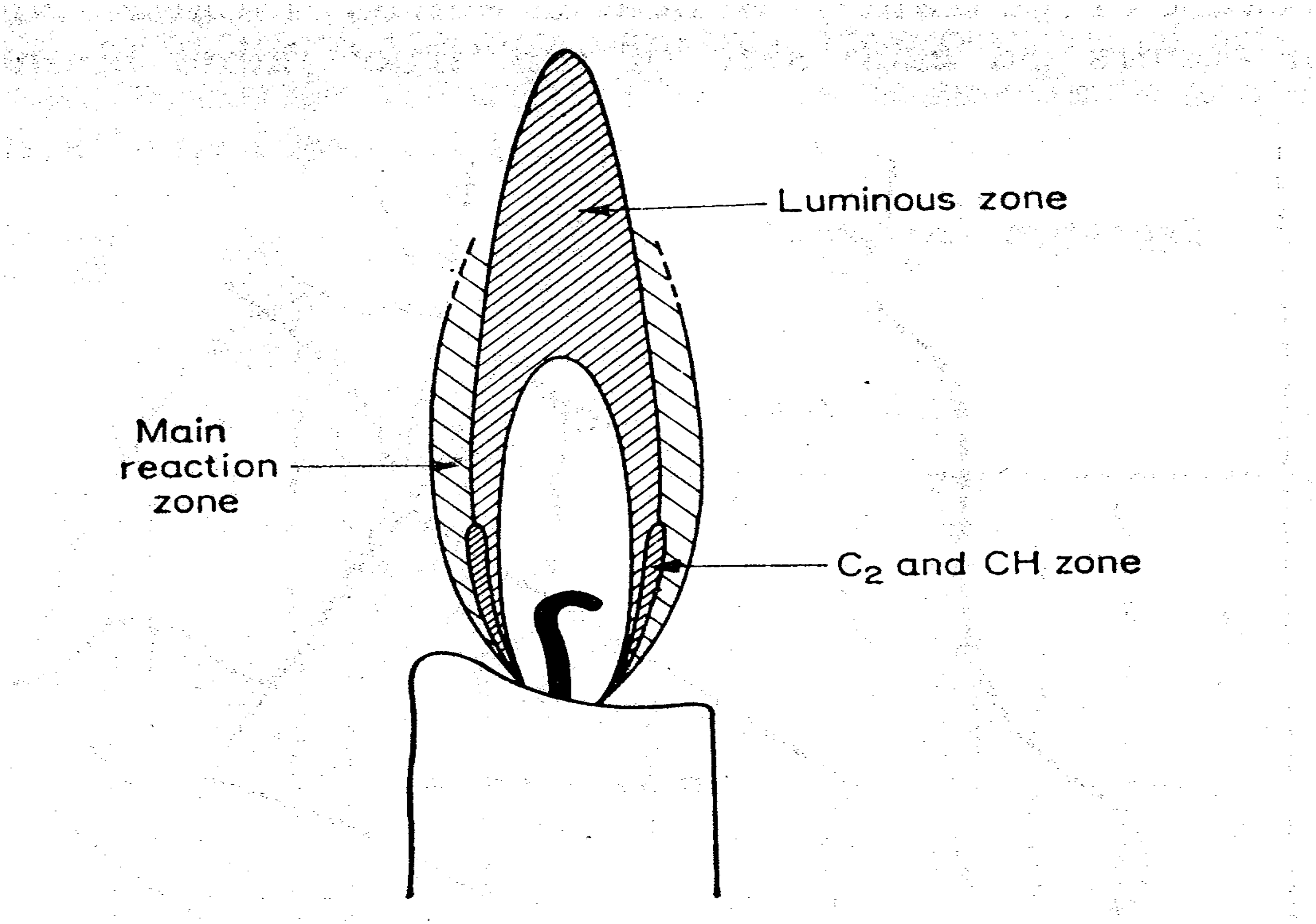
Experimental Measurement Methods:

- Conical stationary flames on cylindrical nozzles.
- Swirling flames.
- Constant volume vessels.
- Stagnation point flames.
  - Laser-based diagnostics to study flame structure.
  - Statistical approaches to estimate the flame front surface area.

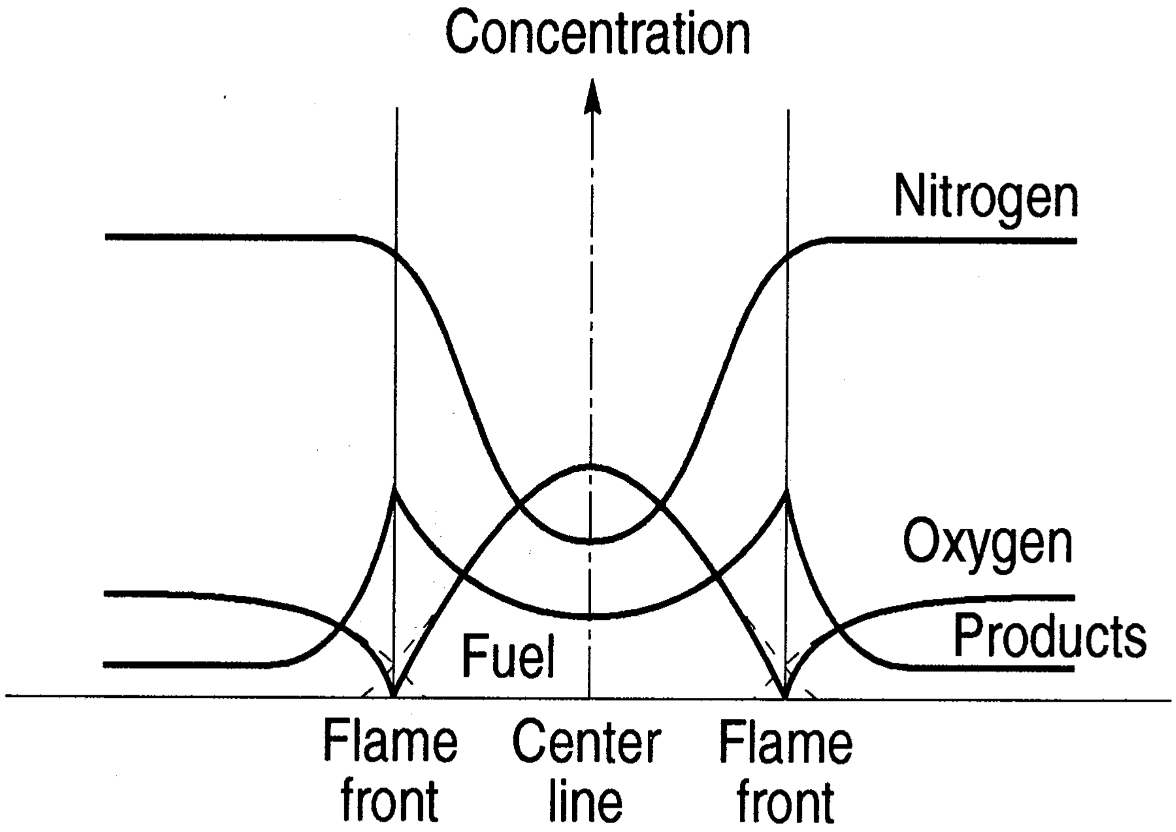
8. Laminar Diffusion Flames (Laminar Non-Premixed Flames)

- In a *diffusion flame* combustion occurs at the interface between the fuel gas and the oxidant gas, and the burning depends more on rate of diffusion of reactants than on the rates of chemical processes involved.
- It is more difficult to give a general treatment of diffusion flames, largely because no simple, measurable parameter, analogous to the burning velocity in premixed flames, can be defined.

- Used in certain applications (e.g., residential gas appliances).
    - mostly partially-premixed flames
- Used in fundamental flame research.
- Primary concern in design is the flame geometry.
- Parameters that control the flame shape,
    - Fuel flow rate
    - Fuel type
    - Other factors

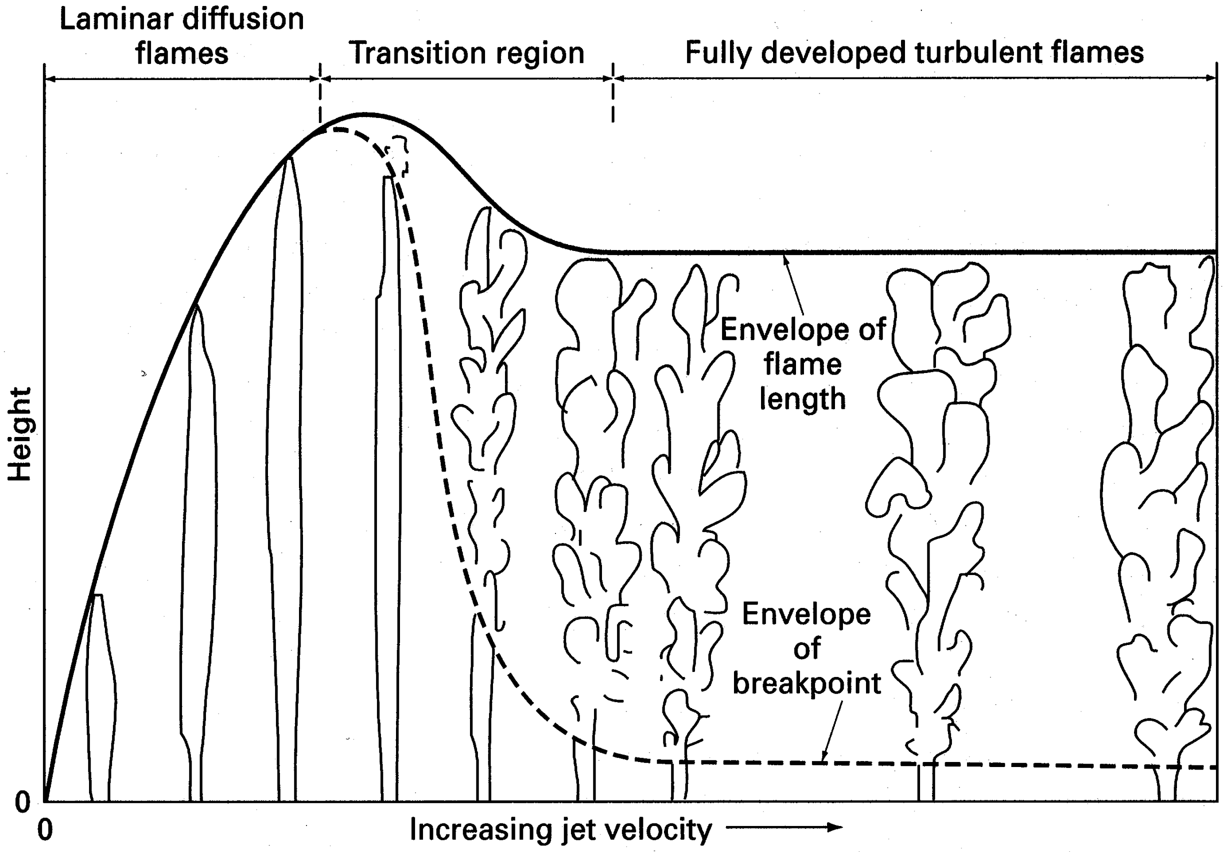


Candle Flame.



Diffusion Flame Structure.

-



Diffusion Flame Regimes.

A Simple Approach

- For simple laminar diffusion flames on circular nozzles (similar to a candle flame), flame height is mostly used to characterize the flame.
- For simple treatments, reaction zone is defined as the region where the fuel and air mixture is stoichiometric. This assumption is, of course, clearly incorrect as reaction will be occuring over an extremely wide range of fuel/air ratios.
- Diffusion process is rate-determining so that rate of reaction is directly related to the amounts of fuel and oxidant diffusing into the reaction zone.

- For a simple conical laminar diffusion flame, molecular diffusion is considered only in radial direction.
- Average square displacement (Einstein diffusion equation) is given by

$$\bar{y}^2 = 2\mathcal{D}t$$

- Height of the flame is taken as the point where the average depth of penetration is equal to the tube radius.
- Approximating $\bar{y}^2$ by R^2 yields

$$t = R^2/2\mathcal{D}$$

- Since

$$t = L_f/v$$

then,

$$L_f \approx \frac{vR^2}{2\mathcal{D}}$$

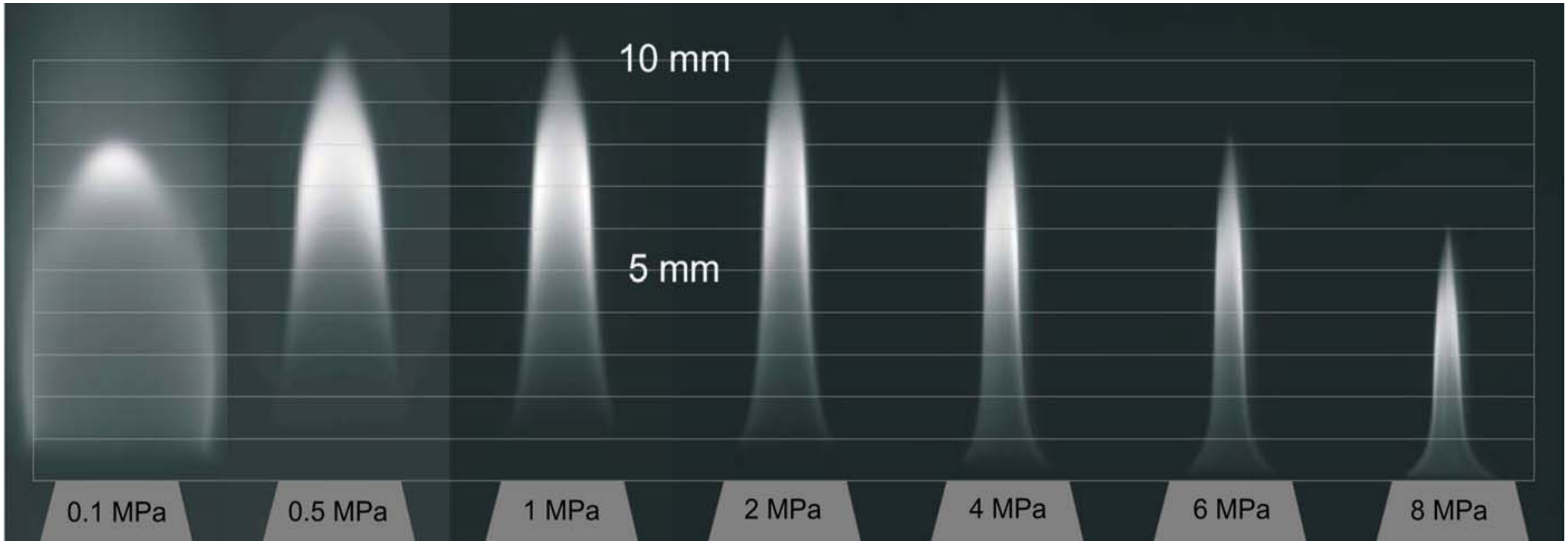
- Volume flow rate

$$Q_{\mathrm{F}} = v\pi R^2$$

so that

$$L_f \approx \frac{Q_{\mathrm{F}}}{\pi\mathcal{D}}$$

- Although very crude, this approximation permits certain predictions:
  - At a given flow rate, flame height is independent of the burner diameter.
  - Since the diffusion coefficent $\mathcal{D}$ is inversely proportional to pressure, the height of the flame is independent of pressure at given mass flow rate.
  - Flame height is proportional to volume flow rate of fuel.

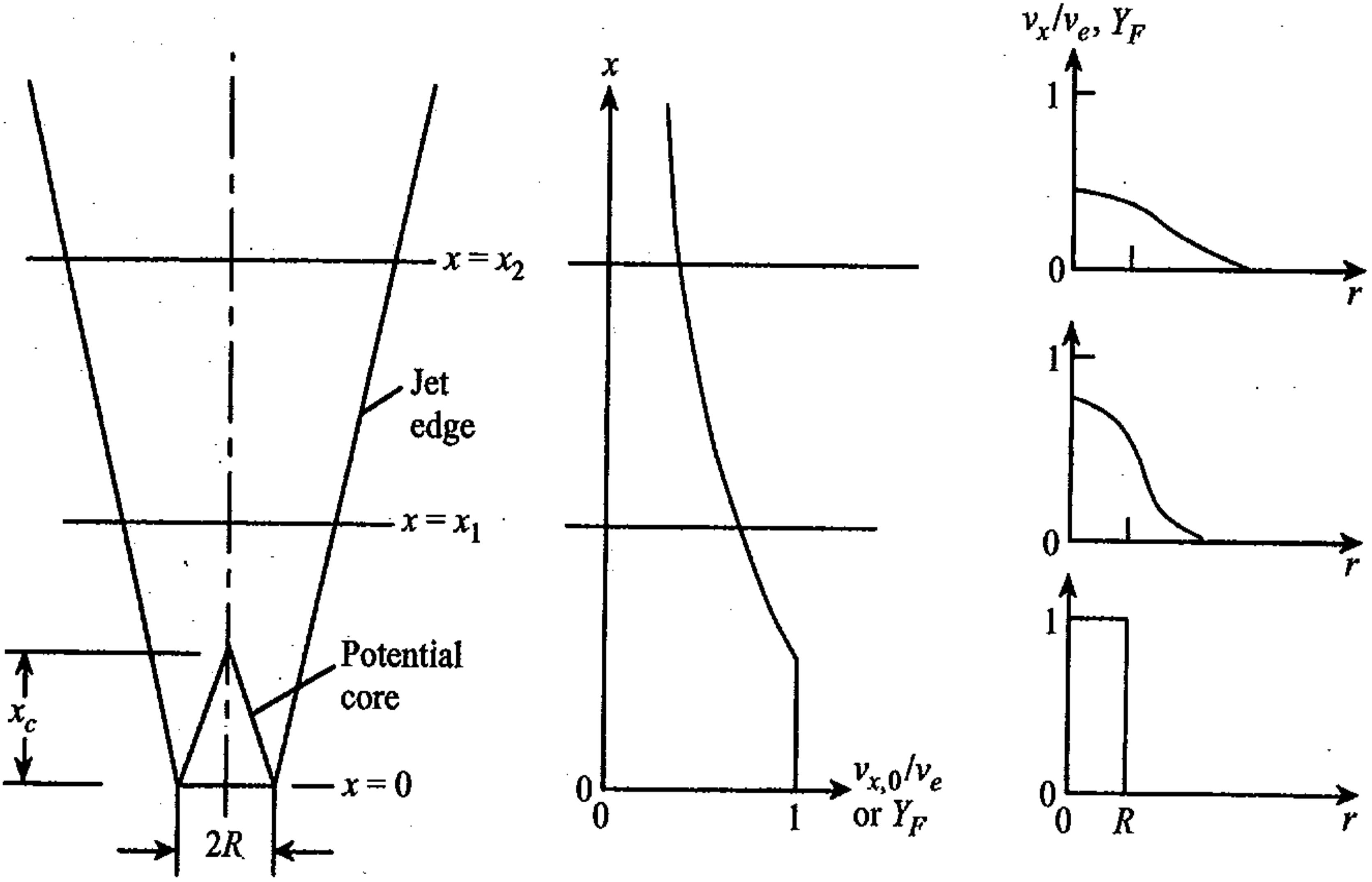


Methane diffusion flames at high pressures.

Nonreacting Constant-Density Laminar Jet

Physical Description:

- Analysis presented in the previous section is very crude and provides only very qualitative features of laminar diffusion flames.
- To develop an understanding of the reacting laminar jet, we start with a nonreacting laminar jet of a fluid flowing into an infinite reservoir.
- Important points: basic flow and diffusional processes.


$x = x_2$
$x = x_1$
$x = 0$
Jet edge
Potential core
x_c
$2R$
x
0
0
1
$v_{x,0}/v_e$ or Y_F
v_x/v_e, Y_F
1
0
r
1
0
r
1
0
0
R
r

- *Potential core:* the effects of viscous shear and molecular diffusion are not in effect yet; so the velocity and nozzle-fluid (fuel) mass fraction remain unchanged from their nozzle-exit values and are uniform in this region.
- In the region between the potential core and the jet edge, both the velocity and fuel concentration decrease monotonically to zero at the jet edge.
- Beyond the potential core the viscous shear and diffusion effects are active across whole field of the jet.

- Initial jet momentum is conserved throughout the entire flowfield.
- As the jet moves into surroundings, some of the momentum is transferred to air, decreasing the velocity of the jet.
- Along the jet increasing quantities of air are entrained into the jet as it proceeds downstream.

\- We can express this mathematically using an integral form of momentum conservation:

$$\underbrace{2\pi\int_0^\infty \rho(r,x)v_x^2(r,x)r\mathrm{d}r}_{\text{Momentum flow of the jet at any } x, J} = \underbrace{\rho_e v_e^2 \pi R^2}_{\text{Momentum flow issuing from the nozzle}, J_e} \qquad (8.1)$$

where subscript e specifies the nozzle exit conditions.

- The process that control the diffusion and convection of momentum are similar to the processes that control the fuel concentration field (convection and diffusion of fuel mass).

- Distribution of fuel mass fraction, $Y_{\mathrm{F}}(r, x)$, should be similar to dimensionless velocity distribution, $v_x(r, x)/v_e$.
- Fuel molecules diffuse radially outward according to Fick's law.
- The effect of moving downstream is to increase time available for diffsuion.
- The width of the region containing fuel grows with x and centerline fuel concentration decays.
- The mass of fluid issuing from nozzle is conserved:

$$2\pi \int_0^\infty \rho(r,x) v_x(r,x) Y_\mathrm{F}(r,x) r \mathrm{d}r = \rho_e v_e \pi R^2 Y_{\mathrm{F},e} \tag{8.2}$$

where $Y_{\mathrm{F},e} = 1$.

- To determine the velocity and mass fraction fields we need to make some asumptions.

Assumptions:

1. $MW_e = MW_\infty$. $P =$const. $T =$ const.: Uniform density field.
2. Species transport is by Fick's diffusion law.

3. Momentum and species diffusivities are constant and equal, i.e. the *Schmidt Number* is unity,

$$\mathrm{Sc} \equiv \nu/\mathcal{D} = 1$$

4. Diffusion is considered only in radial direction; axial diffusion is neglected.

(This may not be a good asumption very near to the nozzle exit; since near the exit it is expected that the axial diffusion will be significant in comparison with the downstream locations.)

Conservation Laws (Boundary-layer equations):

- *Mass Conservation:*

$$\frac{\partial v_x}{\partial x} + \frac{1}{r}\frac{\partial (v_r r)}{\partial r} = 0 \qquad (8.3)$$

- *Axial Momentum Conservation:*

$$v_x \frac{\partial v_x}{\partial x} + v_r \frac{\partial v_x}{\partial r} = \nu \frac{1}{r}\frac{\partial}{\partial r}\left(r \frac{\partial v_x}{\partial r} \right) \qquad (8.4)$$

- *Species Conservation:* For the jet fluid (fuel)

$$v_x \frac{\partial Y_{\mathrm{F}}}{\partial x} + v_r \frac{\partial Y_{\mathrm{F}}}{\partial r} = \mathcal{D} \frac{1}{r}\frac{\partial}{\partial r}\left(r \frac{\partial v_x}{\partial r} \right) \qquad (8.5)$$

- In addition, we have,

$$Y_{\mathrm{Ox}} = 1 - Y_{\mathrm{F}} \tag{8.6}$$

Boundary Conditions:

- To solve Eqns.8.3-8.5 for the unknown functions:
  - $v_x(r,x)$, $v_r(r,x)$, and $Y_{\mathrm{F}}(r,x)$

  requires,
  - three boundary conditions each for v_x and Y_{F}, and
  - one boundary condition for v_r.

- Along the jet centreline, $r = 0$,

$$v_r(0, x) = 0 \tag{8.7a}$$

$$\frac{\partial v_x}{\partial r}(0, x) = 0 \tag{8.7b}$$

$$\frac{\partial Y_{\mathrm{F}}}{\partial r}(0, x) = 0 \tag{8.7c}$$

where the last two result from symmetry.

- At large radii ($r \to \infty$),

$$v_x(\infty, x) = 0 \tag{8.7d}$$

$$Y_{\mathrm{F}}(\infty, x) = 0 \tag{8.7e}$$

- At the jet exit, $x = 0$, we assume uniform axial velocity and fuel mass fraction, and zero elsewhere:

$$\begin{aligned} v_x(r \leq R, 0) &= v_e \\ v_x(r > R, 0) &= 0 \end{aligned} \tag{8.7f}$$

$$\begin{aligned} Y_{\mathrm{F}}(r \leq R, 0) = Y_{\mathrm{F},e} &= 1 \\ Y_{\mathrm{F}}(r > R, 0) &= 0 \end{aligned} \tag{8.7g}$$

Solution:

- Velocity field can be obtained by assuming the profiles to be similar.

- Intrinsic shape of the velocity profiles is the same everywhere in the flowfield.
- Radial distribution of $v_x(r, x)$, when normalized by the local centreline velocity $v_x(0, x)$, is a universal function that depends only on the similarity variable r/x.

\- Solutions for axial and radial velocities:

$$v_x = \frac{3}{8\pi}\frac{J_e}{\mu x}\left[1 + \frac{\xi^2}{4}\right]^{-2} \tag{8.8}$$

$$v_r = \left(\frac{3J_e}{16\pi\rho_e}\right)^{1/2} \frac{1}{x} \frac{\xi - \frac{\xi^3}{4}}{\left(1 + \frac{\xi^2}{4}\right)^2} \qquad (8.9)$$

where J_e is the jet initial momentum flow,

$$J_e = \rho_e v_e^2 \pi R^2 \qquad (8.10)$$

and,

$$\xi = \left(\frac{3\rho_e J_e}{16\pi}\right)^{1/2} \frac{1}{\mu} \frac{r}{x} \qquad (8.11)$$

- Axial velocity distribution in dimensionless form (substitute Eqn.8.10 into 8.8),

$$\frac{v_x}{v_e} = 0.375 \left(\frac{\rho_e v_e R}{\mu}\right) \left(\frac{x}{R}\right)^{-1} \left[1 + \frac{\xi^2}{4}\right]^{-2} \tag{8.12}$$

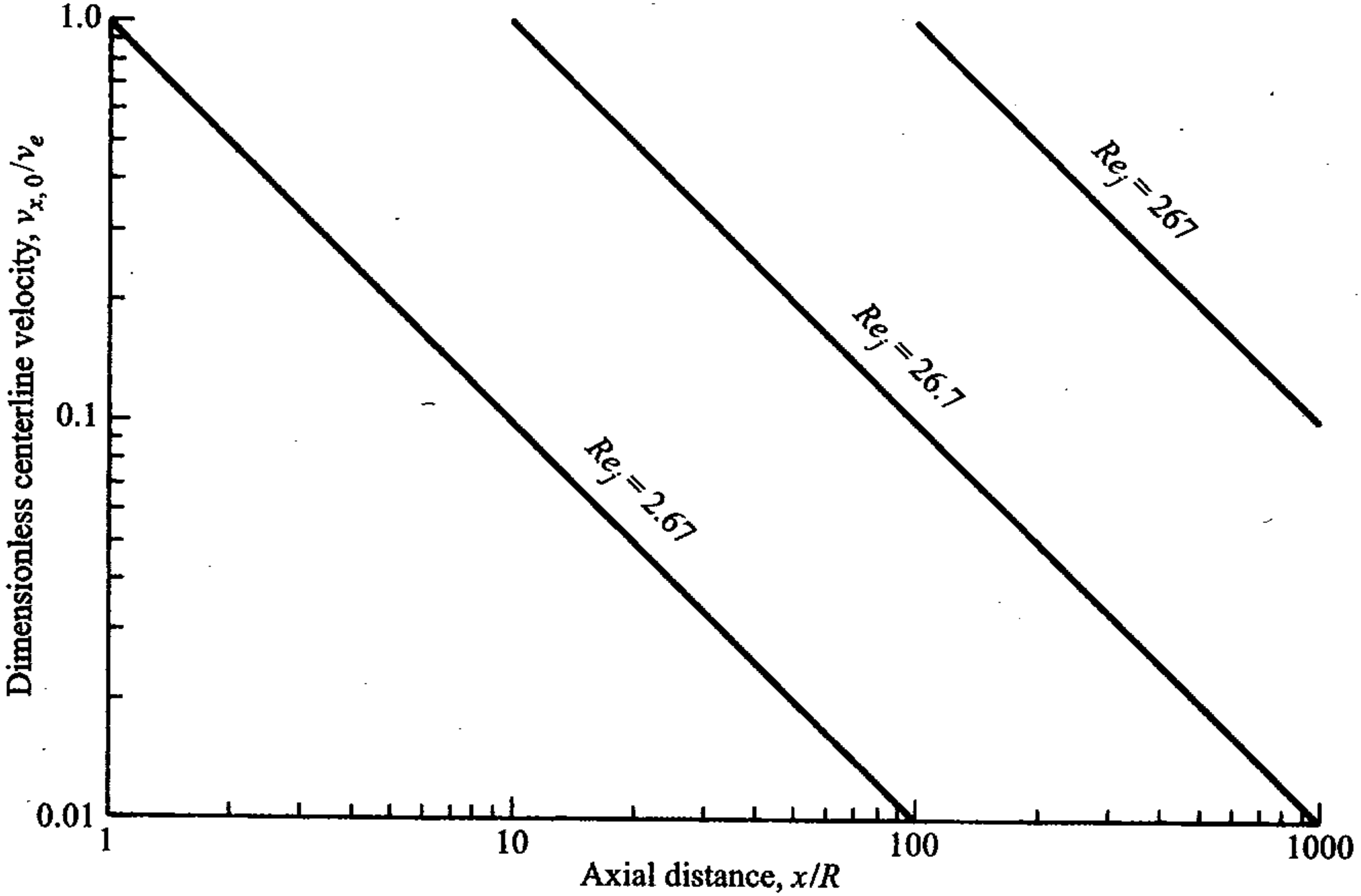
- Dimensionless centreline velocity decay obtained by setting $r = 0$ ($\xi = 0$),

$$\frac{v_{x,0}}{v_e} = 0.375 \left(\frac{\rho_e v_e R}{\mu}\right) \left(\frac{x}{R}\right)^{-1} \tag{8.13}$$

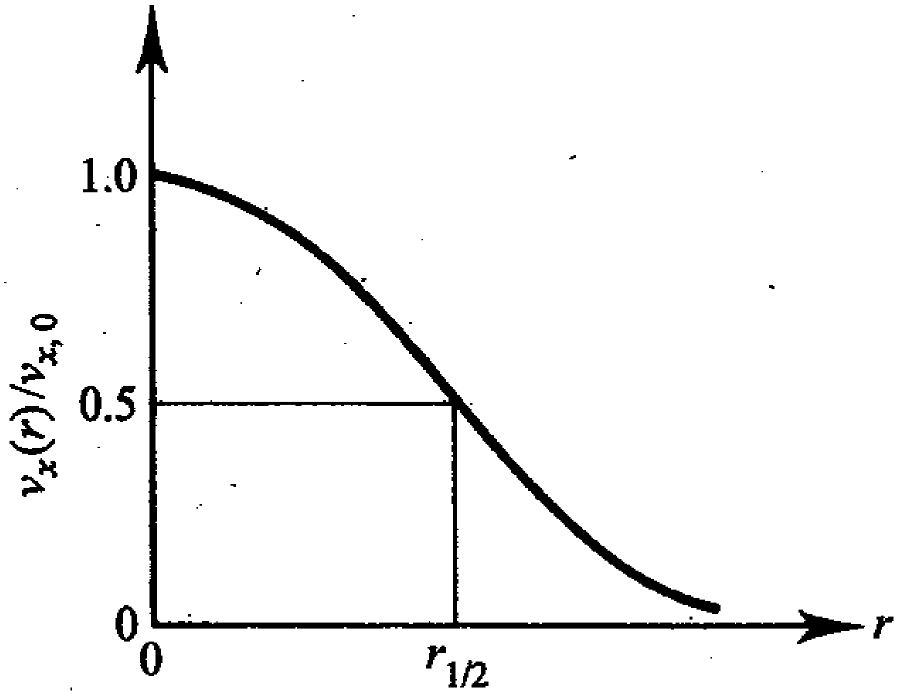
- Velocity decays inversely with axial distance, and proportional to the jet Reynolds number,

$$\mathrm{Re_j} \equiv \frac{\rho_e v_e R}{\mu}$$

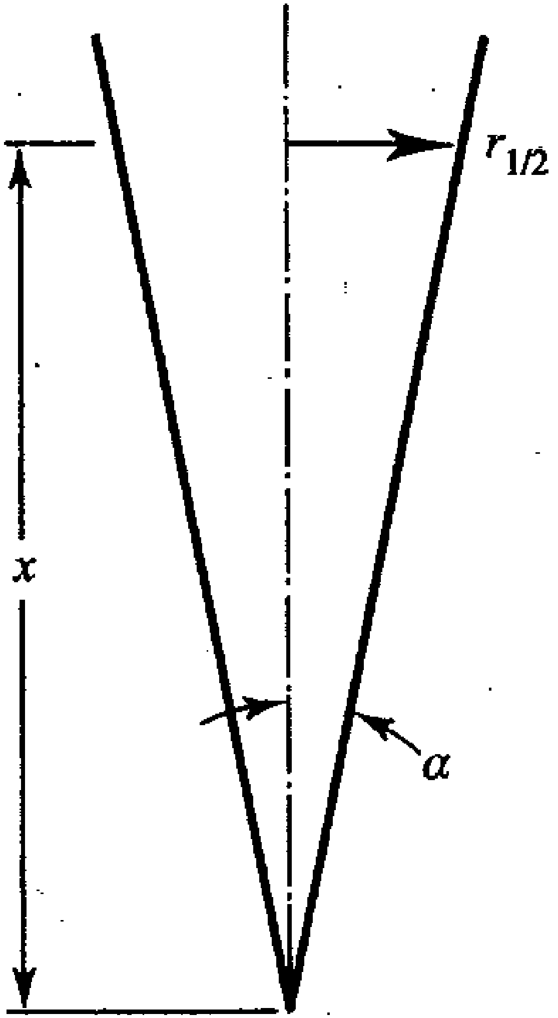
- From Eqn.8.13, we see that the solution is not valid near the nozzle;
  - at small values of x, the dimensionless centerline velocity becomes larger than unity, which is not physically correct.


1.0
0.1
0.01
1
10
100
1000
Dimensionless centerline velocity, $v_{x,0}/v_e$
Axial distance, x/R
$Re_j = 2.67$
$Re_j = 26.7$
$Re_j = 267$

- Other parameters used to characterize jets are the *spreading rate* and *spreading angle,* α.
- We introduce *jet half-width,* $r_{1/2}$.
  - *Half-width*: radial location where jet velocity has decayed to one-half of its centreline value.
- An expression for $r_{1/2}$ can be derived by setting $v_x/v_{x,0}$ to be one half and solving for r.
- *Jet spreading rate*$= r_{1/2}/x$.
- *Jet spreading angle* is the angle whose tangent is the spreading rate.



$v_x(r)/v_{x,0}$
1.0
0.5
0
0
$r_{1/2}$
r



$r_{1/2}$
x
α

$$r_{1/2}/x = 2.97\left(\frac{\mu}{\rho_e v_e R}\right) = 2.97\mathrm{Re_j}^{-1} \qquad (8.14)$$

$$\alpha \equiv \tan^{-1}(r_{1/2}/x) \qquad (8.15)$$

- High-$\mathrm{Re_j}$ jets are narrow, while low-$\mathrm{Re_j}$ jets are wide.
- Comparing Eqns.8.4 and 8.5, we see that Y_{F} plays the same mathematical role as v_x/v_e, if the Schmidt number is unity, i.e., $\nu = \mathcal{D}$.

- Then the functional form of the solution for Y_{F} is identical to that for v_x/v_e,

$$Y_{\mathrm{F}} = \frac{3}{8\pi}\frac{Q_{\mathrm{F}}}{\mathcal{D}x}\left[1+\frac{\xi^2}{4}\right]^{-2} \tag{8.16}$$

where $Q_{\mathrm{F}} = v_e \pi R^2$, volumetric flow rate of fuel.

- By applying $\mathrm{Sc} = 1$ to Eqn.8.16,

$$Y_{\mathrm{F}} = 0.375\mathrm{Re}_{\mathrm{j}}\left(\frac{x}{R}\right)^{-1}\left[1+\frac{\xi^2}{4}\right]^{-2} \tag{8.17}$$

- Centreline values of mass fraction,

$$Y_{\mathrm{F},0} = 0.375\,\mathrm{Re_j}\left(\frac{x}{R}\right)^{-1} \tag{8.18}$$

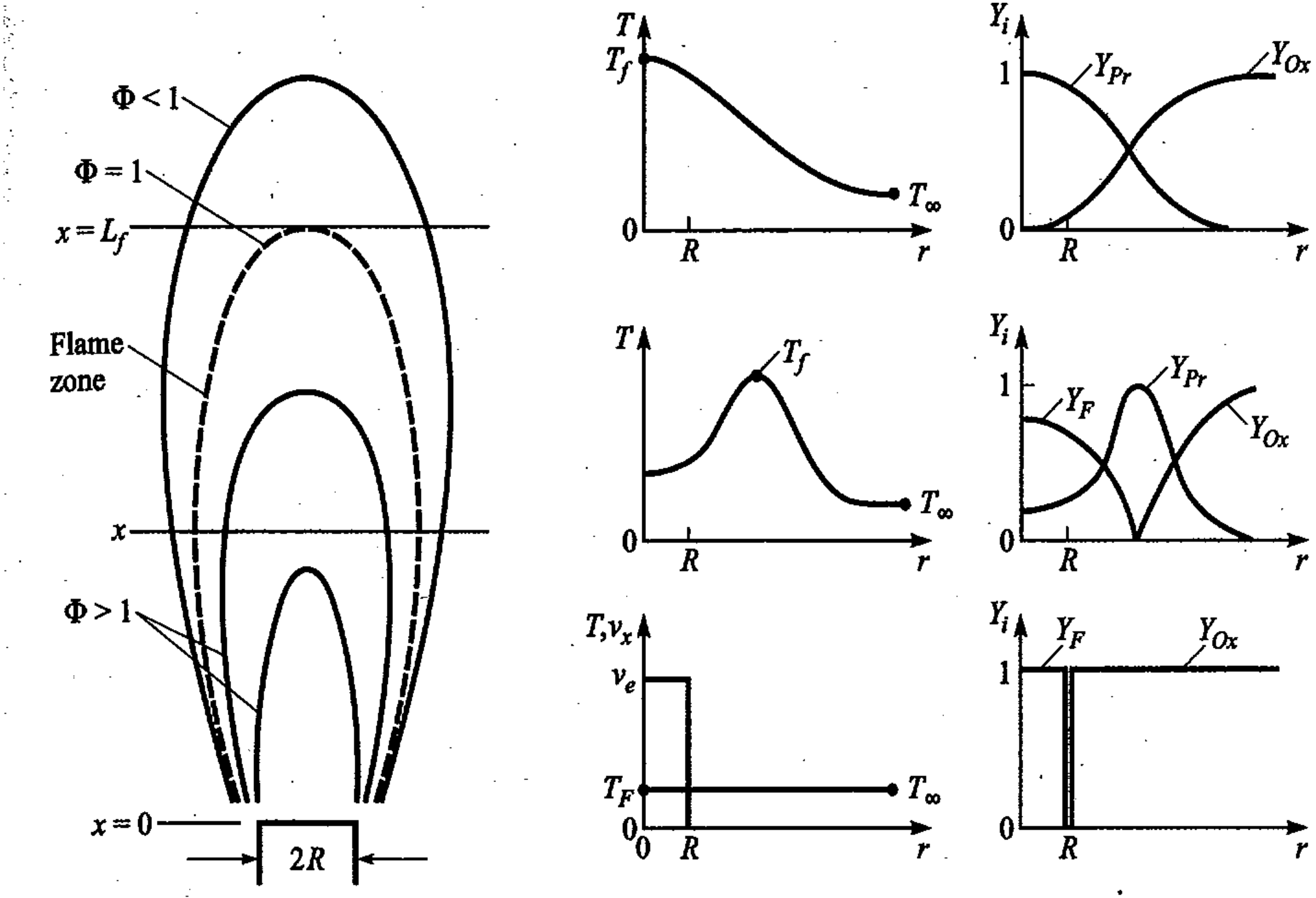
- Again, it should be noted that the solutions are valid far from the nozzle. The dimensionless distance downstream where the solution is valid must exceed the jet Reynolds number, that is,

$$(x/R) \geq 0.375\,\mathrm{Re_j} \tag{8.19}$$

Jet Flame Physical Description

- The burning laminar fuel jet has much in common with our previous discussion of the non-reacting jet.
  - As the fuel flows along the flame axis, it diffuses radially outward, while the oxidizer diffuses radially inward.
  - The "flame surface" can be defined as,

$$\text{Flame Surface} \equiv \begin{array}{c}\text{Locus of points where}\\ \Phi \text{ equals unity}\end{array} \tag{8.20}$$


Φ < 1
Φ = 1
x = L_f
Flame zone
x
Φ > 1
x = 0
2R
T
T_f
0
R
r
T_∞
Y_i
1
Y_{Pr}
Y_{Ox}
Y_F
T, v_x
v_e
T_F

- The products formed at the flame surface diffuse radially both inward and outward.
- An *overventilated flame* is where there is more than enough oxidizer in the immediate surroundings to continuously burn the fuel.
- *Underventilated flame* is the opposite of above.
- Flame length for an overventilated flame is determined at the axial location where,

$$\Phi(r=0, x=L_f)=1 \tag{8.21}$$

- Chemical reaction zone is quite narrow (but significantly larger than laminar flame thickness).
- Flame temperature distribution exhibits an annular shape until the flame tip is reached.
- In the upper regions, the bouyant forces are important.
- As a result, the jet accelerates narrowing the flame.
- The narrowing of the flow increases the fuel concentration gradients, $\mathrm{d}Y_\mathrm{F}/\mathrm{d}r$, thus enhancing diffusion.

- By ignoring the effects of heat released by reaction, Eqn.8.16 provides a crude description of flame boundaries when $Y_{\mathrm{F}} = Y_{\mathrm{F,stoic}}$.

$$Y_{\mathrm{F}} = \frac{3}{8\pi} \frac{Q_{\mathrm{F}}}{\mathcal{D} x} \left[1 + \frac{\xi^2}{4} \right]^{-2} \qquad (8.16)$$

- When r equals zero, we get a flame length,

$$L_f \approx \frac{3}{8\pi} \frac{Q_{\mathrm{F}}}{\mathcal{D} Y_{\mathrm{F,stoic}}} \qquad (8.22)$$

- Flame length is proportional to volumetric flow rate of fuel.
- Flame length is inversely proportional to the stoichiometric fuel mass fraction.
- Since $Q_{\mathrm{F}} = v_e \pi R^2$, various combinations of v_e and R can yield the same flame length.
- Since the diffusion coefficent $\mathcal{D}$ is inversely proportional to pressure, the height of the flame is independent of pressure at given mass flow rate.

Historical Theoretical Formulations:

- Burke and Schumann (1928)
  - constant velocity field parallel to flame axis.
  - reasonable predictions of L_f for round burners.
- Roper and Roper et al (1977)
  - relaxed single constant velocity assumption.
  - provides extremely good predictions.
  - matched by experimental results/correlations.
  - round and slot-burners.

Roper's Solutions and Correlations:

Circular Port:

$$L_{\mathrm{f,thy}} = \frac{Q_{\mathrm{F}}(T_\infty/T_{\mathrm{F}})}{4\pi\mathcal{D}_\infty \ln(1+1/S)} \left(\frac{T_\infty}{T_f}\right)^{0.67} \tag{8.59}$$

$$L_{\mathrm{f,expt}} = 1330 \frac{Q_{\mathrm{F}}(T_\infty/T_{\mathrm{F}})}{\ln(1+1/S)} \tag{8.60}$$

where S is stoichiometric molar oxidizer-fuel ratio, $\mathcal{D}_\infty$ mean diffusion coefficient of oxidizer at T_∞, T_{F} and T_f are fuel stream and mean flame temperatures, respectively.

Square Port:

$$L_{\mathrm{f,thy}} = \frac{Q_{\mathrm{F}}(T_\infty/T_{\mathrm{F}})}{16\mathcal{D}_\infty\left\{\mathrm{inverf}[(1+S)^{-0.5}]\right\}^2}\left(\frac{T_\infty}{T_f}\right)^{0.67} \tag{8.61}$$

$$L_{\mathrm{f,expt}} = 1045\frac{Q_{\mathrm{F}}(T_\infty/T_{\mathrm{F}})}{\left\{\mathrm{inverf}[(1+S)^{-0.5}]\right\}^2} \tag{8.62}$$

where *inverf* is the inverse of error function *Erf*,

$$\mathrm{Erf}w = \frac{2}{\sqrt{\pi}}\int_0^w e^{-t^2}\mathrm{d}t$$

Slot Burner–Momentum Controlled:

$$L_{\mathrm{f,thy}} = \frac{b\beta^2 Q_{\mathrm{F}}}{hI\mathcal{D}_\infty Y_{\mathrm{F,stoic}}} \left(\frac{T_\infty}{T_{\mathrm{F}}}\right)^2 \left(\frac{T_f}{T_\infty}\right)^{0.33} \tag{8.63}$$

$$L_{\mathrm{f,expt}} = 8.6 \cdot 10^4 \frac{b\beta^2 Q_{\mathrm{F}}}{hIY_{\mathrm{F,stoic}}} \left(\frac{T_\infty}{T_{\mathrm{F}}}\right)^2 \tag{8.64}$$

where b is the slot width and h is the length, and,

$$\beta = \frac{1}{4 \times \mathrm{inverf}[1/(1+S)]}$$

I is the ratio of actual initial momentum flow from the slot to that of uniform flow,

$$I = \frac{J_{\mathrm{e,act}}}{\dot{m}_{\mathrm{F}} v_e}$$

For uniform flow $I = 1$. For a fully developed flow, assuming parabolic exit velocity, $I = 1.5$.

- Equations 8.63 and 8.64 are anly applicable to conditions where the oxidizer is stagnant.

Slot Burner–Buoyancy Controlled:

$$L_{\mathrm{f,thy}} = \left[\frac{9\beta^4 Q_{\mathrm{F}}^4 T_\infty^4}{8\mathcal{D}_\infty^2 a h^4 T_{\mathrm{F}}^4} \right]^{1/3} \left(\frac{T_f}{T_\infty} \right)^{2/9} \tag{8.65}$$

$$L_{\mathrm{f,expt}} = 2 \cdot 10^3 \left[\frac{\beta^4 Q_{\mathrm{F}}^4 T_\infty^4}{a h^4 T_{\mathrm{F}}^4} \right]^{1/3} \tag{8.66}$$

where a is the mean buoyant acceleration,

$$a \cong 0.6 g \left(\frac{T_f}{T_\infty} - 1 \right) \tag{8.67}$$

and g is the gravitational acceleration.

Slot Burner–Transition Regime:

- *Froude Number*,

$$\mathrm{Fr_f} \equiv \frac{(v_e I Y_{\mathrm{F,stoic}})^2}{a L_f} \qquad (8.68)$$

- Froude number physically represent the ratio of the initial jet momentum flow to the buoyant force experienced by the flame.

$\mathrm{Fr_f} >> 1$	Momentum-controlled	$(8.69a)$
$\mathrm{Fr_f} \approx 1$	Transition (mixed)	$(8.69b)$
$\mathrm{Fr_f} << 1$	Buoyancy-controlled	$(8.69c)$

- Note that L_f must be known *a priori* to establish the appropriate regime. So it requires a trial and error approach.
- When $\mathrm{Fr_f} \approx 1$,

$$L_{\mathrm{f,T}} = \frac{4}{9} L_{\mathrm{f,M}} \left(\frac{L_{\mathrm{f,B}}}{L_{\mathrm{f,M}}} \right)^3 \times \left\{ \left[1 + 3.38 \left(\frac{L_{\mathrm{f,M}}}{L_{\mathrm{f,B}}} \right)^3 \right]^{2/3} - 1 \right\} \tag{8.70}$$

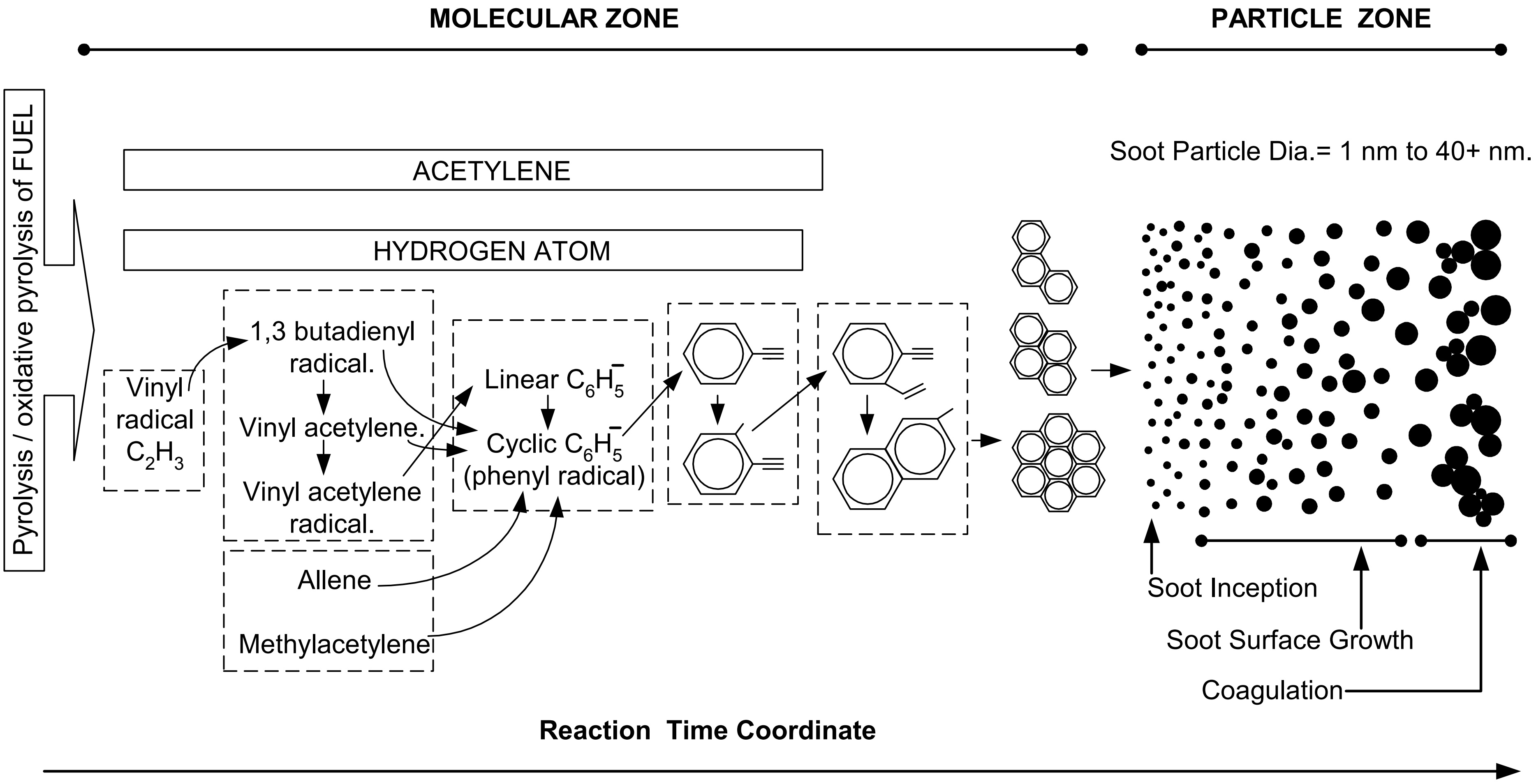
Soot Formation in Diffusion Flames:

- Fuel type
  - Fuel chemical structure and composition
- Dilution
  - Inert or reactive diluents
- Turbulence
  - Turbulence time versus chemical time
- Temperature
- Pressure

- Soot does not form in premixed flames except when $\Phi \geq \Phi_{\mathrm{crit}}$
- The details of soot formation process in diffusion flames is elusive
- Conversion of a hydrocarbon fuel with molecules containing a few carbon atoms into a carbonaceous agglomerate containing some millions of carbon atoms in a few milliseconds.
- Transition from a gaseous to solid phase
- Smallest detectable solid particles are about 1.5 nm in diameter (about 2000 amu)

- Soot formation involves a series of chemical and physical processes:
  - Formation and growth of large aromatic hydrocarbon molecules leading to soot inception, i.e, transition to first solid particles (primary particles)
  - Surface growth and coagulation of primary particles to agglomerates
  - Growth of agglomerates by picking up growth components from the gas phase
  - Oxidation of agglomerates

- **Smoke Point:**
  - An ASTM standard method to determine sooting tendency of a liquid fuel
  - Fuel flow rate is increased until the smoke starts being emitted from the flame tip of a laminar flame on a standard burner
  - Greater the fuel flow rate (height of the flame), the lower is the sooting propensity
  - Generally used for aviation fuel specifications
  - Dependent on the fuel chemical composition



MOLECULAR ZONE

PARTICLE ZONE

Pyrolysis / oxidative pyrolysis of FUEL

ACETYLENE

HYDROGEN ATOM

Vinyl radical C_2H_3

1,3 butadienyl radical.

Vinyl acetylene.

Vinyl acetylene radical.

Allene

Methylacetylene

Linear $C_6H_5^-$

Cyclic $C_6H_5^-$ (phenyl radical)

Soot Particle Dia.= 1 nm to 40+ nm.

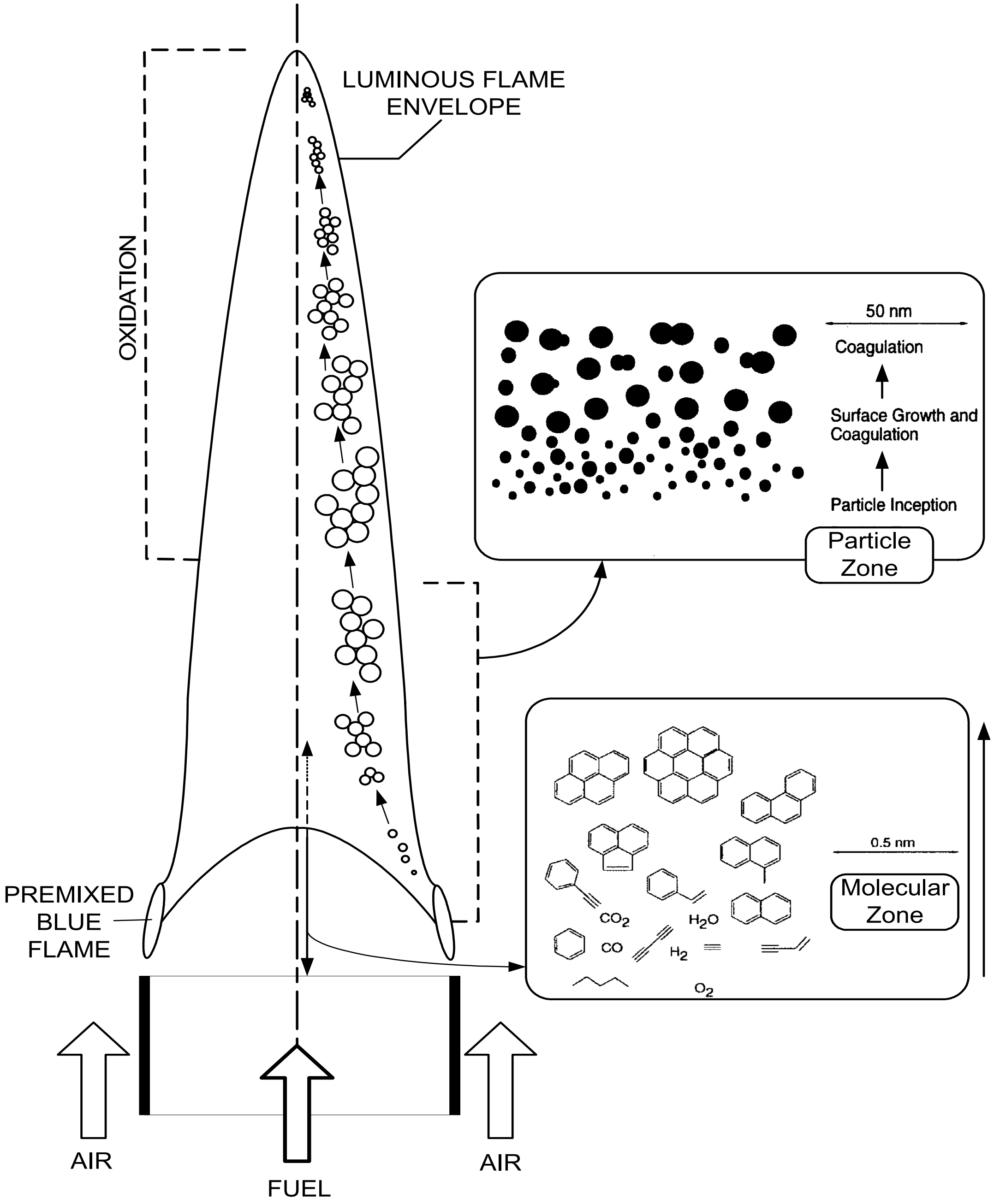
Soot Inception

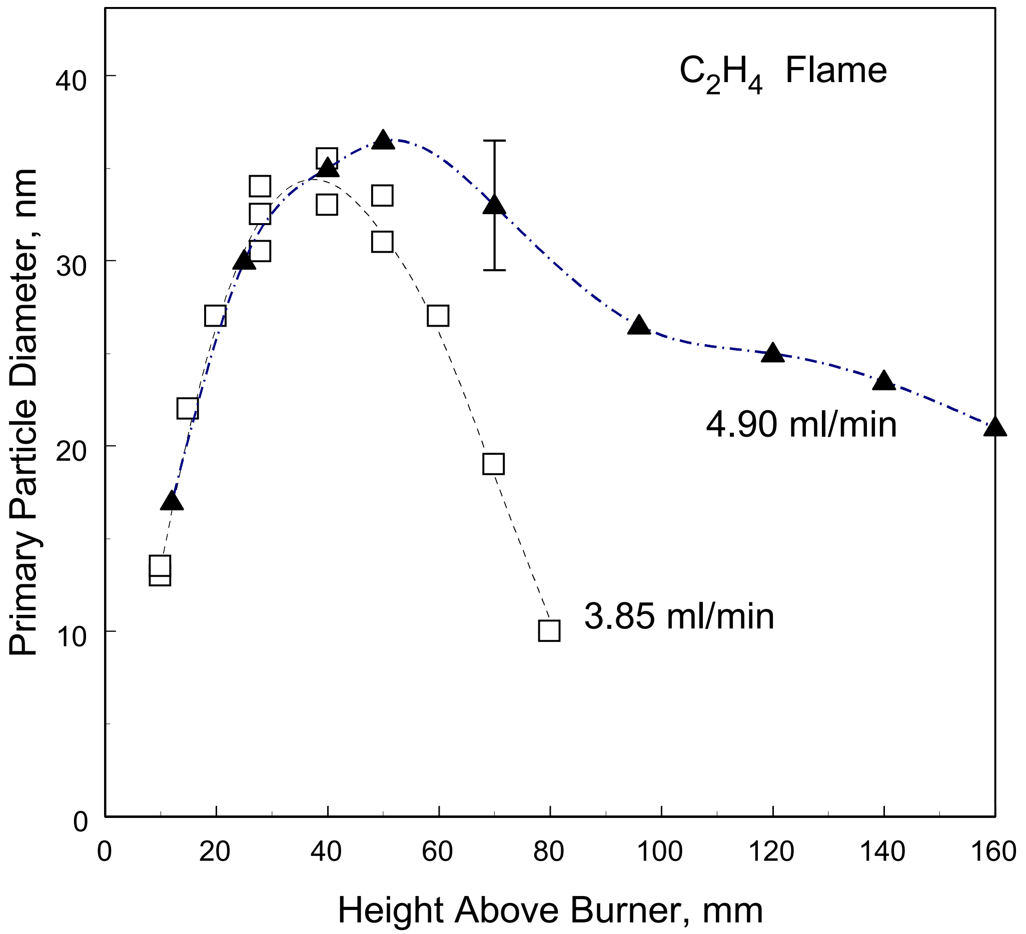
Soot Surface Growth

Coagulation

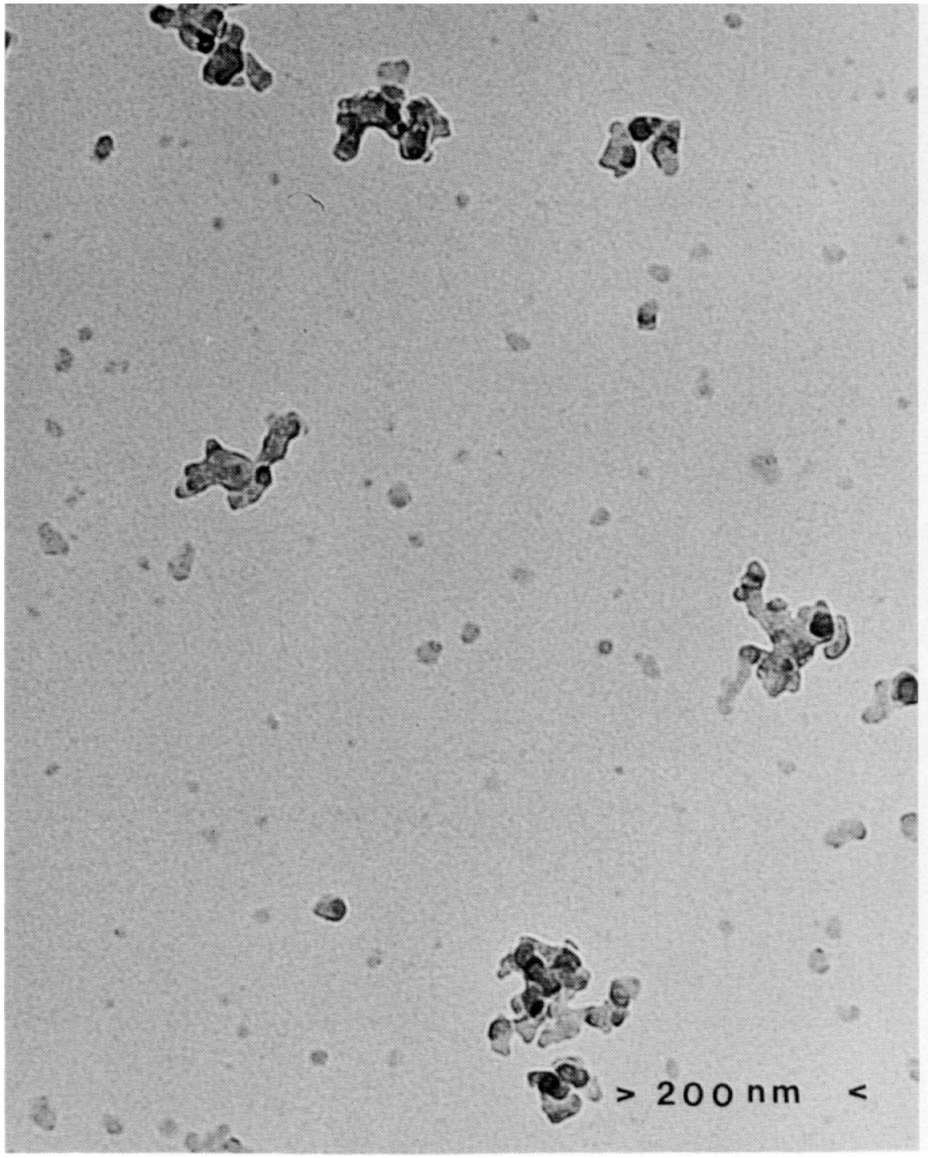
Reaction Time Coordinate

- fuel tube = 11 mm; fuel flow rate = 3.27 cm^3/s
- air nozzle = 100 mm; air flow rate = 170 L/min
- visible flame height = 67 mm (Fuel: C_2H_4)

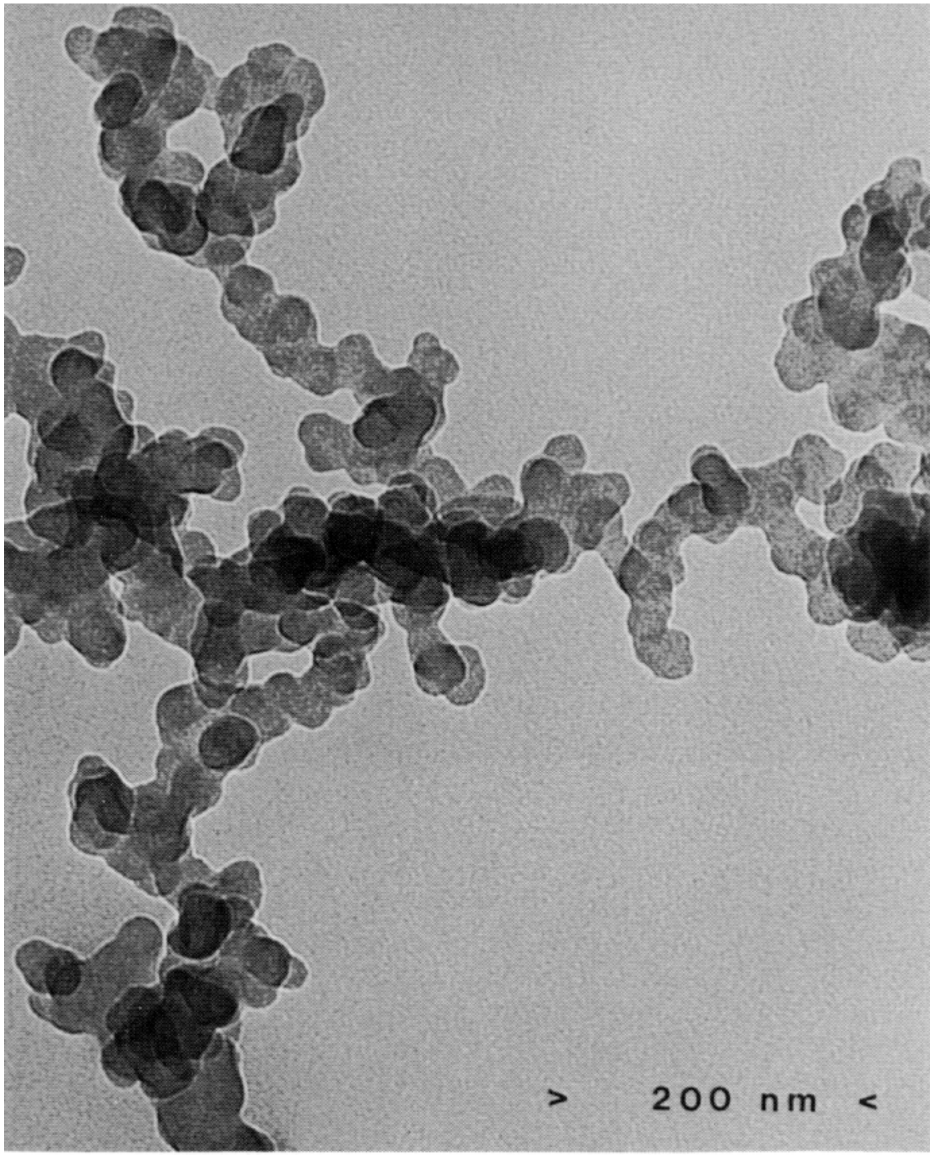

LUMINOUS FLAME ENVELOPE
OXIDATION
50 nm
Coagulation
Surface Growth and Coagulation
Particle Inception
Particle Zone
0.5 nm
Molecular Zone
CO_2
H_2O
CO
H_2
O_2
PREMIXED BLUE FLAME
AIR
FUEL
AIR



C_2H_4 Flame
4.90 ml/min
3.85 ml/min
Primary Particle Diameter, nm
Height Above Burner, mm
0
10
20
30
40
0
20
40
60
80
100
120
140
160

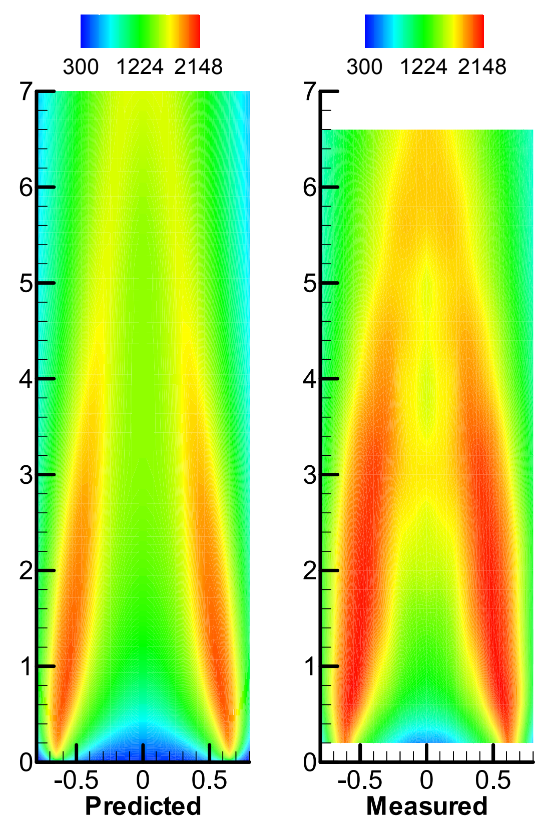


z = 10 mm; r = 5 mm

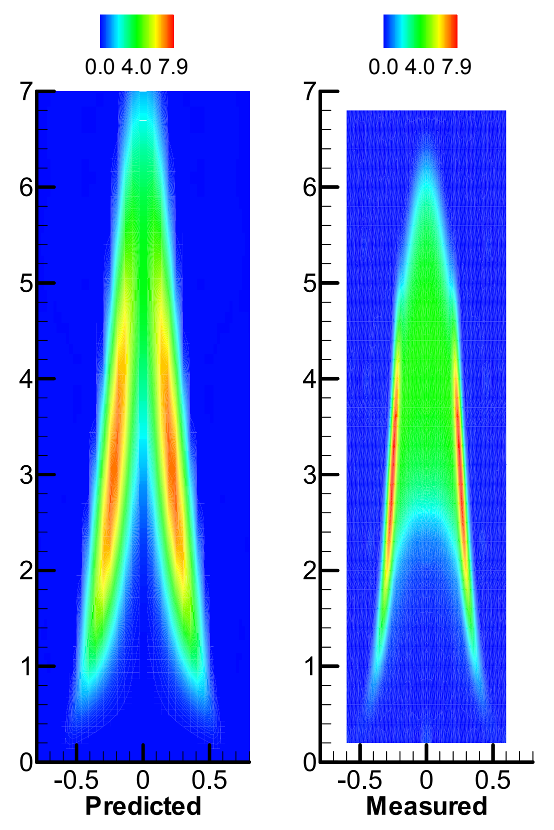


$z = 33$ mm; $r = 0$ mm

Predicted and Measured Results
C_2H_4-Air Flame



Temperature, K

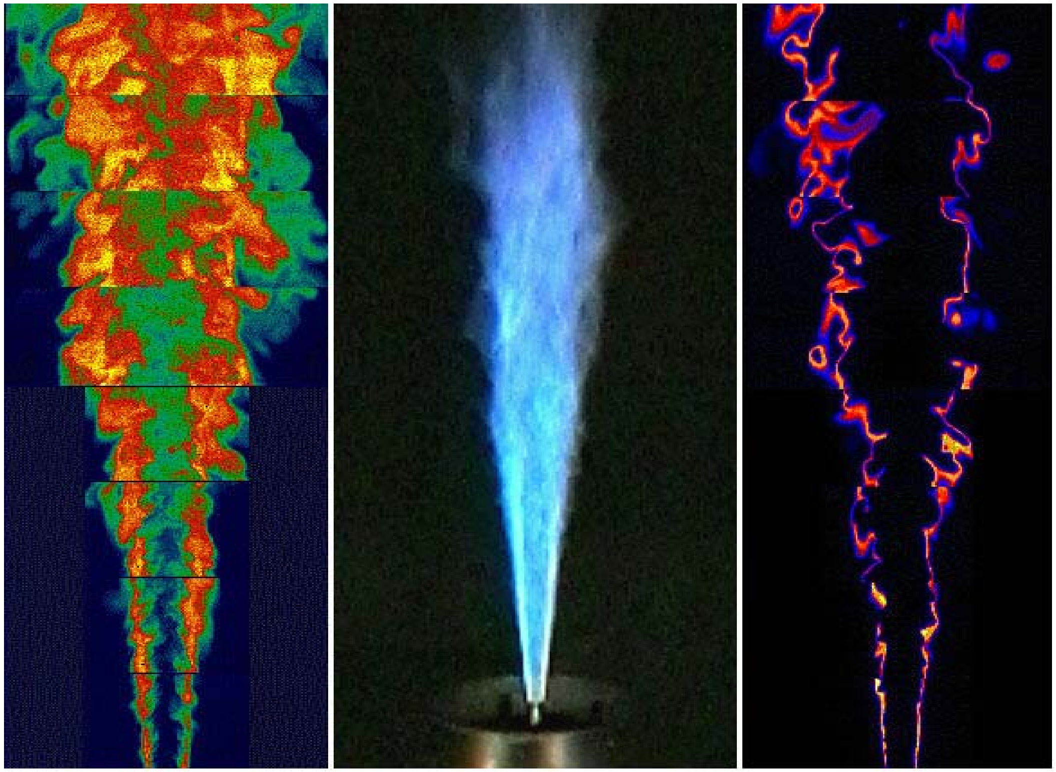


Soot volume fraction, ppm

Turbulent Non-Premixed Flames

- ***Background:***

\- Structure of turbulent non-premixed flames;



- Images of a turbulent non-premixed flame with different diagnostics.

- Examples of turbulent non-premixed flames:
  - Conventional gas turbines
  - Bi-propellant rocket engines
  - Diesel engines
  - Cement kilns, glass furnaces, boiler furnaces
  - Turbojet afterburners
  - Flares in refineries/oil fields
  - Most fires (like forest fires), pool flames
  - Coal/wood combustion

- For any particular application, some of the issues the designer is faced with are as follows (importance of each may change depending on the nature of the application):
    - Combustion intensity and efficiency
    - Flame stability
    - Flame shape and size
    - Heat transport
    - Pollutant emissions

- Conserved scalar concept:
  - The *conserved scalar* concept greatly simplifies the solution of reacting flow problems (i.e., the determination of the fields of velocity, species, and temperature), particularly those involving non-premixed flames.
  - A conserved scalar is any scalar property that is conserved throughout the flowfield. For example, absolute enthalpy would qualify as being a conserved scalar if there are no sinks or sources of thermal energy.

- Element mass fractions are also conserved scalars.
- We will limit our discussion to only one, the mixture fraction:

$$f \equiv \frac{\text{Mass of material having its origin in the fuel stream}}{\text{Mass of mixture}}$$

- Mixture fraction is uniquely related to Φ:

$$f \equiv \frac{\Phi}{(A/F)_{st} + \Phi} \tag{1}$$

- For practical purposes we can define a *flame boundary* where $\Phi = 1$, then the mixture fraction at stoichiometric location:

$$f_s \equiv \frac{1}{(A/F)_{st} + 1} \tag{2}$$

- For a three-*species system*, i.e., fuel, oxidizer, and products:

$$1 \text{ kg fuel} + (A/F) \text{ kg oxidizer} \longrightarrow$$

$$[(A/F) + 1] \text{ kg products}$$

$$\underbrace{f}_{\substack{\text{mass fraction of}\\ \text{material having}\\ \text{its origin in the}\\ \text{fuel stream}}} = \underbrace{(1)}_{\left(\frac{\text{kg fuel stuff}}{\text{kg fuel}}\right)} \underbrace{Y_F}_{\left(\frac{\text{kg fuel}}{\text{kg mixture}}\right)}$$

$$+ \underbrace{\left(\frac{1}{(A/F)+1}\right)}_{\left(\frac{\text{kg fuel stuff}}{\text{kg products}}\right)} \underbrace{Y_{Pr}}_{\left(\frac{\text{kg products}}{\text{kg mixture}}\right)} + \underbrace{(0)}_{\left(\frac{\text{kg fuel stuff}}{\text{kg oxidizer}}\right)} \underbrace{Y_{ox}}_{\left(\frac{\text{kg oxidizer}}{\text{kg mixture}}\right)}$$

- *fuel stuff* is that material originating in the fuel stream. For a hydrocarbon fuel, fuel stuff is carbon and hydrogen. Another way of expressing mixture fraction is, then:

$$f = Y_F + \left(\frac{1}{(A/F)+1}\right) Y_{Pr} \tag{3}$$

- *Example:* Consider a nonpremixed, ethane (C_2H_6) -air flame in which the mole fractions of the following species are measured using various techniques: C_2H_6, CO, CO_2, H_2, H_2O, N_2, O_2, and OH. The mole fractions of all other species are assumed to be negligible. Define a mixture fraction f expressed in terms of the mole fractions of the measured species.
- *Solution:* Approach will be to express f in terms of the known species mass fractions, and then express the mass fractions in terms of mole fractions.

$$f \equiv \frac{\begin{array}{c}\text{Mass of material having its}\\ \text{origin in the fuel stream}\end{array}}{\text{Mass of mixture}}$$

$$= \frac{(m_C + m_H)_{\text{mix}}}{m_{\text{mix}}}$$

- In the flame gases, carbon is present in any unburned fuel and in CO and CO_2; while hydrogen is present in unburned fuel, H_2, H_2O, and OH. Summing the mass fractions of carbon and hydrogen associated with each species yields:

$$
\begin{aligned}
f = {} & Y_{\mathrm{C_2H_6}} \frac{2M_{\mathrm{C}}}{M_{\mathrm{C_2H_6}}} + Y_{\mathrm{CO}} \frac{M_{\mathrm{C}}}{M_{\mathrm{CO}}} + Y_{\mathrm{CO_2}} \frac{M_{\mathrm{C}}}{M_{\mathrm{CO_2}}} \\
& + Y_{\mathrm{C_2H_6}} \frac{3M_{\mathrm{H_2}}}{M_{\mathrm{C_2H_6}}} + Y_{\mathrm{H_2}} + Y_{\mathrm{H_2O}} \frac{M_{\mathrm{H_2}}}{M_{\mathrm{H_2O}}} \\
& + Y_{\mathrm{OH}} \frac{0.5M_{\mathrm{H_2}}}{M_{\mathrm{OH}}}
\end{aligned}
$$

Substituting for the mass fractions,

$$Y_i = \chi_i M_i / M_{\mathrm{mix}}$$

$$f = \chi_{\mathrm{C_2H_6}} \frac{M_{\mathrm{C_2H_6}}}{M_{\mathrm{mix}}} \frac{2M_{\mathrm{C}}}{M_{\mathrm{C_2H_6}}} + \chi_{\mathrm{CO}} \frac{M_{\mathrm{CO}}}{M_{\mathrm{mix}}} \frac{M_{\mathrm{C}}}{M_{\mathrm{CO}}} + \cdots$$

$$f = \frac{(2\chi_{\mathrm{C_2H_6}} + \chi_{\mathrm{CO}} + \chi_{\mathrm{CO_2}})M_{\mathrm{C}}}{M_{\mathrm{mix}}} + \frac{(3\chi_{\mathrm{C_2H_6}} + \chi_{\mathrm{H_2}} + \chi_{\mathrm{H_2O}} + 0.5\chi_{\mathrm{OH}})M_{\mathrm{H_2}}}{M_{\mathrm{mix}}}$$

where,

$$M_{\mathrm{mix}} = \sum \chi_i M_i$$

- ***Non-premixed turbulent flames with equilibrium chemistry:***
  - Chemicals react to equilibrium as fast as they mix.
  - Remaining question is how the fuel mixes with the oxidizer.
  - All scalar diffusivities are equal.
  - By computing the mixing of mixture fraction f, the mixing of everything can be computed.
  - Conservation equation for the mixture fraction can be written.

- If one further assumes that energy diffuses at the same rate for all species, i.e., Lewis number $\mathrm{Le} = k/(D\rho c_p) = 1$, and no heat transfer occurs, then the enthalpy field, as well as the temperature field, can be uniquely described by f.
- Thus, assuming:
    - equilibrium (*fast*) chemistry
    - equal diffusivity and Le=1
    - no heat loss

  all scalar variables (temperature, mass fractions, and density) are known functions of mixture fraction only.

- ***Finite-rate chemistry in non-premixed flames:***

  - If one wishes to relax the fast chemistry assumption, then, in addition to a conservation equation for total mass, energy, and momentum, each species will have a conservation equation with a chemical source term, $M_i\omega_i$. The source term is the sum of all chemical kinetic reactions that involve species i.
  - These kinetic rates depend on other species and, more importantly, have a nonlinear dependence on both species and temperature.

- As the mixing rate increases, one chemical process will emerge at first to depart from chemical equlibrium.
- Increasing the mixing rate further will result in another process departing from equilibrium.
- One by one, processes will depart from equilibrium until the main energy releasing reactions are competing with the mixing rate.
- As the mixing rate increases further, the temperature begins to depart from equilibrium solution.

Flame Length:

- Definition of non-premixed turbulent flame length is not uniform/universal.
    - Visible flame length.
    - Length based on the axial length at which mixture fraction is stoichiometric.
    - Axial location of the average peak centerline temperature.

Factors affecting flame length:

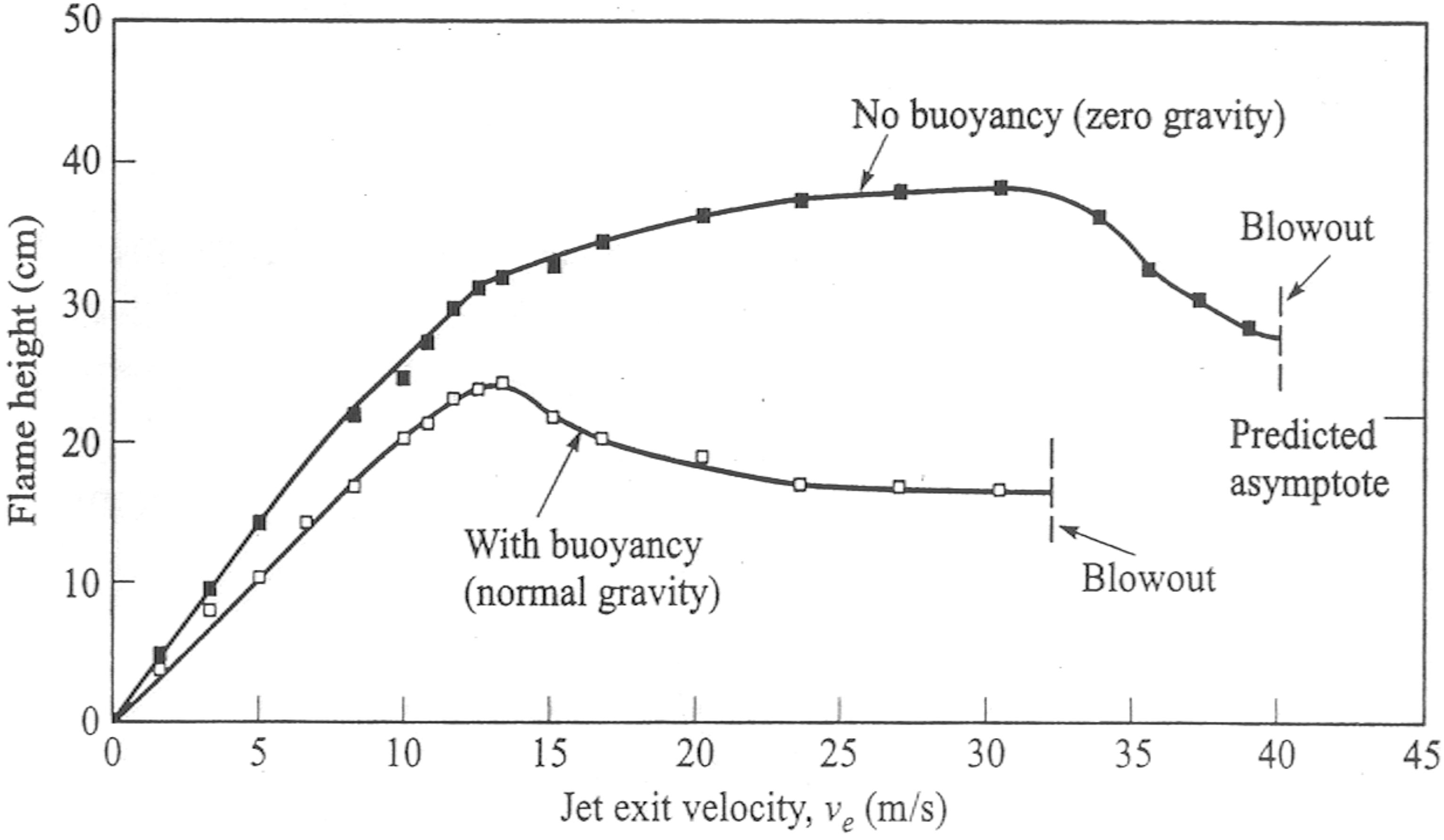
- Relative importance of initial jet momentum flux and buoyant forces acting on the flame - Froude Number
- Stoichiometry - stoichiometric mixture fraction
- Ratio of the nozzle fluid (fuel) to ambient gas density - density ratio
- Initial jet diameter

- For turbulent jet flames, we define the following flame Froude number,

$$\mathrm{Fr_f} = \frac{v_e f_s^{3/2}}{\left(\frac{\rho_e}{\rho_\infty}\right)^{1/4} \left[\frac{\Delta T_f}{T_\infty} g d_j\right]^{1/2}} \tag{4}$$

  where ΔT_f is the characteristic temperature rise as a result of combustion.

  - $\mathrm{Fr_f} < 1$: flames are dominated by buoyancy.
  - $\mathrm{Fr_f} >> 1$: flames dominated by momentum.



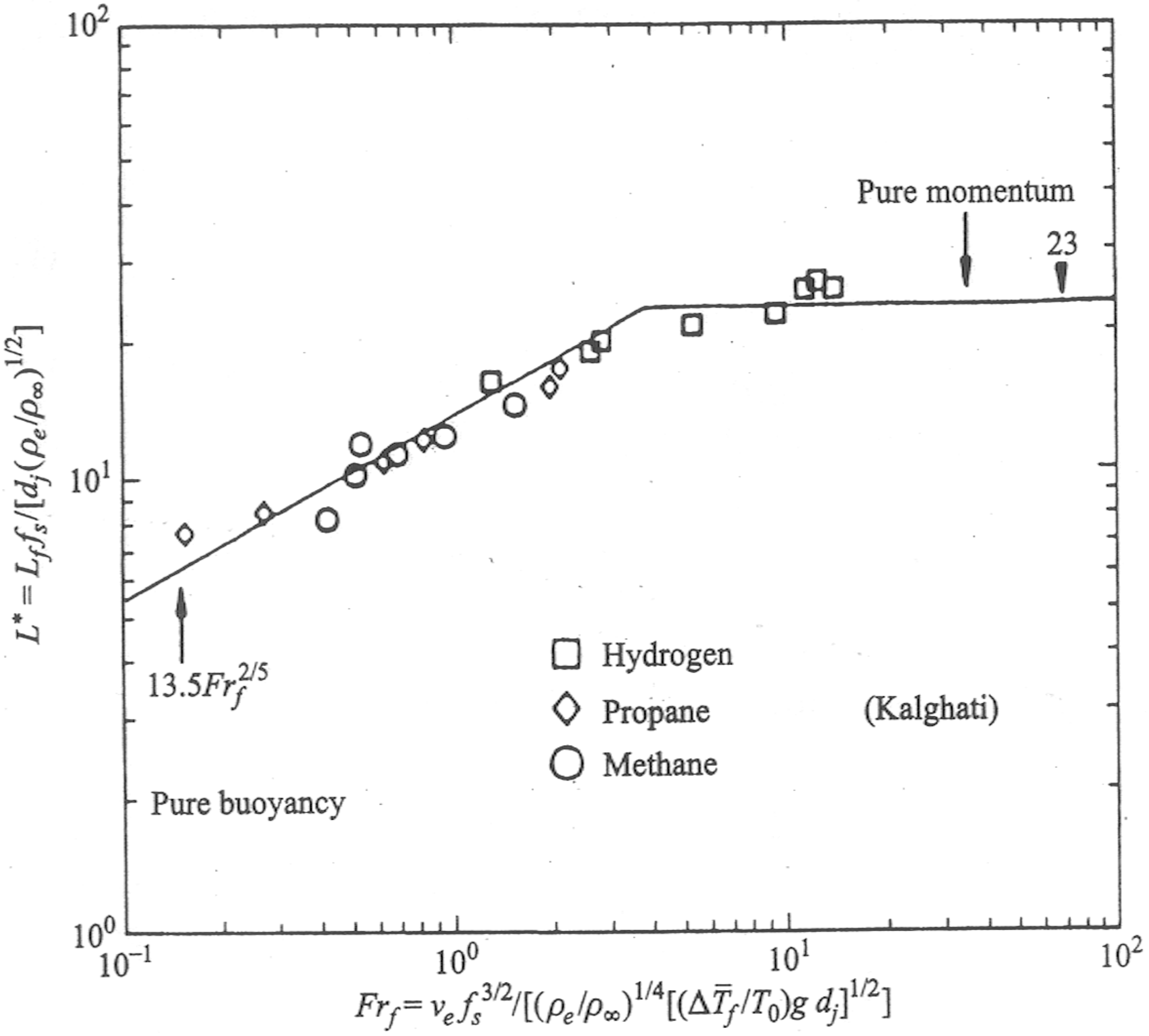
Jet flame heights with and without buoyancy.

- The density ratio and the jet diameter can be combined to give a *momentum diameter*, defined as:

$$d_j^\star = d_j(\rho_e/\rho_\infty)^{1/2} \tag{5}$$

- The basic idea in the above definition is that jets with identical initial jet momentum fluxes should have identical velocity fields.
- Increasing the density of the nozzle fluid produces same effect as increasing the nozzle diameter.

- Correlations of experimental data:



Jet flame heights correlated with Froude number.

- In the previous figure, dimensionless flame length is defined as:

$$L^\star \equiv \frac{L_f f_s}{d_j(\rho_e/\rho_\infty)^{1/2}} \tag{6}$$

or

$$L^\star = \frac{L_f f_s}{d_j^\star} \tag{6a}$$

- Two regimes are identified in previous figure. A buoyancy-dominated regime correlated by:

$$L^\star = \frac{13.5\mathrm{Fr}_\mathrm{f}^{2/5}}{(1+0.07\mathrm{Fr}_\mathrm{f}^2)^{1/5}} \quad \text{for} \quad \mathrm{Fr}_\mathrm{f} < 5 \tag{7}$$

- and a momentum-dominated regime where the dimensionless flame length is constant:

$$L^{\star} = 23 \quad \text{for} \quad \mathrm{Fr_f} \geq 5 \tag{8}$$

- Various other correlations are available in literature. The one discussed above is one of the most used correlations for practical calculations.

- ***Liftoff and Blowout of Non-premixed Flames:***

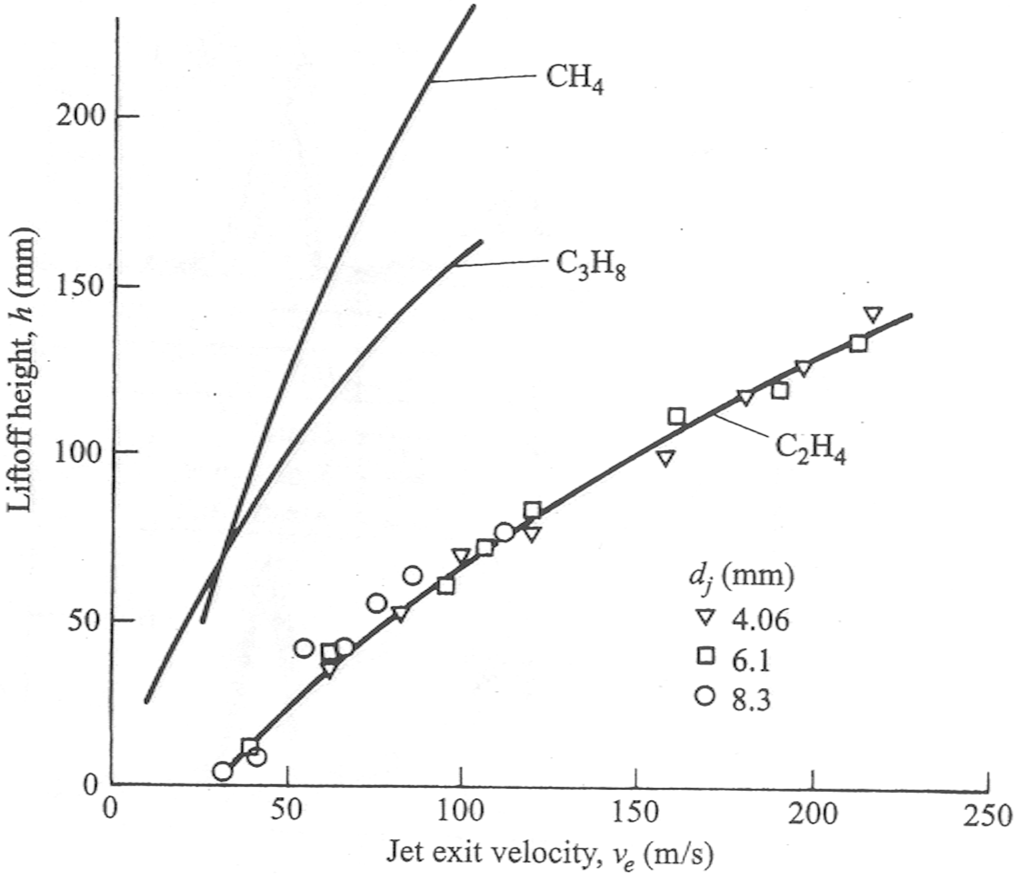
- A jet flame will lift from an attached position at the burner exit if the exit velocity is sufficiently high.
- The *liftoff height*, the distance between the burner tip and the base of the flame, will increase with additional increases in velocity until the flame *blows out*.
- Currently there is no consensus on what determines the liftoff height.

- Three mechanisms below are the most favored ones in literature:
  1. Local flow velocity at the base of the flame matches the turbulent premixed flame velocity corresponding to local conditions at the base of the flame.
  2. Local strain rates in the fluid at the base of the flame exceed the extinction strain rate for a laminar flame corresponding to local conditions at the base of the flame.
  3. The time available for backmixing by large-

scale flow structures of hot products with fresh mixture is less than a critical chemical time required for ignition.

- The following figure shows the liftoff heights for methane, propane, and ethylene jet flames as functions of initial jet velocity.
- For hydrocarbon-air flames, Kalghatgi developed the following correlation:

$$\frac{\rho_e S_{L,\max} h}{\mu_e} = 50 \left(\frac{v_e}{S_{L,\max}} \right) \left(\frac{\rho_e}{\rho_\infty} \right)^{1.5} \qquad (9)$$



Jet flame liftoff heights versus jet exit velocity.

- The following correlation was proposed by Kalghathi to estimate blowout flowrates for jet flames:

$$\frac{v_e}{S_{L,max}}\left(\frac{\rho_e}{\rho_\infty}\right)^{1.5} = 0.017 \cdot \mathrm{Re_H}(1 - 3.5 \cdot 10^{-6}\mathrm{Re_H}) \qquad (10)$$

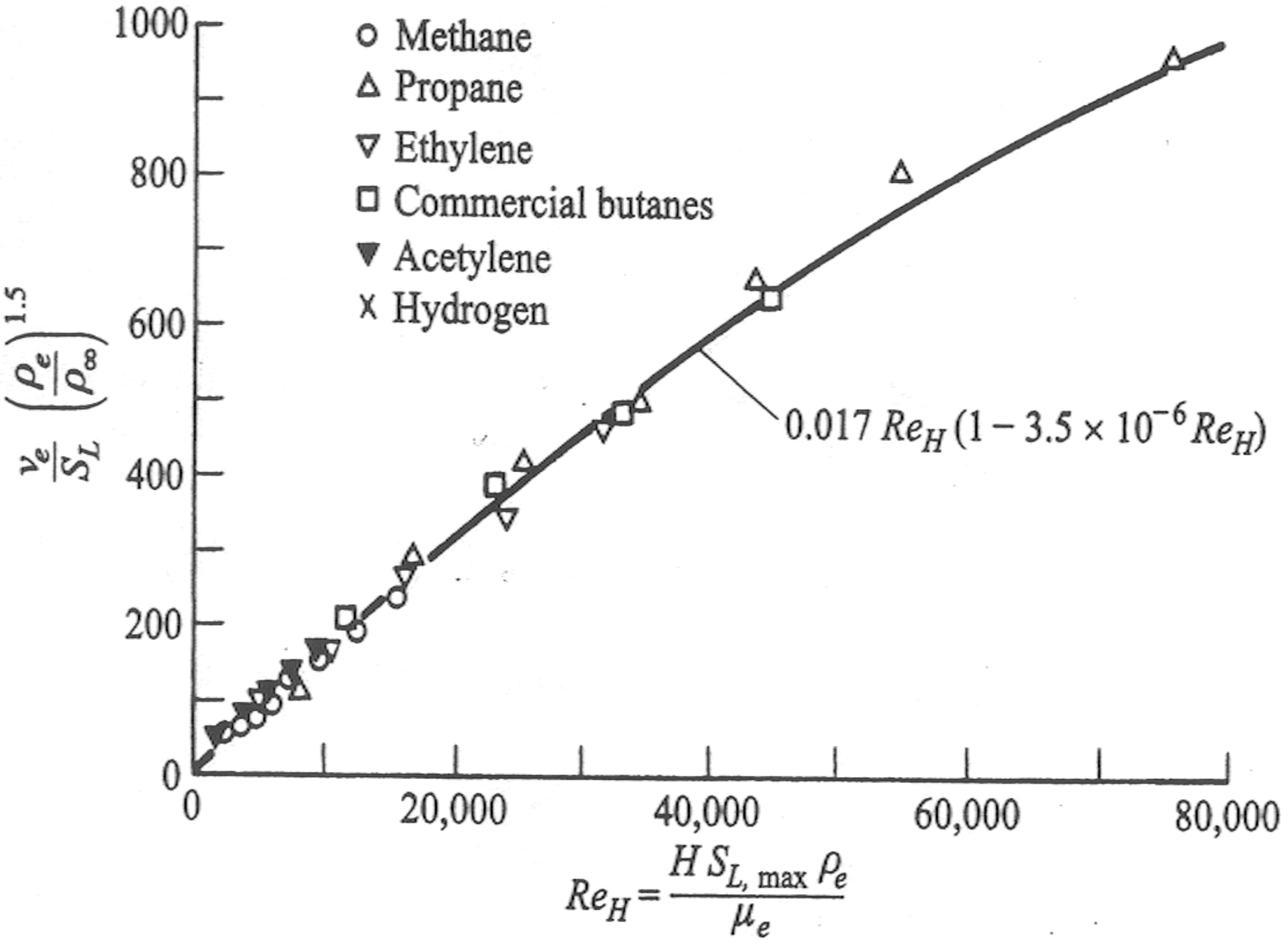
where the Reynolds number, $\mathrm{Re_H}$ is defined as:

$$\mathrm{Re_H} = \frac{\rho_e S_{L,max} H}{\mu_e} \qquad (11)$$

- The characteristic length, H, is the distance along the burner axis where the mean fuel concentration has decreased to its stoichiometric value and can be estimated by:

$$H = 4\left[\frac{Y_{F,e}}{Y_{F,st}}\left(\frac{\rho_e}{\rho_\infty}\right)^{1/2} - 5.8\right]d_j \qquad (12)$$

- The following figure demonstrates the applicability of Eq.(10) to a wide range of fuels.



Universal blowout stability curve.

10. Combustion Engines

Introduction

- This section will address the basic features and operating principles of practical combustion systems, mainly *internal combustion engines*, predominantly used for propulsion.
- *External combustion engines* will be described, but will not be discussed.
- The distinction between internal and external combustion engines is dependent on the nature of the *working fluid*.

- *Working fluid*, as the name implies,
  - produces work by pushing on a piston or turbine blade that in turn rotates a shaft, or
  - works as a high momentum fluid that is used directly for the propulsive force.
- In *internal combustion engines*, the energy source is a combustible mixture, and the combustion products is the working fluid.
- In *external combustion engines*, the combustion products is used to heat a second fluid that acts as the working fluid.

- With this definition, these are the most common internal combustion engines:
    - *Gasoline engines* (also known as spark-ignition, SI): homogeneous/stratified charge.
    - *Diesel engines* (also known as compression-ignition, CI, engines).
    - *HCCI engines* (homogeneous charge compression ignition): currently under-development.
    - *Gas turbine engines*: aircraft propulsion; stationary power production.
    - *Chemical rockets*.

- Examples of external combustion engines:
    - Steam power plants.
    - Home heating furnaces fuelled by gas or oil.
    - Stirling engines.
- What kind of engines are the following?
    - Solar power plant.
    - Nuclear power plant.
    - Fuel cells.
    - Electrical rocket propulsion.

Internal Combustion Engines

- *Steady Flow* internal combustion engines:
  - Gas Turbine
  - Ramjet / Scramjet
  - Chemical Rockets
- *Non-steady Flow* internal combustion engines:
  - Non-premixed charge
  - Premixed charge
  - Stratified charge

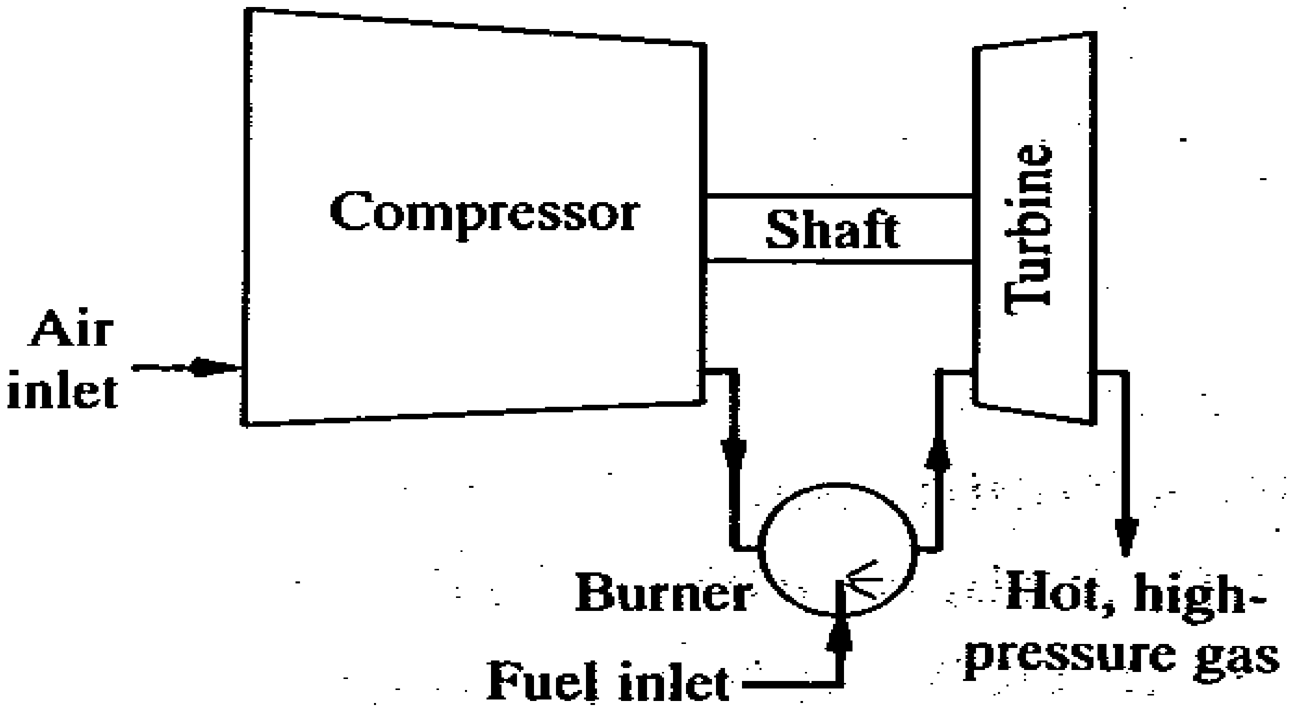
INTERNAL COMBUSTION ENGINES	**STEADY FLOW**	**GAS TURBINE**	TURBOJET	ALL JET EXCEPT FOR WORK NEEDED TO DRIVE COMPRESSOR
			TURBOFAN TURBOPROP	PART JET, PART SHAFT WORK TO DRIVE A FAN/PROPELLER
			TURBOSHAFT	ALL SHAFT WORK TO DRIVE PROPELLER. GENERATOR, OR ROTOR
		RAMJET **SCRAMJET**	NO COMPRESSOR OR TURBINE; USES HIGH MACH NUMBER RAM EFFECT FOR COMPRESSION	
		CHEMICAL ROCKETS	SOLID FUEL	FUEL AND OXIDANT ARE PREMIXED AND PLACED IN CHAMBER
			LIQUID FUEL	FUEL AND OXIDANT ARE PUMPED SEPARATELY TO BE MIXED IN CHAMBER
	NON-STEADY FLOW	**PREMIXED CHARGE**	GASOLINE/ GAS ENGINE	HOMOGENEOUS CHARGE SPARK IGNITION ENGINE
			HCCI ENGINE	HOMOGENEOUS CHARGE COMPRESSION IGNITION ENGINE
		NON-PREMIXED CHARGE	NON-PREMIXED CHARGE, ONLY AIR IS COMPRESSED; FUEL IS INJECTED INTO CYLINDER; COMPRESSION IGNITION (DIESEL), SPARK IGNITION (DISI)	
		STRATIFIED CHARGE	PARTIALLY-PREMIXED CHARGE; EQUIVALENCE RATIO CHANGES SPATIALLY (DISI)	

Gas Turbine Engines

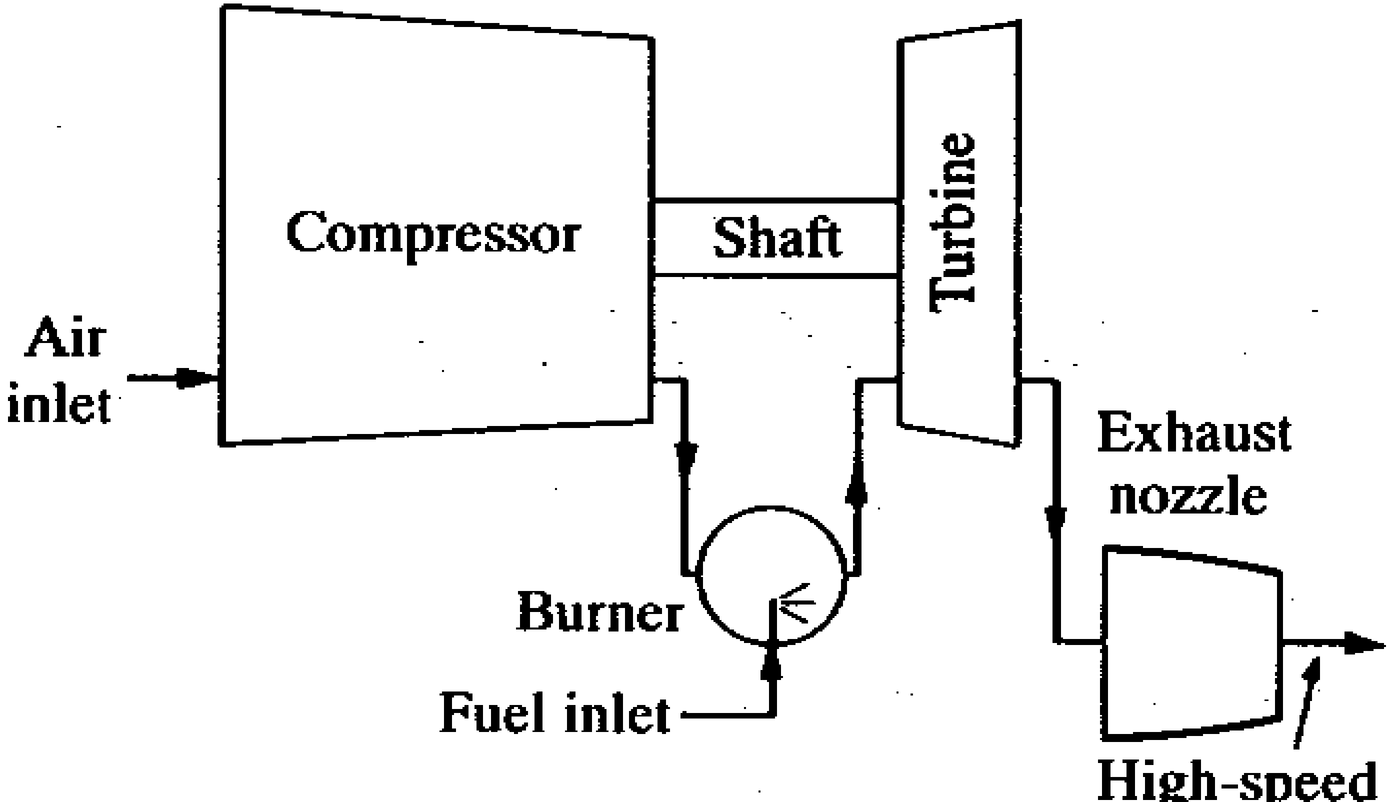
- Aircraft Jet Engines:
  - *Turbojet engines*: all jet except for work needed for the turbine that drives the compressor.
  - *Turbofan engines*: part jet, part shaft work to drive a fan (in addition to the compressor). The fan privides about 5-6 times more air passing around the engine core.

  - *Turboprop engines*: same as turbofan, but the rate of airflow through the propeller may be 25 to 30 times the airflow through the core engine.

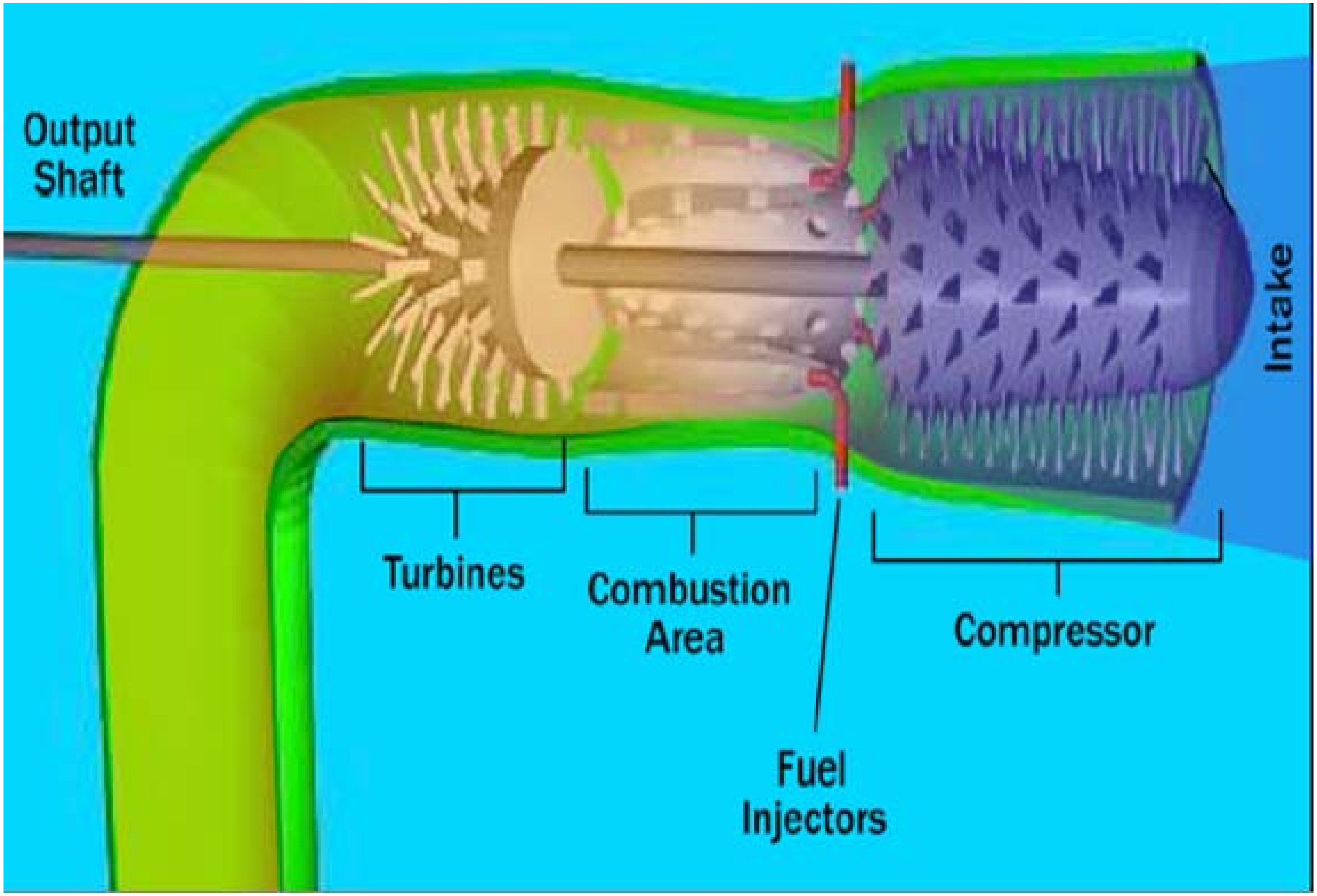
- Turboshaft Engines:
  - Industrial stationary engines used for power production: electricity generation; to drive a pump.
  - To drive a rotor (helicopter), or to drive a ship's propeller.



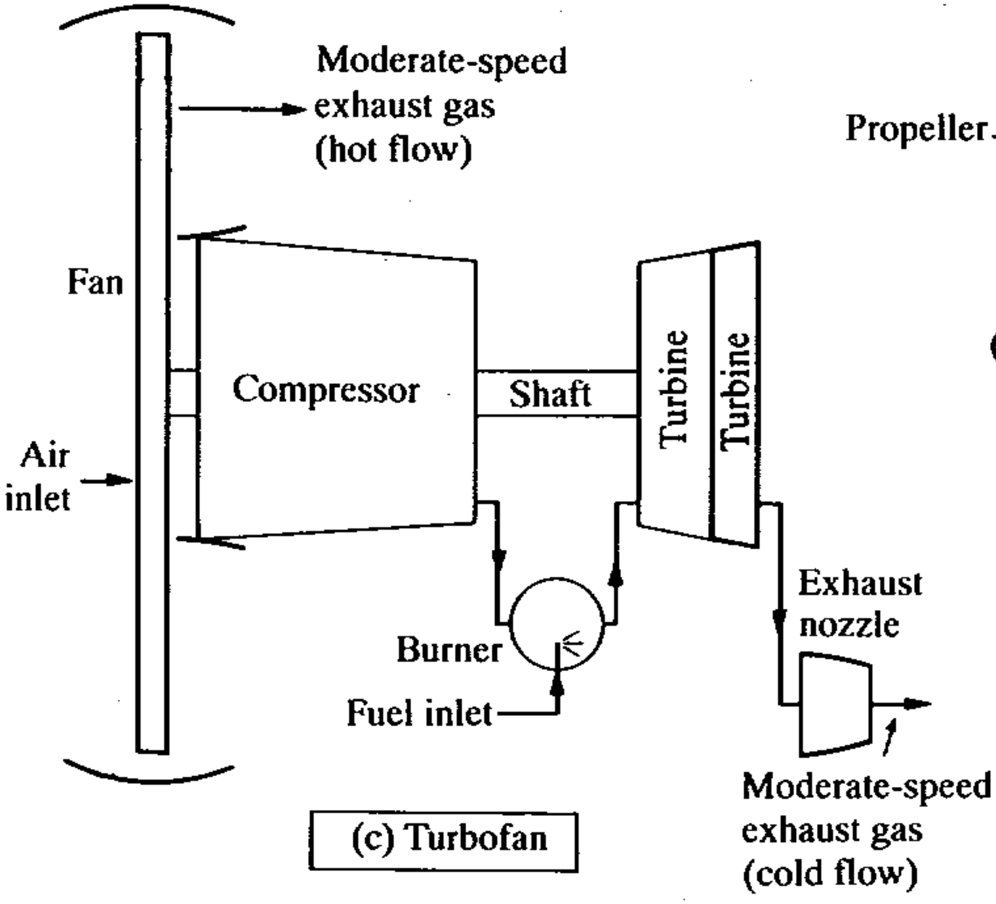
(a) Basic gas generator


Compressor
Shaft
Turbine
Air inlet
Exhaust nozzle
Burner
Fuel inlet
High-speed exhaust gas

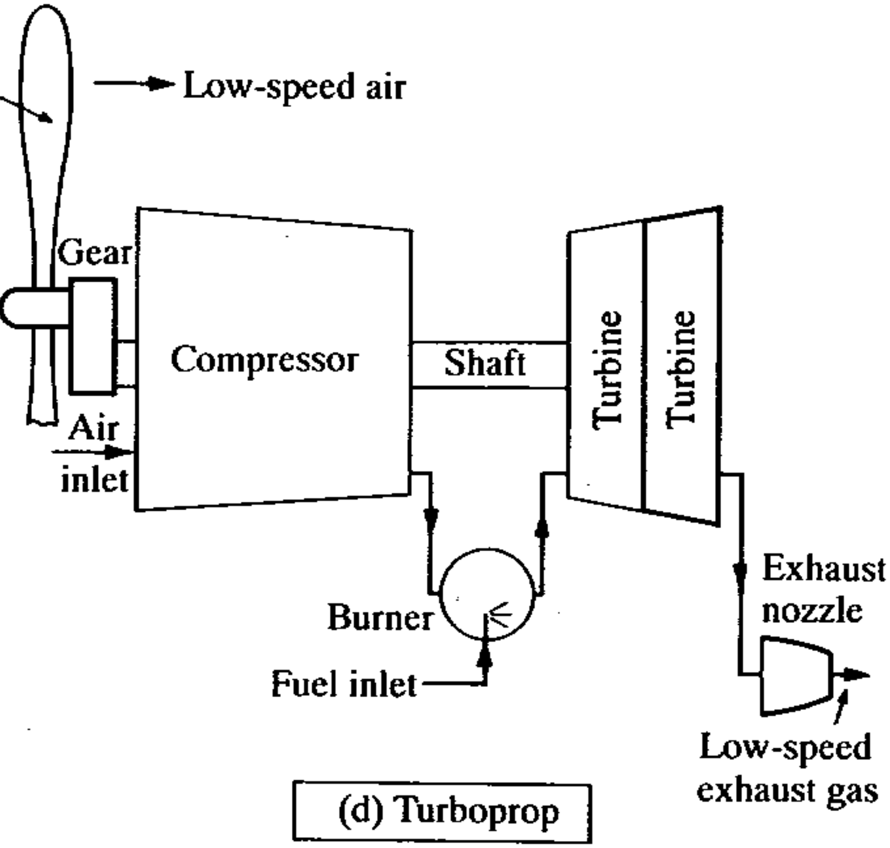
(b) Turbojet



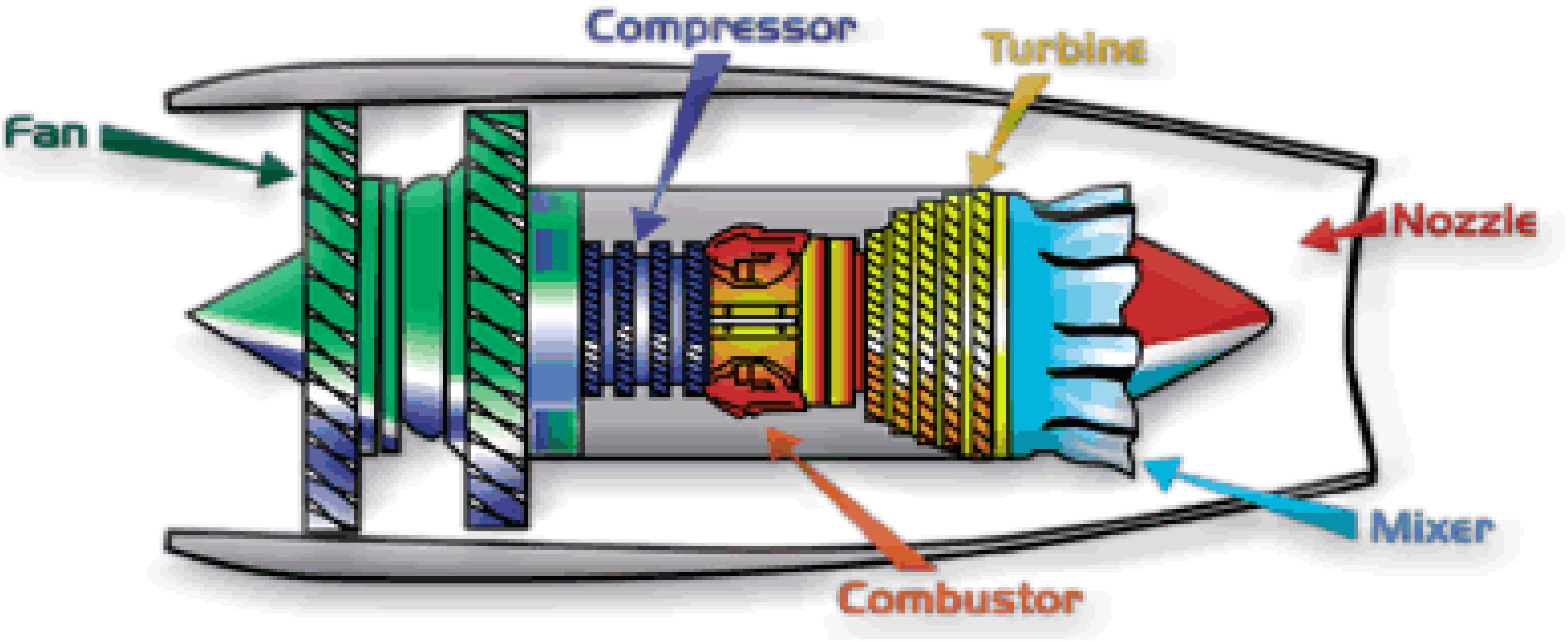
Turboshaft engine.



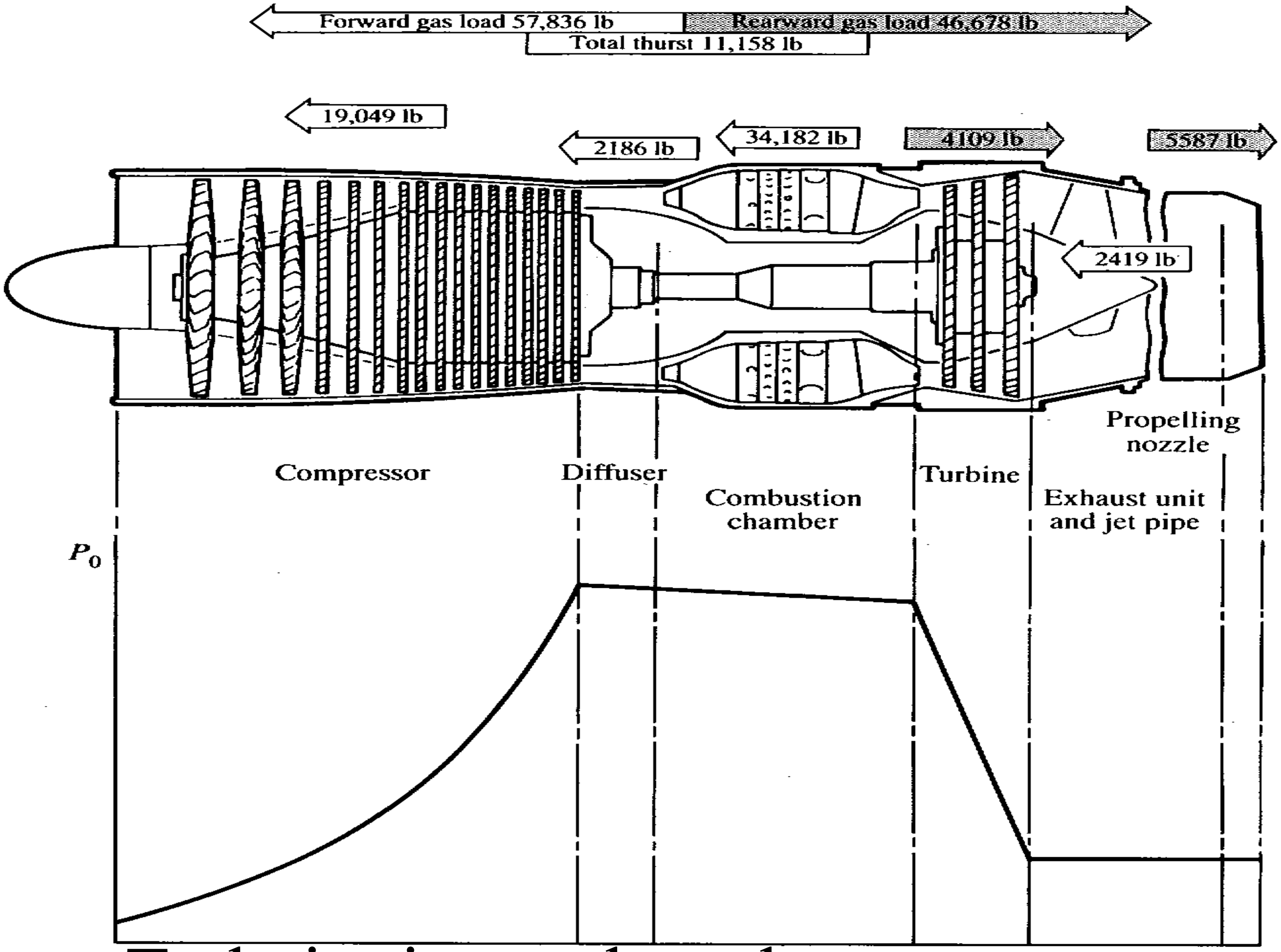
(c) Turbofan



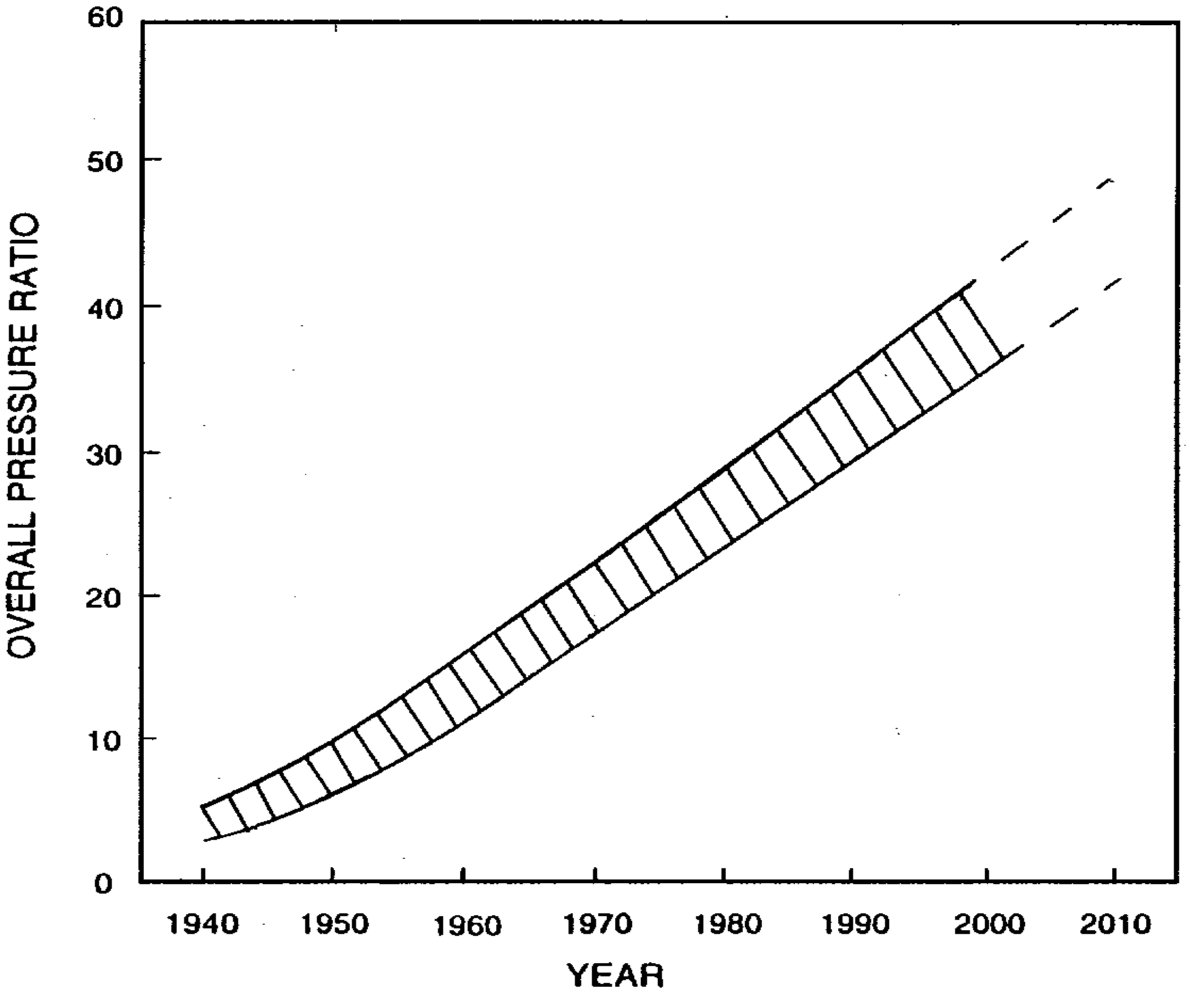
(d) Turboprop



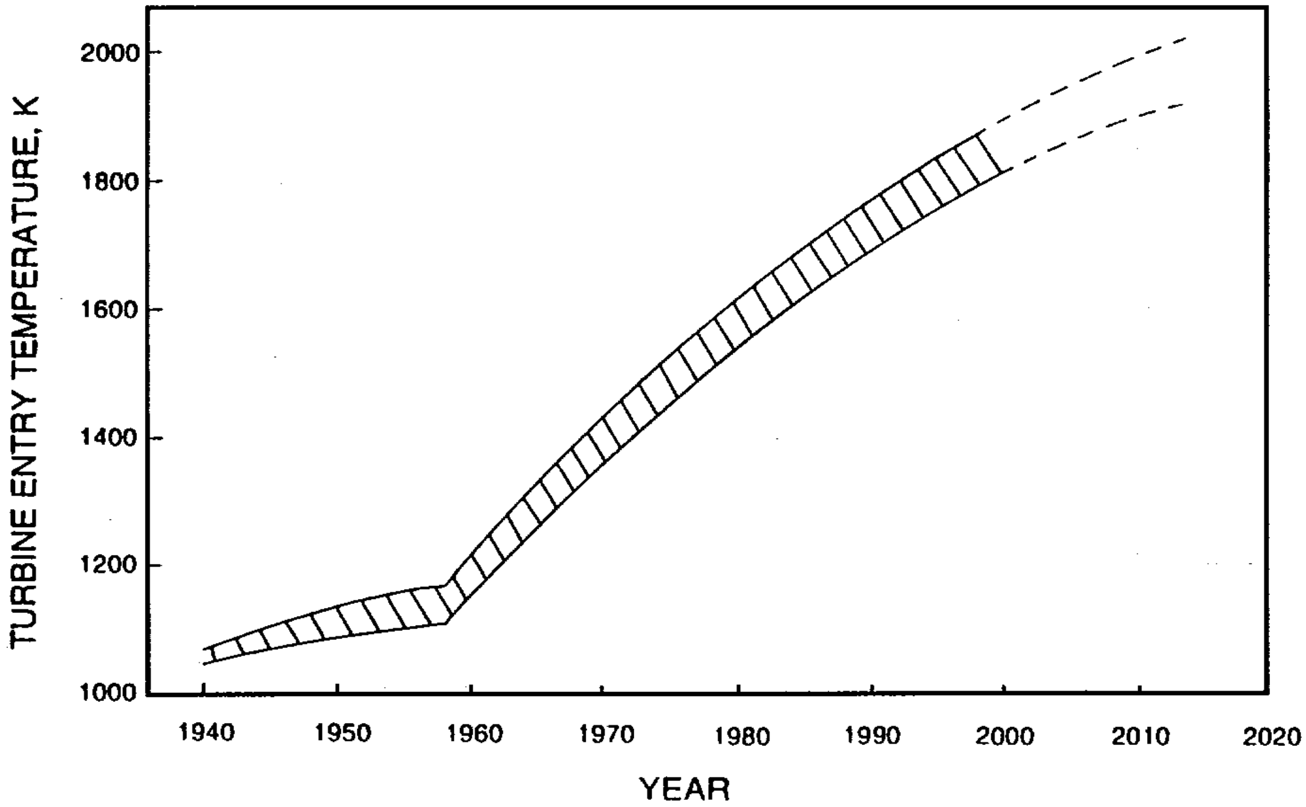
Turbofan engine.



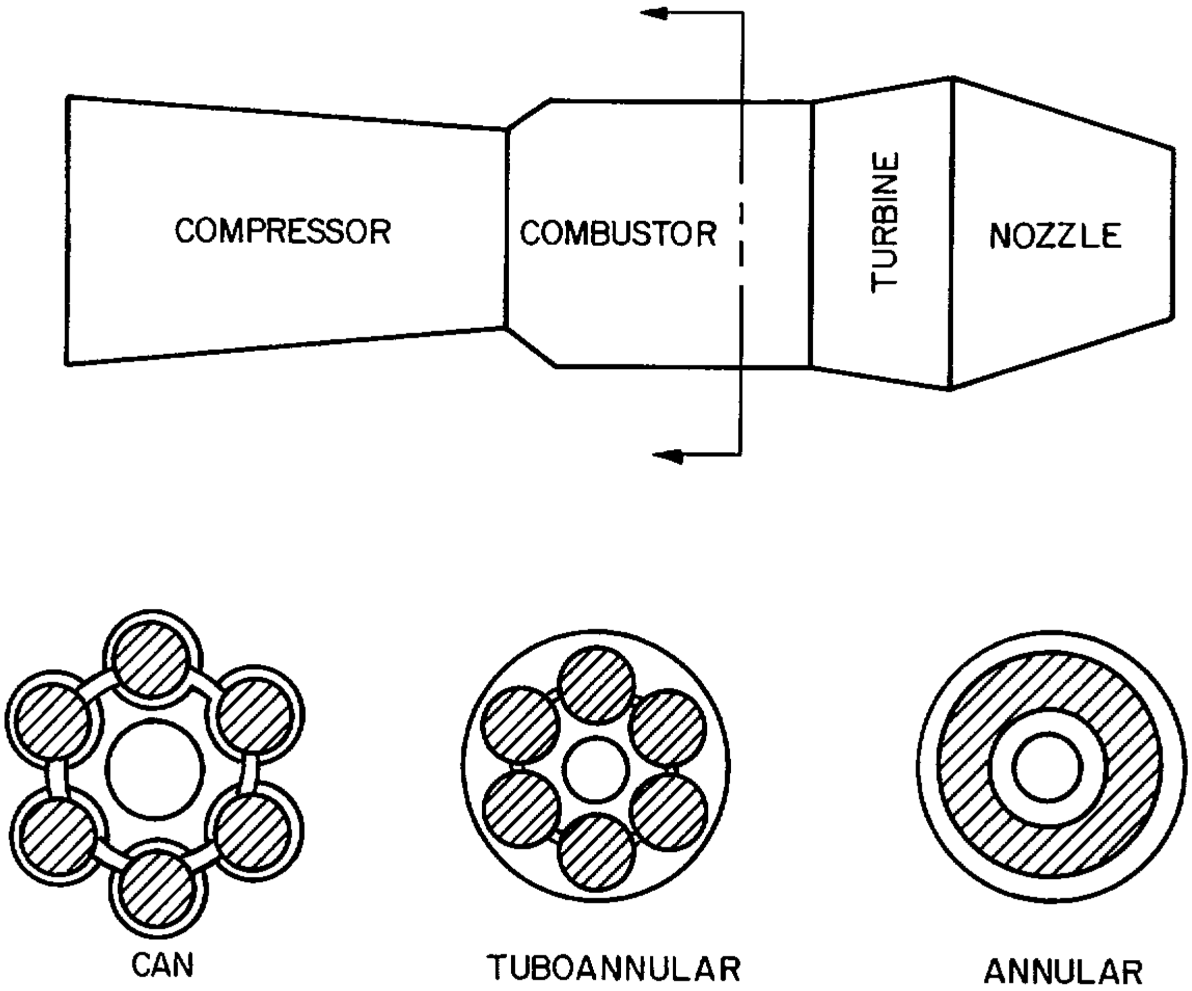
Turbojet internal total pressure.



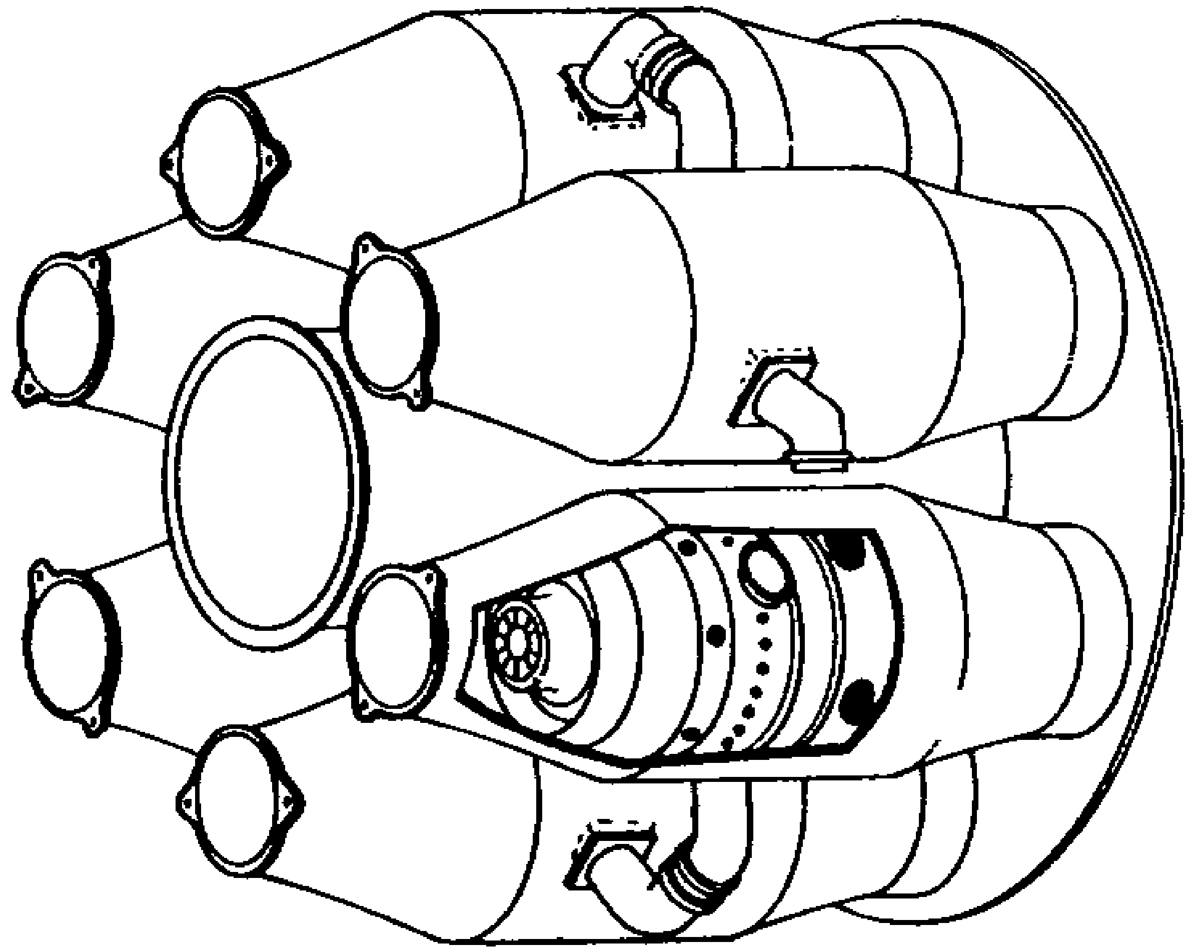
Historical trend of engine pressure ratio.



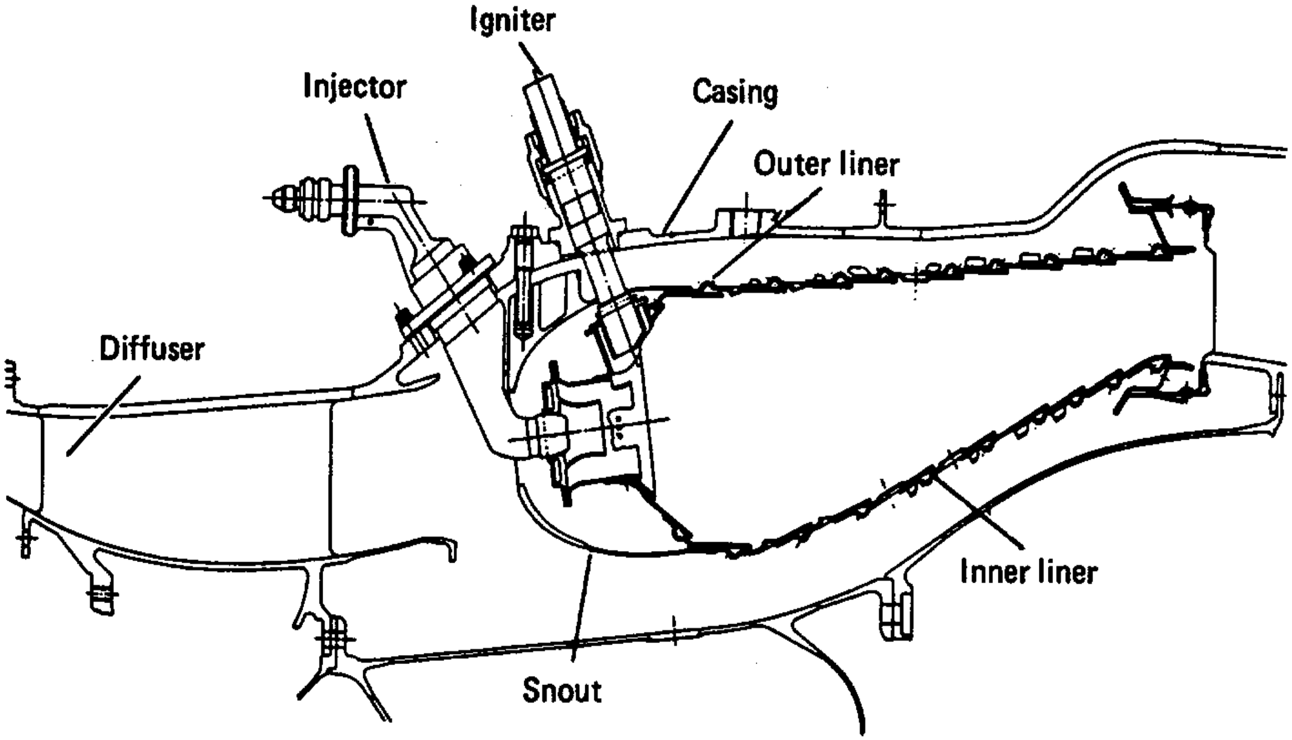
Historical trend of turbine entry temperature.



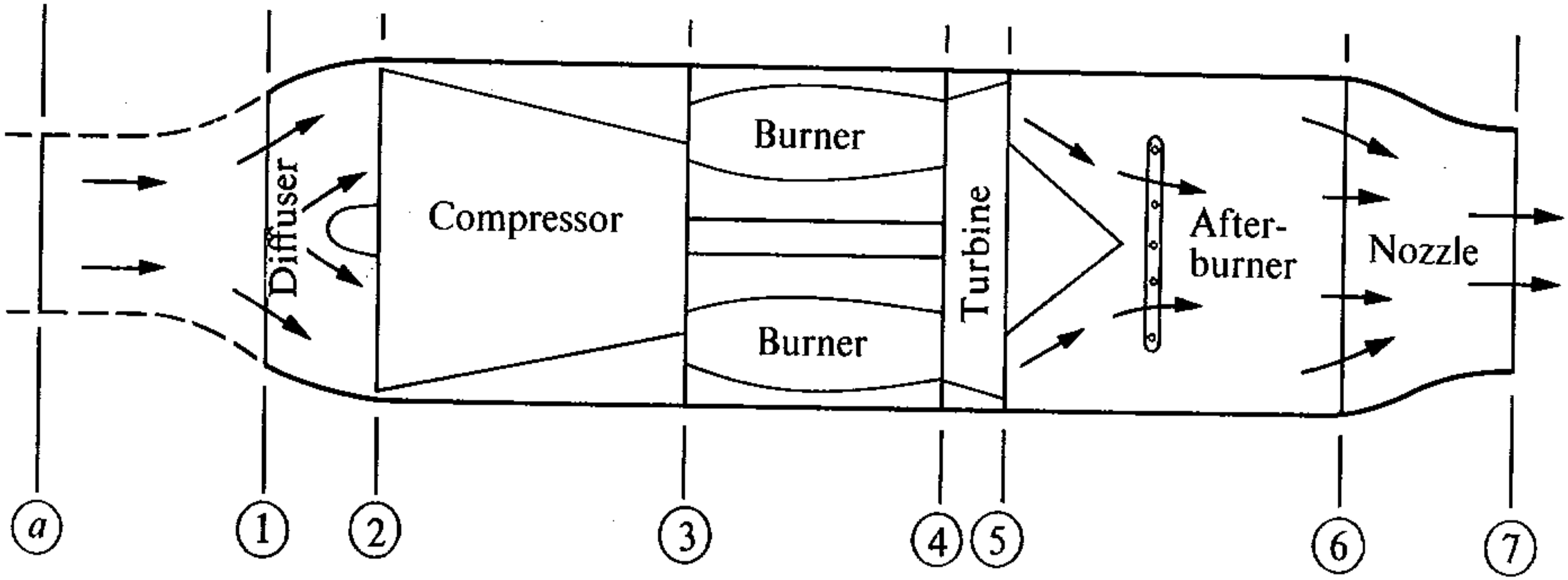
Three main combustor types.



Multi-can combustor arrangement.



Annular Combustor.



Schematic of a turbojet with afterburner.

Combustion in Gas Turbines:

- Spray combustion (liquid fuels)
- Ignition
- Flame stability - combustion noise
- Flame propagation
- Pollutant formation [CO, unburned HC, NO_x, soot]
- Heat transfer
- Cooling / dilution

Current Combustion Problems in Gas Turbines:

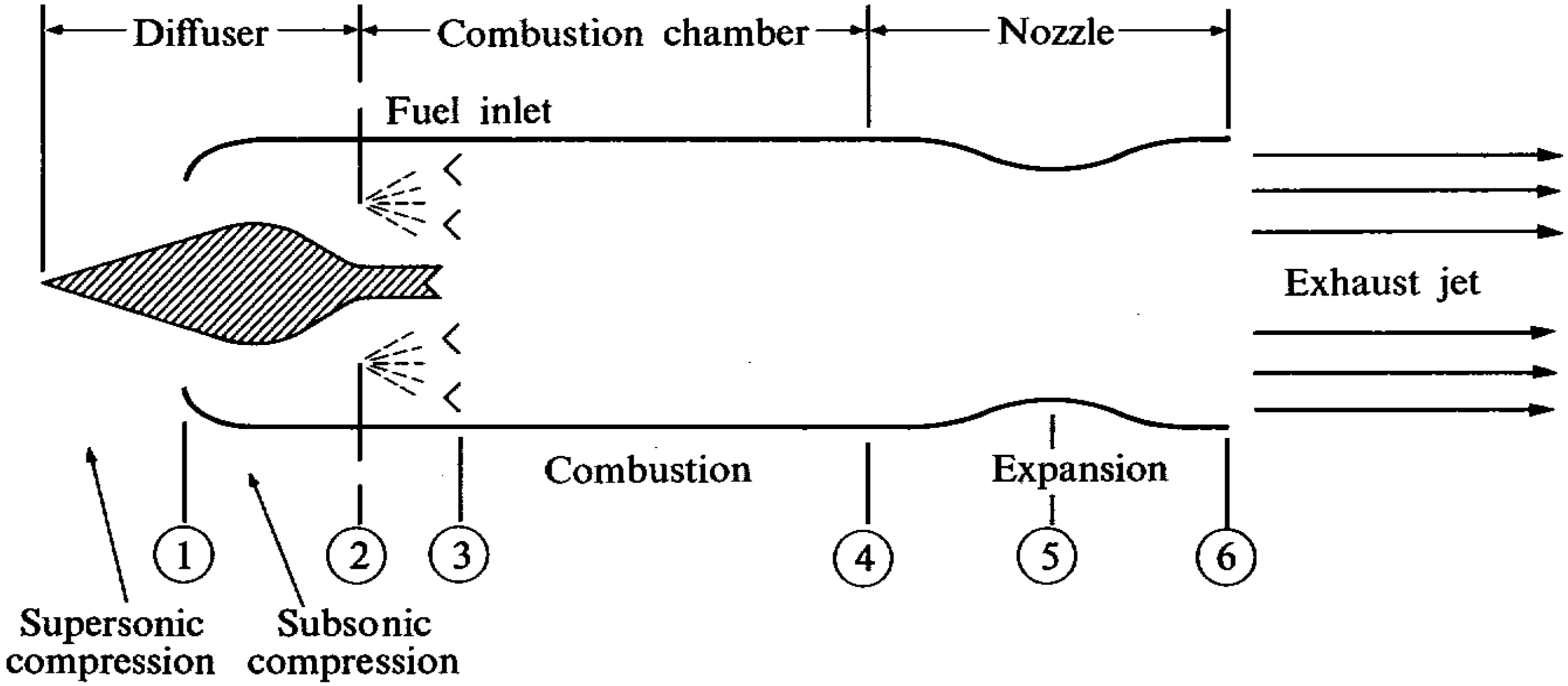
- NO_x control
- Combustion noise (hooting)
- Soot formation (carbon formation)
- Fidelity of CFD of combustion codes

Current Combustion Developments in Gas Turbines:

- Lean-premixed combustion [NO_x control, soot]
- Hydrogen-enrichment [NO_x, efficiency]
- Higher pressure ratios [efficiency]

Ramjets

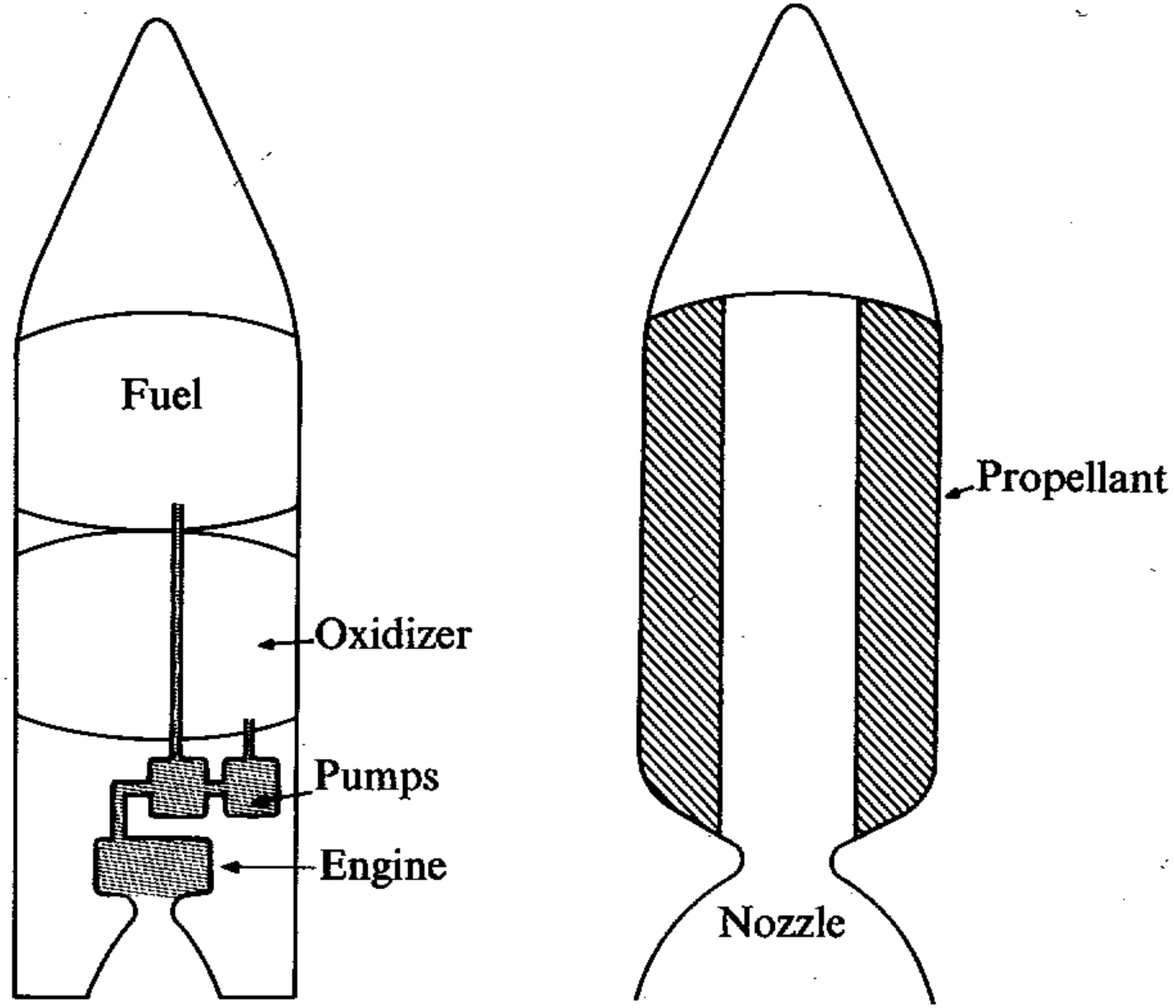
- Simplest of air-breathing engines.
- A diffuser, a combustion chamber, and an exhaust nozzle.
- Most suitable for supersonic speeds.
- Compression by ram effect.
- Fuel injection into compressed flow - flame holders to stabilize flame.
- Combustion gases expand to high velocity in the nozzle.



Schematic diagram of a ramjet engine.

Chemical Rockets

- ***Liquid Fuel Rockets:*** Fuel and oxidizer are stored in separate thin-walled tanks at low pressure. Before combustion, they pass through turbine-driven pumps and are injected to combustion chamber, where they burn at high pressure.
- ***Solid Fuel Rockets:*** Entrire block of propellant (consisting of premixed fuel and oxidizer) stored within the combustion chamber. Combustion proceeds from the surface of the propellant *grain* at a rate that depends on pressure and temperature and geometry of the burning surface.

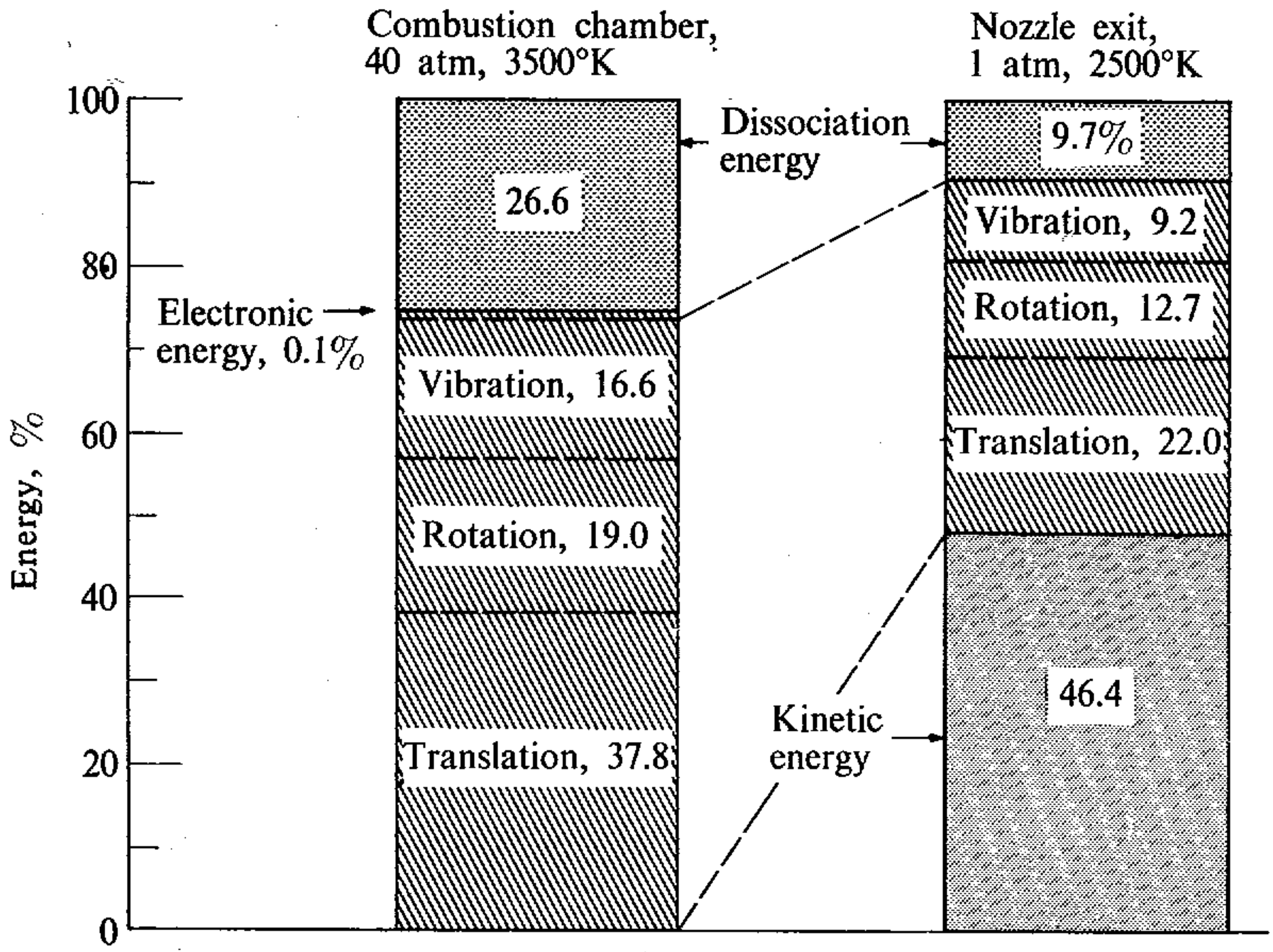


(a) Bipropellant liquid rocket (b) Solid-propellant rocket

Schematic diagram of a rocket engines.

Nonequilibrium expansion:

- Equilibrium composition depends on pressure and temperature, for given fuel and Φ, and may include large quantities of dissociated material.
- In the exhaust nozzle dissociated compounds tend to recombine because of temperature drop.
- This exothermic recombination reactions may act as a heat source in the flow.
- Following Fig. illustrates relative importance of dissociation energies before and after an equilibrium expansion of a stoichiometric H_2-O_2 mixture.


Combustion chamber,
40 atm, 3500°K
Nozzle exit,
1 atm, 2500°K
100
80
60
40
20
0
Energy, %
26.6
Dissociation energy
9.7%
Electronic energy, 0.1%
Vibration, 16.6
Rotation, 19.0
Translation, 37.8
Vibration, 9.2
Rotation, 12.7
Translation, 22.0
46.4
Kinetic energy

- For products to maintain their equilibrium composition as they expand, recombination reactions should be fast enough to keep pace with rapid expansion.
- Since expansion process is very rapid, this condition is not always met.
- In the limit, i.e. $\tau_{\rm recomb} >> \tau_{\rm expan}$

  we have *frozen* flow at constant composition.
- Difference between equilibrium and frozen flow can be appreciable for some propellants.

Current Combustion Problems in Rockets:

- ***Combustion Instabilities:*** Both liquid- and solid-propellant rockets are subject to combustion instabilities in the form of large pressure oscillations within the chamber that may lead to engine failure.
- Low-frequency oscillations (about 100 Hz) due to coupling between combustion and feed system.
- High-frequency oscillations (several thousand Hz): thermo-acoustics, i.e., coupling between combustion and acoustics (and flow field).

- In solid-propellant rockets, burning rate is very sensitive to pressure and velocity.
- Energy release and propellant velocity or pressure pattern that causes nonuniformity can interact to produce sustained oscillations.
- Such oscillations lead to high rates of erosive burning that may change the chamber geometry to stable burning or may lead to engine failure.
- ***Burning rate of solid propellants***
- ***Atomization/mixing*** in liquid-propellant rockets.

Assignment

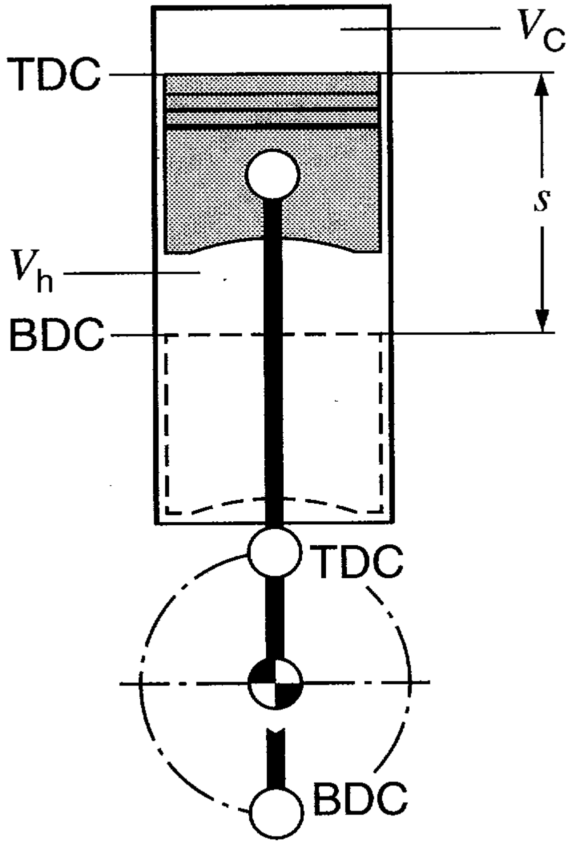
- Visit www.howstuffworks.com and read:
  - How car engines work?
  - How gas turbine engines work?
  - How rockets work?
- From links, visit sites related to gas turbines and rocket propulsion.

Spark-Ignition & Compression-Ignition Engines

- In our formal definition of ***internal combustion engines***, we included the gas turbines and rockets under this classification. Conventionally, however, the term ***internal combustion engines*** is used for spark-ignition and compression-ignition engines.
- Spark-ignition engines (Otto cycle engines, or gasoline engines, or petrol engines, though other fuels can be used).
- Compression-ignition engines (diesel engines and HCCI engines).

Principle of the reciprocating piston engine

TDC Top Dead Center, BDC Bottom Dead Center. V_h Stroke volume, V_C Compression volume, s Piston stroke.



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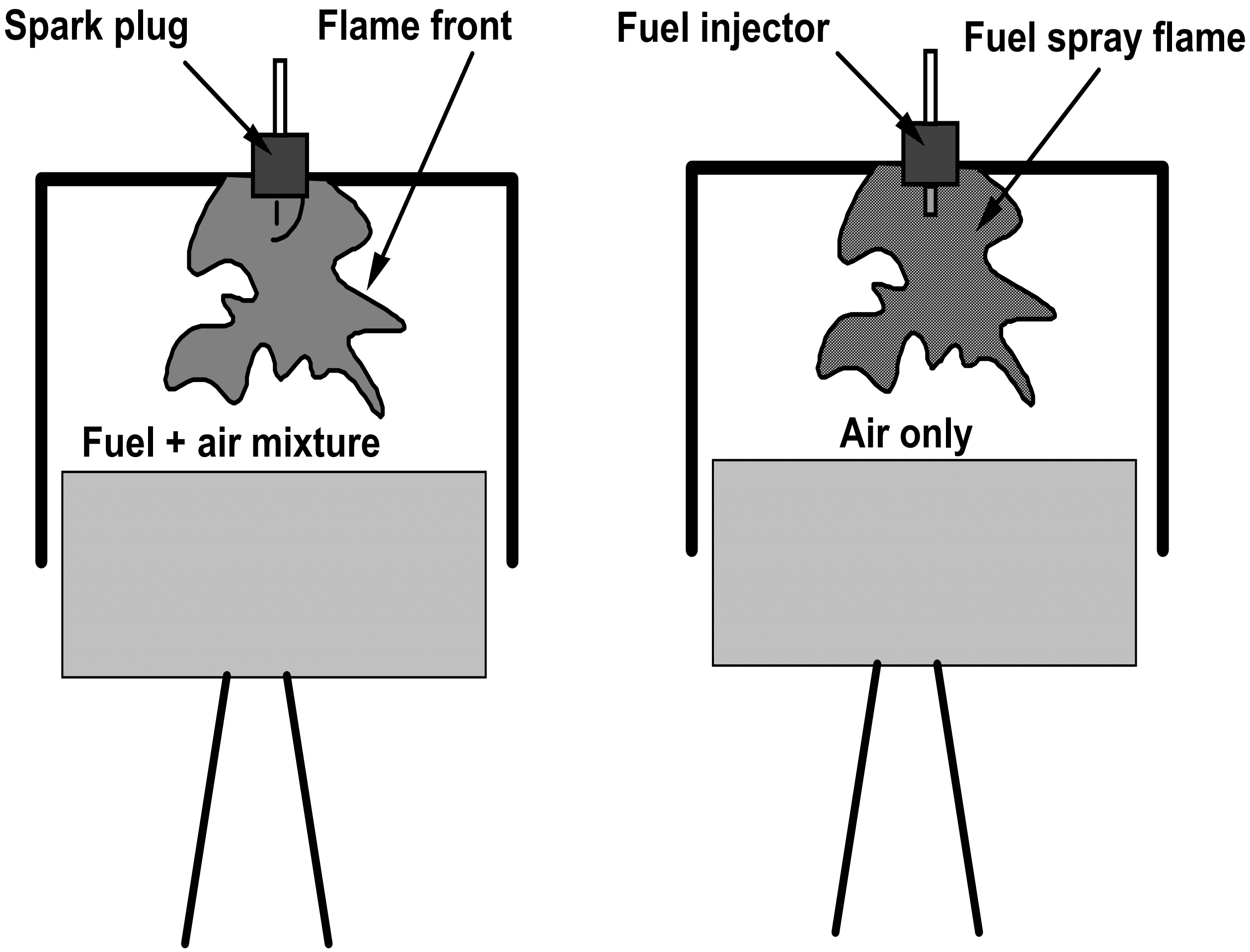
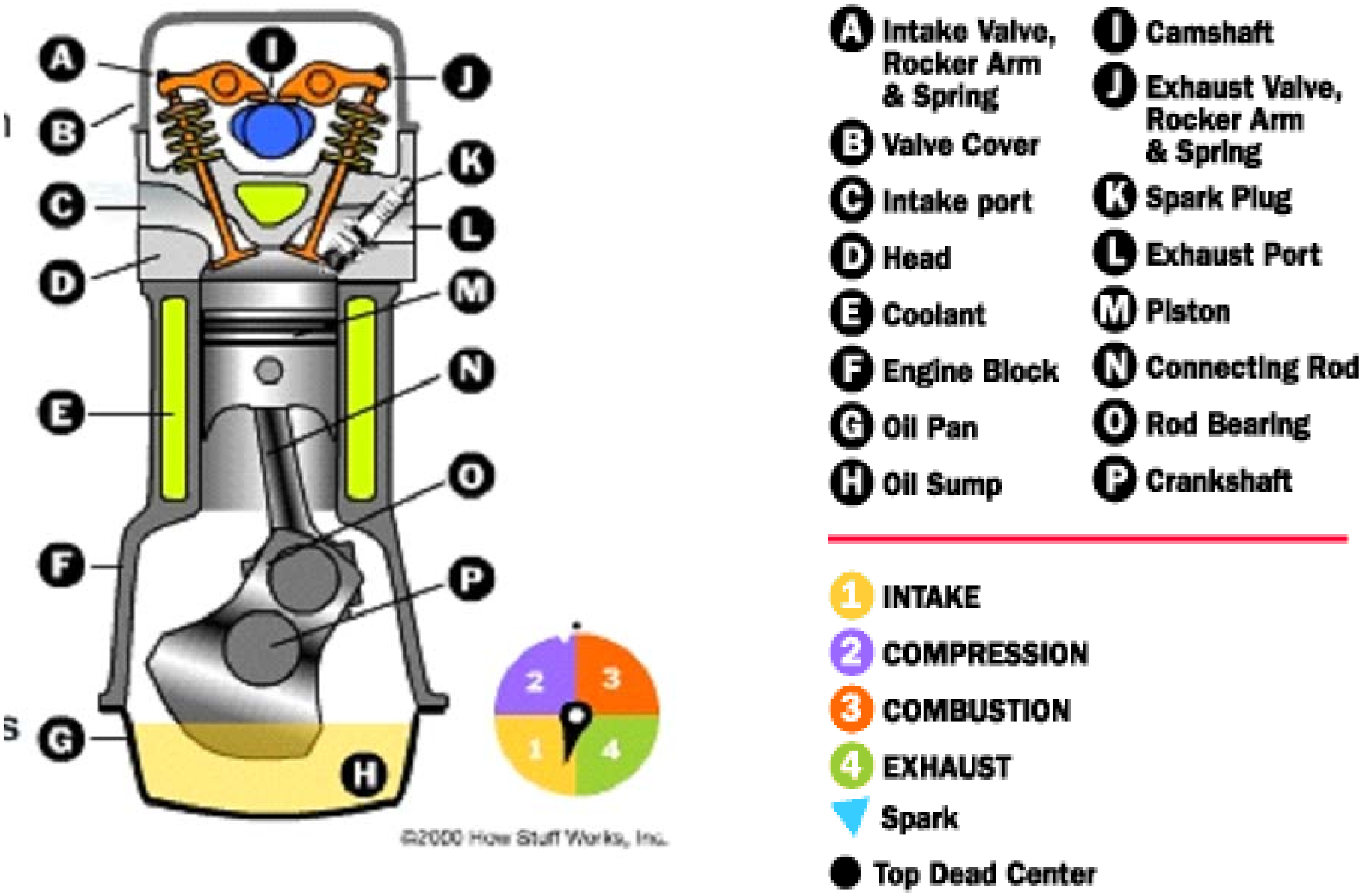


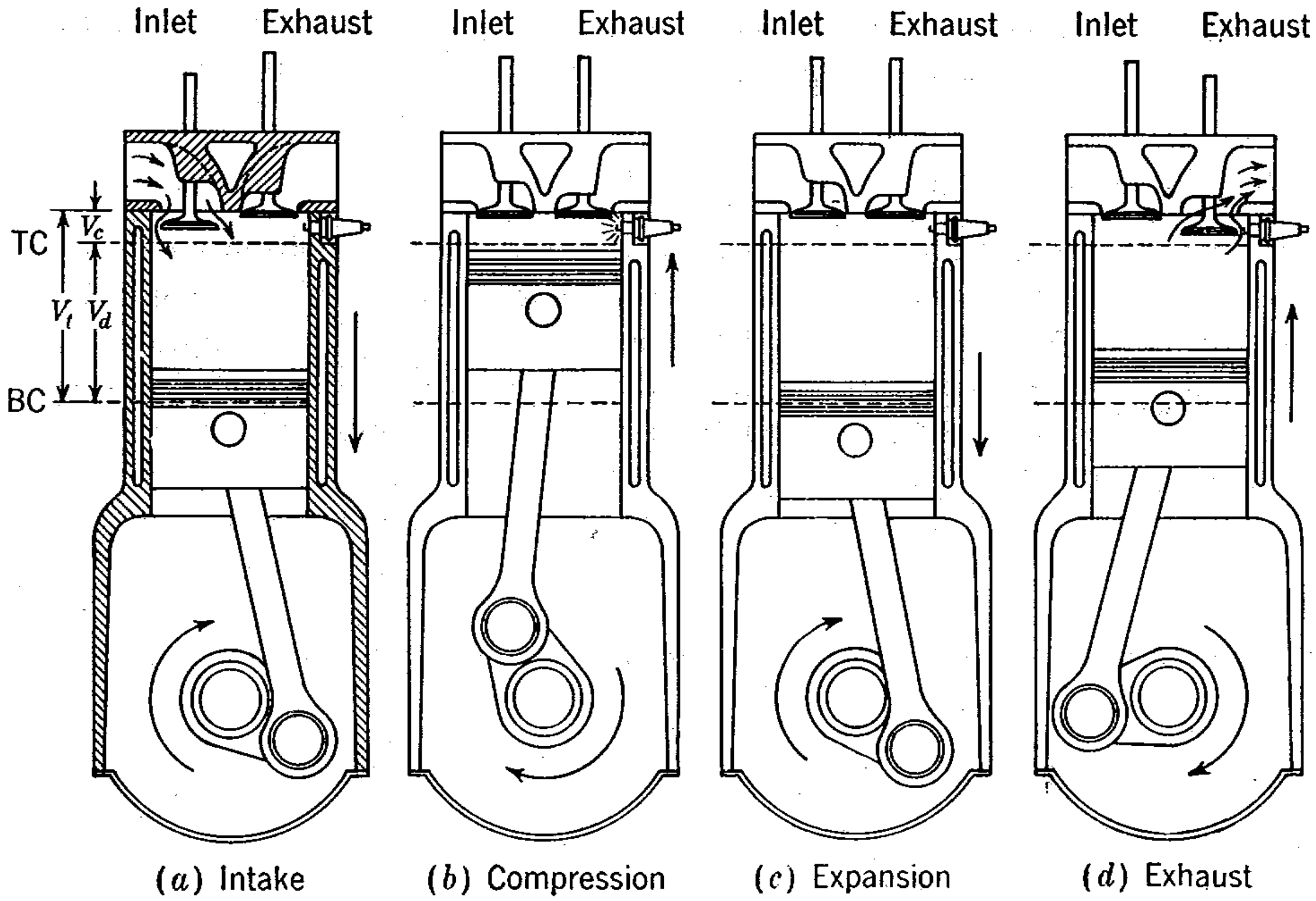
Premixed charge (gasoline)

Non-premixed charge (Diesel)

Schematics of SI and CI engines.



Schematic diagram of a gasoline engine.



Four-stroke SI engine operating cycle.

Four-stroke cycle SI engine:

- Majority of reciprocating engines operate as the *four-stroke cycle*.
- Each cylinder requires four strokes of its piston - two revolutions of the crankshaft - to complete sequence of events which produces one power stroke.
- Both SI and CI engines use this cycle.
- The four strokes are: *Intake, compression, power*, and *exhaust*.

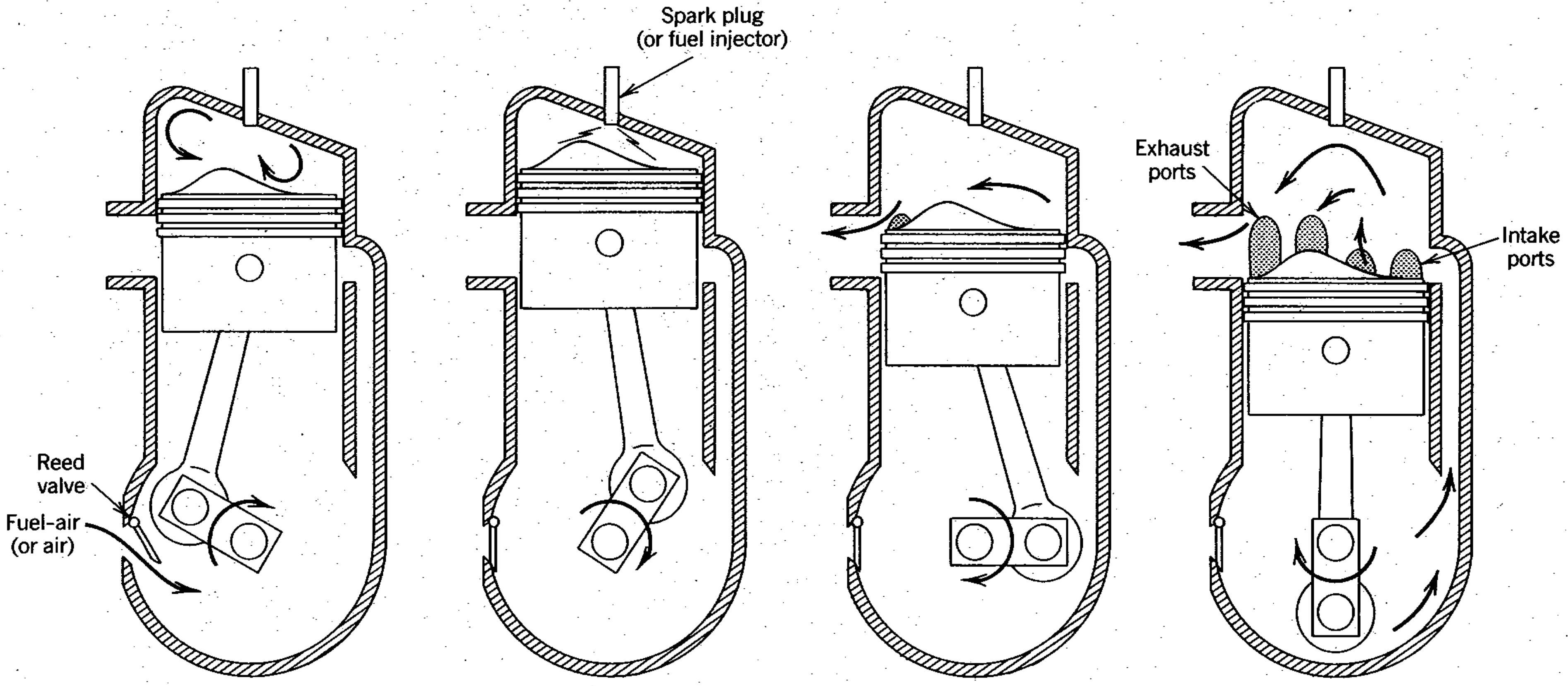
- Intake stroke: starts with piston at TC and ends with piston BC, which draw fresh mixture into cylinder. To increase mass inducted, inlet valve opens shortly before stroke starts and closes after it ends.
- Compression stroke: both valves are closed and the mixture inside the cylinder is compressed to a small fraction of its initial volume. Toward the end of the compression stroke, combustion is initiated and the cylinder pressure rises more rapidly.

- Power stroke: or expansion stroke:
  - starts with the piston at TC and ends at BC as the high-temp., high-pressure, gases push the piston down and force the crank to rotate.
  - About five times as much work is done on the piston during the power stroke as the piston had to do during compression.
  - As the piston approaches BC the exhaust valve opens to initiate the exhaust process and drop the cylinder pressure to close to the exhaust pressure.

- Exhaust stroke: where the remaining burned gases exit the cylinder:
  - first, because the cylinder pressure may be substantially higher than the exhaust pressure;
  - then as they are swept out by the piston as it moves toward TC.
  - As the piston approaches TC the inlet valve opens. Just after TC the exhaust valve closes and the cycle starts again.

Two-stroke cycle SI engine:

- The four-stroke cycle requires, for each engine cylinder, two crankshaft revolutions for each power stroke.
- To obtain a higher output from a given engine size, and a simpler valve design, the *two-stroke cycle* was developed.
- The two-stroke cycle (as four-stroke cycle) is applicable to both SI and CI engines.
- The two strokes are: *compression*, and *power* or *expansion*.



- Compression
- Ports closed
- Air inducted into crankcase

- Combustion, expansion
- Ports closed

- Exhaust
- Intake port closed

Air compressed in crankcase
(Reed valve shut)

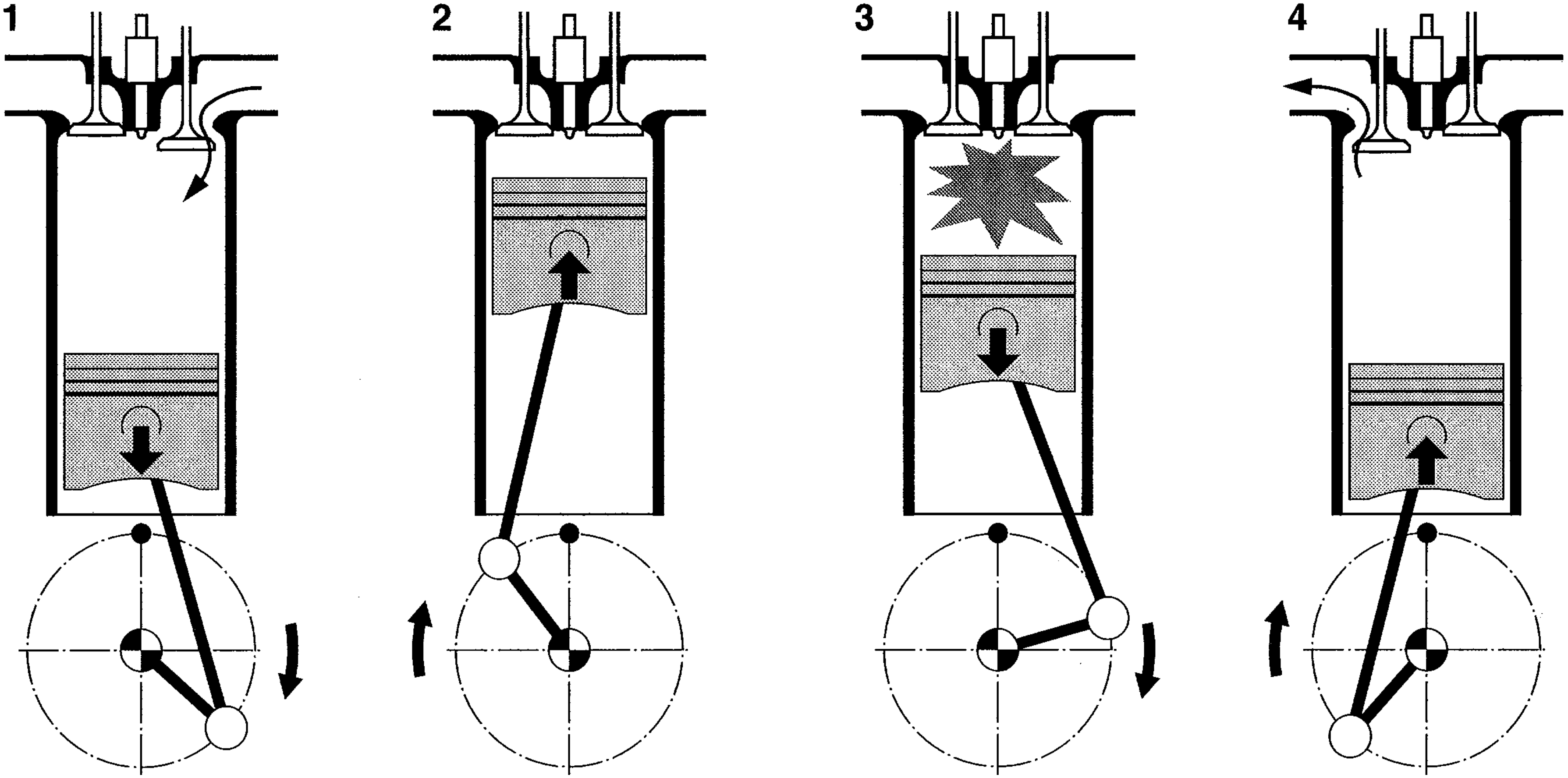
- Scavenging
- Intake
- Ports open
- Reed valve shut

Two-stroke engine operating cycle.

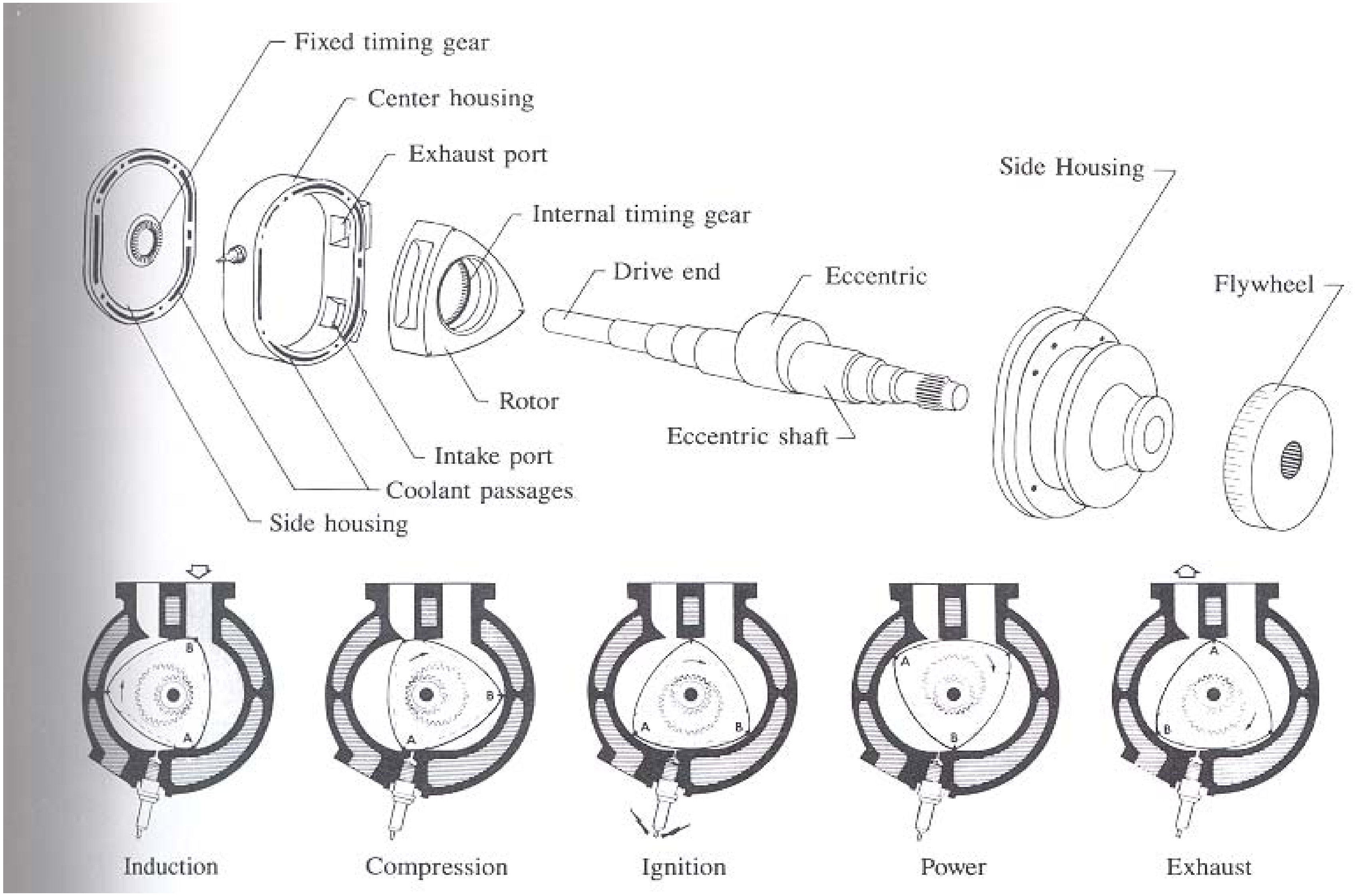
- <u>Compression stroke:</u> starts by closing the inlet and exhaust ports, and then compress the cylinder contents and draws fresh charge into crankcase. As the piston approaches TC, combustion is initiated.
- <u>Power or expansion stroke:</u> similar to that in four-stroke cycle until the piston approaches BC, when first the exhaust ports and then the intake ports are uncovered. Most of burned gases exit cylinder in an exhaust blowdown process. When inlet ports are uncovered, fresh charge which has been compressed in crankcase flows into cylinder.

4-stroke diesel engine

1 Induction stroke, **2** Compression stroke, **3** Power stroke, **4** Exhaust stroke.



Four-stroke CI engine operating cycle.



Wankel engine operating cycle.

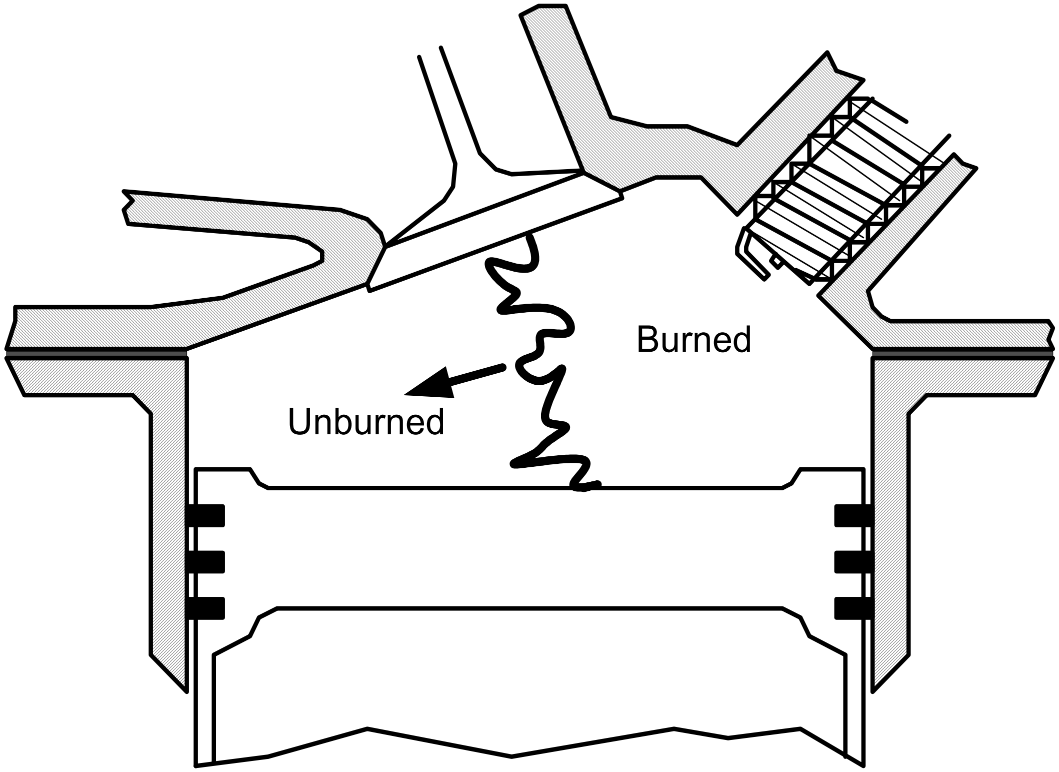
Wankel engine operation:

- Wankel rotary engine operates with the four-stroke cycle.
- As the rotor makes one complete rotation, the eccentric shaft rotates through three revolutions.
- As the rotor makes one rotation, each chamber produces one power stroke.
- Three power pulses occur for each rotor revolution; thus for each eccentric shaft revolution there is one power pulse.

Combustion in SI Engines:

- Mixture preparation:
  - Carburation (no longer used in North American markets).
  - Port injection - fuel is sprayed into the air stream just before the inlet valve.
  - Direct injection - fuel is injected into the cylinder (DISI).
- Ignition: spark plug.
- Flame kernel development and flame propagation.

- Engine knock:
    - Fuel *octane* number
    - Engine compression ratio
- Pollutant formation:
    - Nitric oxides, NO_x
    - Carbon dioxide, CO
    - Unburned hydrocarbons, HC
- Exhaust treatment:
    - Catalytic converters

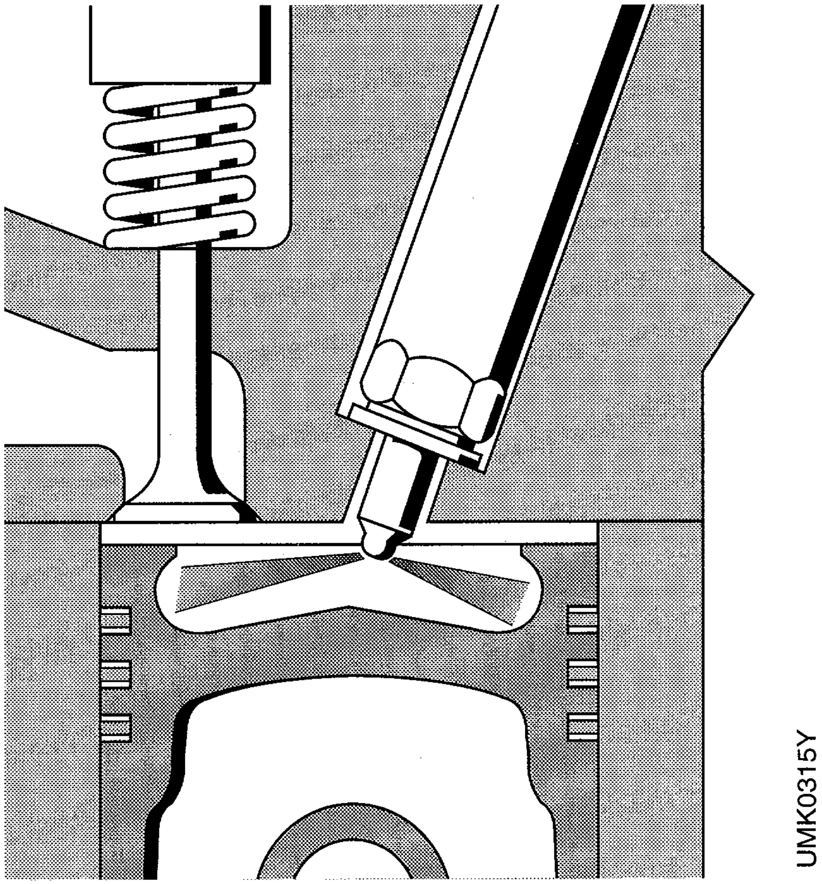


Cross-section of a gasoline engine combustion chamber.

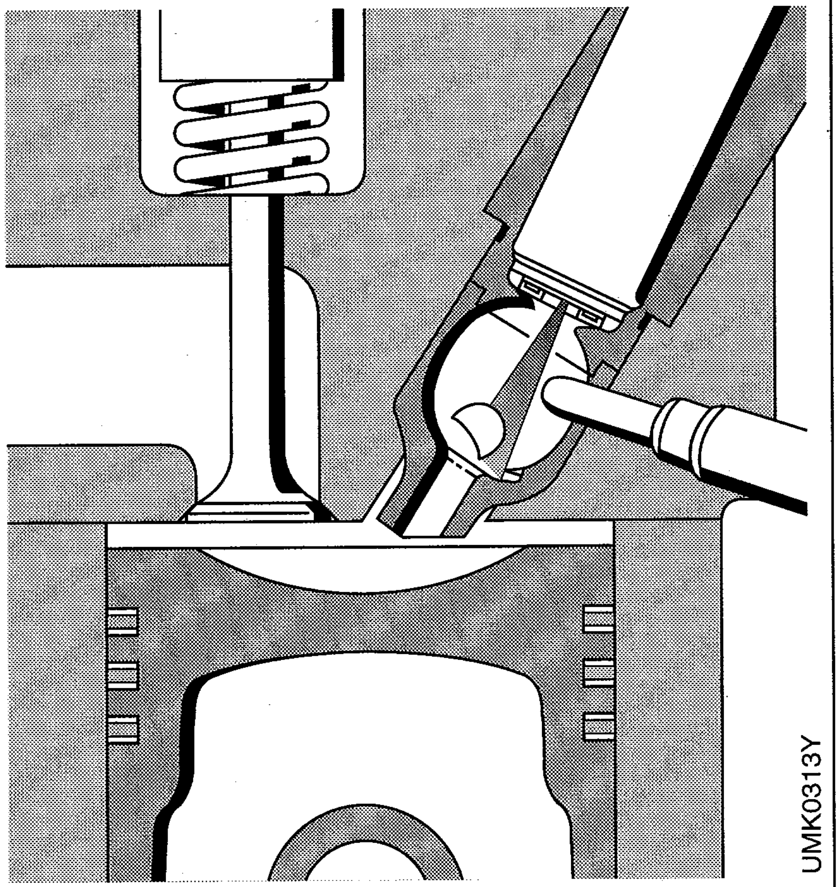
Combustion in a CI engine:

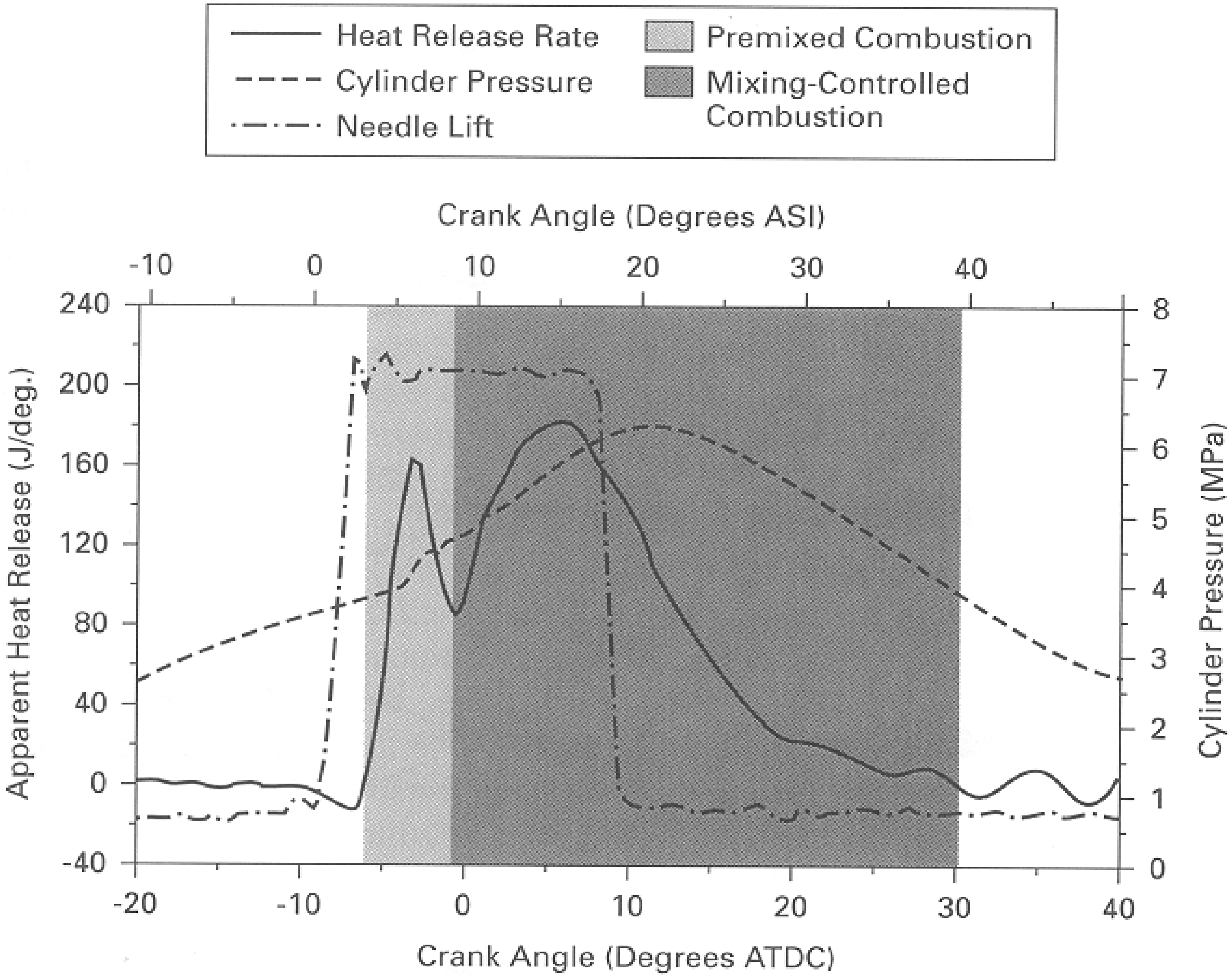
- Direct in-cylinder injection (large engines).
- Prechamber injection (passenger car engines).
- Spray combustion:
  - Compression ignition - ignition delay
  - Diesel fuel *cetane* number
- Pollutant formation:
  - NO_x, CO, HC, Soot (particulates)
- Particulate trap and catalytic converter.

Direct-injection (DI) process

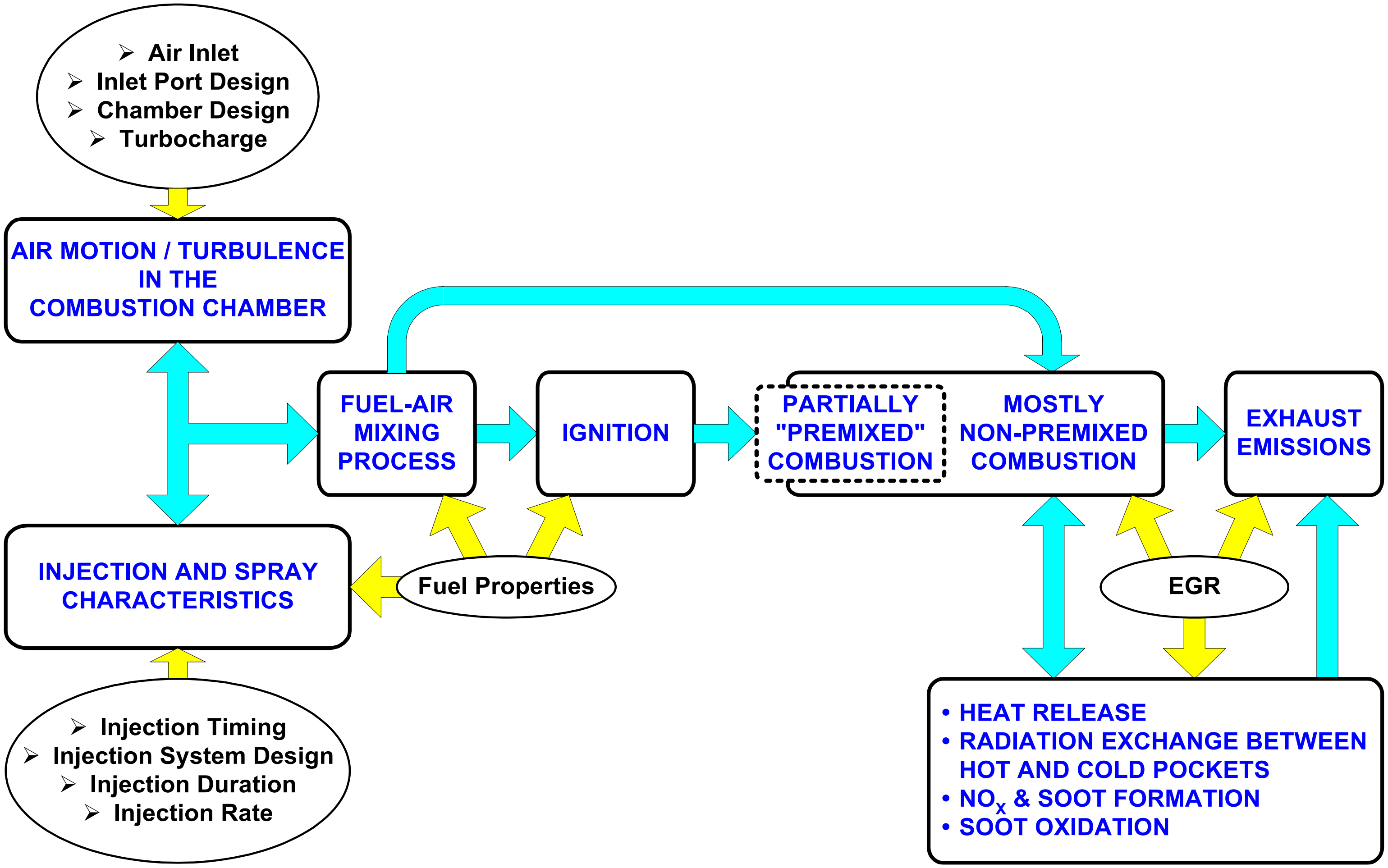


Prechamber process





Heat release in diesel engine combustion.



- Air Inlet
- Inlet Port Design
- Chamber Design
- Turbocharge

AIR MOTION / TURBULENCE IN THE COMBUSTION CHAMBER

FUEL-AIR MIXING PROCESS

IGNITION

PARTIALLY "PREMIXED" COMBUSTION

MOSTLY NON-PREMIXED COMBUSTION

EXHAUST EMISSIONS

INJECTION AND SPRAY CHARACTERISTICS

Fuel Properties

EGR

- Injection Timing
- Injection System Design
- Injection Duration
- Injection Rate

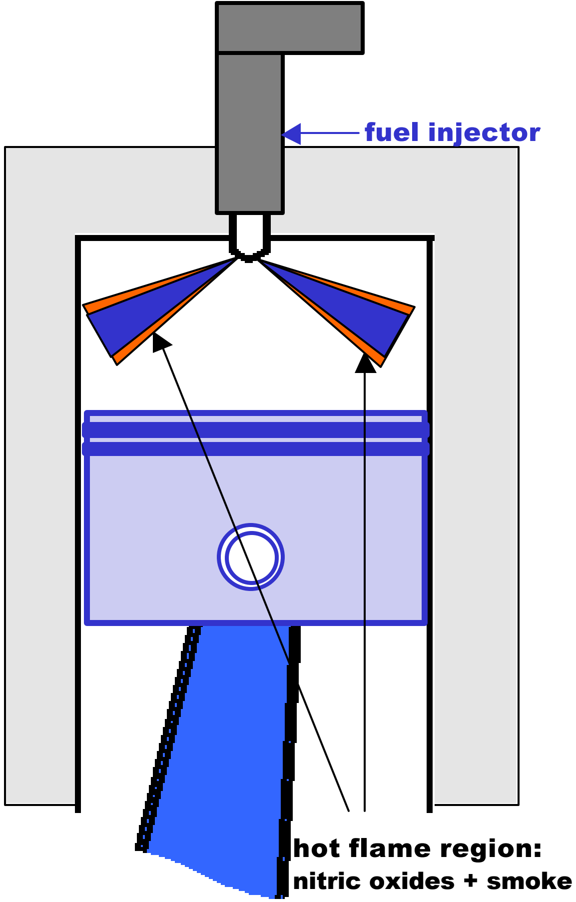
- HEAT RELEASE
- RADIATION EXCHANGE BETWEEN HOT AND COLD POCKETS
- NO_x & SOOT FORMATION
- SOOT OXIDATION

Processes in the diesel engine combustion.

What is HCCI?

Diesel Engine

(compression ignition)

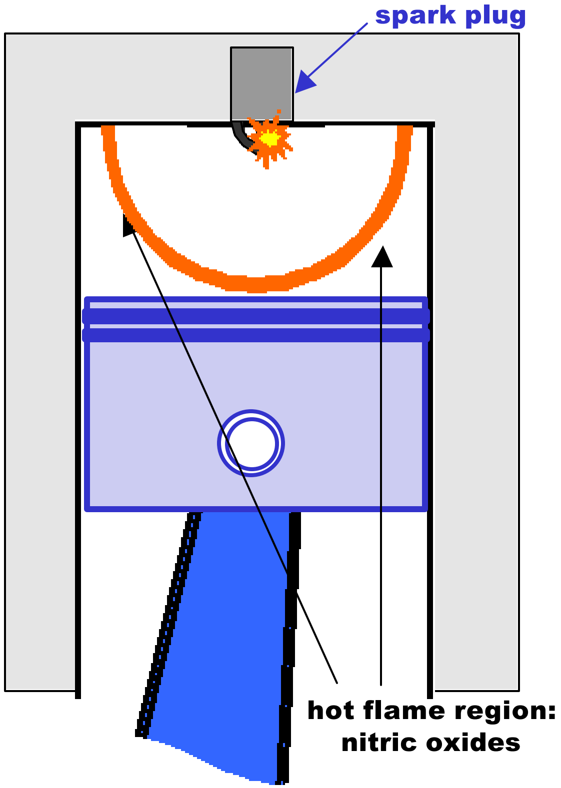


fuel injector

hot flame region:
nitric oxides + smoke

Gasoline Engine

(spark ignited)

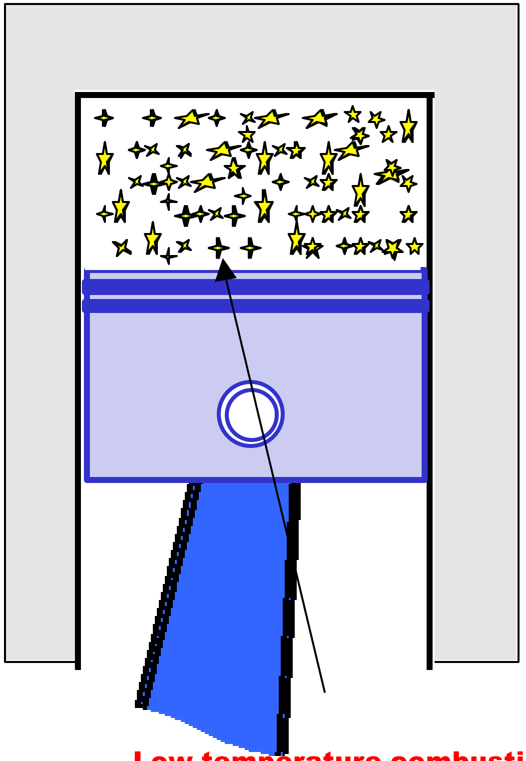


spark plug

hot flame region:
nitric oxides

HCCI Engine

(Homogeneous Charge Compression Ignition)



Low temperature combustion

ultra low emissions

11. Combustion & Pollutants

Introduction:

- Pollutant emission control is a major factor in design of modern combustion devices.
- Control of emissions may sometime involve a compromise of thermal efficiency (fuel consumption).
- Pollutants of concern include: Particulate matter (soot, ash, aerosols); oxides of nitrogen; sulphur oxides; carbon monoxide; unburned hydrocarbons; nitrous oxide, and carbon dioxide.

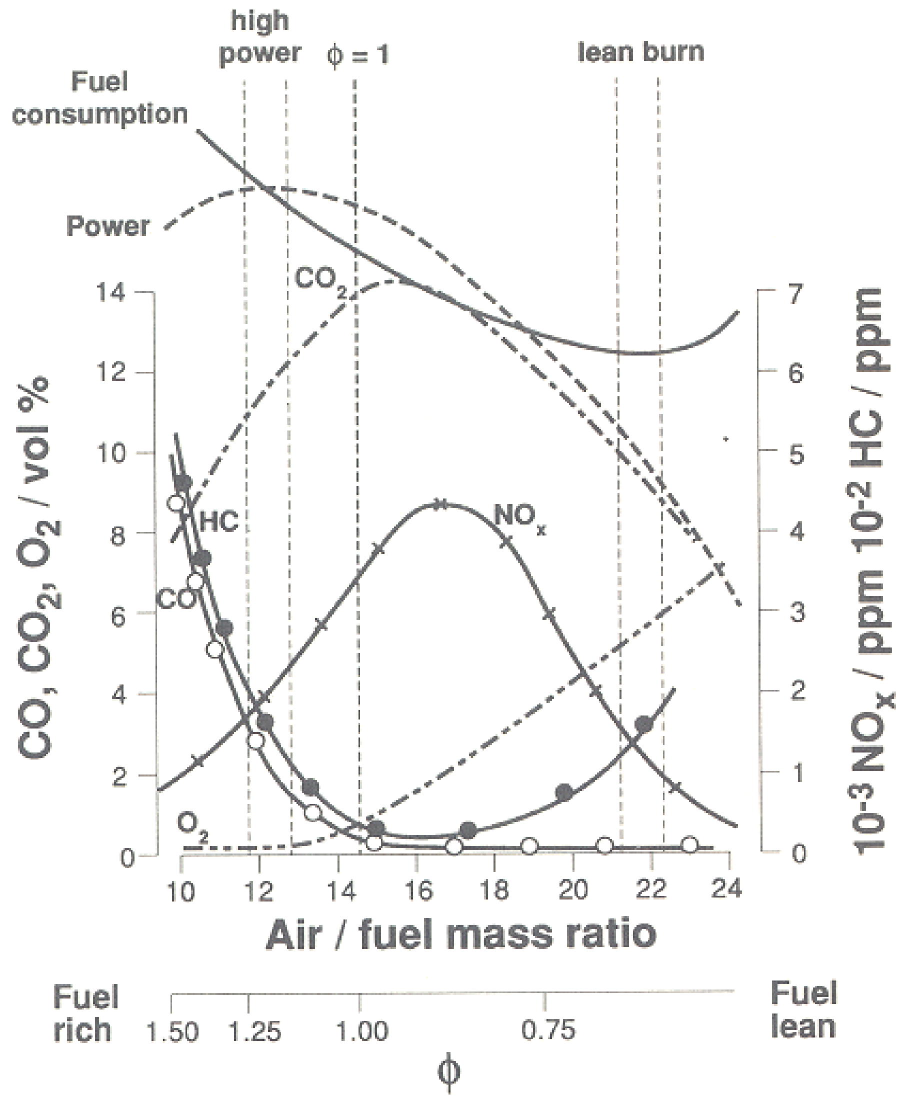
Local/Regional Air Quality Concerns:

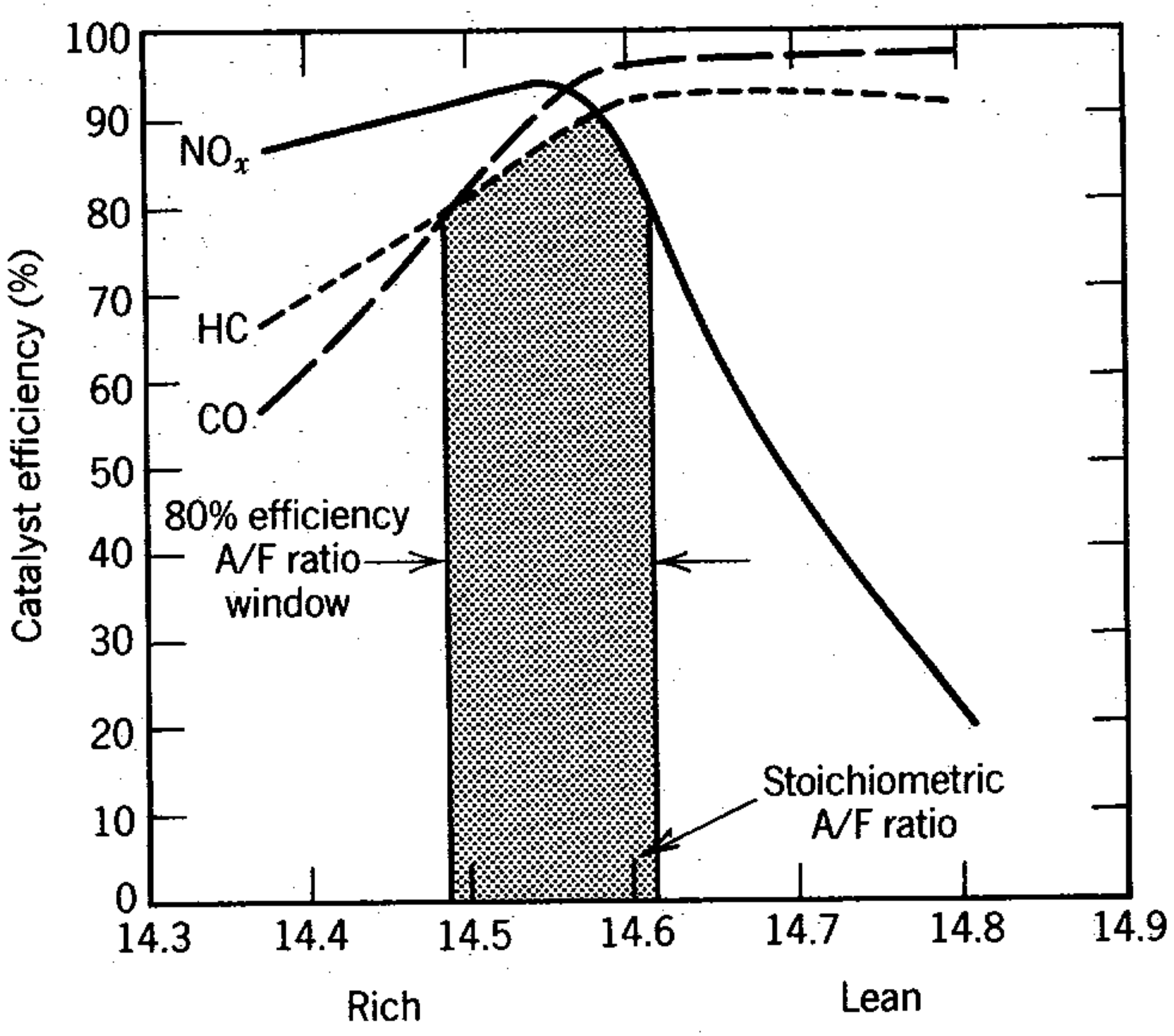
- Combustion generated and regulated pollutants are:
  - Particulate matter; PM_{10} and $PM_{2.5}$
  - Oxides of nitrogen; NO_x (NO and NO_2)
  - Ozone; O_3 (air quality standards).
  - Carbon monoxide; CO
  - Lead
  - Unburned and partially burned hydrocarbons
  - Sulphur dioxide

Regulated emissions:

- Gasoline engines (SI):
    - NO_x, CO, unburned HC
- Diesel engines (CI):
    - NO_x, CO, unburned HC, Particulate Matter
- Gas Turbines (Stationary and aircraft, limited):
    - NO_x
- Power plants:
    - NO_x, CO, Particulate Matter, SO_2

SI engine:


high power
φ = 1
lean burn
Fuel consumption
Power
CO₂
HC
CO
NOₓ
O₂
CO, CO₂, O₂ / vol %
14
12
10
8
6
4
2
0
10
12
14
16
18
20
22
24
Air / fuel mass ratio
10⁻³ NOₓ / ppm 10⁻² HC / ppm
7
6
5
4
3
2
1
0
Fuel rich
1.50
1.25
1.00
0.75
Fuel lean
φ



SI engine 3-Way Catalytic converter

Air Toxics/Hazardous Air Pollutants:

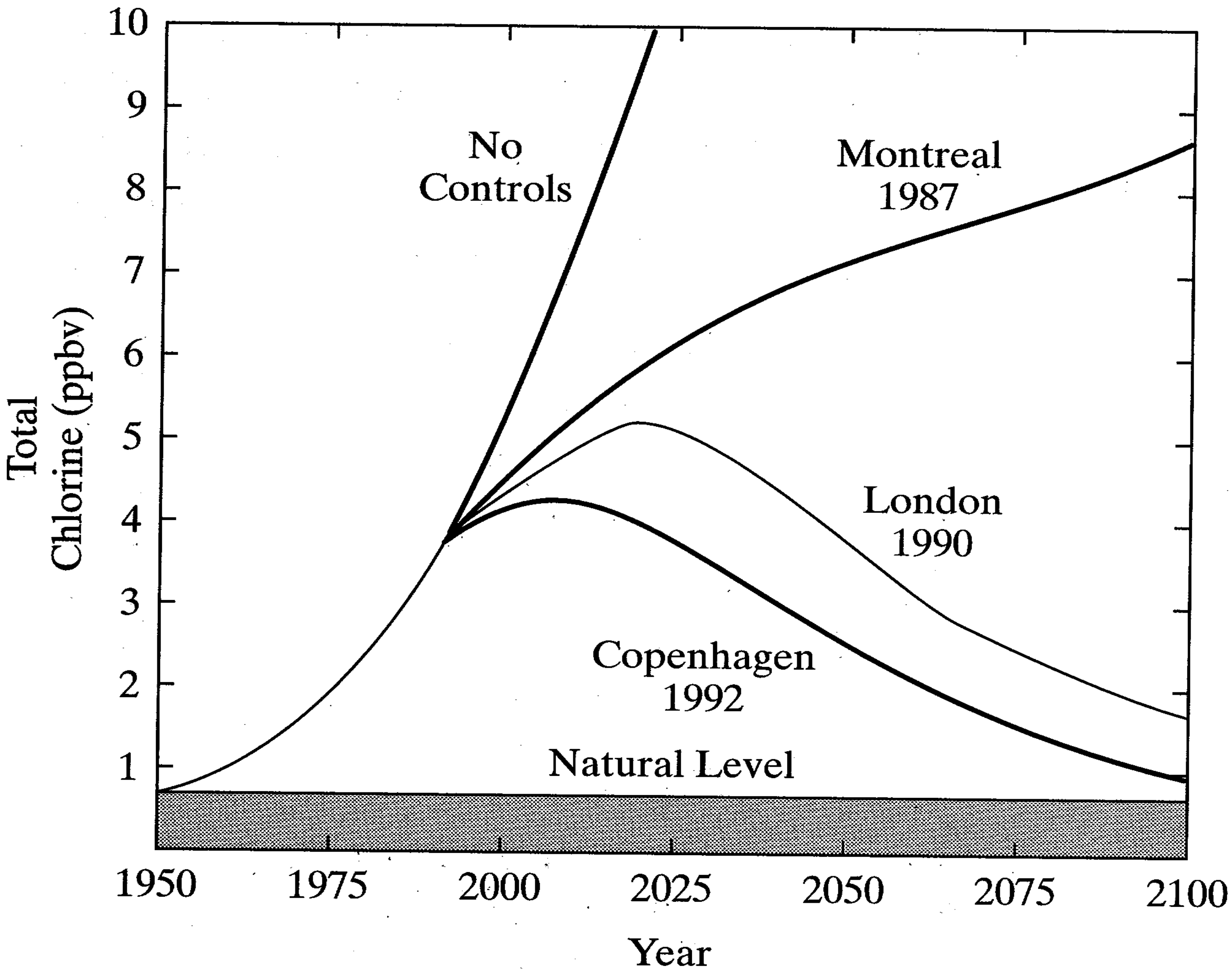
- Close to 200 substances are listed as air toxics:
  - Selected aliphatic, aromatic, and polycyclic aromatic hydrocarbons
  - Selected halogenated hydrocarbons
  - Various oxygenated organic compounds
  - Metals and metal compounds
  - Polycyclic aromatic hydrocarbons with nitrogen atoms in the structure
  - A list of other compounds

Greenhouse Gases tied to Global Warming:

- Kyoto Protocol identifies the following as the Greenhouse gases:
  - Carbon dioxide, CO_2
  - Methane, CH_4
  - Nitrous oxide, N_2O
  - Particulates, soot, aerosols
  - Stratospheric H_2O
  - Tropospheric and stratospheric ozone, O_3
  - Sulphates

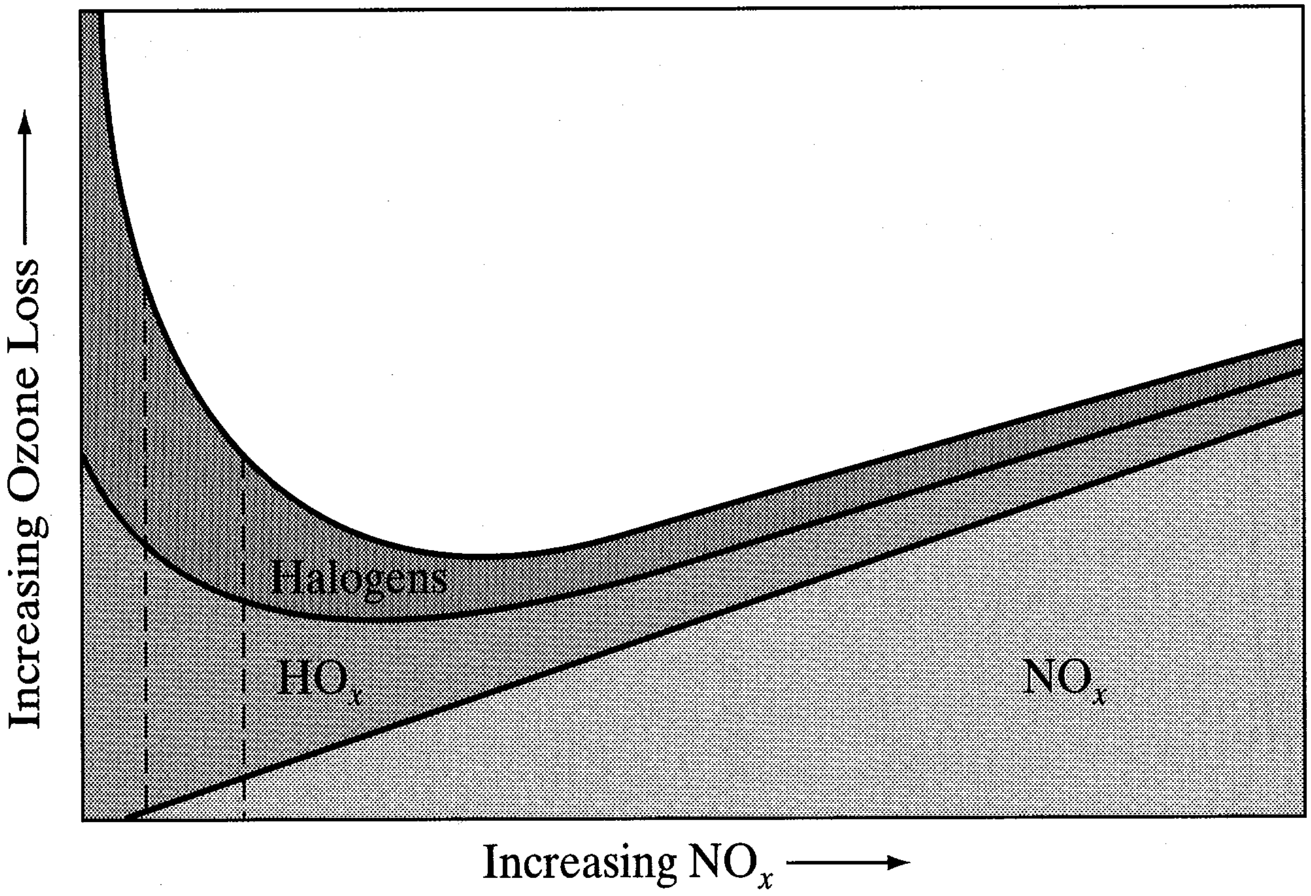
Stratospheric Ozone Destruction:

- Montreal (1987), London (1990) and Copenhagen (1992) Protocols cap the following:
  - Methane, CH_4
  - Nitrous oxide, N_2O
  - Methyl chloride, CH_3Cl
  - Methyl bromide, CH_3Br
  - Stratospheric H_2O
  - Stratospheric ozone, O_3



Chlorine loading of earth's atmosphere

- Stratospheric ozone shields earth from ultraviolet radiation.
- Most of this ozone is contained in a layer between 20 and 50 km altitude.
- Three mechanisms control the level of ozone concentration:
  - HO_x cycle (H, OH, HO_2
  - NO_x cycle (NO, NO_2)
  - ClO_x cycle [halomethanes: $CFCl_3$(Freon-11), CF_2Cl_2 (Freon-12); and CH_3Cl)]



Ozone removal in lower stratosphere

NO_x formation in combustion:

- *Thermal* NO: oxidation of molecular nitrogen in the postflame zone.
- *Prompt* NO: formation of NO in the flame zone (*Fenimore* mechanism).
- N_2O-*intermediate* mechanism.
- *Fuel* NO: oxidation of nitrogen-containing compounds in the fuel.

Relative importance of these three are dependent on the operating conditions and fuel. In most practical combustion devices the thermal NO is the main source.

- The basic mechanism for thermal NO production is given by six reactions known as *extended Zeldovich mechanism*:

$$O + N_2 \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} NO + N \tag{N.1}$$

$$N + O_2 \underset{k_{2r}}{\overset{k_{2f}}{\rightleftharpoons}} NO + O \tag{N.2}$$

$$N + OH \underset{k_{3r}}{\overset{k_{3f}}{\rightleftharpoons}} NO + H \tag{N.3}$$

- The contribution of reaction 3 is small for lean mixtures, but for rich mixtures it should be considered. Forward reaction 1 controls the system, but it is slow at low temperatures (high activation energy). Thus it is effective in post-flame zone where temperature is high and the time is available.
- Concentrations of 1000 to 4000 ppm are typically observed in uncontrolled combustion systems.
- From reactions 1-3, the rate of formation of thermal NO can be calculated:

$$\frac{\mathrm{d[NO]}}{\mathrm{d}t} = k_{1f}[\mathrm{O}][\mathrm{N_2}] - k_{1r}[\mathrm{NO}][\mathrm{N}] + k_{2f}[\mathrm{N}][\mathrm{O_2}]$$

$$-k_{2r}[\mathrm{NO}][\mathrm{O}] + k_{3f}[\mathrm{N}][\mathrm{OH}] - k_{3r}[\mathrm{NO}][\mathrm{H}] \qquad (5.14)$$

- To calculate the NO formation rate, we need the concentrations of O, N, OH, and H.
- In detailed calculations, these are computed using detailed kinetic mechanisms for the fuel used.
- For very approximate calculations, these may be assumed to be in chemical equilibrium.

- At moderately high temperatures N does not stay at thermodynamic equilibrium. A better approximation could be to assume N to be at steady-state.
- From reactions 1-3, we have

$$\frac{\mathrm{d}[\mathrm{N}]}{\mathrm{d}t} = k_{1f}[\mathrm{O}][\mathrm{N}_2] - k_{1r}[\mathrm{NO}][\mathrm{N}] - k_{2f}[\mathrm{N}][\mathrm{O}_2]$$

$$+k_{2r}[\mathrm{NO}][\mathrm{O}] - k_{3f}[\mathrm{N}][\mathrm{OH}] + k_{3r}[\mathrm{NO}][\mathrm{H}] = 0$$

$$[\mathrm{N}]_{\mathrm{ss}} = \frac{k_{1f}[\mathrm{O}][\mathrm{N}_2] + k_{2r}[\mathrm{NO}][\mathrm{O}] + k_{3r}[\mathrm{NO}][\mathrm{H}]}{k_{1r}[\mathrm{NO}] + k_{2f}[\mathrm{O}_2] + k_{3f}[\mathrm{OH}]} \tag{5.15}$$

- The reaction rate constants, in [m^3/ kmol s], for 1-3 are as follows:

$$
\begin{aligned}
k_{1f} &= 1.8 \cdot 10^{11} \exp\left(-38,370/T\right) \\
k_{1r} &= 3.8 \cdot 10^{10} \exp\left(-425/T\right) \\
k_{2f} &= 1.8 \cdot 10^{7} T \exp\left(-4680/T\right) \\
k_{2r} &= 3.8 \cdot 10^{6} T \exp\left(-20,820/T\right) \\
k_{3f} &= 7.1 \cdot 10^{10} \exp\left(-450/T\right) \\
k_{3r} &= 1.7 \cdot 10^{11} \exp\left(-24,560/T\right)
\end{aligned}
\tag{5.16}
$$

- N_2O-*intermediate mechanism* is important in very-lean combustion ($\Phi < 0.8$). This mechanism can be represented by:

$$
\begin{aligned}
O + N_2 + M &\rightleftharpoons N_2O + M && \text{(N.4)}\\
H + N_2O &\rightleftharpoons NO + NH && \text{(N.5)}\\
O + N_2O &\rightleftharpoons NO + NO && \text{(N.6)}
\end{aligned}
$$

- This mechanism is important in NO control strategies in lean-premixed gas turbine combustion applications.

- It has been shown that some NO is rapidly produced in the flame zone long before there would be time to form NO by the thermal mechanism. This is also known as the *Fenimore mechanism*:
- The general scheme is that hydrocarbon radicals form CN and HCN

$$\mathrm{CH} + \mathrm{N_2} \rightleftharpoons \mathrm{HCN} + \mathrm{N} \qquad \text{(N.7)}$$

$$\mathrm{C} + \mathrm{N_2} \rightleftharpoons \mathrm{CN} + \mathrm{N} \qquad \text{(N.8)}$$

- The conversion of hydrogen cyanide, HCN, to form NO is as follows

$$\mathrm{HCN + O \rightleftharpoons NCO + H} \tag{N.9}$$

$$\mathrm{NCO + H \rightleftharpoons NH + CO} \tag{N.10}$$

$$\mathrm{NH + H \rightleftharpoons N + H_2} \tag{N.11}$$

$$\mathrm{N + OH \rightleftharpoons NO + H} \tag{N.3}$$

- For equivalence ratios higher than 1.2, chemistry becomes more complex and it couples with the thermal mechanism.

NO_x ***emissions from SI engines:***

- Nitric oxide forms in the high temperature burned gases during the combustion process. During expansion, as the burned gas temperature falls, NO freezes out as the decomposition chemistry becomes extremely slow.
- The burned gas temperature, and the amount of oxygen in the burned gases, are the primary variables affecting NO formation.

NO_x ***emissions from SI engines (Cont'd):***

- Dilution of the unburned mixture with EGR leads to lower burned gas temperature due to increased heat capacity of the mixture per unit mass of fuel.
- Dilution with air also increases the heat capacity, but increasing the oxygen content has a greater impact on NO formation rate.
- Spark retard reduces NO formation rate because it reduces peak cylinder pressures and burned gas temperatures.

Unburned HC emissions from SI engines:

- Unburned HC emissions are various compounds of hydrogen and carbon.
- They are unburned or partially burned fuel, and to a lessor extent, oil.
- About 1000-3000 ppm under normal operating conditions (before catalyst).
- This corresponds to about 1 to 2 % of the fuel flow into the engine.

CO emissions from SI engines:

- Carbon monoxide (CO) is the incomplete oxidation product of the fuel carbon. It is present in significant amounts in fuel-rich combustion products, and in high-temperature burned gases.
- Effectively determined by fuel-air ratio.
- Although in chemical equilibrium during combustion, recombination with oxygen is slow and CO levels freeze during expansion and exhaust strokes.

Unburned HC emissions from CI engines:

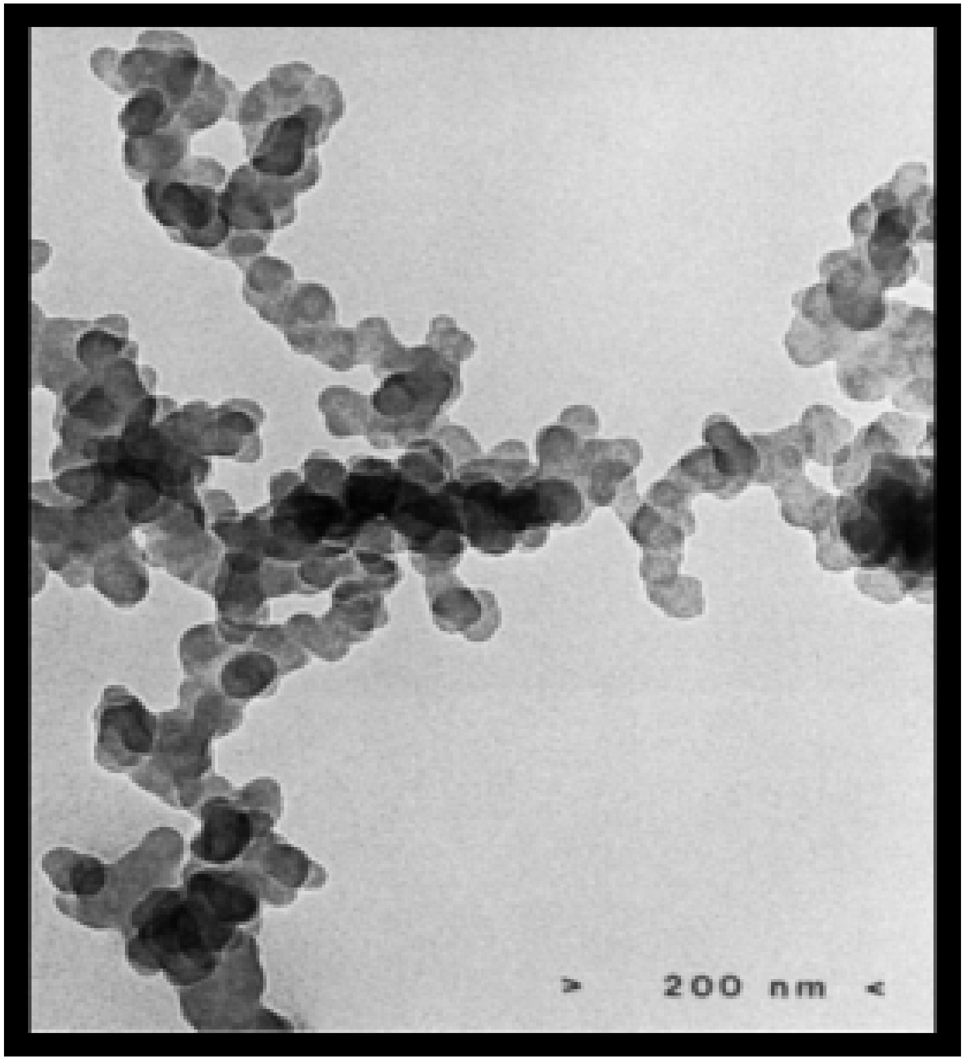
- The unburned hydrocarbons in the diesel exhaust come from fuel which escapes combustion because it is:
  - too lean to burn due to over-mixing with air
  - too rich to burn because it did not mix with enough air
- The lubricating oil contributes high molecular mass HC which condense on the soot particles in the exhaust and contribute to the particulates.

What is Particulate Matter?

- Soot:
  - Carbonaceous particles produced through gas-phase combustion process
- Coke or cenospheres:
  - Carbonaceous particles formed as a result of direct pyrolysis of liquid hydrocarbon fuels
- Particulate Matter (PM):
  - Particles that can be collected on the probes of measuring instruments such as filters
  - Originate from a variety of sources

Soot formation in combustion:

- Conversion of a hydrocarbon fuel with molecules containing a few carbon atoms into a carbonaceous agglomerate containing some millions of carbon atoms in a few milliseconds
- Transition from a gaseous to solid phase
- Smallest detectable solid particles are about 1.5 nm in diameter (about 2000 amu)
- It is an artifact of diffusive combustion. In premixed systems soot does not form unless the equivalence ratio is richer than 1.7-2.0



Combustion soot

Soot/particulates in gas turbine and diesel engines:

- The soot particles form in the extremely fuel-rich zones of the burning fuel spray as the fuel molecules pyrolyze and break down and then form increasingly higher molecular mass polycyclic aromatics and polyacetylenes.
- These eventually form nuclei for soot particles which grow and agglomerate.
- A substantial fraction of the soot formed oxidizes within the combustion chamber (more than 90-95 %).

Soot/particulates in gas turbine and diesel engines:

- PM emissions from diesel engines and gas turbines consist of soot particles and volatile organics (hydrocarbons and sulfates) absorbed into the particles in the exhaust.
- Particles are agglomerates of 5 to 30 nm diameter primary soot particles. Aerodynamic dimensions of agglomerates range from 10 to 1000 nm.
- For regulatory purposes, PM emissions are defined as mass of matter that can be collected from a diluted exhaust stream on a filter kept at 52^o C.

Reading Assignment

- **Study Chapter 15 in the Textbook**

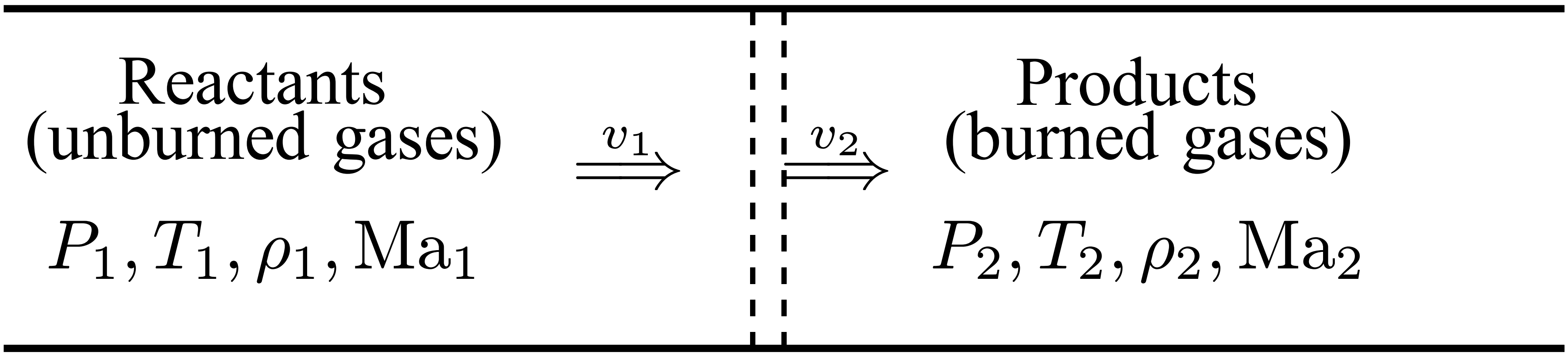
12. Rankine-Hugoniot Relations

- For steady one-dimensional flow of a combustible gas that burns to completion, equations relating initial and final conditions are readily derived from conservation equations.
- Consider a premixed flammable mixture in a long tube ignited from one end. A combustion wave will travel down the tube starting from the ignition point. If the both ends of the tube are open to atmosphere, the velocity of the combustion wave would be in the order of one meter per second.

- For most hydrocarbon-air stoichiometric mixtures, this velocity is about 0.4 to 0.6 m/s.
- The velocity of this wave is controlled by the diffusion of heat and active radicals.
- This combustion wave is normally called as a *flame*. Since it is treated as a fluid flow entity, it may also be called a deflagration.
- If the tube is closed at one end and it is ignited there, the propagating wave undergoes a transition from subsonic to supersonic speeds under the right conditions.

- The supersonic wave is called a detonation.
- In detonation, heat and radical diffusion do not control the velocity; rather, the shock wave structure of the developed supersonic wave raises the temperature and pressure substantially to cause very high reaction rates and energy release that sustain the wave propagation.
- Although the structure of a detonation wave is highly three-dimensional, we can gain considerable insight by carrying out a one-dimensional analysis of a detonation wave.

- Assumptions:
  - One-dimensional steady flow.
  - Constant area tube.
  - Ideal-gas; constant and equal specific heats.
  - Adiabatic conditions.
  - Body forces are negligible.



Reactants
(unburned gases)

$P_1, T_1, \rho_1, \mathrm{Ma}_1$

$\xRightarrow{v_1}$ $\xRightarrow{v_2}$

Products
(burned gases)

$P_2, T_2, \rho_2, \mathrm{Ma}_2$

- Mass conservation:

$$\dot{m}'' = \rho_1 v_1 = \rho_2 v_2 \tag{12.1}$$

- Momentum conservation: Only force acting on the control volume is pressure.

$$P_1 + \rho_1 v_1^2 = P_2 + \rho_2 v_2^2 \tag{12.2}$$

- Energy conservation:

$$h_1 + \frac{v_1^2}{2} = h_2 + \frac{v_2^2}{2} \tag{12.3}$$

- If we split the total enthalpy to *sensible* and *heat of formation* contributions, we can write:

$$h(T) = \sum Y_i h^o_{fi} + \sum Y_i \int_{T_o}^{T} c_{pi} \mathrm{d}T \qquad (12.4)$$

- With constant specific heat assumption

$$h(T) = \sum Y_i h^o_{fi} + c_p (T - T_o) \qquad (12.5)$$

- Substituting eq.(12.5) into eq.(12.3)

$$c_pT_1 + \frac{v_1^2}{2} + \underbrace{\sum_{\mathrm{state\,1}} Y_i h_{fi}^o - \sum_{\mathrm{state\,2}} Y_i h_{fi}^o}_{\mathrm{Heat Addition},q} = c_pT_2 + \frac{v_2^2}{2} \tag{12.6}$$

- Then, energy equation is:

$$c_pT_1 + v_1^2/2 + q = c_pT_2 + v_2^2/2 \tag{12.8}$$

- Ideal gas assumption yields:

$$P_1 = \rho_1 R_1 T_1 \tag{12.9}$$

$$P_2 = \rho_2 R_2 T_2 \tag{12.10}$$

- Rayleigh Line: Combining eqs(12.1) and (12.2):

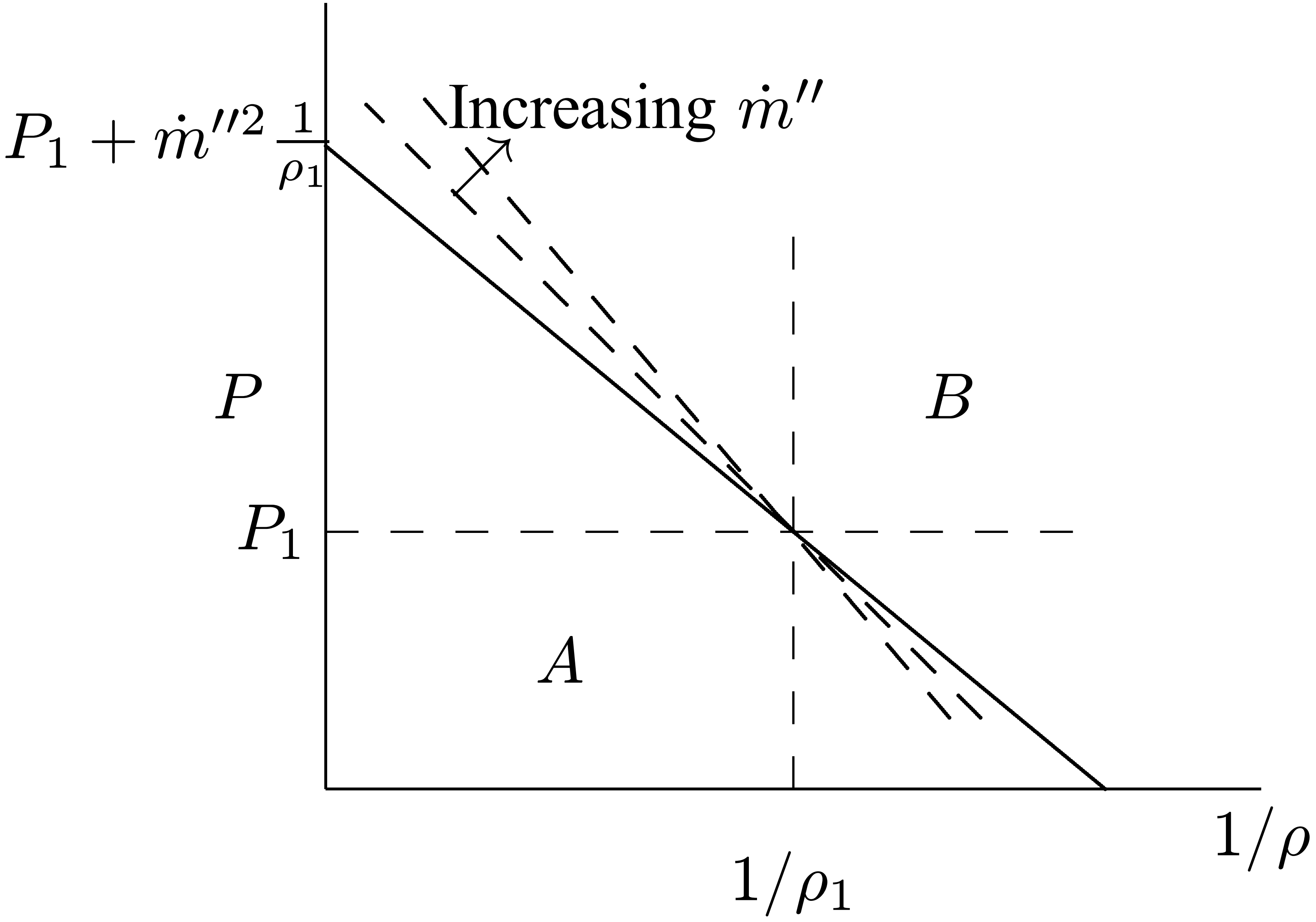
$$\frac{P_2 - P_1}{1/\rho_2 - 1/\rho_1} = -\dot{m}''^2 \qquad (12.11)$$

- Plotting P versus $1/\rho$ for a fixed flow rate $\dot{m}''$ gives the Rayleigh line. For fixed values of P_1 and ρ_1

$$P = a(1/\rho_2) + b \qquad (12.12a)$$

- where the slope a and intercept b are

$$a = -\dot{m}''^2 \quad \text{and} \quad b = P_1 + \dot{m}''^2(1/\rho_1) \qquad (12.12b\&c)$$


Increasing $\dot{m}''$
$P_1 + \dot{m}''^2 \frac{1}{\rho_1}$
P
B
P_1
A
$1/\rho$
$1/\rho_1$

- Rayleigh line for state 1 fixed by P_1 and $1/\rho_1$.
- Increasing mass flux $\dot{m}''$ causes the line steepen.
- In the limit of infinite mass flux, Rayleigh line would be vertical; while at the opposing limit of zero flux, it is horizontal.
- Two quadrants labeled A and B are physically inaccessible.
- This will be used later to help in deciding what final states are possible for detonation waves.

- ***Rankine-Hugoniot*** curve is obtained when we require that the energy equation (12.8) be satisfied in addition to the continuity and momentum. Combining eqs(12.1), (12.2), and (12.8), and using ideal gas relations (e.g., $\gamma \equiv c_p/c_v$):

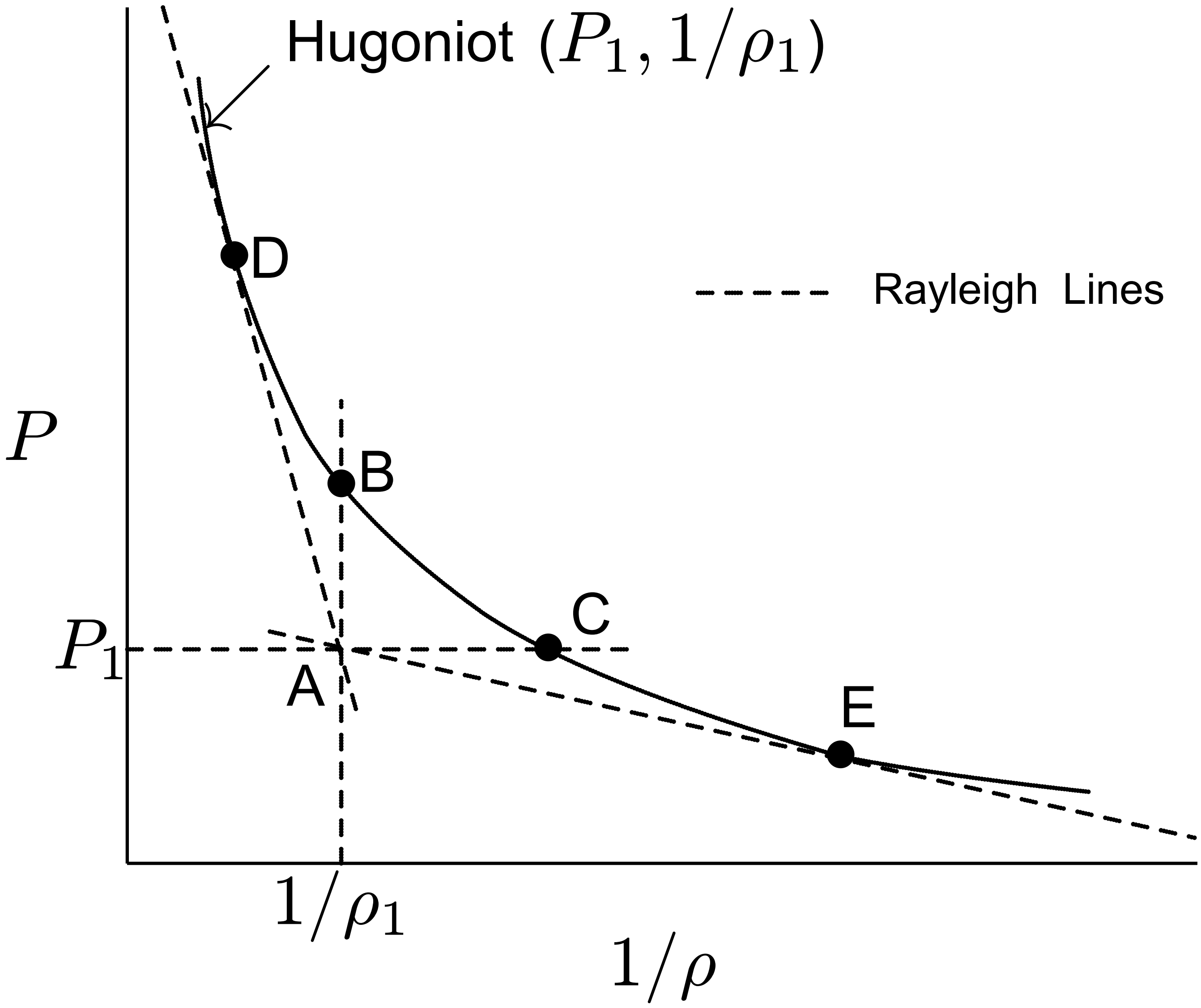
$$\frac{\gamma}{\gamma-1}\left(\frac{P_2}{\rho_2}-\frac{P_1}{\rho_1}\right)-\frac{1}{2}\left(P_2-P_1\right)\left(\frac{1}{\rho_1}+\frac{1}{\rho_2}\right)-q=0 \tag{12.13}$$

- We assume that q is a known parameter. Further, we fix the values of P_1 and $1/\rho_1$.

- Then, eq(12.13) becomes a transcendental relation between P_2 and $1/\rho_2$, or more generically between P and $1/\rho$,

$$f(P, 1/\rho) = 0 \tag{12.14}$$

- We can now plot P as a function of $1/\rho$ for P_1, $1/\rho_1$, and q fixed at particular known values. The point $(P_1, 1/\rho_1)$ is known as the origin of the Rankine-Hugoniot curve.
- Note that the Rankine-Hugoniot curve does not pass through the so-called origin.


Hugoniot $(P_1, 1/\rho_1)$
D
Rayleigh Lines
P
B
C
P_1
A
E
$1/\rho_1$
$1/\rho$

- What points on the Hugoniot curve correspond to realizable physical states?
- Any real process going from 1 to 2 must satisfy both Rayleigh and Hugoniot relations.
- The four limiting Rayleigh lines divide the Hugoniot into five segments.
- Above D: strong detonations
- D-B: weak detonations
- C-E: weak deflagrations
- Below E: strong deflagrations

- ***Detonation Velocity:***

- Define detonation velocity, v_D, to be equal to the velocity at which the unburned mixture enters the detonation wave,

$$v_D \equiv v_1 \tag{12.15}$$

- Remembering that detonation for state 2 is the upper C-J point at which velocity is sonic, then eq(12.1) reads

$$\rho_1 v_1 = \rho_2 c_2 \tag{12.16}$$

- where $c_2 = \sqrt{\gamma R_2 T_2}$ is the sonic velocity, then

$$v_1 = \frac{\rho_2}{\rho_1}(\gamma R_2 T_2)^{1/2} \tag{12.17}$$

- Now we try to relate the density ratio, ρ_2/ρ_1, and T_2 to state 1 or other known quantities. We divide eq.(12.2) by ρ_2/v_2^2, and neglect P_1 as compared to P_2:

$$\frac{\rho_1 v_1^2}{\rho_2 v_2^2} - \frac{P_2}{\rho_2 v_2^2} = 1 \tag{12.18}$$

- Apply continuity eq(12.1) into eq(12.18) to eliminate v_1

$$\frac{\rho_2}{\rho_1} = 1 + \frac{P_2}{\rho_2 v_2^2} \tag{12.19}$$

- Replace v_2 with $c_2(=\sqrt{\gamma R_2 T_2})$; then

$$\frac{\rho_2}{\rho_1} = 1 + \frac{P_2}{\rho_2 \gamma R_2 T_2} \tag{12.20}$$

- Using $P_2 = \rho_2 R_2 T_2$ will yield:

$$\frac{\rho_2}{\rho_1} = \frac{\gamma + 1}{\gamma} \tag{12.21}$$

- Solving the energy conservation equation for T_2 yields

$$T_2 = T_1 + \frac{v_1^2 - v_2^2}{2c_p} + \frac{q}{c_p} \tag{22}$$

- Eliminating v_1 using the continuity equation, substituting $c_2 = v_2$, and using eq(12.21) in eq(12.22) we obtain

$$T_2 = T_1 + \frac{q}{c_p} + \frac{\gamma R_2 T_2}{2c_p}\left[\left(\frac{\gamma+1}{\gamma}\right)^2 - 1\right] \tag{12.23}$$

- Solving for T_2, and using $(\gamma - 1) = (\gamma R_2/c_p)$ result in

$$T_2 = \frac{\gamma^2}{\gamma+1}\Big(T_1 + \frac{q}{c_p}\Big) \tag{12.24}$$

- If we substitute eqs(12.21) and (12.24) into eq(12.17), we obtain

$$v_D = v_1 = [2(\gamma+1)\gamma R_2(T_1 + q/c_p)]^{1/2} \tag{12.25}$$

- Eq(12.25) is approximate, because of the simplifying physical assumptions employed, and the assumption that $P_2 \gg P_1$.

- If we relax the assumption of constant and equal specific heats, we get more accurate but still very approximate expressions

$$T_2 = \frac{2\gamma_2^2}{\gamma_2 + 1}\left(\frac{c_{p1}}{c_{p2}}T_1 + \frac{q}{c_{p2}}\right) \tag{12.26}$$

$$v_d = \left[2(\gamma_2+1)\gamma_2 R_2\left(\frac{c_{p1}}{c_{p2}}T_1 + \frac{q}{c_{p2}}\right)\right]^{1/2} \tag{12.27}$$

$$\rho_2/\rho_1 = (\gamma_2 + 1)/\gamma_2 \tag{12.28}$$

Segment	Characteristic	Burned Gas Velocity	Remarks
Above **D**	Strong Detonation	Subsonic	Seldom observed Special exp. equip.
Point **D**	Upper C-J point	Sonic	Observed in tubes
D–B	Weak Detonation	Supersonic	Seldom observed
B-C	Inaccessible		
C-E	Weak Deflagration	Subsonic	Often observed $P \sim 1$
Point **E**	Lower C-J point	Sonic	Not observed
Below **E**	Strong Deflagration	Supersonic	Not observed

University of Toronto Institute for Aerospace Studies

Faculty of Applied Science And Engineering

AER 1304 Fundamentals of Combustion - Fall 2012
Final Exam : December 6, 2012

Room: UTIAS - LH & SL — Professor O. L. Gulder
Starting Time: 14:00 — Duration of the Exam: 150 min

NOTE: •This is an ‘‘open-book" exam. •You are permitted to use your notes, textbooks, reference books, and non-communicating hand-held calculators during the exam. •Percentage value of each question is shown in the left margin preceding the question number. •Attempt all questions. •Do not forget to write your name and student number on the front cover of all answer booklets.

READ FIRST: ♣ Show the correct units of quantities during the solution as well as the final answer. ♣ Pay attention during stoichiometry related calculations: no partial marks will be awarded for the wrong numerical results, even if the procedure is right. ♣ Do not use averaged specific heats for adiabatic flame calculations; if you do, you do not get any marks unless your answer is numerically correct. ♣ All gases obey the ideal gas law.

QUESTIONS

1. Hydrazine (N_2H_4) is used as a liquid rocket fuel with liquid hydrogen peroxide (H_2O_2) as the oxidant.

10% **a.** Calculate the stoichiometric oxidant-to-fuel ratio.

10% **b.** Assume that the combustion products are in equilibrium at 2600 K and 50 atm in the rocket combustion chamber. If the mole fractions of OH and H_2O are known, how can we calculate the equilibrium mole fractions of H_2, H, and O? No numerical solution is required, however, you should show all necessary steps by providing the required number of equations and relationships to find the answers.

15% **2.** Consider the combustion of a methanol (CH_3OH) and air mixture with an equivalence ratio of 0.5. The reactants enter an adiabatic steady-flow reactor at 500 K and the pressure in the reactor is kept at 1 atm. Assuming that the combustion in the reactor is complete and no dissociation occurs, calculate the adiabatic flame temperature. Standard enthalpy of formation of methanol at 298 K and 1 atm is $\bar{h}_f^o =$ -201,200 kJ/kmol, and its sensible enthalpy at 500 K is about 11,500 kJ/kmol.

Continued overleaf

3. In a jet diffusion flame, the fuel is ethanol vapour (C_2H_5OH) and the oxidant is an equimolar mixture of oxygen and carbon dioxide . The species existing within the flame are C_2H_5OH, CO_2, CO, H_2O, H_2, O_2, and OH.

5% **a.** What is the stoichiometric mixture fraction?

10% **b.** Derive an expression for the mixture fraction at any location within the flame in terms of species mass fractions.

4. Two atmospheric laminar diffusion flames on square burners are fuelled by methane (CH_4) with equal mass flow rates of 9×10^{-6} kg/s.

5% **a.** If the first burner's exit nozzle is 1 cm×1 cm, and the second burner's exit nozzle is 1.3 cm×1.3 cm, what is the ratio of flame heights of the two diffusion flames? Fuel and air are at 300 K in both burners.

10% **b.** If the fuel temperature in the second burner is increased to 600 K while keeping the air temperature at 300 K, what is the ratio of flame heights of the two diffusion flames?

10% **5.** Show that the pressure has no effect on a gaseous equilibrium system (i.e., the equlibrium composition will not change if the pressure is changed at constant temperature) such as

$$\mathrm{H} + \mathrm{O_2} \rightleftharpoons \mathrm{OH} + \mathrm{O}$$

in which the total number of moles of reactants is equal to the total number of moles of products in the chemical equation, and gases involved obey the ideal gas law.

15% **6.** A turbulent non-premixed propane-air jet flame has a nozzle exit velocity of 168 m/s. Determine the minimum nozzle exit diameter required to prevent the flame being blown out.

10% **7.** A fuel developer claims that she produced a synthetic fuel from a certain biomass feed stock. The fuel's closed form formula is thought to be $C_6O_3N_4$. If its standard enthalpy of formation is estimated as 105,000 kJ/kmol at 298 K, what would be the difference between higher and lower heating values of this fuel?

University of Toronto Institute for Aerospace Studies

Faculty of Applied Science And Engineering

AER 1304 Fundamentals of Combustion - Fall 2012

Midterm Test: November 8, 2012

Room: Staff Lounge & Lecture Hall
Time: 14:00 pm

Professor O. L. Gulder
Time Allocated : 120 min

NOTE: •This is an ‘‘open-book" exam. •You are permitted to use your notes, textbooks, reference books, and non-communicating hand-held calculators during the exam. •Percentage value of each question is shown in the left margin preceding the question number. •Attempt all questions. •Do not forget to write your name and student number on the front cover of all answer booklets.

QUESTIONS

1. Relatively small liquid fuel rockets are used in space crafts for orbital maneuvering and control . One common fuel used for these types of rockets is monomethyl hydrazine (CH_6N_2) with nitrogen tetroxide (N_2O_4) and nitric acid (HNO_3) as the oxidizers.

10% **a.** In a certain application, the rocket uses an equimolar mixture of N_2O_4 and HNO_3 as the oxidant, whereas the fuel is CH_6N_2. What is the stoichiometric oxidant to fuel mass ratio for this fuel-oxidant system?

10% **b.** If a stoichiometric mixture as described in **a** is reacting in the rocket combustion chamber at 70 atm and 2800 K, what is the equilibrium composition of the combustion products? Assume that combustion products consist of CO_2, CO, H_2O, H_2, O_2, and N_2. No numerical solution is required. However, show and explain how to find the gas composition by providing the necessary chemical reactions, equations, and the related steps required for the solution.

15% **2.** In a mixture of combustion products consisting of several tens of species at 3000 K and 50 atm, the mole fractions of O_2 and O are 0.04 and 0.001, respectively. Are these species in equilibrium? Justify your answer.

10% **3.** Estimate the molecular diffusion coefficient of toluene vapour into air at 600 K and 15 atm pressure. What would be the thermal diffusivity if the Lewis number is assumed to be unity?

Continued overleaf

4.

$\boxed{20\%}$ **a.** A mixture of biogas and syngas contains two mols of methane (CH_4) for each mols of hydrogen (H_2) and carbon monoxide (CO). This fuel is mixed with air and burned adiabatically in a constant volume vessel. If the initial temperature and pressure in the vessel are 298 K and 1 atm, respectively, and the equivalence ratio is 0.4, estimate the adiabatic flame temperature and the final pressure in the vessel. Assume that the combustion in the vessel is complete and no dissociation occurs.

$\boxed{10\%}$ **b.** If the combustion is non-adiabatic and 20% of the enthalpy of the combustion (total heat release by combustion) is lost by heat transfer to the combustion chamber walls, how would you modify your solution to problem **2.a**? You are not required to provide a numerical answer, but explain how you would proceed to calculate the temperature of the final products in case of 20% loss of the enthalpy of combustion.

$\boxed{10\%}$ **5.** One of the potential alternative aviation jet fuels is n-pentanol. Its closed form formula is $C_5H_{12}O$, and its higher heating value (HHV) in liquid state at 298 K has been measured as 38,359 kJ/kg. Calculate the standard enthalpy of formation of n-pentanol at gaseous state, if its enthalpy of vaporization (latent heat) is 44,400 kJ/kmol at 298 K. Molecular mass of n-pentanol is 88 g/mol.

6.

$\boxed{5\%}$ **a.** A stoichiometric propane-air mixture is diluted with some combustion products, pressurized to 10 atm, and heated to 650 K. If the mass fraction of the combustion products in the unburned mixture is 0.15, estimate the laminar burning speed.

$\boxed{10\%}$ **b.** What would be the approximate value of the quenching diameter for this mixture at 650 K and 10 atm? The transport properties of this mixture can be approximated by using the properties of air.