Aerospace Engineering 533
Combustion Processes Fall 2018

Instructor: J. F. Driscoll
Class time: Tues & Thurs 10:30 to 12:00 noon in 1008 FXB
Office hours: Tues & Wed 1:30 to 3:00 pm in 3004 FXB jamesfd@umich.edu
Textbook: Kuo, K., Principles of Combustion, Second Edition, Wiley Pub.
References: Turns, S.R., An Introduction to Combustion
Glassman, I., Combustion, and Williams, F.A., Combustion Theory

Grading: Two exams, no final 65%
Homework problems 35%: put in Driscoll's mailbox by 5 pm on Thursdays

Week	Week of	Topic	Reading: Chapters in Kuo's text
1	Sept 3	Fuels, Alternate Fuels, Gas properties	handouts
2	Sept 10	Equilibrium Chemistry, Flame Temp	Chpt 1
3	Sept 17	Dissociation, frozen flow	
4	Sept 24	Chemkin code	handouts
5	Oct 1	Hugoniot Relation, Detonations	4.1-4.5
6	Oct 8	Chemical Kinetics – Arrhenius relation	2.1-2.8
7	Oct 15	Hydrocarbon kinetics	2.14-2.17
8	Oct 22	NOx, CO pollutant kinetics	
9	Oct 29	Laminar Premixed Flames	Chpts 3, 5
	Oct 30 **EXAM #1**	in-class, open notes, covers weeks 1-7	
10	Nov 5	Laminar Premixed Flames: Flame speed, effect of pressure	Chpts 3, 5
11	Nov 12	Laminar Jet Nonpremixed Flames	6.1-6.4
12	Nov 19	Mixture fraction theory	
13	Nov 26	Applications	
14	Dec 3	Applications	handouts
	Dec 6 **EXAM #2**	in-class, open notes, covers weeks 8-13	

No final exam will be given.

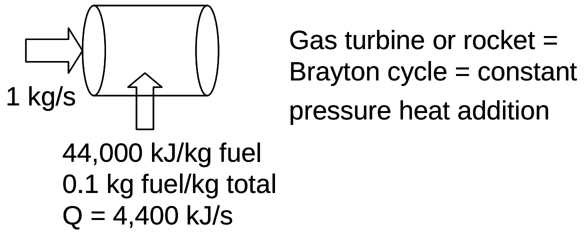
Topics Read Kuo Chapter 1
Fuels, Alternate Fuels, Gas properties handouts
Equilibrium Chemistry, Flame Temp

Handout #1

Properties of Fuels and Gas Mixtures
AE 533 Combustion Processes

1. Why study combustion ?

After you take your thermodynamics or propulsion classes, you may think that you know most of what you need to design an engine.



We know that >98% of the fuel burns in an engine combustor, so we do not need to study combustion to know how much heat is added, or what the final gas temperature will be. We need to study combustion to understand:

(a) **Rate of combustion**	tells us where the flame is located, how far the flame is from the walls, the heat release distribution in space, engine knock, liner lifetime, scramjet coolant required, time required for flame or detonation wave to propagate across a chamber
(b) **Size of combustor**	need to predict flame length, avoid heat release in turbine
(c) **Uniformity**	of the heat release – avoid hot spots, good pattern factor
(d) **Blowout**	due to high velocity during a dive, or due to high altitude – puts a ceiling on operation, low pressure = slow chemistry
(e) **Reduce pollutants**	ICAO international standards, FAA U.S. compliance with NOx (typ. 50 g NO/kN thrust), CO and soot (Concorde too dirty)
(f) **Alternate fuels**	ethanol from corn, methanol from coal, can be done today Fischer-Tropsch synthetic liquid diesel or aviation fuel from coal or natural gas natural gas (CH4), used during WWII hydrogen for buses (today), for aircraft (need cryotanks) Can we predict combustion properties of alternate fuels ?
(g) **Specialty fuels**	JP-7 (Blackbird fuel), JP-10 (cruise missile/scramjet fuel) new rocket propellants: boron, silane (SiH4), “smokeless” aluminum-ammonium perchlorate

2. Common fuels

(a) Parafins (C_nH_{2n+2})

Methane (CH_4) – a gas at STP, the major component of “natural gas”, also distilled from crude oil, seeps into mine shafts to cause explosions, the gas that we cook with, not very portable, used in cars – stored as a gas in high pressure tanks, used in rockets –stored as a liquid in cryogenically cooled tanks.

Propane (C_3H_8) a gas at STP, used in barbeque grills, stored as a liquid at 40 psi in tanks; called LPG = liquid petroleum gas, used in propane cutting torches, used in cars - stored as a liquid in 40 psi tanks

Butane (C_4H_{10}) a liquid at STP, used in cigarette lighters
Octane (C_8H_{18}) a liquid at STP, the primary ingredient in gasoline, low vapor pressure, evaporates away in an unconfined area, does not "knock" so want a high octane rating to prevent knocking
Dodecane ($C_{12}H_{26}$) the primary ingredient in diesel fuel, liquid, not very volatile, knocks easily so it is best for diesel engines that have no spark so they always knock, viscous when cold, very sooty

(b) Alcohols (something + OH)
Ethanol (ethyl alcohol = C_2H_5+OH) - liquid we can drink, made from corn, grain, added to gasoline
Methanol (methyl alcohol = CH_3-OH) – poisonous but works well in cars, can be made from coal – a synfuel

(c) Kerosenes -$C_{10}H_{20}$ (Kuo p112)- volatile (easy to form spray), not very viscous
Jet-A : standard commercial aviation fuel = kerosene + lubricants, corrosion and icing inhibitors, has an anti-static additive since it builds up static electricity when flowing through pipes, similar to JP-8
JP-4 : military fuel used by USAF prior to 1996, replaced with the less flammable, less hazardous JP-8
JP-5 : used now by the NAVY, their version of JP-8
JP-7 : used by USAF supersonic aircraft because of its high flashpoint and thermal stability. Used in Pratt & Whitney J58 turbojet engines, used in the Lockheed SR-71 Blackbird. The very low volatility and relative unwillingness of JP-7 to be ignited required triethylborane to be injected into the engine in order to light it up, and to light up the afterburner in flight. An endothermic fuel – excellent for cooling the walls, degrades into ethylene
JP-8 : main fuel of the USAF, less flammable, less hazardous than JP-4
JP-10 : "missile fuel" - USAF fuel used in cruise missiles, pulse detonation engines and scramjets, an endothermic fuel excellent for cooling the walls

(see: J. PROPULSION AND POWER Vol. 19, No. 6, 2003 "Liquid Fuels and Propellants for Aerospace Propulsion: 1903–2003" by Tim Edwards *USAF Research Laboratory,Wright–Patterson AFB Base)*

(d) Other fuels
Acetylene (C_2H_2), liquid used in acetylyene-oxygen torches, very hot flames, sooty
Hydrogen – H_2, normally obtained from crude oil but can be electrolyzed from water, very clean, not a greenhouse gas, used in main propulsion system of space shuttle and upper stages of other rockets, used on some buses, requires large tank to be stored as a gas at room temperature, or as a liquid if cryogenically cooled
Hydrazene (N_2H_4) – liquid monopropellant used in rockets, carcinogenic
Nitromethane (CH_3NO_2) – liquid rocket propellant
Ammonium perchlorate (NH_4ClO_4) – solid rocket propellant
Aluminum, Boron, Magnesium, Carbon – solid metal fuels used in rockets

Ideal Gases

A. Ideal Gas Law: $p = \rho R T$

R = gas constant for a specific gas = **287.0** $(N/m^2) / ((kg/m^3)K)$ for air
R_u= universal gas constant = **8.314** N m / (mole K)

$R = R_u / \overline{MW}$

$\overline{MW}$ = molecular weight of gas = **29.0** g/mol for air

ex.: for air at STP (standard temperature and pressure) the ideal gas law is:

$(1.01325 \times 10^5 \ N/m^2) = (1.18 \ kg/m^3) \ (287.0 \ N/m^3) \ (298.15 \ K)$

E = kJoules, e = kJoules/kg, $\bar{e}$ = kJoules/kmole

Internal energy $E_2 - E_1 = m \int c_v \, dT$, $e_2 - e_1 = \int c_v \, dT$, $\bar{e}_2 - \bar{e}_1 = \int \bar{c}_v \, dT$

Enthalpy $H_2 - H_1 = m \int c_p \, dT$ $h_2 - h_1 = \int c_p \, dT$ $\bar{h}_2 - \bar{h}_1 = \int \bar{c}_p \, dT$

For a calorically perfect ideal gas (c_p = constant) then the entropy is
$S_2 - S_1 = m [c_p \ln (T_2/T_1) - R \ln (p_2/p_1)]$, $s_2 - s_1 = c_p \ln (T_2/T_1) - R \ln (p_2/p_1)$

m = mass of gas $\bar{s}_2 - \bar{s}_1 = \bar{c}_p \ln (T_2/T_1) - R \ln (p_2/p_1)$
For air at STP c_p = 1.0035 kJ /(kg K) $\bar{c}_p$ = 29.10 kJ /(kmol K) $= c_p \overline{MW}$
c_v = 0.7165 kJ /(kg K) $\bar{c}_v$ = 20.78 kJ /(kmol K) $= c_v \overline{MW}$
R = 0.2870 kJ /(kg K) $\overline{R_u}$ = 8.31 kJ /(kmol K) $= R_u \overline{MW}$

English units: To convert anything to English units all you need is:
1 slug = 32.2 lbm 1 slug = a mass that weighs 32.2 lbf
1 lbf = 1 slug ft/s^2 1 lbm = a mass that weighs 1 lbf
1 lbf = 32.2 lbm ft/s^2 1 lbf = 4.448 N
1 N = 1 kg m/s^2 1 kg = 2.206 lbm

"You can always multiply by one"; and
"Remember to write down the units and cancel them out". For example:

27 lbm is equal to 27 lbm (1 slug/32.2 lbm) = 0.838 slug

10 N is equal to 10 N (1 lbf / 4.448 N) = 2.248 lbf

"my dog SLUG" = a way to remember that a slug is a mass that weights 32.2 lbf

Gas Mixtures

(a) **Density** - of a gas mixture (see Kuo's textbook, page 8)

Since $p = \rho R T$ and R = gas constant for the mixture = $R_u / \overline{MW}$

Therefore the density of a mixture is: $\rho = \frac{p}{R_u T} \overline{MW}$

Where the molecular weight of a mixture is: $\overline{MW} = \sum_{i=1}^{n} X_i \ MW_i$

X_i = mole fraction of i-th species, Y_i is mass fraction of i-th species, related by:

$$Y_i = X_i \frac{MW_i}{\overline{MW}} \quad \text{and} \quad X_i = \frac{Y_i / MW_i}{\sum_{j=1}^{n} (Y_j / MW_j)}$$

Ex.: natural gas is 85% methane (CH4) and 15% ethane (C2H6) by volume. What is the density of the gas mixture at 1 atm, 25^oC ?

$X_{CH4} = 0.85$, $X_{C2H6} = 0.15$, $MW_{CH4} = 16$, $MW_{C2H6} = 30$, so $\overline{MW} = 18.1$ g/mol

$$\rho = \frac{p}{R_u T} \overline{MW} = 1.013\ 10^5\ N/m^2\ (18.1\ g/mol) / [\ 8.314\ N\ m / (mole\ K) \quad 298]$$

$$= 740\ g/m^3 = 0.74\ kg/m^3$$

(b) **Concentration (C) of the entire mixture** (moles/cc)

$$C = n / V = p / (R_u T)$$

Concentration C_i of the i-th species:

$C_i = n_i / V = (X_i \ p) / (R_u T)$ used often in chemical kinetics

(c) **Enthalpy of a mixture**: H = enthalpy (kJ), $\overline{h}$ = enthalpy/mole, h_i = enthalpy /mass

$$H = \sum_{i=1}^{n} X_i \overline{h}_i = \sum_{i=1}^{n} Y_i h_i$$

(d) **Viscosity or diffusion coefficient** of a mixture: see handout or use formulas in
The Properties of Gases and Liquids, Robert C. Reid, J. Prausnitz, B. Poling, McGraw Hill
Transport Phenomena, R. Bird, W. Stewart, E. Lightfoot, Wiley Pub.

Alternate (Fischer Tropsch) aviation fuel from natural gas (or coal)

In 2006 the Air Force will fly a B-52 that is powered by an alternate (synthetic Fischer-Tropsch FT) liquid kerosene fuel derived from natural gas (mixed in with standard JP-8). See: http://www.af.mil/news/story.asp?storyID=123020290 This FT fuel also can be produced from coal, and the USA has abundant coal and natural gas reserves. The Fischer-Tropsch process was developed by the Germans to produce synthetic diesel fuel during World War II. Germany's yearly production was 124,000 barrels per day from 25 plants in 1944.

Today Sasol Chevron produces liquid synthetic diesel fuel from natural gas and coal (see http://www.sasolchevron.com/technology.htm). The three main processing steps are:

Reforming - of Natural Gas or Coal into Syngas (H2 and CO) by:
  $\mathrm{CH4} + \frac{1}{2}\,\mathrm{O2} \rightarrow 2\,\mathrm{H2} + \mathrm{CO}$ and by:
  $\mathrm{CH4} + \mathrm{H_2O}$ (steam) $\rightarrow \mathrm{CO} + 3\,\mathrm{H2}$
Fischer-Tropsch Conversion of Syngas to simple hydrocarbons by:
  $\mathrm{CO} + 2\mathrm{H2}$ + cobalt catalyst $\rightarrow \mathrm{CH2} + \mathrm{H2O}$
  The gases bubble through the catalyst particles
Product Upgrading 12 $\mathrm{CH_2} \rightarrow \mathrm{C_{12}H_{24}}$ (kersosene, H/C= 2, MW = 168)

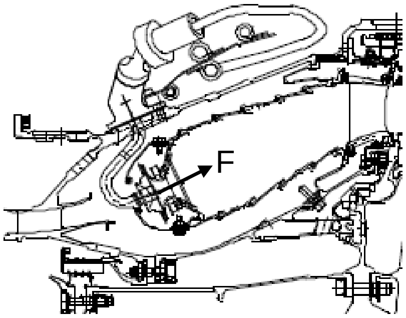
Cost and environmental concerns. While synthetic FT fuels reduce the dependency on foreign oil, they are expensive and add significant CO2 greenhouse gas to the atmosphere during their production. Carbon sequestration is being considered (dissolving the CO2 into ocean water or feeding it to plants to create oxygen). The fuel must pass severe tests after additives are added: altitude relight, cold start, proper atomization/volatility, avoid coking (gummy deposits) at high temperatures, low emissions, non-corrosive, proper viscosity for pumping, not too flammable if spilled in an accident, low sulfur, stable when stored for long times, have similar energy content as Jet-A. Things look promising but the price is high.

Ethanol: has only 60% of the energy content as Jet-A; Boeing calculates that an ethanol airplane requires 50% larger engines, 25% larger wings than Jet-A (see http://www.trbav030.org/pdf2006/265_Dagget.pdf).

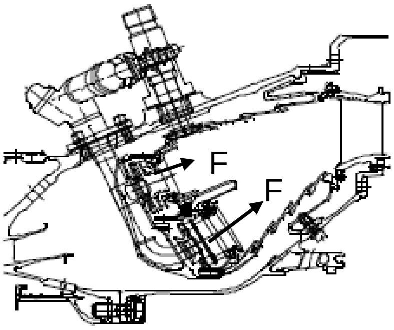
	Density (kg m^{-3})	**Specific Energy MJ kg^{-1})**	**Energy Density (10^{3} MJ m^{-3})**
Kerosene (typical)	783	43.2	33.8
Ethanol	785	21.8	17.1
Methanol	786	19.6	15.4
Methane (liquid)	421	50.0	21.0
Hydrogen (liquid)	70	119.7	8.4

Hydrogen: 2.6 times more energy per unit weight than Jet-A (heating value of 119,000 kJ/kg vs. 45,000 kJ/kg) but much larger diameter aircraft fuselage needed to hold the cryogenically-cooled fuel tanks. More drag. Compared to Jet-A, an airplane fueled by hydrogen needs 25% smaller engines, uses 28% less energy than Jet-A, according to Boeing. Very clean burning – produces no CO2 greenhouse gas. A better fuel than Jet-A but very dangerous during an accident or during normal fueling. Safety issues.

New, clean gas turbine engine combustors



First generation
gas turbine combustor
Single annular
combustor (SAC)
Nonpremixed, fuel
injected at one radial
Location (F)



Second generation:
Dual annular
Combustor (DAC)
Nonpremixed,
Fuel injected at two
Radial locations:
inner = Pilot fuel,
outer = MAIN fuel

Third generation: operate DAC nonpremixed but overall lean
Fourth generation = TAPS
TAPS – twin annular premixed swirler - will be
used on GE-90 and GE CFM engines to
achieve reduced NOx levels of 20 g/kN
Looks like the DAC – has dual annular fuel injectors
each injector has an inner pilot (nonpremixed)
and outer MAIN fuel injector (premixed).
MAIN fuel is injected several cm upstream as
a jet in a crossflow – to premix fuel and air

Ref: AIAA Paper 2003-2657 "TAPS –A 4th Generation Propulsion Combustor Technology for Low Emissions" Hukam C. Mongia, GE Aircraft Engines, Cincinnati

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Is ammonium perchlorate (NH4ClO4) a fuel or an oxidizer ?

Fuel = compound with a negative saturated valence
Oxidizer = compound with an positive saturated valence
Saturated valence of a compound is the sum of the saturated valences of each atom
Valence electrons: electrons in the outer shell

Hydrogen has one valence electron, it has a saturated valence of -1
Chlorine has 17 electrons, 7 in its outer shell, so it needs one electron to complete its shell and have 8 electrons, so its saturated valence is +1

Saturated valence = number of electrons that a molecule or atom will “gain” if it forms a covalent bond with another atom or molecule
Hydrogen loses one electron, so its net gain is -1
Chlorine gains one electron, so its net gain is +1

Fuel Like	Saturated Valence	Oxidizer Like	Saturated Valence	Inert	Saturated Valence
H	-1	O	+2	He	0
Li	-1	F	+1	Ne	0
Be	-2	S	+2	N	0 (usually)
B	-3	Cl	+1	Ar	0
C	-4	N	+ (in some cases, if double or triple covalent bonds form)		
Na	-1				
Mg	-2				
Al	-3	Br	+1		
Si	-4	I	+1		
K	-1				

Ex. Hydrogen peroxide H2O2 contains both fuel-like and oxidizer-like atoms. Is this compound a fuel or an oxidizer ? Its saturated valence is $2(-1) + 2(+2) = +2$ (oxidizer).

Radical: an atom or molecule that does not have a completed outer shell – it does not have 2 or 8 electrons in its outer shell. Ex.: the H atom is a radical because it has only one electron it its outer shell. It is very reactive and has a short lifetime. Radicals give off the colors that are observed in flames:
Violet color & UV = OH radicals – hydrogen Bunsen flames
Blue color (431 nm) = CH radicals – methane Bunsen flames
Green color (516 nm) = C2 radicals – propane Bunsen flames

Diffusion coefficients (D) of gas mixtures
from Reid, R.C,
Prausnitz, J.M, Poling B.
Properties of Gases and
Liquids, McGraw Hill

11-3 Diffusion Coefficients for Binary Gas Systems at Low Pressures: Prediction from Theory

The theory describing diffusion in binary gas mixtures at low to moderate pressures has been well developed. As noted earlier in Chaps. 9 (Viscosity) and 10 (Thermal Conductivity), the theory results from solving the Boltzmann equation, and the results are usually credited to both Chapman and Enskog, who independently derived the working equation

$$\boxed{D_{AB} = \frac{3}{16}\frac{(4\pi kT/M_{AB})^{1/2}}{n\pi\sigma_{AB}^2\Omega_D}f_D} \qquad (11\text{-}3.1)$$

where M_A, M_B = molecular weights of A and B
$M_{AB} = 2[(1/M_A) + (1/M_B)]^{-1}$
n = number density of molecules in the mixture
k = Boltzmann's constant
T = absolute temperature

Ω_D, the collision integral for diffusion, is a function of temperature; it depends upon the choice of the intermolecular force law between collidin molecules. σ_{AB} is a characteristic length; it also depends upon the inter molecular force law selected. Finally, f_D is a correction term which is o the order of unity. If M_A is of the same order as M_B, f_D lies between 1. and 1.02 regardless of composition or intermolecular forces. Only if th molecular masses are very unequal and the light component is present in trace amounts is the value of f_D significantly different from unity, and even in such cases, f_D is usually between 1.0 and 1.1 [138].

If f_D is chosen as unity and n is expressed by the ideal-gas law, Eq. (11 3.1) may be written as

$$\boxed{D_{AB} = \frac{0.00266T^{3/2}}{PM_{AB}^{1/2}\sigma_{AB}^2\Omega_D}} \qquad (11\text{-}$$

where D_{AB} = diffusion coefficient, cm^2/s
T = temperature, K
P = pressure, bar
σ_{AB} = characteristic length, Å
Ω_D = diffusion collision integral, dimensionless

and M_{AB} is defined under Eq. (11-3.1). The key to the use of Eq. (11-3. is the selection of an intermolecular force law and the evaluation of σ and Ω_D.

Lennard-Jones 12-6 potential

As noted earlier [Eq. (9-4.2)], a popular correlation relating the interm lecular energy ψ between two molecules to the distance of separation r, given by

$$\psi = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{11-3.3}$$

with ϵ and σ as the characteristic Lennard-Jones energy and length, respectively. Application of the Chapman-Enskog theory to the viscosity of pure gases has led to the determination of many values of ϵ and σ; some of them are given in Appendix B.

To use Eq. (11-3.2), some rule must be chosen to obtain the interaction value σ_{AB} from σ_A and σ_B. Also, it can be shown that Ω_D is a function only of kT/ϵ_{AB}, where again some rule must be selected to relate ϵ_{AB} to ϵ_A and ϵ_B. The simple rules shown below are usually employed:

$$\epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2} \tag{11-3.4}$$

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \tag{11-3.5}$$

Ω_D is tabulated as a function of kT/ϵ for the 12-6 Lennard-Jones potential [100], and various analytical approximations also are available [92, 109, 112, 158]. The accurate relation of Neufield et al. [158] is

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)} \tag{11-3.6}$$

where $T^* = kT/\epsilon_{AB}$ $\quad A = 1.06036 \quad B = 0.15610$

$C = 0.19300 \quad D = 0.47635 \quad E = 1.03587$

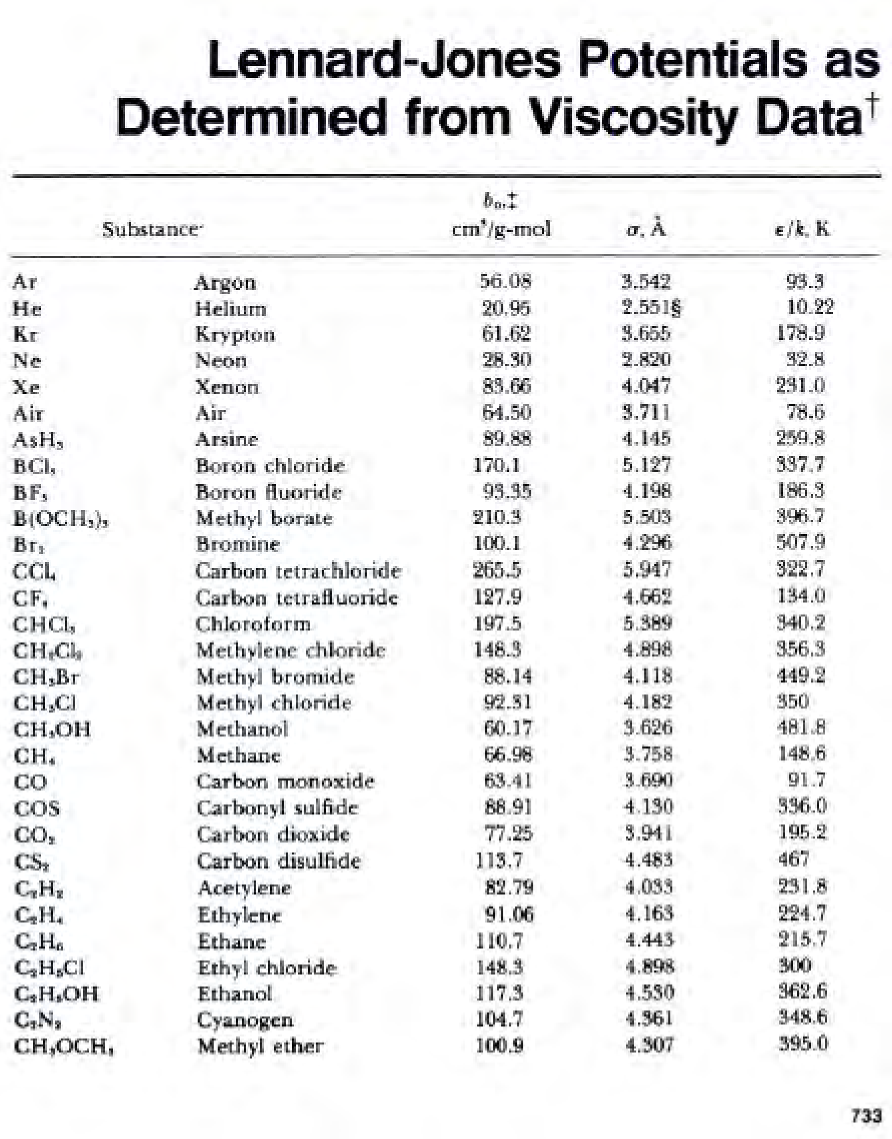
$F = 1.52996 \quad G = 1.76474 \quad H = 3.89411$

Example 11-1 Estimate the diffusion coefficient for the system N_2-CO_2 at 590 K and 1 bar. The experimental value reported by Ellis and Holsen [61] is 0.583 cm^2/s.

solution To use Eq. (11-3.2), values of σ (CO_2), σ (N_2), ϵ (CO_2), and ϵ (N_2) must be obtained. Using the values in Appendix B with Eqs. (11-3.4) and (11-3.5) gives σ (CO_2) = 3.941 Å, σ (N_2) = 3.798 Å; σ (CO_2-N_2) = (3.941 + 3.798)/2 = 3.8695 Å; ϵ (CO_2)/k = 195.2 K, ϵ (N_2)/k = 71.4 K; ϵ (CO_2-N_2)/k = $[(195.2)(71.4)]^{1/2}$ = 118 K. Then $T^* = kT/\epsilon$ (CO_2-N_2) = 590/118 = 5.0. With Eq. (11-3.6), Ω_D = 0.842. Since M (CO_2) = 44.0 and M (N_2) = 28.0, $M_{AB} = (2)[(1/44.0) + (1/28.0)]^{-1} = 34.22$. With Eq. (11-3.2),

$$D\,(CO_2\text{-}N_2) = \frac{(0.00266)(590)^{3/2}}{(1)(34.22)^{1/2}(3.8695)^2(0.842)} = 0.52\ \text{cm}^2/\text{s}$$

The error is 11 percent. Ellis and Holsen recommend values of ϵ (CO_2-N_2) = 134 K and σ (CO_2-N_2) = 3.660 Å. With these parameters, they predicted D to be 0.56 cm^2/s, a value closer to that found experimentally.



Lennard-Jones Potentials as Determined from Viscosity Data†

Substance		b_0,‡ cm^3/g-mol	σ, Å	ϵ/k, K
Ar	Argon	56.08	3.542	93.3
He	Helium	20.95	2.551§	10.22
Kr	Krypton	61.62	3.655	178.9
Ne	Neon	28.30	2.820	32.8
Xe	Xenon	83.66	4.047	231.0
Air	Air	64.50	3.711	78.6
AsH_3	Arsine	89.88	4.145	259.8
BCl_3	Boron chloride	170.1	5.127	337.7
BF_3	Boron fluoride	93.35	4.198	186.3
$B(OCH_3)_3$	Methyl borate	210.3	5.503	396.7
Br_2	Bromine	100.1	4.296	507.9
CCl_4	Carbon tetrachloride	265.5	5.947	322.7
CF_4	Carbon tetrafluoride	127.9	4.662	134.0
$CHCl_3$	Chloroform	197.5	5.389	340.2
CH_2Cl_2	Methylene chloride	148.3	4.898	356.3
CH_3Br	Methyl bromide	88.14	4.118	449.2
CH_3Cl	Methyl chloride	92.31	4.182	350
CH_3OH	Methanol	60.17	3.626	481.8
CH_4	Methane	66.98	3.758	148.6
CO	Carbon monoxide	63.41	3.690	91.7
COS	Carbonyl sulfide	88.91	4.130	336.0
CO_2	Carbon dioxide	77.25	3.941	195.2
CS_2	Carbon disulfide	113.7	4.483	467
C_2H_2	Acetylene	82.79	4.033	231.8
C_2H_4	Ethylene	91.06	4.163	224.7
C_2H_6	Ethane	110.7	4.443	215.7
C_2H_5Cl	Ethyl chloride	148.3	4.898	300
C_2H_5OH	Ethanol	117.3	4.530	362.6
C_2N_2	Cyanogen	104.7	4.361	348.6
CH_3OCH_3	Methyl ether	100.9	4.307	395.0

Substance		b_0,‡ cm^3/g-mol	σ, Å	ϵ/k, K
CH_2CHCH_3	Propylene	129.2	4.678	298.9
CH_3CCH	Methylacetylene	136.2	4.761	251.8
C_3H_6	Cyclopropane	140.2	4.807	248.9
C_3H_8	Propane	169.2	5.118	237.1
n-C_3H_7OH	n-Propyl alcohol	118.8	4.549	576.7
CH_3COCH_3	Acetone	122.8	4.600	560.2
CH_3COOCH_3	Methyl acetate	151.8	4.936	469.8
n-C_4H_{10}	n-Butane	130.0	4.687	531.4
iso-C_4H_{10}	Isobutane	185.6	5.278	330.1
$C_2H_5OC_2H_5$	Ethyl ether	231.0	5.678	313.8
$CH_3COOC_2H_5$	Ethyl acetate	178.0	5.205	521.3
n-C_5H_{12}	n-Pentane	244.2	5.784	341.1
$C(CH_3)_4$	2,2-Dimethylpropane	340.9	6.464	193.4
C_6H_6	Benzene	193.2	5.349	412.3
C_6H_{12}	Cyclohexane	298.2	6.182	297.1
n-C_6H_{14}	n-Hexane	265.7	5.949	399.3
Cl_2	Chlorine	94.65	4.217	316.0
F_2	Fluorine	47.75	3.357	112.6
HBr	Hydrogen bromide	47.58	3.353	449
HCN	Hydrogen cyanide	60.37	3.630	569.1
HCl	Hydrogen chloride	46.98	3.339	344.7
HF	Hydrogen fluoride	39.37	3.148	330
HI	Hydrogen iodide	94.24	4.211	288.7
H_2	Hydrogen	28.51	2.827	59.7
H_2O	Water	23.25	2.641	809.1
H_2O_2	Hydrogen peroxide	93.24	4.196	289.3
H_2S	Hydrogen sulfide	60.02	3.623	301.1
Hg	Mercury	33.03	2.969	750
$HgBr_2$	Mercuric bromide	165.5	5.080	686.2
$HgCl_2$	Mercuric chloride	118.9	4.550	750
HgI_2	Mercuric iodide	224.6	5.625	695.6
I_2	Iodine	173.4	5.160	474.2
NH_3	Ammonia	30.78	2.900	558.3
NO	Nitric oxide	53.74	3.492	116.7
NOCl	Nitrosyl chloride	87.75	4.112	395.3
N_2	Nitrogen	69.14	3.798	71.4
N_2O	Nitrous oxide	70.80	3.828	232.4
O_2	Oxygen	52.60	3.467	106.7
PH_3	Phosphine	79.63	3.981	251.5
SF_6	Sulfur hexafluoride	170.2	5.128	222.1
SO_2	Sulfur dioxide	87.75	4.112	335.4
SiF_4	Silicon tetrafluoride	146.7	4.880	171.9
SiH_4	Silicon hydride	85.97	4.084	207.6
$SnBr_4$	Stannic bromide	329.0	6.388	563.7
UF_6	Uranium hexafluoride	268.1	5.967	236.8

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†R. A. Svehla, *NASA Tech. Rep.* R-132, Lewis Research Center, Cleveland, Ohio, 1962.

‡$b_0 = \frac{2}{3}\pi N_0 \sigma^3$, where N_0 is Avogadro's number.

§The parameter σ was determined by quantum-mechanical formulas.

Viscosity of a gas mixture

Method of Wilke

In a further simplification of the kinetic theory approach, Wilke [221] neglected second-order effects and proposed:

$$\eta_m = \sum_{i=1}^{n} \frac{y_i \eta_i}{\sum_{j=1}^{n} y_j \phi_{ij}} \tag{9-5.13}$$

where

$$\phi_{ij} = \frac{[1 + (\eta_i/\eta_j)^{1/2}(M_j/M_i)^{1/4}]^2}{[8(1 + M_i/M_j)]^{1/2}} \tag{9-5.14}$$

ϕ_{ji} is found by interchanging subscripts or by

$$\phi_{ji} = \frac{\eta_j}{\eta_i}\frac{M_i}{M_j}\phi_{ij} \tag{9-5.15}$$

For a binary system of 1 and 2, with Eqs. (9-5.13) to (9-5.15),

$$\eta_m = \frac{y_1\eta_1}{y_1 + y_2\phi_{12}} + \frac{y_2\eta_2}{y_2 + y_1\phi_{21}} \tag{9-5.16}$$

where η_m = viscosity of the mixture
η_1, η_2 = pure component viscosities
y_1, y_2 = mole fractions

and
$$\phi_{12} = \frac{[1 + (\eta_1/\eta_2)^{1/2}(M_2/M_1)^{1/4}]^2}{\{8[1 + (M_1/M_2)]\}^{1/2}}$$

$$\phi_{21} = \phi_{12}\frac{\eta_2}{\eta_1}\frac{M_1}{M_2}$$

Equation (9-5.13), with ϕ_{ij} from Eq. (9-5.14), has been extensively tested. Wilke [221] compared values with data on 17 binary systems and reported an average deviation of less than 1 percent; several cases in which η_m passed through a maximum were included. Many other investigators have tested this method [4, 28, 42, 51, 78, 161, 176, 177, 191, 214, 223]. In most cases, only nonpolar mixtures were compared, and very good results obtained. For some systems containing hydrogen as one component, less satisfactory agreement was noted. In Table 9-4, Wilke's method predicted mixture viscosities that were larger than experimental for the H_2-N_2 system, but for H_2-NH_3, it underestimated the viscosities. Gururaja et al. [91] found that this method also overpredicted in the H_2-O_2 case but was quite accurate for the H_2-CO_2 system. Wilke's approximation has proved reliable even for polar-polar gas mixtures of aliphatic alcohols [169]. The principal reservation appears to lie in those cases where $M_i \gg M_j$ and $\eta_i \gg \eta_j$.

Example 9-5 Kestin and Yata [124] report that the viscosity of a mixture of methane and n-butane is 93.35 μP at 293 K when the mole fraction of n-butane is 0.303. Compare this result with the value estimated by Wilke's method. For pure methane and n-butane, these same authors report viscosities of 109.4 and 72.74 μP.

solution Let 1 refer to methane and 2 to n-butane. $M_1 = 16.043$ and $M_2 = 58.124$.

$$\phi_{12} = \frac{[1 + (109.4/72.74)^{1/2}(58.124/16.043)^{1/4}]^2}{\{8[1 + (16.043/58.124)]\}^{1/2}} = 2.268$$

$$\phi_{21} = 2.268 \frac{72.74}{109.4} \frac{16.043}{58.124} = 0.416$$

$$\eta_m = \frac{(0.697)(109.4)}{0.697 + (0.303)(2.268)} + \frac{(0.303)(72.74)}{0.303 + (0.697)(0.416)}$$

$$= 92.26\ \mu\text{P}$$

$$\text{Error} = \frac{92.26 - 93.35}{93.35} \times 100 = -1.2\%$$

SEE NEXT PAGE

TABLE 332.—VISCOSITY OF GASES

Variation of viscosity with pressure and temperature

According to the kinetic theory of gases the coefficient of viscosity $\eta = \frac{1}{3}(\rho \bar{c} l)$, ρ being the density, $\bar{c}$ the average velocity of the molecules, l the average path. Since l varies inversely as the number of molecules per unit volume, ρl is a constant and η should be independent of the density and pressure of a gas (Maxwell's law). This has been found true for ordinary pressures; below 1/60 atmosphere it may fail, and for certain gases it has been proved untrue for high pressures, e.g., CO_2 at 33° and above 50 atm. See Jeans, "Dynamical Theory of Gases."

If B is the amount of momentum transferred from a plane moving with velocity U and parallel to a stationary plane distant d, and s is a quantity (coefficient of slip) to allow for the slipping of the gas molecules over the plane, then $\eta = (B/U)(d+2s)$; s is of the same magnitude as l, probably between .7 (Timiriazeff) and .9 (Knudsen) of it; at low pressures d becomes negligible compared with $2s$ and the viscosity should vary inversely as the pressure.

$\bar{c}$ depends only on the temperature and the molecular weight. $\bar{c}$ varies as the $\sqrt{T}$, but η has been found to increase much more rapidly. Meyer's formula, $\eta_t = \eta_0(1 + at)$, where a is a constant and η_0 the viscosity at 0°C, is a convenient approximate relation. Sutherland's formula

$$\eta_t = \eta_0 \frac{273 + C}{T + C}\left(\frac{T}{273}\right)^{\frac{3}{2}}$$

is the most accurate formula in use, taking into account the effect of molecular forces. It holds for temperatures above the critical and for pressures following approximately Boyle's law. It may be thrown into the form $T = KT^{\frac{3}{2}}/\eta - C$ which is linear of T and $T^{\frac{3}{2}}/\eta$, with a slope equal to K and the ordinate intercept equal to $-C$. Onnes (see Jeans) shows that this formula does not represent helium at low temperatures with anything like the accuracy of the simpler formula $\eta = \eta_0(T/273.1)^n = AT^n$.

The following table[125] contains the constant a of Meyers formula, C and K of Sutherland's formula, n and A of the exponential formula, and the temperature range for which the constants of the latter two are applicable.

Gas	Temperature range °C	$a \times 10^3$	C	$K \times 10^6$	n	$A \times 10^6$
Air	23 to 750	2.90	117.9	14.82	.754	2.490
Ammonia	− 77 to 441	. . .	472	15.42	1.041	.274
Argon	−183 to 827	1.78	133	19.00	.766	2.782
Benzene	0 to 313	. . .	403	10.33	.974	.299
Carbon dioxide	− 98 to 1052	3.48	233	15.52	.868	1.057
Carbon monoxide	. . .	2.69	102	13.5	.74	. . .
Chloroform	. . .	. . .	454	15.9	. . .	. . .
Ethylene	. . .	3.50	226	10.6	. . .	. . .
Helium	−258 to 817	. . .	97.6	15.13	.653	4.894
Hydrogen	−258 to 825	. . .	70.6	6.48	.678	1.860
Krypton	. . .	. . .	188	. . .	. . .	. . .
Mercury	−218 to 610	. . .	996	63.00	1.082	.573
Methane	18 to 499	. . .	155	9.82	.770	1.360
Neon	. . .	. . .	252	. . .	. . .	. . .
Nitrogen	−191 to 825	2.69	102	13.85	.702	3.213
Nitrous oxide	. . .	3.45	313	17.2	.93	. . .
Oxygen	−191 to 829	. . .	110	16.49	.721	3.355
Water vapor	0 to 407	. . .	659	18.31	1.116	.170
Xenon	. . .	. . .	252	. . .	. . .	. . .

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[125] Dushman, S., Vacuum technique, p. 37, John Wiley & Sons, New York, 1949; Banerjea, G. B., and Plattanaik, B., Zeit. Physik, vol. 110, p. 676, 1938; Partington, J. R., Phys. Zeit., vol. 34, p. 289, 1933; Fisher, Phys. Rev., vol. 24, 1907.

① $\mu = AT^n$

or

$\mu = A(273.1)^n \left[\frac{273+C}{T+C}\right]\left(\frac{T}{273}\right)^{3/2}$

$\mu_0 = A(273.1)^n$

$\mu_{0_{air}} = 2.49 \times 10^{-6}(273.1)^{.745}$

$\mu_{0_{air}} = 1.71 \times 10^{-4} \frac{g}{cm\,s}$

μ_{air} (Kreith) $= 1.71\,10^{-4}$ g/cm s

TABLE 333.—VISCOSITY OF GASES AND VAPORS

Part 1.—Viscosity of vapors

The values of η given in the table are 10^6 times the coefficients of viscosity in cgs units.

Substance	Temp. °C	η	Substance	Temp. °C	η
Acetone	18.0	78.	Ether	16.1	73.2
Alcohol, Methyl	66.8	135.	"	36.5	79.3
Alcohol, Ethyl	78.4	142.	Ethyl chloride	0.	93.5
Alcohol, Propyl, norm	97.4	142.	Ethyl iodide	72.3	216.0
Alcohol, Isopropyl	82.8	162.	Ethylene	0.0	96.1
Alcohol, Butyl, norm	116.9	143.	Mercury	270.0	489.
Alcohol, Isobutyl	108.4	144.	"	300.0	532.
Alcohol, Tert. butyl	82.9	160.	"	330.0	582.
Ammonia	20.0	108.	"	360.0	627.
Benzene	0.	70.	"	390.0	671.
"	19.0	79.	Methane	20.0	120.1
"	100.0	118.	Methyl chloride	0.0	98.8
Carbon bisulfide	16.9	92.4	" "	15.0	105.2
Carbon monoxide	20.0	184.0	" "	302.0	213.9
Chloroform	0.0	95.9	Methyl iodide	44.0	232.
"	17.4	102.9	Water vapor	0.0	90.4
"	61.2	189.0	" "	16.7	96.7
Ether	0.0	68.9	" "	100.0	132.0

Part 2.—Viscosity of gases and vapors [illegible]

(Temperature variation)

Temp. °C	Viscosity in millipoises							
	Air	Argon	Carbon dioxide	Chlorine	Helium	Hydrogen	Nitrogen	Oxygen
—200	.053	...	...	...	...	.033	...	...
—150	.081	...	...	...	...	.047	...	...
—100	.111	...	.087	...	...	.061	...	...
— 50	.139	...	.112	...	...	.073	...	...
0	.175 *	...	.135	...	...	.083	...	...
50	.193	.241	.159	.147	.207	.093	.189	.217
100	.216	.269	.181	.167	.228	.102	.207	.241
150	.237	.297	.203	.189	.247	.111	.226	.264
200	.256	.321	.225	.208	.267	.120	.245	.287
250	.275	.346	.245	.228	.285	.129	.263	.309
300	.293	.367	.262	...	.305	.137	.280	.330
350	.310	.389	.280	...	.323	.145	.296	.349
400	.327	.410	.299	...	.341	.153	.311	.368
500	.357	.450	.331	...	.375	.167	.341	.403
600	.384	.488	.362	...	.408	.181	.367	.435
700	.411	.521	.391	...	.438	.195	.391	.466
800	.437	.554	.417	...	.467	.208	.414	.494
900	.463	...	.421	...	...	...	...	...
1000	.499	...	.465	...	...	...	...	...
1100	.511	...	...	...	...	...	...	...

Xenon
.222 (15°C)

Nitric oxide
.179 (0°C)

Nitrous oxide
.138 (0°C)

Krypton
.246 (15°C)

Carbon monoxide
.163 (0°C)

Ammonia
.096 (0°C)

[illegible] Based on data from Landolt and Börnstein, 3d supplementary vol., pt. 1, p. 184, 1935.

$\mu_{air} = .175 \underbrace{\times 10^{-3}\ g/cm\text{-}sec}_{millipoise}$

$= .175 \times 10^{-4}\ kg/m\text{-}sec$

$\nu_{air} = \frac{.175 \times 10^{-3}\ g/cm\text{-}sec}{1.22 \times 10^{-3}\ g/cm^3}$

$= .143\ cm^2/s$

go over handout sheet p 7
(− = fuel) valencies of elements
valencies of compounds

Fuel or Oxidizer?
or saturated product

Saturated valence - see handout

carbon monoxide $CO = -4 + 2 = -2$ = fuel

silane $SiH_4 = -4 - 4 = -8$ = fuel

methanol $CH_3OH = -4 - 3 + 2 - 1 = -6$ = fuel

Ammonium perchlorate $NH_4ClO_4 = 0 - 4 + 1 + 8 = +5$ = oxidizer

CO_2 carbon dioxide $= -4 + 4 = 0$ saturated product

H_2O water $= -2 + 2 = 0$ saturated product

when boron (B) is reacted with oxygen gas (O_2) what is the saturated product?

the saturated product must be the compound: B_xO_y

saturated valence of B_xO_y must be <u>zero</u> (product)

~~to~~ sat. valence of compound is sum of sat. valence of atoms

$(-3)x + (+2)y = 0$ so $x = 2/3\,y$ but x, y are integers, so

$x = 2$ $y = 3$ $B_xO_y = B_2O_3$

Note: if compound has a saturated valence of zero ~~it~~ is either

a) saturated product

b) saturated monopropellant (has both fuel & ox in stoich proportions)

Stoichiometry   Kuo p. 40   lecture 2

(a) assume methane-air, stoichiometric, only saturated products (final T not so high as to dissociate products)

assume basis = 1 kmole fuel

$$1\,CH_4 + \underline{2}\;O_2 + \underline{2}\,\tfrac{79}{21}\,N_2 \rightarrow \underline{1}\;CO_2 + \underline{2}\,H_2O + \underline{2\tfrac{79}{21}}\,N_2$$

same

(b) now define $r = $ mass fuel/mass air $= \dfrac{12\text{ kg} + 4\text{ kg}}{2(32) + 2\,\frac{79}{21}(28)\text{ kg}} = 0.058$

"fuel-air ratio"

$r_s = $ stoich fuel air ratio value of r if stoich. $= .058$

~~fuel-air~~ equivalence ratio $\boxed{\phi \equiv \dfrac{r}{r_s}} = 1.0$ for stoichiometric

fuel-lean conditions $\phi < 1$ put O_2 on RHS!

$$1\,CH_4 + m\,O_2 + m\,\tfrac{79}{21}\,N_2 \rightarrow \underline{1}\,CO_2 + 2\,H_2O + m\,\tfrac{79}{21}\,N_2 + (m-2)\,O_2$$

How is m related to ϕ?

$$r = \frac{16\text{kg}}{m\,32 + m\,\frac{79}{21}\,28} \qquad r_s = \frac{16\text{ kg}}{2(32) + 2\,\frac{79}{21}\,28}$$

$\therefore\ \phi = \dfrac{r}{r_s} = \dfrac{2}{m}$ or $m = \dfrac{2}{\phi}$ so we write

lean case: $\phi<1$ no dissoc.

$$\boxed{CH_4 + \frac{2}{\phi}\,O_2 + \frac{2}{\phi}\,\frac{79}{21}\,N_2 \rightarrow CO_2 + 2\,H_2O + \frac{2}{\phi}\,\frac{79}{21}\,N_2 + \left(\frac{2}{\phi} - 2\right)O_2} \quad (a)$$

fuel-rich conditions $\phi > 1$ put CH_4 on RHS

omit

$$1\,CH_4 + m\,O_2 + n\,\frac{79}{21}N_2 \rightarrow a\,CO_2 + b\,H_2O + c\,N_2 + d\,CH_4$$

solve atom balance for: $a = n/2$ $b = n$

$c = n\frac{79}{21}$ $d = 1 - \frac{n}{2}$

$$\phi = \frac{r}{r_s} = \left(\frac{16}{n\,32 + n\frac{79}{21}28}\right) \Big/ \frac{16}{2(32) + 2\frac{79}{21}28} = \frac{2}{n}$$

so $n = \frac{2}{\phi}$ find result

rich $\phi > 1$ no dissoc

$$\boxed{CH_4 + \frac{2}{\phi}O_2 + \frac{2}{\phi}\frac{79}{21}N_2 \rightarrow \left(\frac{1}{\phi}\right)CO_2 + \left(\frac{2}{\phi}\right)H_2O + \frac{2}{\phi}\frac{79}{21}N_2 + \left(1 - \frac{1}{\phi}\right)CH_4}$$

(b)

if methane does not dissociate.

realistic rich conditions – if CH_4 dissociates:

($\phi > 1$) (rich case with dissoc)

$$CH_4 + \frac{2}{\phi}O_2 + \frac{2}{\phi}\frac{79}{21}N_2 \rightarrow a\,CO_2 + b\,CO + c\,H_2O + d\,H_2 + \frac{2}{\phi}\frac{79}{21}N_2 + f\,H$$

(c)

have CHO atom balances (3 eqns)

have 5 unknowns a, b c d, f (ϕ = given)

need 2 equilibrium relations

Ex. aluminum and AP (ammonium perchlorate) react to form saturated products. $\left\{\begin{matrix} Al_2O_3 \\ HCl \\ H_2O \\ N_2 \end{matrix}\right\}$ what is the stoich fuel-oxidizer mass ratio?

$$1\ Al + a\ NH_4ClO_4 \rightarrow b\ Al_2O_3 + c\ N_2 + d\ HCl + e\ H_2O$$

Al $\quad 1 = 2b$

N $\quad a = 2c$

H $\quad 4a = d + 2e$

Cl $\quad a = d$

O $\quad 4a = 3b + e$

$b = 0.50$

elim a: $\quad 8c = d + 2e$

$2c = d$

$8c = 3b + e$

elim d: $\quad 6c = \cancel{2c} + 2e \quad 3c = e$

$8c = 3/2 + e$

$5c\ \cancel{8c} = 3/2 + \cancel{3c} \Rightarrow c = 0.3$

$\therefore e = 0.9 \quad d = 2c = 0.6$

$1.5\ \cancel{2.4} = 3b\ \cancel{+0.9} \quad a = 2c = 0.6$

$\therefore$ $\boxed{\begin{matrix} a = 0.60 \\ b = 0.50 \\ c = 0.30 \\ d = 0.60 \\ e = 0.90 \end{matrix}}$

$$\frac{\text{mass Al}}{\text{mass AP}} = \frac{(1\ \text{kmole})\cdot(27\ \text{kg/kmol})}{0.60\,(14 + 4 + 71 + 64)} = 0.29$$

First Law of Thermodynamics for SSSF = Steady State Steady Flow Reacting System

(see thermo text by Borgnakke and Sonntag or similar text)

combustor
or compressor
or turbine

Assume: steady state, 1-D, neglect KE, PE = low speed
Variable area, pressure may vary (p_e does not have to equal p_i)
Do not assume heat capacity c_p is constant, so not calorically perfect
Assume ideal gas law holds $p = \rho RT$

Ex. $CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$

$\bar{h}_i$ = enthalpy per mole (J/mole or kJ/kmole) of species i

$$\bar{h}_i = \bar{h}^o_{f,i} + \Delta\bar{h}_i \qquad \text{where } \Delta\bar{h}_i = \bar{h}_i - \bar{h}_{298}$$

$\bar{h}^o_{f,i}$: enthalpy/mole of formation (chemical enthalpy/mole) see table on p. 2-3

$\Delta\bar{h}_i$: sensible or thermal enthalpy/mole see tables on pp. 2-4 to 2-6

Ex: $\bar{h}_{f,CO2} = -393{,}522$ kJ/kmol see p 2-3

$$\Delta\bar{h}_{CO2} = \bar{h}_{CO2} - \bar{h}_{298,CO2} = \int_{298K}^{T} \bar{c}_p(T)\,dT = 44{,}484\ \frac{kJ}{kmol}$$

if $T = 1200K$
(see p 2-5)

First Law:

$$\boxed{Q_{cv} + \sum_R \nu_i'\left(\bar{h}^o_{f,i} + \Delta\bar{h}_i\right) = W_{cv} + \sum_P \nu_i''\left(\bar{h}^o_{f,i} + \Delta\bar{h}_i\right)}$$

Heat/kmole fuel added TO the CV across the CV boundaries (normally negative)	enthalpy/kmole fuel of reactants entering the CV	Work/kmole fuel done by CV across the CV boundaries (zero unless turbine or compressor exists)	enthalpy/kmole fuel of products leaving the CV

Compact Notation (Kuo p. 18)

consider methane - oxygen stoichiometric

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

Kuo's compact notation for this is: (p. 18)

$$\sum_i \nu_i' A_i \rightarrow \sum_i \nu_i'' A_i$$

A_i = species i $A_1 = CH_4$, $A_2 = O_2$ . . .

ν_i' = reactant stoich. coeff = LHS

ν_i'' = product stoich. coeff = RHS

i =	1	2	3	4
A_i =	CH_4	O_2	CO_2	H_2O
ν_i' = LHS =	1	2	0	0
ν_i'' = RHS =	0	0	1	2

Ex. stoich methane-O_2, non-adiabatic walls, no work $W_{cv} = 0$

$T_i = 298K$ initial T, $T_e = 1000K$ final T

⇒ what is heat transfer Q_{cv}? kJ (per kmol fuel)

$1\,CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$ get ν_i', ν_i'' from p. 1-18

$$Q_{cv} + 1\left(\bar{h}^o_{f\,CH4} + \Delta\bar{h}_{CH4}\right) + 2\left(\bar{h}^o_{f\,O2} + \Delta\bar{h}_{O2}\right) = \left(\bar{h}^o_{f\,CO2} + \Delta\bar{h}_{CO2}\right) + 2\left(\bar{h}^o_{f\,H2O} + \Delta\bar{h}_{H2O}\right)$$

from handouts Thermo, p. 2-3

	Enthalpy of Formation $\bar{h}^o_f$
CH_4	$-74{,}873$ $\frac{kJ}{kmol}$
O_2	0
CO_2	$-393{,}522$
H_2O	$-241{,}827$

	Enthalpy (w.r.t. 298K) $\Delta\bar{h}_i$ at 298K
CH_4	0
O_2	0

	Enthalpy w.r.t 298K $\Delta\bar{h}_e$ at 1000K
CO_2	$33{,}405$ $\frac{kJ}{kmol}$
H_2O	$25{,}978$

note: $\boxed{\Delta\bar{h}_i = \bar{h}_i - \bar{h}_{298}}$ = thermo handout pages 2-4 to 2-6

plug in, solve for Q_{cv}

$$\boxed{Q_{cv} = -716{,}942\ \frac{kJ}{kmol\ fuel}}$$

Q_{cv} = heat added across C.V. walls – if heat is lost, Q_{cv} = negative

note: ν_i' (Kuo) = n_i (Sonntag)
ν_i'' (Kuo) = n_e (Sonntag)

Another way to do the example problem on p 2-2.
(Not recommended. It uses Kuo's notation on p. 71)

Kuo uses capital H's for enthalpy/mole

Kuo's tables are in Kcal/mole

Kuo defines $\Delta H^\circ_{f\,T_0}$ = heat of formation of the species

Kuo p. 71:

$$\boxed{\begin{aligned}\Delta H = Q_{cv} - W_{cv} = &\sum_P \nu_j''\left\{\left(H^\circ_{Tf} - H^\circ_{T_0}\right) + \Delta H^\circ_{f\,T_0}\right\}_j \\ &- \sum_R \nu_i'\left\{\left(H^\circ_{Ti} - H^\circ_{T_0}\right) + \Delta H^\circ_{f,T_0}\right\}_i\end{aligned}}$$

$\Delta H^\circ_{f_{T_0}}$ = heat of formation of the species

for: $CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$

$T_i = 298K$, $T_e = 1000\,K$ $Q_{cv} = ?$

above eqn gives

$$\begin{aligned}Q_{cv} &= 1\Big(\underset{\text{Table 1.5a}}{7.982\,\tfrac{kcal}{mol}} + \underset{\text{Table 1.2}}{-94.054\,\tfrac{kcal}{mol}}\Big) \\ &\quad + 2\left(6.214 - 57.798\right) \\ &\quad - 1\left(0 + -17.895\right) \\ &\quad - 2\left(0 + 0\right) \\ &= -171.3\ kcal/mol_{fuel} \cdot \frac{4.1855\,kJ}{kcal}\end{aligned}$$

$$\boxed{Q_{cv} = -717{,}100\ kJ/kmol\,fuel}$$

Same as on p. 2-2

Enthalpy of Combustion of Some Hydrocarbons at 25°C

= −LHV

		Liquid H_2O in Products (Negative of Higher Heating Value)		Vapor H_2O in Products (Negative of Lower Heating Value)	
Hyrocarbon	Formula	Liquid Hydrocarbon, kJ/kg fuel	Gaseous Hydrocarbon, kJ/kg fuel	Liquid Hydrocarbon, kJ/kg fuel	Gaseous Hydrocarbon, kJ/kg fuel
Paraffin Family					
Methane	CH_4		−55 496		−50 010
Ethane	C_2H_6		−51 875		−47 484
Propane	C_3H_8	−49 975	−50 345	−45 983	−46 353
Butane	C_4H_{10}	−49 130	−49 500	−45 344	−45 714
Pentane	C_5H_{12}	−48 643	−49 011	−44 983	−45 351
Hexane	C_6H_{14}	−48 308	−48 676	−44 733	−45 101
Heptane	C_7H_{16}	−48 071	−48 436	−44 557	−44 922
Octane	C_8H_{18}	−47 893	−48 256	−44 425	−44 788
Decane	$C_{10}H_{22}$	−47 641	−48 000	−44 239	−44 598
Dodecane	$C_{12}H_{26}$	−47 470	−47 828	−44 109	−44 467
Olefin Family					
Ethene	C_2H_4		−50 296		−47 158
Propene	C_3H_6		−48 917		−45 780
Butene	C_4H_8		−48 453		−45 316
Pentene	C_5H_{10}		−48 134		−44 996
Hexene	C_6H_{12}		−47 937		−44 800
Heptene	C_7H_{14}		−47 800		−44 662
Octene	C_8H_{16}		−47 693		−44 556
Nonene	C_9H_{18}		−47 612		−44 475
Decene	$C_{10}H_{20}$		−47 547		−44 410
Alkylbenzene Family					
Benzene	C_6H_6	−41 831	−42 266	−40 141	−40 576
Methylbenzene	C_7H_8	−42 437	−42 847	−40 527	−40 937
Ethylbenzene	C_8H_{10}	−42 997	−43 395	−40 924	−41 322
Propylbenzene	C_9H_{12}	−43 416	−43 800	−41 219	−41 603
Butylbenzene	$C_{10}H_{14}$	−43 748	−44 123	−41 453	−41 828
Hydrogen	H_2		−142919		−119,954

Enthalpy of Formation, Gibbs Function of Formation and Absolute Entropy of Various Substances at 25°C, 0.1 MPa Pressure

				$\bar{h}_f^\circ$	$\bar{g}_f^\circ$	$\bar{s}^\circ$
Substance	Formula	M	State	kJ/kmol	kJ/kmol	kJ/kmol K
Carbon monoxide[a]	CO	28.011	gas	−110 529	−137 150	197.653
Carbon dioxide[a]	CO_2	44.011	gas	−393 522	−394 374	213.795
Water[a,b]	H_2O	18.015	gas	−241 827	−228 583	188.833
Water[b]	H_2O	18.015	liq.	−285 838	−237 178	70.049
Methane[a]	CH_4	16.043	gas	− 74 873	− 50 751	186.256
Acetylene[a]	C_2H_2	26.038	gas	+226 731	+209 234	200.958
Ethene[a]	C_2H_4	28.054	gas	+ 52 283	+ 68 207	219.548
Ethane[c]	C_2H_6	30.070	gas	− 84 667	− 32 777	229.602
Propane[c]	C_3H_8	44.097	gas	−103 847	− 23 316	270.019
Butane[c]	C_4H_{10}	58.124	gas	−126 148	− 16 914	310.227
Octane[c] gas	C_8H_{18}	114.23	gas	−208 447	+ 16 859	466.835
Octane[c] liquid	C_8H_{18}	114.23	liq.	−249 952	+ 6 940	360.896
Carbon[a] (graphite)	C	12.011	solid	0	0	5.795

Enthalpy of Formation at 25°C, Ideal Gas Enthalpy and Absolute Entropy at 0.1 MPa (1 bar) Pressure

$\Delta\bar{h}_{N2}$

	Nitrogen, Diatomic (N_2) (9/30/65)		Nitrogen, Monatomic (N) (3/31/61)	
	$(\bar{h}_f^\circ)_{298} = 0$ kJ/kmol $M = 28.013$		$(\bar{h}_f^\circ)_{298} = 472\ 646$ kJ/kmol $M = 14.007$	
Temp. K	$(\bar{h}^\circ - \bar{h}^\circ_{298})$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K	$(\bar{h}^\circ - \bar{h}^\circ_{298})$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K
0	−8 669	0	−6 197	0
100	−5 770	159.813	−4 117	130.596
200	−2 858	179.988	−2 042	145.006
298	0	191.611	0	153.302
300	54	191.791	38	153.432
400	2 971	200.180	2 117	159.411
500	5 912	206.740	4 197	164.051
600	8 891	212.175	6 276	167.842
700	11 937	216.866	8 351	171.047
800	15 046	221.016	10 431	173.821
900	18 221	224.757	12 510	176.268
1000	21 460	228.167	14 590	178.461
1100	24 757	231.309	16 669	180.440
1200	28 108	234.225	18 749	182.247
1300	31 501	236.941	20 824	183.803
1400	34 936	239.484	22 903	185.452
1500	38 405	241.878	24 983	186.887
1600	41 903	244.137	27 062	188.230
1700	45 430	246.275	29 142	189.490
1800	48 982	248.304	31 217	190.678
1900	52 551	250.237	33 296	191.799
2000	56 141	252.078	35 376	192.866
2100	59 748	253.836	37 455	193.883
2200	63 371	255.522	39 535	194.850
2300	67 007	257.137	41 614	195.774
2400	70 651	258.689	43 698	196.661
2500	74 312	260.183	45 777	197.511
2600	77 973	261.622	47 861	198.326
2700	81 659	263.011	49 949	199.113
2800	85 345	264.350	52 036	199.875
2900	89 036	265.647	54 124	200.607
3000	92 738	266.902	56 220	201.318
3200	100 161	269.295	60 421	202.674
3400	107 608	271.555	64 647	203.954
3600	115 081	273.689	68 906	205.171
3800	122 570	275.714	73 199	206.330
4000	130 076	277.638	77 534	207.443
4200	137 603	279.475	81 923	208.514
4400	145 143	281.228	86 370	209.548
4600	152 699	282.910	90 881	210.552
4800	160 272	284.521	95 462	211.527
5000	167 858	286.069	100 115	212.477
5200	175 456	287.559	104 847	213.401
5400	183 071	288.994	109 663	214.309
5600	190 703	290.383	114 558	215.201
5800	198 347	291.726	119 537	216.075
6000	206 008	293.023	124 600	216.933

Enthalpy of Formation at 25°C, Ideal Gas Enthalpy and Absolute Entropy at 0.1 MPa (1 bar) Pressure

$\Delta\bar{h}_{O2}$

	Oxygen, Diatomic (O_2) (9/30/65)		Oxygen, Monatomic (O) (6/30/62)	
	$(\bar{h}_f^\circ)_{298} = 0$ kJ/kmol $M = 31.999$		$(\bar{h}_f^\circ)_{298} = 249\ 195$ kJ/kmol $M = 16.00$	
Temp. K	$(\bar{h}^\circ - \bar{h}^\circ_{298})$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K	$(\bar{h}^\circ - \bar{h}^\circ_{298})$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K
0	−8 682	0	−6 728	0
100	−5 778	173.306	−4 519	135.947
200	−2 866	193.486	−2 188	152.156
298	0	205.142	0	161.060
300	54	205.322	42	161.198
400	3 029	213.874	2 209	167.432
500	6 088	220.698	4 343	172.202
600	9 247	226.455	6 460	176.063
700	12 502	231.272	8 569	179.314
800	15 841	235.924	10 669	182.118
900	19 246	239.936	12 770	184.590
1000	22 707	243.585	14 862	186.795
1100	26 217	246.928	16 949	188.787
1200	29 765	250.016	19 041	190.603
1300	33 351	252.886	21 125	192.272
1400	36 966	255.564	23 213	193.820
1500	40 610	258.078	25 296	195.260
1600	44 279	260.446	27 380	196.603
1700	47 970	262.685	29 464	197.866
1800	51 689	264.810	31 547	199.059
1900	55 434	266.835	33 631	200.184
2000	59 199	268.764	35 715	201.251
2100	62 986	270.613	37 798	202.268
2200	66 802	272.387	39 882	203.238
2300	70 634	274.090	41 961	204.163
2400	74 492	275.735	44 045	205.050
2500	78 375	277.316	46 133	205.899
2600	82 274	278.848	48 216	206.720
2700	86 199	280.329	50 304	207.506
2800	90 144	281.764	52 392	208.268
2900	94 111	283.157	54 484	209.000
3000	98 098	284.508	56 576	209.711
3200	106 127	287.098	60 768	211.063
3400	114 232	289.554	64 973	212.339
3600	122 399	291.889	69 191	213.544
3800	130 629	294.115	73 425	214.686
4000	138 913	296.236	77 676	215.778
4200	147 248	298.270	81 948	216.820
4400	155 628	300.219	86 236	217.816
4600	164 046	302.094	90 546	218.774
4800	172 502	303.893	94 876	219.694
5000	180 987	305.621	99 224	220.585
5200	189 502	307.290	103 596	221.439
5400	198 037	308.901	107 985	222.267
5600	206 593	310.458	112 395	223.071
5800	215 166	311.964	116 821	223.849
6000	223 756	313.420	121 269	224.602

	Carbon Dioxide (CO_2) (9/30/65)		Carbon Monoxide (CO) (9/30/65)	
	$(\bar{h}_f^\circ)_{298} = -393\,522$ kJ/kmol $M = 44.01$		$(\bar{h}_f^\circ)_{298} = -110\,529$ kJ/kmol $M = 28.01$	
K	$(\bar{h}^\circ - \bar{h}^\circ_{298})$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K	$(\bar{h}^\circ - \bar{h}^\circ_{298})$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K
0	−9 364	0	−8 669	0
100	−6 456	179.109	−5 770	165.850
200	−3 414	199.975	−2 858	186.025
298	0	213.795	0	197.653
300	67	214.025	54	197.833
400	4 008	225.334	2 975	206.234
500	8 314	234.924	5 929	212.828
600	12 916	243.309	8 941	218.313
700	17 761	250.773	12 021	223.062
800	22 815	257.517	15 175	227.271
900	28 041	263.668	18 397	231.066
1000	33 405	269.325	21 686	234.531
1100	38 894	274.555	25 033	237.719
1200	44 484	279.417	28 426	240.673
1300	50 158	283.956	31 865	243.426
1400	55 907	288.216	35 338	245.999
1500	61 714	292.224	38 848	248.421
1600	67 580	296.010	42 384	250.702
1700	73 492	299.592	45 940	252.861
1800	79 442	302.993	49 522	254.907
1900	85 429	306.232	53 124	256.852
2000	91 450	309.320	56 739	258.710
2100	97 500	312.269	60 375	260.480
2200	103 575	315.098	64 019	262.174
2300	109 671	317.805	67 676	263.802
2400	115 788	320.411	71 346	265.362
2500	121 926	322.918	75 023	266.865
2600	128 085	325.332	78 714	268.312
2700	134 256	327.658	82 408	269.705
2800	140 444	329.909	86 115	271.053
00	146 645	332.085	89 826	272.358
0	152 862	334.193	93 542	273.618
0	165 331	338.218	100 998	276.023
400	177 849	342.013	108 479	278.291
3600	190 405	345.599	115 976	280.433
3800	202 999	349.005	123 495	282.467
4000	215 635	352.243	131 026	284.396
4200	228 304	355.335	138 578	286.241
4400	241 003	358.289	146 147	287.998
4600	253 734	361.122	153 724	289.684
4800	266 500	363.837	161 322	291.299
5000	279 295	366.448	168 929	292.851
5200	292 123	368.963	176 548	294.349
5400	304 984	371.389	184 184	295.789
5600	317 884	373.736	191 832	297.178
5800	330 821	376.004	199 489	298.521
6000	343 791	378.205	207 162	299.822

$\Delta \bar{h}_{H2O}$

	Water (H_2O) (3/31/61)		Hydroxyl (OH) (3/31/66)	
	$(\bar{h}_f^\circ)_{298} = -241\,827$ kJ/kmol $M = 18.015$		$(\bar{h}_f^\circ)_{298} = 39\,463$ kJ/kmol $M = 17.007$	
Temp. K	$(\bar{h}^\circ - \bar{h}^\circ_{298})$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K	$(\bar{h}^\circ - \bar{h}^\circ_{298})$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K
0	−9 904	0	−9 171	0
100	−6 615	152.390	−6 138	149.587
200	−3 280	175.486	−2 975	171.591
298	0	188.833	0	183.703
300	63	189.038	54	183.892
400	3 452	198.783	3 033	192.465
500	6 920	206.523	5 991	199.063
600	10 498	213.037	8 941	204.443
700	14 184	218.719	11 903	209.004
800	17 991	223.803	14 878	212.979
900	21 924	228.430	17 887	216.523
1000	25 978	232.706	20 933	219.732
1100	30 167	236.694	24 025	222.677
1200	34 476	240.443	27 158	225.405
1300	38 903	243.986	30 342	227.949
1400	43 447	247.350	33 568	230.342
1500	48 095	250.560	36 840	232.598
1600	52 844	253.622	40 150	234.736
1700	57 685	256.559	43 501	236.769
1800	62 609	259.371	46 890	238.702
1900	67 613	262.078	50 308	240.551
2000	72 689	264.681	53 760	242.325
2100	77 831	267.191	57 241	244.020
2200	83 036	269.609	60 752	245.652
2300	88 295	271.948	64 283	247.225
2400	93 604	274.207	67 839	248.739
2500	98 964	276.396	71 417	250.200
2600	104 370	278.517	75 015	251.610
2700	109 813	280.571	78 634	252.974
2800	115 294	282.563	82 266	254.296
2900	120 813	284.500	85 918	255.576
3000	126 361	286.383	89 584	256.819
3200	137 553	289.994	96 960	259.199
3400	148 854	293.416	104 387	261.450
3600	160 247	296.676	111 859	263.588
3800	171 724	299.776	119 378	265.618
4000	183 280	302.742	126 934	267.559
4200	194 903	305.575	134 528	269.408
4400	206 585	308.295	142 156	271.182
4600	218 325	310.901	149 816	272.885
4800	230 120	313.412	157 502	274.521
5000	241 957	315.830	165 222	276.099
5200	253 839	318.160	172 967	277.617
5400	265 768	320.407	180 736	279.082
5600	277 738	322.587	188 531	280.500
5800	289 746	324.692	196 351	281.873
6000	301 796	326.733	204 192	283.203

2-5

	Hydrogen, Diatomic (H_2) (3/31/61)		Hydrogen, Monatomic (H) (9/30/65)	
	$(\bar{h}_f^\circ)_{298} = 0$ kJ/kmol $M = 2.016$		$(\bar{h}_f^\circ)_{298} = 217\ 986$ kJ/kmol $M = 1.008$	
Temp. K	$(\bar{h}^\circ - \bar{h}^\circ_{298})$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K	$(\bar{h}^\circ - \bar{h}^\circ_{298})$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K
0	−8 468	0	−6 197	0
100	−5 293	102.145	−4 117	92.011
200	−2 770	119.437	−2 042	106.417
298	0	130.684	0	114.718
300	54	130.864	38	114.847
400	2 958	139.215	2 117	120.826
500	5 883	145.738	4 197	125.466
600	8 812	151.077	6 276	129.257
700	11 749	155.608	8 351	132.458
800	14 703	159.549	10 431	135.236
900	17 682	163.060	12 510	137.684
1000	20 686	166.223	14 590	139.872
1100	23 723	169.118	16 669	141.855
1200	26 794	171.792	18 749	143.662
1300	29 907	174.281	20 824	145.328
1400	33 062	176.620	22 903	146.867
1500	36 267	178.833	24 983	148.303
1600	39 522	180.929	27 062	149.641
1700	42 815	182.929	29 142	150.905
1800	46 150	184.833	31 217	152.093
1900	49 522	186.657	33 296	153.215
2000	52 932	188.406	35 376	154.281
2100	56 379	190.088	37 455	155.294
2200	59 860	191.707	39 535	156.265
2300	63 371	193.268	41 610	157.185
2400	66 915	194.778	43 689	158.072
2500	70 492	196.234	45 769	158.922
2600	74 090	197.649	47 848	159.737
2700	77 718	199.017	49 928	160.520
2800	81 370	200.343	52 007	161.277
2900	85 044	201.636	54 082	162.005
3000	88 743	202.887	56 162	162.708
3200	96 199	205.293	60 321	164.051
3400	103 738	207.577	64 475	165.311
3600	111 361	209.757	68 634	166.499
3800	119 064	211.841	72 793	167.624
4000	126 846	213.837	76 948	168.691
4200	134 700	215.753	81 107	169.704
4400	142 624	217.594	85 266	170.670
4600	150 620	219.372	89 420	171.595
4800	158 682	221.087	93 579	172.482
5000	166 808	222.744	97 734	173.327
5200	174 996	224.351	101 893	174.143
5400	183 247	225.907	106 052	174.930
5600	191 556	227.418	110 207	175.683
5800	199 924	228.886	114 365	176.415
6000	208 346	230.313	118 524	177.118

Equilibrium Constants (Kp)

$H \rightleftharpoons \frac{1}{2}H_2$ $K_p = \exp(-\frac{1}{2} \cdot \text{value in col 2})$

$OH \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}O_2$ $K_p = \exp(\text{col 5} - \text{col 6})$

Table A.12

Logarithms to the Base e of the Equilibrium Constant K_p

For the reaction $\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$ the equilibrium constant K is defined as

$$K = \frac{a_C^{\nu_C} a_D^{\nu_D}}{a_A^{\nu_A} a_B^{\nu_B}} = K_p \text{ for gases}$$

$K_p = \exp(-92.208)$

Base on thermodynamic data given in the JANAF Thermochemical Tables, Thermal Research Laboratory, The Dow Chemical Company, Midland, Michigan.

Temp. K	col 2 $H_2 \rightleftharpoons 2H$	$O_2 \rightleftharpoons 2O$	$N_2 \rightleftharpoons 2N$	col 5 $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$	col 6 $H_2O \rightleftharpoons \frac{1}{2}H_2 + OH$	col 7 $CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$	$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO$
298	−164.005	−186.975	−367.480	−92.208	−106.208	−103.762	−35.052
500	−92.827	−105.630	−213.372	−52.691	−60.281	−57.616	−20.295
1000	−39.803	−45.150	−99.127	−23.163	−26.034	−23.529	−9.388
1200	−30.874	−35.005	−80.011	−18.182	−20.283	−17.871	−7.569
1400	−24.463	−27.742	−66.329	−14.609	−16.099	−13.842	−6.270
1600	−19.637	−22.285	−56.055	−11.921	−13.066	−10.830	−5.294
1800	−15.866	−18.030	−48.051	−9.826	−10.657	−8.497	−4.536
2000	−12.840	−14.622	−41.645	−8.145	−8.728	−6.635	−3.931
2200	−10.353	−11.827	−36.391	−6.768	−7.148	−5.120	−3.433
2400	−8.276	−9.497	−32.011	−5.619	−5.832	−3.860	−3.019
[illegible]0	−6.517	−7.521	−28.304	−4.648	−4.719	−2.801	−2.671
2800	−5.002	−5.826	−25.117	−3.812	−3.763	−1.894	−2.372
3000	−3.685	−4.357	−22.359	−3.086	−2.937	−1.111	−2.114
3200	−2.534	−3.072	−19.937	−2.451	−2.212	−0.429	−1.888
3400	−1.516	−1.935	−17.800	−1.891	−1.576	0.169	−1.690
3600	−0.609	−0.926	−15.898	−1.392	−1.088	0.701	−1.513
3800	0.202	−0.019	−14.199	−0.945	−0.501	1.176	−1.356
4000	0.934	0.796	−12.660	−0.542	−0.044	1.599	−1.216
4500	2.486	2.513	−9.414	0.312	0.920	2.490	−0.921
5000	3.725	3.895	−6.807	0.996	1.689	3.197	−0.686
5500	4.743	5.023	−4.666	1.560	2.318	3.771	−0.497
6000	5.590	5.963	−2.865	2.032	2.843	4.245	−0.341

most stable (most neg)

least stable (least neg)
CO_2

ex.

Water-gas reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$

you can show that for this reaction: $K_p = \exp\left(\begin{matrix}\text{value in}\\ \text{col 5}\end{matrix} - \begin{matrix}\text{value in}\\ \text{col. 7}\end{matrix}\right)$

ex. at $T = 2000K$ $K_p = \exp(-8.145 + 6.635)$

$= 0.22$

a) Heat of formation **(of a compound) Kuo p. 43**
b) Heat of reaction **(of a constant pressure reaction) Kuo p. 52**
c) Lower heating value **(of a fuel) Kuo p. 61**

Heat of formation of a compound (= "enthalpy" of formation)

Each compound, such as H_2O, has a heat of formation.
Symbol for heat of formation is $\bar{h}_f^o$ (Borgnakke text), is ΔH_f^o (Kuo's text, p. 46).
Heat of formation is the negative of the heat released (kJ) per kmole of the compound when the compound is produced from elements in their standard states. Standard states of hydrogen and oxygen are H_2 and O_2. So:

$H_2 + (1/2)\, O_2 \rightarrow H_2O$ and $\bar{h}_f^o = -241{,}827$ kJ/kmol (First Law handout, p. 2-3) or
$\Delta H_f^o = -57.798$ kcal/mol (Kuo p. 45)
note: same number since 1 kcal = 4184 J.

$O_2 \rightarrow 2\,O$ $\Delta H_f^o = +\,59.553$ kcal/mol (Kuo p. 47)
Note: stable species (H_2O) have negative heat of formation while O has a positive value.

Heat of reaction Kuo p. 52
The heat of reaction is amount of heat that must be added during a chemical reaction to keep all of the substances present at the same temperature. If the pressure is kept constant the heat of reaction is the difference between the enthalpy of the substances present at the end of the reaction and the enthalpy of the substances present at the start of the reaction.

First Law

$$Q_{cv} + \sum_R{}' \nu_i' \left(\bar{h}^o_{f,i} + \Delta\bar{h}_i\right) = W_{cv} + \sum_P{}' \left(\bar{h}^o_{f,i} + \Delta\bar{h}_i\right)\nu_i''$$

heat of formation (kJ/kmol)

thermal enthalpy = $(h_i - h_{298}) = \int_{298K}^{T} \bar{c}_p \, dT$

For an isothermal reaction $\Delta\bar{h}_i = 0$ (remove heat quickly)
no work done $W_{cv} = 0$

$\therefore Q_{cv} =$ heat of reaction kJ/kmol, kcal/mol

$$\boxed{\begin{aligned} \bar{h}_{RP} &= \sum_P{}' \nu_i'' \bar{h}^o_{f,i} - \sum_R{}' \nu_i' \bar{h}^o_{f,i} \\ \Delta H_{r,T_0} &= \sum_P{}' \nu_i'' \Delta H^o_{f_i} - \sum_R{}' \nu_i' \Delta H^o_{f,i} \end{aligned}}$$

Borgnakke
p 2-3 handout

Kuo
Kuo p. 45

Example:

What is the heat of reaction for hydrogen reacting with oxygen, if water is in vapor state ?

$H_2 + (1/2)\, O_2 \rightarrow H_2O$ Heat of reaction: $\bar{h}_{rp} = 1\, \bar{h}^o_{f,H2O} - 1\, \bar{h}^o_{f,H2} - (1/2)\, \bar{h}^o_{f,O2}$

$= -241{,}913$ kJ/kmol - 0 - 0

(handout p. 2-3 for water vapor)

or $\Delta H_{r,T0} = 1\, \Delta H^o_{f,H2O} - 1\, \Delta H^o_{f,H2} - (1/2)\, \Delta H^o_{f,O2}$

$= -57.789$ kcal /mol Kuo p. 45

Note: we always deal with exothermic reactions (that release heat), and they always have a negative heat of reaction.

Note: if we reacted hydrogen with air, we would get the same value as with pure oxygen since N_2 has a zero heat of formation.

Note: the "Heat of combustion" is ambiguous, is defined differently in each textbook, let's not use it.

Lower Heating Value (LHV) of a fuel

LHV is a measure of how good a fuel is. It is the kJ of heat released per unit mass of the fuel. Thus, LHV is the negative of the heat of reaction divided by the molecular weight of the fuel, when product temperature is so high that all water is in the vapor state (typical of all our combustion problems).

$$\text{LHV} = -\bar{h}_{rp} \,/\, \text{MW}_{\text{fuel}}$$

Ex. For hydrogen LHV = - (-241,913 kJ/kmol) / 2.016 kg/kmol

= 119,996 kJ/kg fuel

Values of Lower Heating Value are listed for various fuels on First Law handout p. 2-3.

LHV of methane is – 50,010 kJ/kmol

Hydrogen has by far the largest LHV of any fuel.

Note: the "higher heating value HHV" of a fuel is something we don't use. It is the heat of combustion divided by the molecular weight of fuel, when the product temperature is so low that all of the water is in the liquid form. To determine HHV, we look up the heat of formation of water (liquid) to be -285,838 kJ/kmol (First Law handout p. 2-3) which also is -68.315 kcal/mol (Kuo p. 45). This might occur in your home furnace but not in a propulsion device.

Adiabatic Flame Temperature (T_{ad})

T_{ad} the final temperature of the product gases if a premixed mixture of fuel and oxidizer at initial temperature T_i is burned in a Steady State, Steady Flow reactor at constant pressure, for adiabatic conditions ($Q_{cv} = 0$) and no work extracted ($W_{cv} = 0$). How to compute T_{ad} = ? We solve the First Law of Thermodynamics. After rearrangement it becomes, for a general reaction (with dissociation, heat capacity not constant):

$$\boxed{\underset{\text{thermal enthalpy of products}}{\sum_P \nu_i'' \Delta\bar{h}_i} - \underset{\text{thermal enthalpy of reactants}}{\sum_R \nu_i' \Delta\bar{h}_i} = -\underbrace{\bar{h}_{rp}}_{\text{kJ/kmole liberated}} = (LHV)\cdot(MW_{fuel})} \quad (2)$$

Example: consider the following lean hydrogen-oxygen mixture with no dissociation:

($H_2 + 2.5\ O_2 \rightarrow H_2O + O_2$), and T_i = 298 K, so the above equation becomes:

$$\Delta\bar{h}_{H2O} + 2\,\Delta\bar{h}_{O2} = (LHV)\,(MW_{fuel}) \quad (3)$$

(recall that the first term is $\Delta\bar{h}_{H2O} = [\bar{h}_{H2O}(T_{ad}) - \bar{h}_{H2O}(298\ K)]$; this is the thermal enthalpy of water vapor, referenced to its enthalpy at 298 K.)

The only unknown here is T_{ad}. Solve this equation by first guessing values of T_{ad} then look up the values of $\Delta\bar{h}_{H2O}$ *and* $\Delta\bar{h}_{O2}$ and insert these values into LHS until it equals the RHS. Guess T_{ad} = 2400 K. On First Law handout p. 2-5 and 2-4 find $\Delta\bar{h}_{H2O}$ = 93,604 kJ/kmol and $\Delta\bar{h}_{O2}$ = 74,492 kJ/kmol. RHS equals LHS which is 241,827 kJ/kmol so T_{ad} is 2400 K.

a) A simplified method (not accurate, but used for a first approximation) is to assume that c_p is constant and is the same as $c_{p,02}$ for all species. Rearrangement of the last equation yields:

$$c_{p,O2}\,(T_{ad} - 298\ K) = (r)\,(LHV)\,(MW_{fuel}) \quad (4)$$

where r is the fuel to oxidizer mass ratio and $c_{p,O2}$ is the heat capacity of O_2 per unit mass.

b) The most accurate way to compute T_{ad} would be to include dissociation.

$$H_2 + 2.5\ O_2 \rightarrow a\ H_2O + b\ O_2 + c\ OH + d\ H + e\ O$$

To compute the adiabatic flame temperature T_{ad}, you need to combine

- atom balance for H and O atoms
- three equilibrium relations involving Kp_1, Kp_2 and Kp_3
- First Law (Eq. 2 above) to get T_{ad}

Kuo's example: adiabatic flame temperature (page 72)

$$CH_4 + 15(0.21 O_2 + 0.79 N_2) \rightarrow CO_2 + 2 H_2O + 11.85 N_2 + 1.15 O_2$$

(assume no dissociation) $T_i = 298K$

a) Borgnakke/Sonntag method:

$$\sum_{P}^{i} \nu_i'' \Delta \bar{h}_i - \sum_{R}^{i} \nu_i' \Delta \bar{h}_i = -\bar{h}_{rp} = (LHV)(mW_{fuel})$$

$$\Delta \bar{h}_{CO_2} + 2 \Delta \bar{h}_{H_2O} + 11.85 \Delta \bar{h}_{N_2} + 1.15 \Delta \bar{h}_{O_2} - 0 = \left(50,010 \frac{kJ}{kg}\right)\left(16 \frac{kJ}{kmol}\right)$$

guess $T_{AD} = 1700K$, look up on handout p. 2-4 → 2-6

$\Delta \bar{h}_{CO_2} = 73,492$ kJ/kgmole $\quad \Delta \bar{h}_{N_2} = 45,430$ kJ/kmol

$\Delta \bar{h}_{H_2O} = 57,685$ kJ/kmol $\quad \Delta \bar{h}_{O_2} = 47,970$ kJ/kmol

$LHS = 782,373$ kJ/kmol $\quad RHS = 800,160$ kJ/kmol

interpolate after selecting $T_{AD} = 1750$ to get $\underline{\underline{T_{AD} = 1732K}}$

(see Kuo p. 72)

b) Kuo's method – see p. 72

Note: nitrogen (N_2) does not take part in the chemical reaction, but it acts like a "sponge" to absorb the heat liberated and it reduces

Chemical equilibrium

- equilibrium = wait long time, isolated $d/dt = 0$
- kinetics = rate at which arrive at equil.

Arrhenius relation $\frac{d[CH_4]}{dt} = \cdots$

general case of chemical equilibrium:

$$1\ CH_4 + \frac{2}{1.2} O_2 + \frac{2}{1.2} N_2 \rightarrow a\ CO_2 + b\ CO + c\ H_2O + d\ H_2 + e\ N_2 + f\ OH + g\ H + h\ C + i\ O + j\ N + k\ H_2O_2 + l\ O_2 + m\ CH4$$

Note

i.) this is fuel rich ($\phi = 1.2$)

ii) this is a one-way reaction

reactants are <u>not</u> in equil. with products!

iii) after long time <u>all</u> product species are in equil. with each other!

iv) <u>Chemists have a rule</u>

"put any species you want on RHS, but then write an equil. relation for every compound (on RHS) with its elements in their standard state"

(also: must put every element in its standard state on RHS!)

so we write:

a) $CO_2 \rightleftharpoons C + O_2$ K_{pCO2}

b) $CO \rightleftharpoons C + \frac{1}{2}O_2$ K_{pCO}

c) $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$ K_{pH2O}

d) $OH \rightleftharpoons \frac{1}{2}O + \frac{1}{2}H_2$ K_{pOH}

e) $H \rightleftharpoons \frac{1}{2}H_2$ K_{pH}

f) $O \rightleftharpoons \frac{1}{2}O_2$ K_{pO}

g) $N \rightleftharpoons \frac{1}{2}N_2$ K_{pN}

h) $H_2O_2 \rightleftharpoons H_2 + O_2$ K_{pH2O2}

i) $CH_4 \rightleftharpoons C + 2H_2$ K_{pCH4}

4 atom balance for C, H, O, N, } 13 eqns 13 unknowns CHEMKIN will solve it!
9 equil relns.

one more unknown is T → 1st law thermo.

Simplification

we know that for fuel-rich conditions oxidizer concentration will be negligible, and CH_4 will totally dissociate and N_2 will not dissociate

$\therefore f = g = h = i = j = k = l = m = 0$

also, since C and O_2 do not appear on RHS any more, let's eliminate $C + O_2$ from the equil. relns.

Equil relation

(a) $CO_2 \rightleftharpoons C + O_2$

subtract in order to eliminate C

(-b) $-[CO \rightleftharpoons C + \frac{1}{2}O_2]$

$CO_2 - CO \rightleftharpoons \frac{1}{2}O_2$

$\therefore CO_2 \rightleftharpoons \frac{1}{2}O_2 + CO$

add these two to eliminate O_2

also rewrite (-c) $-[H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2]$

$CO_2 - H_2O \rightleftharpoons CO - H_2$

or $\boxed{CO + H_2O \rightleftharpoons CO_2 + H_2}$

water-gas equil. rela.

$K_{P_{W-G}}$

what is $K_{P_{W-G}}$? ← all 4 stoich coeffs are one

$$K_{PWG} = \frac{a \cdot d}{b \cdot c}\left(\frac{P/P_0}{n_T}\right)^{1+1-1-1}$$

$P_0 = 1 atm$

n_T = total # moles

$n_T = a + b + \ldots$

$$\boxed{K_{PWG} = \frac{a \cdot d}{b \cdot c}}$$

Law of Mass Action

there is no table for water gas reaction on handout P. 2-7 what is $K_{P_{WG}}$ for $CO + H_2O \rightleftharpoons CO_2 + H_2$?

all we have is ~~p~~, 2-7

(a) handout. (Borgnakke text)

species

elements in their standard states

T	$H_2 \rightleftharpoons 2H$	$O_2 \rightleftharpoons 2O$	$H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$	$CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$
298	-164		-92.208	
⋮			column 5	col. 7
6000				

K_P of this equil relation $= \exp(-92.208)$ (at 298K)

col. 5: $K_{P5} = \frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \Rightarrow P_{H_2O} = \frac{P_{H_2} P_{O_2}^{1/2}}{K_{P5}}$

col 7: $K_{P7} = \frac{P_{CO} P_{O_2}^{1/2}}{P_{CO_2}} \Rightarrow P_{CO_2} = \frac{P_{CO} P_{O_2}^{1/2}}{K_{P7}}$

we want $K_{PWG} = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = \frac{\cancel{P_{CO}} \cancel{P_{O_2}^{1/2}}}{K_{P7}} \frac{\cancel{P_{H_2}}}{\cancel{P_{CO}}} \frac{K_{P5}}{\cancel{P_{H_2}} \cancel{P_{O_2}^{1/2}}}$

$K_{PWG} = K_{P5} / K_{P7}$

$\therefore K_{P_{WG}} = \exp$ (value in col 5 − value in col 7)

at 2000K $K_{P_{WG}} = \exp(-8.145 + 6.635) = 0.22$

Example Determine adiabatic flame temperature for methane-air (298K, 1atm) at fuel rich conditions for $\Phi = 1.2$. Include dissociation of major species

---

basis = 1 kmole fuel

$$\hookrightarrow 1\ CH_4 + \frac{2}{1.2} O_2 + \frac{2}{1.2}\frac{79}{21} N_2 \rightarrow a\ CO_2 + b\ CO + c\ H_2O + d\ H_2 + e\ N_2$$

$$\left.\begin{aligned} C&:\ 1 = a + b \\ H&:\ 4 = 2c + 2d \\ O&:\ \frac{4}{1.2} = 2a + b + c \\ N&:\ \frac{4}{1.2}\frac{79}{21} = 2e \end{aligned}\right\}$$

choose to put everything in terms of a: (elim b, c, d, e)

$$\boxed{\begin{aligned} b &= 1 - a & ① \\ c &= 2.33 - a & ② \\ d &= a - 0.33 & ③ \\ e &= 6.27 & ④ \end{aligned}}$$

We have to find one new equation to give us "a".

reactants are not in equil to products
products are in equil

water-gas equilibrium relation

$$\boxed{K_{p,WG} = \frac{a \cdot d}{b \cdot c}} \quad ⑤$$

⑥ = First Law

six unknowns: $a, b, c, d, e, T (= T_{ad})$

$K_{p,WG}$ = exp (value in Col. 5 − value in col 7) of table on p. 2-7 handout solution:

2 eqns, 2 unknowns

$$K_p(T) = \frac{a\,(a-0.33)}{(1-a)\,(2.33-a)}$$

(a = kmols CO_2)

First Law: (kJ/kmol)

$$-74,873 = a\left(-393,522 + \Delta\bar{h}_{CO2}\right) + (1-a)\left(-110,529 + \Delta\bar{h}_{CO}\right)$$
$$+ (2.33-a)\left(-241,827 + \Delta\bar{h}_{H2O}\right) + (a-0.33)\left(\Delta\bar{h}_{H2}\right) + 6.27\,\Delta\bar{h}_{N2}$$

a) guess $T_1 = 2000\,K$

$\Delta\bar{h}_{CO2} = 91450$

$\Delta\bar{h}_{CO} = 56,739$

$\Delta\bar{h}_{H2O} = 72,689$

$\Delta\bar{h}_{H2} = 52,932$

$\Delta\bar{h}_{N2} = 56,141$

$K_p = 0.22 \rightarrow a = 0.59$

$$-74,873 = .59(-302,072) + .41(-53,790) + 1.74(-169,138)$$
$$+ 0.26(52,939) + 6.27(56,141)$$

$$\underset{-74,873}{LHS} \neq RHS1$$

(b) guess $T_2 = 2200\,K$

$$\underset{-74,873}{LHS} \neq RHS2$$

interpolate using

$$\boxed{T = \frac{(LHS - RHS1)(T_1 - T_2) + (RHS1 - RHS2)T_1}{(RHS1 - RHS2)}}$$

LHS = −74,873 = known

RHS1 = right side when guess T = T_1

RHS2 = " " T = T_2

T = correct answer - solve for T

interpolation gives $T = \underline{2134K}$

First law (using sensible enthalpies in table on previous page)

$1(-74{,}873) = .58(-393{,}522 + 99{,}808) + 1.75(-241{,}827 + 79{,}809)$

$+ .42(-110{,}529 + 61{,}759) + .25(57{,}701) + 6.27(61{,}124)$

$-74{,}873 = -170{,}354 - 283{,}531 - 20{,}483 + 14{,}425 + 383{,}247$

$-74{,}873 = -76{,}695$ agrees! our guess of 2134K is correct!

$K_p = 0.201$ $a = 0.58$ $d = 0.25$

$b = 0.42$ $e = 6.27$

$c = 1.75$ $n_T = 9.27 = a+b+c+d+e$

Compare our results to CHEMKIN computer program for methane-air, 1atm, initial temp = 298K, $\phi = 1.2$:

	our calculation	CHEMKIN
Adiabatic flame temperature =	2134K	2134K
mole fractions		
$X_{CO_2} = \frac{.58}{9.27} = \frac{a}{n_T}$	.0625	.06269
$X_{H_2O} = \frac{1.75}{9.27} = \frac{c}{n_T}$	.188	.18716
$X_{CO} = \frac{.42}{9.27} = \frac{b}{n_T}$	.045	.04488
$X_{H_2} = \frac{.25}{9.27} = \frac{d}{n_T}$	.027	.02689
$X_{N_2} = \frac{6.27}{9.27} = \frac{e}{n_T}$	0.676	.669
Total	1.00	

Minor species

We also can solve for mole fraction of minor species:

$X_H,\ X_O,\ X_{OH},\ X_{NO},\ X_{CH4}$ $\left(X_H = \frac{g}{n_T}\right)$

$n_T = a + + b + \ldots$

Assume:

"mole fractions of minor species are so small that they do not affect Tad, or mole fractions of major species"

$$\therefore CH_4 + \frac{2}{1.2} O_2 + \frac{2}{1.2} N_2 \rightarrow 0.58\, CO_2 + 0.42\, CO + 1.75\, H_2O + f\, OH + 0.25\, H_2 + 6.27\, N_2 + g\, H + h\, C + i\, O + j\, N + m\, CH4 + k\, H_2O_2 + l\, O_2 +$$

- solve for g

$H \rightleftharpoons \frac{1}{2} H_2$

$$K_{PH} = \frac{(0.25)^{1/2}}{g}\left(\frac{P}{n_T}\right)^{-1/2}$$

$K_{PH} = \exp\left(-\frac{1}{2} \cdot \text{value in col 2, p. 2-7}\right)$ (at 2134K)

$$\begin{cases} K_{PH} = \exp\left(-\frac{1}{2}(-11.12)\right) = 259.8 \\ P = 1.0 \text{ atm} \\ n_T = 9.27 \text{ kmol} \quad \text{basis} = 1 \text{ kmol fuel} \end{cases}$$

$\therefore g = 0.00585$

$$X_H = \frac{0.00585}{9.27}$$

$$\boxed{X_H = 0.00063}$$

chemkin result: $X_H = 0.00062$!

CHEMKIN for equilibrium conditions (2013)

In AE 533 we will run four sample projects in CHEMKIN, the files end in .ckprj - this means that they are sample projects with all the input data already put into the file.

a)	equilibrium_gas.ckprj	this gives final temperature, mole fractions after a long time
b)	psr_gas.ckprj	this is a perfectly stirred reactor; the species and T change in time, and eventually reach equilibrium values
c)	opposed_flame_h2_air.ckprj	this an opposed flow non-premixed flame project
d)	pre-mixed_burner_burner_stabilized.ckprj	this is a premixed Bunsen burner flame

Run the Equilibrium Project (equilibrium_gas.ckprj)

and turn in a plot of adiabatic flame temperature for three different initial temperatures

A. Open the Equilibrium_gas project

1. Go to a CAEN workstation in basement of FXB or library or 2230 Space Research
2. Log on, select circle on bottom left of PC, All Programs, Engr Applications, Chemkin
3. Note that there is pdf file in documentation / tutorials, but do not read tutorials now
4. Click on Chemkin and then Projects / OPEN / samples 2010 / equilibrium_gas.ckprj
5. In box on left, see the words: Open projects, and under it see: equilibrium_gas.
6. Double click on Diagram View, see an icon for equilibrium (a scale)
7. Now double click on Pre-processing. See:

Working directory: …equilibrium \ gas	
Chemistry set: … equilibrium_gas.cks	(.cks indicates a chemical kinetics file)
Gas Phase kinetics file …chem.inp	(.inp indicates an input file)
Thermodynamic data: …therm.dat	(.dat indicates a data file)

8. Click on the pencil icon on right of gas-phase kinetics and a box opens that shows the species in the kinetics data file. This one is only hydrogen-oxygen-nitrogen kinetics.
9. Click on the pencil icon on right of therm.dat file: see many heats of formation, Kp's
10. Click on Equilibrium on the left, click on Mechanism in center, see species properties
11. Select Run Pre-processor button in middle. This runs a check on the input data files. The window at the bottom should say chemistry set has no problems.

B. Input the initial conditions

12. Double click on C1_equilibrium on left. Click on reactor physical properties. See that this example has selected the constant pressure and enthalpy box. Intital temperature is seen to be set to 300 K, initial pressure is 1 atm. Click on species tab in the middle. This table is where you enter the moles of H2, N2 and O2. If you click normalize, the number of moles turns into mole fraction. You should not change these values.

C. Set up a batch of several runs

13. Click on Continuation on the left. Click on the box run #1 and see that the initial T is 400 K. Click on the box new run #2 and see that the initial T is 500 K. This project is set up to make three runs, with initial T = 300, 400 and 500 K and plot results versus initial T. Notice that you could select different equivalence ratios for the different runs, but we don't do that in this example problem.

D. Run CHEMKIN

14. Click on Run calculations and begin. Look in the bottom box and see: success and done.
15. Click on Process Solution Data, then move the right hand slider down to see a button that says Display Plot near the bottom of the page.
16. Highlight the words Initial Temperature and click Display Plot. See a graph of initial temperature for solutions 1, 2 and 3 equal to 300 K, 400K and 500 K.
17. Now highlight the words Equilibrium Temperature and select Display plot. The graph shows the final equilibrium adiabatic flame temperature for the three cases.
18. Print out this graph and turn it in.
19. Highlight some other final results such as mole fractions of different species and see the graphs that show how they vary with initial temperature. No need to print them.
20. Finally sign off by clicking PC circle in bottom left and select Log Off.

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Recent Developments in the Research on Pulse Detonation Engines

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Introduction

IN principle, detonations are an extremely efficient means of combusting a fuel-oxidizer mixture and releasing its chemical energy content. During the past 60 years or so, there have been numerous research efforts at harnessing the potential of detonations for propulsion applications.[1] There is a renewed interest lately on intermittent or pulsed detonations engines. Eidelman et al.[2] and Eidelman and Grossmann[3] have reviewed some of the initial research as well as work done in the late 1980s on pulse detonation engines (PDEs). The basic theory, design concepts, and the work in the early 1990s related to pulse detonation engines have been discussed by Bussing and Pappas.[4] The focus of a more recent review[5] is on performance estimates from various experimental, theoretical and computational studies. More recently, work related to nozzles for PDEs has been discussed.[6] Other reviews[7–9] discussing the objectives and accomplishments of various programs are also available. The objective of this paper is to update the previous reviews, focusing on the more recent developments in the research on PDEs. The review is restricted to work openly available in the literature but includes ongoing efforts around the world.

Currently, there are several programs sponsored by Office of Naval Research (ONR), U.S. Air Force, NASA, Defense Advanced Research Projects Agency, and other agencies in the United States as well as several parallel efforts in Belarus, Canada, France, Japan, Russia, Sweden, and other countries. The results from some of these programs are just beginning to be published. A summary of recent progress and the various organizations and people involved in PDE research in Japan has been presented.[9] Reports of the basic PDE research sponsored by ONR are available in the proceedings of a recurring annual meeting (for example, see Ref. 10). Recent work conducted outside the United States has been reported at international meetings on detonations such as those held in Seattle[11] (for more information, see http://www.engr.washington.edu/epp/icders/) and Moscow.[12] Although an attempt is made to cover a broad range of the reported research, the shear volume of papers presented with PDEs in the title make it impractical to be exhaustive.

Rather than providing a chronological report, an attempt is made here to discuss the recent progress in terms of broad topic areas. The key issues that need to be resolved have been addressed in a number of papers (e.g., Refs. 13 and 14). The specific order in which to discuss the various topics was determined by considering the schematic of an idealized, laboratory pulse detonation engine shown in Fig. 1. This idealized engine is representative of the device used in many of the recent experimental and computational studies and consists of a tube closed at one end and open at the other. Typically, fuel and oxidizer are injected and mixed near the head end to achieve a nearly homogeneous mixture and ignited. Depending on the mixture and ignition energies involved, a detonation, which travels towards the open end of the tube leaving behind a high-pressure, high-temperature gas that generates thrust as it expands and leaves the tube, might-form. The first topic discussed covers the injection and atomization of liquid fuels and fuel-air mixing. Even if the fuel and air are premixed, rapid deposition of energy into the mixture does not necessarily mean that a detonation wave will be formed. Issues involved and recent successes in the initiation of detonations are addressed next. Developments in diagnostics and computations of the detonation wave are then briefly discussed as they provide a good characterization of the pressure, temperature, and velocity flowfields within the tube. This leads to the issue of the performance of pulse detonation engines. The performance of idealized laboratory pulse detonation engines has received significant attention recently, and, as this review will show, it is one of the topics that appears to be resolved. However, the performance of these devices at flight conditions is still a controversial topic. This is partly because of the uncertainty concerning the "proper" design of nozzles and inlets for these engines. Nozzles for the PDE present challenging design and integration issues because of the inherently unsteady nature of the pulse detonation process. For a high-frequency, multitube system, where the overall system might appear to be nearly steady, there are issues in designing a common flow path for the exhaust from the individual thrust tubes. Issues concerning global performance estimation and the results from recent analysis of some of the applications proposed for the PDE are also presented. It is hoped that this review provides a clearer picture of our current understanding and highlights the need for additional research on PDEs.

Atomization and Fuel–Oxidizer Mixing

Detonations are essentially a premixed combustion process. The well-known detonation parameters such as the Chapman–Jouguet (CJ) velocities and CJ pressures are derived with the implicit assumption of a perfectly mixed fuel–oxidizer or fuel–air mixture. The importance of adequately mixing the fuel and oxidizer was highlighted by the experimental investigations of Stanley et al.,[15] who obtained very low sub-CJ velocities when injecting the fuel and oxidizer at different times and not invoking additional measures to

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Chemical kinetics read Kuo 2.1 - 2.8

equilibrium chemistry - tells you final products but not how fast the reaction was (Law of Mass Action)

chemical kinetics - tells you how fast reaction occurs (unsteady soln)

(Arrhenius rate equation)

second order reactions (two reactants) Kuo p. 144

$$H_2 + O \xrightarrow{k_f} H_2O$$

$$\frac{d\,C_{H_2}}{dt} = -k_f\, C_{H_2}\, C_O$$

$$\frac{d\,C_O}{dt} = -k_f\, C_{H_2}\, C_O$$

$$\frac{d\,C_{H_2O}}{dt} = +k_f\, C_{H_2}\, C_O$$

double the moles of H_2 → double # collisions between H_2 + O
∴ double the rate at which H_2 disappears

C_{H_2} = concentration H_2 in $\frac{\text{moles}}{\text{cm}^3} = X_{H_2} \cdot \frac{P}{R_u T}$

$R_u = 8.315 \frac{N \cdot m}{mole\ K} = 1.987 \times 10^{-3} \frac{kcal}{mol\ K}$

ex $X_{N_2} = .738$

$P = 3$ atm

$T = 2500K$

→ use the R_u with $\frac{N \cdot m}{mol K}$

$$C_{N_2} = ? = X_{N_2} \frac{P}{R_u T}$$

$$= (.738) \frac{3(101,325 \ N/m^2)}{8.315 \frac{N-m}{mole \ K} (2500 \ K)}$$

$$= 10.79 \frac{moles}{m^3} \cdot \left[\frac{1 m^3}{10^6 cm^3}\right] = 10.79 \times 10^{-6} \frac{moles}{cc}$$

<u>Arrhenius rate constant</u> Kuo p. 119

$$k = A T^b \exp\left(-\frac{E_a}{R_u T}\right)$$

for second order reaction, previous Arrhenius eqn shows that

$$k = \frac{1}{\left(\frac{moles}{cm^3}\right) sec}$$

A = whatever units that give $k = \frac{1}{\left(\frac{moles}{cm^3}\right) sec}$
with T = Kelvin

E_a = activation energy - note

whatever units E_a is given, use R_u such that the units in the exponential cancel!

ex.: $E_a = 13.8 \frac{kJ}{mol}$ (Kuo p. 226)

$T = 2000\ K$

$$\exp\left(\frac{-E_a}{R_u T}\right) = \exp\left[\frac{-13{,}800 \frac{J}{mol}}{8.315 \frac{J}{mol\,K}(2000\ K)}\right]$$

$$= 0.436 \quad \text{(no units)}$$

Opposing reactions – (p. 150)

example #1 $\quad 2H + N_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} H_2 + N_2$

$$\frac{dC_H}{dt} = -2k_f\, C_H^2\, C_{N_2} + 2\, k_b\, C_{H_2}\, C_{N_2}$$

forward reaction is 3rd order (3 molecules on left)
reverse reaction is 2nd order (2 molecules on right)

order of a reaction in forward direction $\quad \boxed{m = \sum_{LHS}' \nu_i'}$ $\quad$ p128

General Arrhenius relation for opposing reactions (p. 151)

$$\frac{dC_{m_i}}{dt} = (\nu_i'' - \nu_i')\, k_f \prod_{j=1}^{N} (C_{m_j})^{\nu_i'}$$
$$+ (\nu_i' - \nu_i'')\, k_b \prod (C_{m_j})^{\nu_i''}$$

reaction is (p. 118)

$$\sum_i{}' \nu_i' M_i \rightleftharpoons \sum_i{}' \nu_i'' M_i \qquad 2H + N_2 \rightleftharpoons H_2 + N_2$$

↑ left side

↑ right side

$i=1$ $M_1 = H$ $\nu_1' = 2$ $\nu_1'' = 0$

$i=2$ $M_2 = N_2$ $\nu_2' = 1$ $\nu_2'' = 1$

$i=3$ $M_3 = H_2$ $\nu_3' = 0$ $\nu_3'' = 1$

$i=1$
$$\frac{dC_H}{dt} = (0-2)\, k_f\, C_H^2\, C_{N_2}$$
$$+ (2-0)\, k_b\, C_{H_2}\, C_{N_2}$$

example #2
$$H + O_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} OH + O$$

$$\frac{dC_H}{dt} = -k_f\, C_H\, C_{O_2} + k_b\, C_{OH}\, C_O$$

Derivation of the Arrhenius relation   Kuo p. 120

$$H + O_2 \xrightarrow{k_f} OH + O$$

$$\frac{dC_H}{dt} = -k_f\, C_H\, C_{O2}$$

rate of increase

$$\frac{\text{moles H/cm}^3}{\text{sec}} = -\begin{pmatrix}\text{collision frequency}\\ \text{between } H + O_2\end{pmatrix} \cdot \begin{pmatrix}\text{fraction of H and } O_2\\ \text{that have energy that}\\ \text{exceeds the}\\ \text{activation energy}\end{pmatrix}$$

— required to break apart O_2 + get H + O to connect

collision frequency $\sim T^{1/2}\, C_H\, C_{O2}$

(fraction of $H + O_2$ exceeding activation energy) $\sim \exp\left(\frac{-E_A}{R_u T}\right)$

so $k_f \sim T^{1/2} \exp\left(\frac{-E_A}{R_u T}\right)$

Rate at which a First Order reaction proceeds

Kuo p.141

$$H_2 \xrightarrow{k_f} 2H$$

suppose we shine laser energy into H_2; it will dissociate into 2 H without any collisions between H_2 and anything else.

at $t=0$ $C_{H2} = C_{H2,0}$, $C_{H,0}=0$

① $$\frac{dC_H}{dt} = 2k_f C_{H2}$$

② $$\frac{dC_{H2}}{dt} = -k_f C_{H2}$$

two ODEs
1 indep. variable (time)
2 dependent variables C_H C_{H2}

solve eq 2 – put all C_{H2} on LHS, all t's on RHS

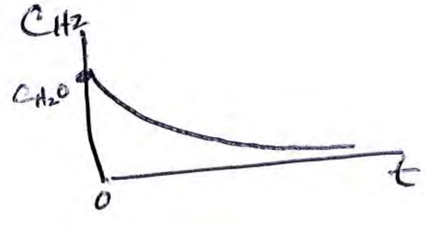
assume T remains constant in time during the reaction

$$\int \frac{dC_{H2}}{C_{H2}} = -k_f \int dt$$

$$\ln C_{H2}\Big|_{C_{H_2,0}}^{C_{H2}} = -k_f(t-0)$$

$$\cancel{\ln}\ \frac{C_{H2}}{C_{H_2,0}} = \underset{\exp}{(-k_f\ t)}$$

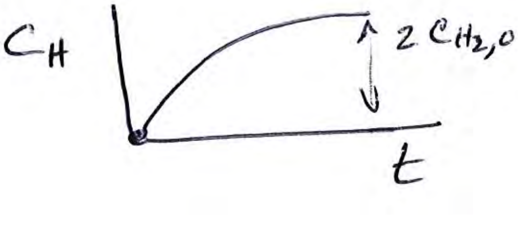
$$\boxed{C_{H2}(t) = C_{H_2,0}\exp(-k_f t)}$$



①&②:

$$\int \frac{dC_H}{\cancel{dt}} = -2\int\frac{dC_{H2}}{\cancel{dt}} \Rightarrow (C_H - \cancel{C_{H,0}}^{\,0}) = -2(C_{H_2} - C_{H_2,0})$$

$$C_H(t) = 2\left(C_{H_2,0} - C_{H_2,0}\exp(-k_f t)\right)$$



if you started with 1 $\frac{mole}{cm^3}$ H_2
you end up with 2 $\frac{moles}{cm^3}$ H

Second order reaction

- we start with $C_{H,0}$ moles/cm³ of H atoms at time = 0
and $C_{O_2,0}$ moles/cm³ of O_2 atoms at time = 0
and zero $\frac{\text{moles}}{cm^3}$ of OH, zero $\frac{\text{moles}}{cm^3}$ O at t = 0

then we react according to :

Second Order Reaction (Kuo p 144)

temp. = constant in time

$$\boxed{H + O_2 \xrightarrow{k_f} OH + O}$$

$$1)\quad \frac{d\,C_H}{dt} = -k_f\, C_H\, C_{O2}$$

$$2)\quad \frac{d\,C_{O2}}{dt} = -k_f\, C_H\, C_{O2}$$

$$3)\quad \frac{d\,C_{OH}}{dt} = +k_f\, C_H\, C_{O2}$$

$$4)\quad \frac{d\,C_O}{dt} = +k_f\, C_H\, C_{O2}$$

we wrote; last page

Consider Eqns ① + ②:
note RHS same so solve. →

$$\int \frac{d\,C_H}{\cancel{dt}} = \int \frac{d\,C_{O2}}{\cancel{dt}}$$

$$C_H - C_{H,0} = C_{O2} - C_{O2,0}$$

$$\text{then } C_{O2} = C_H - C_{H,0} + C_{O2,0}$$

plug into first eqn ①
$$\frac{d\,C_H}{dt} = -k_f\, C_H \left(C_H - C_{H,0} + C_{O2,0}\right)$$

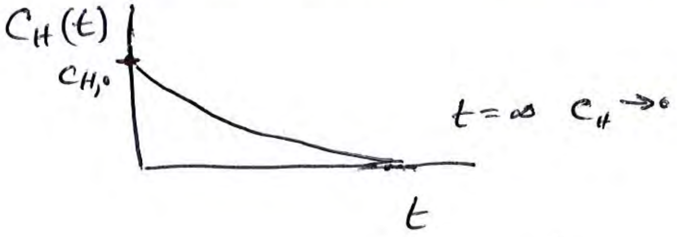
separate variable:

$$\int_{C_{H,0}}^{C_H} \frac{d\,C_H}{C_H\left(C_H - C_{H,0} + C_{O2,0}\right)} = -k_f \int_0^t dt$$

since $\displaystyle\int \frac{dx}{x(x+a)} = -\frac{1}{a} \ln\left(\frac{x+a}{x}\right)$ $\qquad a = C_{O2,0} - C_{H,0}$

solution for $C_H(t)$

$$\boxed{\left(\frac{C_H + C_{O2,0} - C_{H,0}}{C_H}\right)\left(\frac{C_{H,0}}{C_{O2,0}}\right) = \exp\left[\left(C_{O2,0} - C_{H,0}\right) k_f\, t\right] \quad \text{Kuo p. 145}}$$

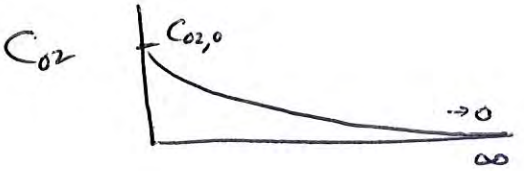


at $t=0$ $\quad RHS = 1$

$LHS \Rightarrow C_H - C_{H0} = C_{O2} - C_{O2,0}$

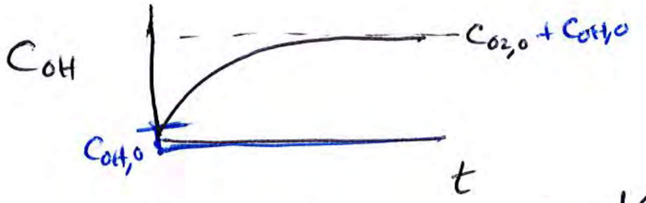
$LHS = \left.\dfrac{C_{O2,0}}{C_{O20}}\,\dfrac{C_{H,0}}{C_H}\right|_{t=0} = 1$ ✓

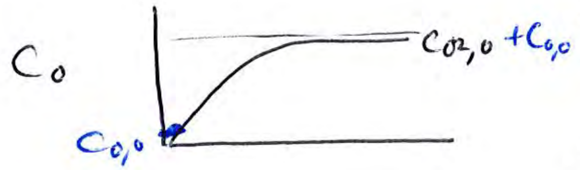
$$C_{O2} = C_{O2,0} + C_H - C_{H,0}$$



$$\frac{dC_{OH}}{dt} = -\frac{dC_{O2}}{dt}$$

$$C_{OH} - C_{OH,0} = -\left(C_{O2} - C_{O2,0}\right)$$





$$\frac{dC_O}{dt} = \frac{dC_{OH}}{dt}$$

$$C_O - C_{O,0} = C_{OH} - C_{OH,0}$$

Note: if we require $C_{O2} \to 0$ at $t = \infty$ and
$C_H \to 0$ at $t = \infty$
since they both go to zero at the same rate, $\therefore C_{O2,0} = C_{H,0}$!

Chain reactions (Kuo p. 155)

steady state approximation (p. 157 / p. 246) reasons why?

partial equilibrium assumption (p 246)

Lindeman theory (p. 156)

H_2 - Br_2 case (p. 159)

Chemkin (p. 169)

H_2 - O_2 (p. 215)

explosion limits H_2-O_2 (p. 221)

CO oxidation p. 233

HC → path

NO path 263

Kinetics - closure

- write all elementary reactions ... i.e. ..

$$H_2 + N_2 \xrightarrow{k_1} 2H + N_2$$

$$H + O_2 \xrightarrow{k_2} OH + O$$

$$O + H_2 \xrightarrow{k_3} OH + H$$

$$\vdots$$

- for each species write

$$\frac{d\,C_H}{dt} = 2k_1\, C_{H2}\, C_{N2} - k_2\, C_H\, C_{O2} + k_3\, C_O\, C_{H2} + \dots$$

you automatically have one Arrhenius eqn. for each species - closed set of ODEs if you know all the k_i's !

Chain reactions – consist of 3 types of reactions

a) Chain initiating reaction

$$H_2 + M \rightarrow 2H + M$$

collisional dissociation of H_2

b) Chain branching reactions - more radicals formed than lost

$$\underset{\text{one radical}}{H} + O_2 \rightarrow \underbrace{OH + O}_{\text{two radicals}}$$

c) Chain carrying reactions – do not change number of radicals

$$CO + \underbrace{OH}_{\text{one radical}} \rightarrow CO_2 + \underbrace{H}_{\text{one radical}}$$

d) chain terminating reactions – reduce number of radicals (recombination collisions)

$$M + 2O \rightarrow O_2 + M$$

Steady state approximation

- used to eliminate variables (such as C_H = concentration of a radical) in a complex mechanism ⇒ generate a reduced mechanism

For any radical - since radicals are very reactive

rate of depletion of radicals >> rate of creation of radicals

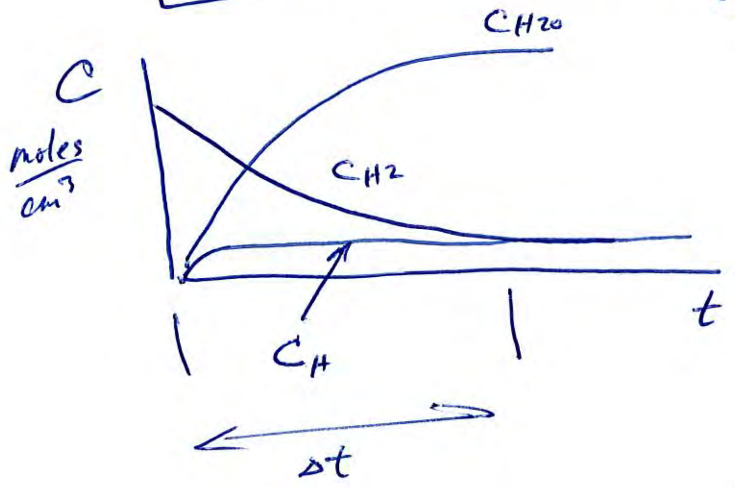
ex.

reaction 1 $H_2 \xrightarrow{k_1} 2H$ creates H radicals = SLOW

reaction 2 $H + OH \xrightarrow{k_2} H_2O$ depletes H radicals = fast

we conclude that for any radical $\boxed{\frac{dC_H}{dt} = 0}$ $\frac{dC_N}{dt} = 0$ $\frac{dC_O}{dt} = 0$

"steady state approx"



C_H never can build up - it is depleted faster than it is created

over time Δt

$$dC_{H_2O}/dt \approx C_{H_2O,max}/\Delta t$$
$$dC_{H_2}/dt \approx C_{H_2,max}/\Delta t$$
$$dC_H/dt \approx C_{H,max}/\Delta t$$

since $C_{H,max} << C_{H_2O,max}$

$$\therefore \frac{d\,C_H}{dt} << \frac{d\,C_{H_2O}}{dt} \quad \text{proof.}$$

- real proof is to run full chemistry <u>once</u> on large computer
- then show that $dC_H/dt << dC_{H_2O}/dt$ for many cases!

How does this approximation help?

we have one more equation

$$\frac{d\,C_H}{dt} = 2\,k_1\,C_{H_2} - k_2\,C_H\,C_{OH} = 0$$

solve for $\boxed{C_H = \frac{2\,k_1}{k_2}\,\frac{C_{H_2}}{C_{OH}}}$

We now can eliminate C_H from all the Arrhenius reaction rate terms - one less unknown.

Partial equilibrium assumption if ⇒ ★

if both k_f and k_r are large

ex. Turns prob. 4.20 for next HW

$$H + O_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} OH + O$$

we can assume partial-equilibrium – that

$$K_c = \frac{[OH][O]}{[H][O_2]} = K_p = \frac{k_f}{k_r} \qquad (4.43)$$

∴ we eliminate one diff. eqn & replace it with an algebraic eqn (above)

Why? Turbulent combustion models -
Laminar flame models -

chemical reaction rate term in a PDE x, y, z, t are now variables $\dot{\omega} = \frac{\text{mass } H_2 \text{ consumed}}{\text{sec} \cdot \text{vol}} = \overline{k_1 [H_2][OH] + \ldots}$

very complicated when reaction rate varies in x, y, z, t so want only one PDE and many algebraic eqns if possible!

ex. NO is produced by:

$$O + N_2 \xrightarrow{k_1} NO + N \qquad \text{slow} \qquad k_2 >> k_1$$

$$N + O_2 \xrightarrow[k_2]{} NO + O \qquad \text{fast} \qquad \text{N depleted as soon as it forms}$$

① $$\frac{dC_{NO}}{dt} = k_1 C_O C_{N2} + k_2 C_N C_{O2}$$

we can simplify this by assuming

a) N is steady state $\frac{dC_N}{dt} = 0$

b) O is in partial equilibrium with O_2 (k_f + k_b below are both large)

a) → $$\frac{dC_N}{dt} = k_1 C_O C_{N2} - k_2 C_N C_{O2} = 0$$

$$\text{so } k_1 C_O C_{N2} = k_2 C_N C_{O2}$$

insert into ①
(eliminate C_N) $$\therefore \frac{dC_{NO}}{dt} = 2 k_1 C_O C_{N2} \quad ②$$

b) → $$O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \frac{1}{2} O_2$$

$$K_p = \frac{C_{O2}^{1/2}}{C_O} \left(\frac{P}{n_T}\right)^{-1/2}$$

solve for C_O
insert into ②

$$\therefore \boxed{\frac{dC_{NO}}{dt} = 2 k_1 C_{N2} C_{O2}^{1/2} \left(\frac{P}{n_T}\right)^{-1/2} K_p^{-1}}$$

assume $C_{NO} << C_{N2}$ or C_{O2} so

$$CH_4 + \frac{2 O_2}{0.8} + \frac{2}{0.8}\frac{79}{21} N_2 \rightarrow CO_2 + 2 H_2O + 2 \frac{79}{21}\frac{1}{0.8} N_2 + \left(\frac{2}{0.8} - 2\right) O_2$$

$$C_{N2} = X_{N2} \frac{P}{R_u T}$$

$$X_{N2} = \frac{\frac{2}{0.8}\frac{79}{21}}{3 + \frac{2}{0.8}\frac{79}{21} + \left(2 - \frac{2}{0.8}\right)}$$

← moles N_2

← n_T

$$C_{O2} = \ldots$$

Nitric Oxide Chemistry

Regulations

100 ppm NO or NO_2 = toxic

cars: 0.07 grams NO_x/mile

jet aircraft: $\boxed{EI = 50 \text{ grams } NO_x \text{ / kg fuel}}$

$= 0.5 \, \frac{\text{g/sec } NO_x}{\text{kN thrust}}$

NO = nitric oxide = invisible, produced in flame by $N_2 + O \rightarrow NO + N$
converted to NO_2 (smog) in atmosphere,
NO destroys ozone layer at high alt.

NO_2 = nitrogen dioxide = brown, toxic, very stable, see it in LA
creates O_3 ozone at low altitudes
LA ozone alert irritates eyes
dissolves in water to from nitric acid
ie. acid rain

N_2O = nitrous oxide = not toxic, laughing gas but still a pollutant since it destroys ozone layer

NO created by combustion (not NO_2)

Upper atmosphere has lots of ozone (O_3)

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

NO destroys ozone layer at high altitude

Lower atmosphere - has little ozone (O_3)

$$NO + O_2 + \overset{\text{sun}}{\text{light}} \rightarrow NO_2 \text{ (smog)} + O$$

photochemical smog production - 1 day

$$NO_2 + O_2 \rightarrow NO + O_3 \text{ (eye irritant)}$$

smog (NO_2) creates ozone at low altitudes.

∴ NO from engine does two bad things -
destroys ozone at high altitude
creates ozone at low altitudes

NO eventually all goes to NO_2

NO_2 eventually all dissolves in rain water to form nitric acid

$$NO_2 + H_2O \Rightarrow HNO_3 + H$$

HNO_3 = acid rain = bad for trees, good for soil
good for us = washes out the smog!

Creation of NO in engines

a) Zeldovich "thermal" NO: $N_2 + O \rightarrow NO + N$

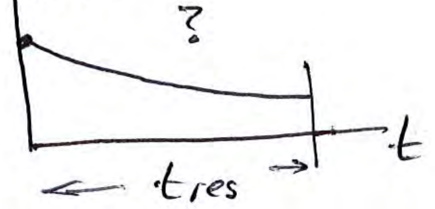
b) Fenimore prompt NO: $CH + N_2 \rightarrow HCN + N$
(see Turns) $N + OH \rightarrow NO + H$

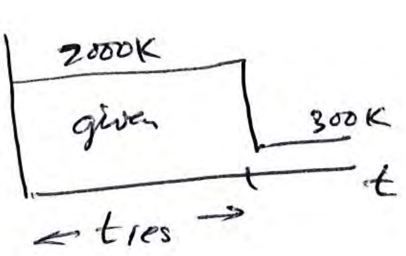
Zeldovich is primary mechanism - is very temperature dependent
+ 40 ppm for every 10 K rise in temperature
goal - lower the regions of high T, but eventually Zeldovich
goes away at low T but still have prompt NO to
get rid of in "ultra low NOx" devices.

Ex. Oxidation of CO carbon monoxide

Suppose fuel + air are burned then at $t=0$ the hot (lean) products sit at constant T, P of (2000K, 10 atm) and concentrations of major species ($C_{O_2}, C_{H_2O}, C_{CO_2}$) known to do not change in time. After $t = t_{res}$ $T \Rightarrow 300K$ reactions stop

- at $t=0$ we are given $C_{CO,0}$ = initial amount of unburned CO
- compute $C_{CO}(t)$





- assume reaction that consumes the CO is.

$$CO + OH \xrightarrow{k_1} CO_2 + H$$

Arrhenius says

$$\frac{d\,C_{CO}}{dt} = -k_1 C_{CO} C_{OH}$$

- question: replace unknown C_{OH} & put it in terms of the known $C_{O_2}, C_{H_2O}, C_{CO_2}$

partial equilibrium

#2. When hydrocarbon fuels are oxidized in flames, the first stage of the process involves the formation of carbon monoxide (CO) and water vapor (H2O). The second stage of the process (which is relatively slow) involves the final oxidation of carbon monoxide to carbon dioxide (CO2) by the following reaction with the hydroxyl radical (OH):

$$CO + OH \rightarrow CO2 + H,\ k_1 \qquad (1)$$

SLOW COMPARED to (2) + (3)

For the conditions of interest, early in the oxidation of carbon monoxide, the reverse reaction of Reaction (1) is slow, and other reactions involving CO and CO2 are slow. Reaction (1) also proceeds slowly in comparison to other reactions involving hydrogen (H2), oxygen (O2), water vapor (H2O), the hydroxyl radical (OH) and atomic oxygen (H) so that these species are maintained in local thermodynamic equilibrium; this can be represented by the following equilibrium reactions for OH and H2O:

$$H2 + O2 \leftrightarrow 2OH,\ K_{C2} \qquad (2)$$

FAST-FORWARD & REVERSE

and

$$H2 + (1/2)O2 \leftrightarrow H2O,\ K_{C3} \qquad (3)$$

FAST-FORWARD & REVERSE

where K_{C2} and K_{C3} are based on the molal concentrations (kgmol/m^3) of the species involved. Using this information, it is desired to develop a simplified global reaction rate expression for the oxidation of CO in terms of the concentrations of other major species in the system, e.g., CO, CO2, H2O and O2. To carry this out, please do the following:

(a) Find an expression giving the concentration of OH in terms of the major stable species concentrations, e.g., H2, O2, H2O.

(b) Find an expression for the rate of reaction of CO, d(CO)/dt, in terms of the concentrations of major species, and k_1, K_{C2} and K_{C3}.
(CO, H_2O, O_2)

(a) partial equilibrium assumptions:

$$K_{c2} = \frac{[OH]^2}{[H_2][O_2]} \quad \text{so} \quad [OH] = K_{c2}^{1/2}[H_2]^{1/2}[O_2]^{1/2}$$

$$K_{c3} = \frac{[H_2O]}{[H_2][O_2]^{1/2}} \quad \text{so} \quad [H_2] = \frac{[H_2O]}{K_{c3}[O_2]^{1/2}}$$

(b)

$$\frac{d[CO]}{dt} = -k_1[CO][OH]$$

now replace [OH] with above equation, so

$$\frac{d[CO]}{dt} = -k_1[CO]\,K_{c2}^{1/2}[H_2]^{1/2}[O_2]^{1/2}$$

now replace $[H_2]$

$$\boxed{\frac{d[CO]}{dt} = -k_1[CO]\,K_{c2}^{1/2}\frac{[O_2]^{1/4}[H_2O]^{1/2}}{K_{c3}^{1/2}}}$$

we have eliminated ✓ [OH] and $[H_2]$

We can integrate this based on our assumptions

$$\int_{C_{CO,0}}^{C_{CO}} \frac{d\,C_{CO}}{C_{CO}} = -k_1 \cancel{C_{CO}} \frac{K_{C2}^{1/2}}{K_{C3}^{1/2}} C_{O2}^{1/4} C_{H2O}^{1/2} \int_0^t dt$$

$$\left(\frac{C_{CO}(t)}{C_{CO,0}}\right) = 1 - \exp(-t/\tau)$$

where $$\tau = \left[k_1 \left(\frac{K_{C2}}{K_{C3}}\right)^{1/2} C_{O2}^{1/4} C_{H2O}^{1/2}\right]^{-1}$$

Chemkin – "tuning"

- disagreement on values of A, b, E_a for each elementary reaction

- disagreement about importance of the many elementary reactions

- approach
  - make many redundant measurements of major elementary reactions

    i.e.: $H + O_2 \rightarrow OH + O$

  - adjust the A, b, E_a to give CHEMKIN predictions of
    - laminar burning velocity
    - ignition delay time

Complex Reactions

Read: Lindemann Theory (p. 156)
Hydrogen-Bromine (p. 159)

OMIT

suppose you put C_2H_6 (ethane) and N_2 in a box and heat to 1300 K.
much of the C_2H_6 will break down into CH_3 radicals

Our first guess: $C_2H_6 \rightarrow 2\,CH_3$

with this mechanism C_m is not important,

If so then $$\frac{dC_{CH3}}{dt} = 2\,C_{C2H6}$$

No. experiment does not agree

Our second guess (the right one) is:

$$C_2H_6 + M \underset{k_b}{\overset{k_f}{\rightleftarrows}} C_2H_6^{*} + M$$

$$C_2H_6^{*} \xrightarrow[k_f']{} 2\,CH_3$$

write an Arrhenius relation for each species

1 $$\frac{dC_{C2H6}}{dt} = -k_f\,C_{C2H6}\,C_m + k_b\,C_{C2H6^*}\,C_m$$

2 $$\frac{dC_{C2H6^*}}{dt} = k_f\,C_{C2H6}\,C_m - k_b\,C_{C2H6^*}\,C_m - k_f'\,C_{C2H6^*}$$

3 $$\frac{dC_{CH3}}{dt} = 2\,k_f'\,C_{C2H6^*}$$

4 $$\frac{dC_m}{dt} = 0 \quad \text{since } \nu'' = \nu'$$

simplify using steady state approx: $\frac{dC_{C2H6^*}}{dt} = 0$,

⑤ eqn 2 yields:

$$C_{C2H6^*} = \frac{k_f\,C_{C2H6}\,C_m}{k_b C_m + k_f'}$$

combine eqn ①, ③, ④, ⑤:

$$\boxed{\frac{dC_{CH3}}{dt} = \left[\frac{k_f(k_f')C_m}{k_b C_m + k_f'}\right] C_{C2H6}}$$

agrees with experiment.

Kuo P 159

6.3 Complex Reactions

6.3.1 Hydrogen–Bromine Reaction A classical example of a complex reaction mechanism is provided by the formation of HBr from H_2 and Br_2. Bromine is a heavy, volatile, corrosive, reddish-brown, nonmetallic liquid element that has a highly irritating vapor with boiling point of 58.78°C. The global (overall) gas-phase reaction for the generation of hydrogen bromide is

$$H_2 + Br_2 \rightarrow 2HBr$$

The rate of production of HBr does not follow the law of mass action given by Eq. (2-13). Instead, the experimentally determined rate law for the reaction is

$$\frac{dC_{\mathrm{HBr}}}{dt} = \frac{a_1 C_{\mathrm{H_2}} C_{\mathrm{Br_2}}^{1/2}}{1 + C_{\mathrm{HBr}}/(a_2 C_{\mathrm{Br_2}})}$$

where a_1 and a_2 are constants at a given temperature.

In the following, we shall first consider the detailed reaction mechanism, which consists of an interplay of various elementary reactions, then apply the steady-state treatment to free H and Br radicals, and finally derive a rate expression in the same form as that obtained experimentally. The H_2–Br_2 reaction also serves as an example of how a complex reaction mechanism can be proposed and verified.

To initiate this chemical reaction, heat is added. Br_2 begins to decompose first, since H_2 is more stable than Br_2 (note: $\Delta\mathcal{H}^o_{f,\mathrm{Br}} = 6.71$ kcal/mol, $\Delta\mathcal{H}^o_{f,\mathrm{H}} =$ 52 kcal/mol). Once bromine atoms are formed, these free radicals can react

5-24

readily with H_2. Therefore, a series of reactions are followed:

$$M + Br_2 \xrightarrow{k_1} 2Br + M \qquad \text{chain-initiating} \tag{2-44}$$

$$\left.\begin{aligned} Br + H_2 &\xrightarrow{k_2} HBr + H \\ H + Br_2 &\xrightarrow{k_3} HBr + Br \\ HBr + H &\xrightarrow{k_4} H_2 + Br \end{aligned}\right\} \qquad \text{chain-carrying} \qquad \begin{aligned} &(2\text{-}45) \\ &(2\text{-}46) \\ &(2\text{-}47) \end{aligned}$$

$$M + Br + Br \xrightarrow{k_5} Br_2 + M \qquad \text{chain-terminating} \tag{2-48}$$

In reactions (2-44) and (2-48), the symbol M represents a third body, that is, any of the chemical species H, Br, H_2, Br_2, or HBr which may be present in the system. The relationships showing the effectiveness between different collision partners are called chaperon relationship [see, for example, Eq. (5-52) and(5-53)]. Initially, Br_2 or H_2 molecules are the collision partners with Br_2 molecules.

Reaction (2-44) is a chain-initiating step. Reactions (2-45) and (2-46) represent the chain-carrying reactions in which an atom (either Br or H) is produced for each atom which reacts. Reaction (2-47) is the inverse of (2-45); the inverse of (2-46) is relatively slow and is therefore unimportant. Reaction (2-46) represents the chain-terminating (also called chain-breaking or chain-killing) step. The chain-breaking step according to the recombination process

$$2H + M \rightarrow H_2 + M$$

is not important in the present case, since the concentration of H atoms is generally small compared with that of Br atoms. However, at higher temperatures the following two reactions

$$Br + HBr \rightarrow Br_2 + H$$

$$2H + M \rightarrow H_2 + M$$

can become quite influential. After examining the above set of opposing and consecutive reactions, it is easy to understand why the rate law derived from the global reaction has very little significance.

Following the law of mass action, a set of equations for the rate of change of concentration is obtained:

$$\frac{dC_{Br}}{dt} = 2k_1 C_M C_{Br_2} - k_2 C_{Br} C_{H_2} + k_3 C_H C_{Br_2} + k_4 C_H C_{HBr} - 2k_5 C_M C_{Br}^2 \tag{2-49}$$

$$\frac{dC_H}{dt} = k_2 C_{Br} C_{H_2} - k_3 C_H C_{Br_2} - k_4 C_H C_{HBr} \tag{2-50}$$

$$\frac{dC_{Br_2}}{dt} = -k_1 C_{Br_2} C_M - k_3 C_H C_{Br_2} + k_5 C_{Br}^2 C_M \tag{2-51}$$

$$\frac{dC_{H_2}}{dt} = -k_2 C_{Br} C_{H_2} + k_4 C_H C_{HBr} \tag{2-52}$$

$$\frac{dC_{HBr}}{dt} = k_2 C_{Br} C_{H_2} + k_3 C_H C_{Br_2} - k_4 C_H C_{HBr} \tag{2-53}$$

Applying the steady-state assumption that the mean concentrations of the free radicals H and Br remain nearly constant, we have

$$\frac{dC_{\mathrm{H}}}{dt} = \frac{dC_{\mathrm{Br}}}{dt} = 0 \tag{2-54}$$

In actuality, the concentrations of H and Br will not remain constant throughout the reaction process, but they will remain constant throughout the major portion of the reaction period, except for short initial and final periods. Thus, the concentration of the free radicals can be treated as nearly constant.

Using Eq. (2-54) to equate Eqs. (2-49) and (2-50), and then rearranging the result, we have

$$C_{\mathrm{Br}} = \sqrt{\frac{k_1}{k_5}}\sqrt{C_{\mathrm{Br}_2}} \tag{2-55}$$

Solving for C_{H} after setting the left-hand-side term of Eq. (2-50) equal to zero, we have

$$C_{\mathrm{H}} = \frac{k_2 C_{\mathrm{Br}} C_{\mathrm{H}_2}}{k_3 C_{\mathrm{Br}_2} + k_4 C_{\mathrm{HBr}}} \tag{2-56}$$

Note that Eqs. (2-55) and (2-56) were obtained under the steady-state assumption. If the equilibrium assumption were used instead of the steady-state assumption, Eq. (2-56) would be different, since equilibrium-constant equations would be used to replace the rate expressions. It is obvious that these two assumptions are not interchangeable. Under either the steady-state assumption or the equilibrium assumption, the total number of unknowns is equal to six, namely

$$T_f,\ C_{\mathrm{H}},\ C_{\mathrm{Br}},\ C_{\mathrm{H}_2},\ C_{\mathrm{Br}_2},\ C_{\mathrm{HBr}}$$

In addition to Eqs. (2-49) through (2-53), we have one enthalpy-balance equation to make the system completely defined. By solving these six simultaneous equations as a function of time, the reaction history of this combustion problem is obtained.

Now, if we follow the steady-state assumption for H and Br atoms and substitute Eqs. (2-55) and (2-56) into Eq. (2-53), we have

$$\frac{dC_{\mathrm{HBr}}}{dt} = k_2\sqrt{\frac{k_1 C_{\mathrm{Br}_2}}{k_5}}C_{\mathrm{H}_2} + \frac{k_3 C_{\mathrm{Br}_2} - k_4 C_{\mathrm{HBr}}}{k_3 C_{\mathrm{Br}_2} + k_4 C_{\mathrm{HBr}}} k_2 C_{\mathrm{Br}} C_{\mathrm{H}_2}$$

or

$$\frac{dC_{\mathrm{HBr}}}{dt} = k_2\sqrt{\frac{k_1 C_{\mathrm{Br}_2}}{k_5}}C_{\mathrm{H}_2}\left(\frac{2k_3 C_{\mathrm{Br}_2}}{k_3 C_{\mathrm{Br}_2} + k_4 C_{\mathrm{HBr}}}\right)$$

which simplifies to

$$\frac{dC_{\mathrm{HBr}}}{dt} = \frac{2k_2\sqrt{k_1/k_5}\sqrt{C_{\mathrm{Br}_2}}C_{\mathrm{H}_2}}{1 + (k_4/k_3)C_{\mathrm{HBr}}/C_{\mathrm{Br}_2}} \tag{2-57}$$

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Equation (2-57) matches the empirical relation obtained from experimental measurements,

$$\frac{dC_{\mathrm{HBr}}}{dt} = \frac{2k_t C_{\mathrm{H_2}} \sqrt{C_{\mathrm{Br_2}}}}{1 + C_{\mathrm{HBr}}/(10C_{\mathrm{Br_2}})} \tag{2-58}$$

At the beginning of the reaction process, the concentration of HBr is very small, that is,

$$1 \gg \frac{C_{\mathrm{HBr}}}{10C_{\mathrm{Br_2}}}$$

In this case, Eq. (2-58) reduces to the Arrhenius form in which

$$\frac{dC_{\mathrm{HBr}}}{dt} = kC_{\mathrm{H_2}}C_{\mathrm{Br_2}}^{1/2} \tag{2-59}$$

The overall order of the reaction is $1\frac{1}{2}$.

For the other case, corresponding to

$$\frac{C_{\mathrm{HBr}}}{10C_{\mathrm{Br_2}}} \gg 1$$

the Arrhenius form is again obtained. In general, the order of complex reactions changes as a function of time.

5-29

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Elementary Reactions – Hydrogen

Kuo p. 216

H_2/O_2 Reaction Systems

The initiation reactions are

no radicals $\boxed{H_2 + M \rightarrow 2H + M}$ ← one radical

Chain-reaction steps involving O, H, and OH radicals are

one radical → $H + O_2 \leftrightharpoons OH + O$ ← two radicals (H4)

chain branching

$O + H_2 \leftrightharpoons H + OH$ (H5)

$O + H_2O \leftrightharpoons 2OH$ (H7)

Chain-terminating steps involving O, H, and OH radicals are the three-body recombination reactions:

$H + H + M \rightarrow H_2 + M$ (H8)

$O + O + M \rightarrow O_2 + M$ (H9)

$H + O + M \rightarrow OH + M$ (H10)

two radicals → $H + OH + M \rightarrow \boxed{H_2O} + M$ ← no radicals (H11)

The above mechanism is realistic, for many cases. To make it even better, add the following less-important reactions.

When the HO_2, hydroperoxyl radical and H_2O_2 species are considered

$H + O_2 + M \rightarrow HO_2 + M$ (H12)

$HO_2 + H \rightarrow 2OH$ (H13)

$HO_2 + H \rightarrow H_2O + O$ (H14)

$HO_2 + O \rightarrow O_2 + OH$ (H15)

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (H16)

$HO_2 + H_2 \rightarrow H_2O_2 + H$ (H17)

$H_2O_2 + OH \rightarrow H_2O + HO_2$ (H18)

$H_2O_2 + H \rightarrow H_2 + HO_2$ (H19)

$H_2O_2 + H \rightarrow H_2O + OH$ (H20)

$H_2O_2 + M \rightarrow 2OH + M$ (H21)

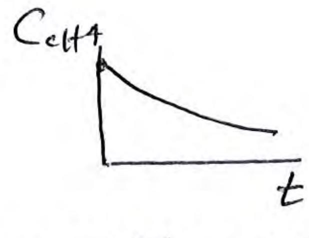
$H_2O_2 + O_2 \rightarrow 2HO_2$ (H22)

Measure Reaction Rates

- Shock tube, fast reactions or rapid compression machine (Wooldridge)
- Flow reactor slow reactions diluted with Argon
- Flame – measure profiles of

– shock tube - raise T, p to desired value instantaneously

$$CH_4 + O_2 \xrightarrow{k} CH_3 + HO_2$$

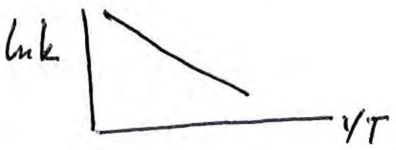


$$\frac{d\,C_{CH4}}{dt} = -k(T)\,C_{CH4}\,C_{O2}$$

measure $C_{CH4}(t)$ at $T = 1000K, 1200K, 1400K \ldots$ $p = 1$ atm

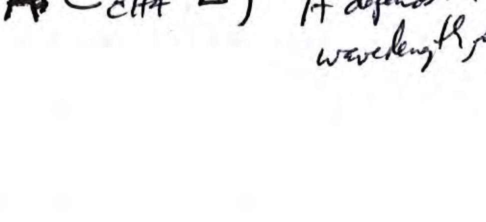
measure $C_{O2}(t)$ too

deduce $K(T)$



$k \sim \exp\left(\frac{-E_A}{R_uT}\right)$ log k $\ln k \sim -\frac{E_A}{R_uT}$

C_{CH4} from diode laser absorption



Beers Law $\frac{I_{detector}}{\underbrace{I_{laser}}_{0.90}} = \exp(-A\,C_{CH4}\,L)$ A depends on wavelength, etc

Zeldovich (thermal NO) mechanism

Kuo p. 255
Turns p. 168
p. 559

(A) $O_2 + M \underset{k_{Ab}}{\overset{k_{Af}}{\rightleftharpoons}} 2O + M$

(N1) $O + N_2 \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} NO + N$

(N2) $N + O_2 \underset{k_{2b}}{\overset{k_{2f}}{\rightleftharpoons}} NO + O$

– general CHEMKIN method: 5 unknowns: C_{O2} C_{N2} C_{NO} C_O C_N

write 5 Arrhenius relns $\frac{dC_{O2}}{dt} = \ldots$ etc & solve!

– develop a simplified "Reduced Mechanism" – only one differential eqn!

assume: – NO is not in partial equilibrium –
(NO reactions are slow, so part. equil. not good assumpt)

O + O_2 in reactions A are in partial equilibrium (O + O_2)

– N radicals are in "steady state" $dC_N/dt = 0$

– consider only initial buildup of small amts of NO
so ignore k_{1b} and k_{2b} which are significant
only when appreciable NO is present

– ignore the $N + OH \rightarrow NO + H$ reaction

(A) partial equil yields:

$$\frac{d\,C_{O2}}{dt} = -k_{Af}\, C_{O2}\, C_M + k_{Ab}\, C_O^2\, C_M = 0$$

$$\therefore\ K_N = \frac{k_{Af}}{k_{Ab}}\ \cancel{C_{O2}}\ \cancel{C_M} = \cancel{k_{Ab}}\ \frac{C_O^2}{C_{O2}}\ \cancel{C_M}$$

$$\text{but}\quad K_N = K_P \left(\frac{P}{n_T}\right)^{-1} \qquad \frac{P}{n_T} = R_u T$$

$$\text{so} \quad ①\ \boxed{C_O = C_{O2}^{1/2}\, (K_P)^{1/2}\, (R_u T)^{-1/2}}$$

partial equil allows us to eliminate C_O in our "reduced" description

now:

$$② \quad \frac{d\,C_{NO}}{dt} = k_{1f}\, C_O\, C_{N2} + k_{2f}\, C_N\, C_{O2} - k_{1b}\, \underbrace{\cancel{C_{NO}\, C_M}}_{\text{small}} - k_{2b}\, \underbrace{\cancel{C_{NO}\, C_O}}_{\text{small}}$$

ignore   ignore

$$\frac{d\,C_N}{dt} = k_{1f}\, C_O\, C_{N2} \mp k_{2f}\, C_N\, C_{O2} - k_{1b}\, \cancel{C_{NO}\, C_N} + k_{2b}\, \cancel{C_{NO}\, C_O}$$

ignore

use steady state assumption for N: $\frac{d\,C_N}{dt} = 0$

$$\therefore\ k_{1f}\, C_O\, C_{N2} = k_{2f}\, C_N\, C_{O2} \qquad \text{solve for } C_N$$

$$③ \quad \boxed{C_N = \frac{k_{1f}}{k_{2f}}\ \frac{C_O\, C_{N2}}{C_{O2}}}$$

steady state assump. allows us to eliminate C_N using this plug ① and ③ into ②:

same

$$\frac{d\,C_{NO}}{dt} = 2k_{1f}\,C_O C_{N_2} + \cancel{k_{2f}}\,\frac{k_{1f}}{\cancel{k_{2f}}}\,\frac{C_O C_{N2}}{\cancel{C_{O2}}}\,\cancel{C_{O2}}$$

$$\boxed{\frac{d\,C_{NO}}{dt} = 2\,k_{1f}\,C_{O2}^{1/2}\,C_{N2}\left(K_p\right)^{1/2}\left(R_u T\right)^{-1/2}}$$

Turns p. 131

where $\boxed{k_1 = 1.82\times10^{14}\exp\left(\frac{-38,370\,K}{T}\right)}$ (K_p is for $O_2 \rightleftharpoons 2O$)

in $\left(\frac{m^3}{kmol\,sec}\right)$

$$K_p = \frac{\left(P_O/P^\circ\right)^2}{\left(P_{O2}/P^\circ\right)}$$

ex. lean CH_4-air $\phi = 2/3$ at $T = 2500K$, 3 atm compute dX_{NO}/dt.

in an IC engine if residence time is 10° crank angle at 2000 RPM compute X_{NO}.

$$CH_4 + \frac{2O_2}{(2/3)} + \frac{2(3.76)N_2}{(2/3)} \longrightarrow CO_2 + 2H_2O + \frac{2(3.76)N_2}{2/3} + 1\,O_2$$

behind flame in product gases

$$X_{N2} = \frac{3(3.76)}{1+2+1+3(3.76)} = 0.738$$

$R_u = 8.315 \frac{J}{mol\,K}$

$= 8315 \frac{N \cdot m}{kmol\,K}$

$$X_{O2} = \frac{1}{1+2+1+3(3.76)} = .0654$$

$$C_{N2} = [N_2] = X_{N2}\frac{P}{R_uT} = .738\,\frac{\overset{3\,atm}{3}(101325)}{8315\;2500} = 1.08\,10^{-2}\ \frac{kmol}{m^3}$$

$$C_{O2} = [O_2] = X_{O2}\frac{P}{R_uT} = .0654\,\frac{3(101325)}{8315(2500)} = 0.96\times10^{-3}\ \frac{kmol}{m^3}$$

$$k_f = 1.82\times10^{14}\exp\left(\frac{-38370\,K}{T}\right)$$

$$k_f = 3.93\times10^{4}\ \frac{m^3}{kmol \cdot s}$$

$$K_p = \exp\begin{pmatrix}\text{value in Col 3}\\ \text{of handout}\\ \text{at 2500K}\end{pmatrix} = \exp(-8.509) = 2.00\times10^{-4}$$

$P_0 = 1\,atm$, $T = 2500K$

must use $P_0 = 101{,}325\ Pa$

Kuo p.84 $K_{p_1}(2500K) = .0153$

$$K_p = K_{p_1}^{-2} = \underline{2.1\times10^{-4}}$$

$$\frac{dC_{NO}}{dt} = \frac{d\,[NO]}{dt} = 2\underbrace{\left(3.93\times10^{4}\ \frac{m^3}{kmol\ s}\right)}_{k_{1f}}\left[\frac{\overbrace{2.10\times10^{-4}}^{K_P}\left(101{,}325\ \frac{N}{m^2}\right)}{8315\ \frac{J}{kmol\ K}\ 2500K}\right]^{1/2}$$

$$\underbrace{\left(1.08\ 10^{-2}\ \frac{kmol}{m^3}\right)}_{C_{N_2}}\underbrace{\left(0.96\times10^{-3}\ \frac{kmol}{m^3}\right)^{1/2}}_{C_{O_2}^{1/2}}$$

$$= 2.63\times10^{1}\left(1.00\ 10^{-3}\right) = 0.026\ \frac{kmol}{m^3\text{-}s}$$

$$\frac{dX_{NO}}{dt} = \frac{d[NO]}{dt}\ \frac{R_uT}{P} = \frac{8315(2500)}{3(101{,}325)}\,.026 = 1.77\ s^{-1}$$

$$\boxed{\frac{dX_{NO}}{dt} = 1.77\times10^{6}\ ppm/s}$$

suppose

$2000\ \frac{rev}{min} \Rightarrow .03$ sec/rev

30 msec/rev = 360°

10° → .08 ms = 0.1 ms

residence time at 2500K = 0.10 msec $= 10^{-4}$ s

10° out of 360° at 2000rpm

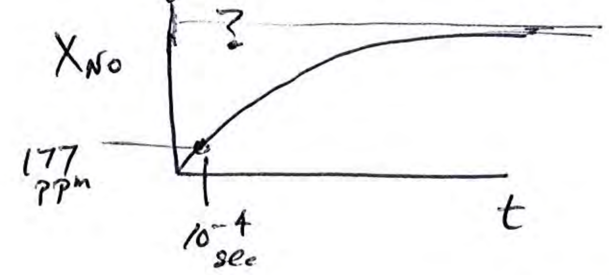
$$X_{NO\ \text{created}} = \frac{dX_{NO}}{dt}\cdot t_{res} = \boxed{177\ ppm}$$

idea – reduce T or reduce residence time

5-51

~~4-27~~ 6-~~23~~

Ex. if we allowed the residence time to be very large such that X_{NO} reached its equil. value, what would X_{NO} be?



$X_{NO,eq} = ?$

$P = 3\,atm \qquad T = 2500\,K$

$$X_{N2} = \frac{P_{N2}}{P} = .738 \qquad X_{O2} = \frac{P_{O2}}{P} = .654$$

K_{NO} p. 85

$$K_{p6} = \frac{P_{NO}}{P_{N2}^{1/2} P_{O2}^{1/2}}$$

for $\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO$

at $T = 2500$

$\log_{10} K_{p6} = -1.22$

$$= \frac{P_{NO}/P}{(P_{N2}/P)^{1/2}(P_{O2}/P)^{1/2}} = \frac{X_{NO}}{X_{N2}^{1/2} X_{O2}^{1/2}}$$

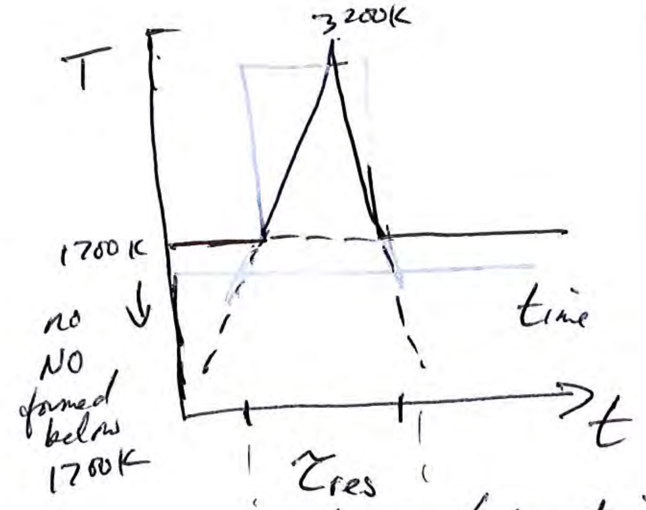
$K_{p6} = 0.0602$

$$X_{NO} = .0602(.738)^{1/2}(.654)^{1/2} = .041 = 41{,}000\ ppm!$$

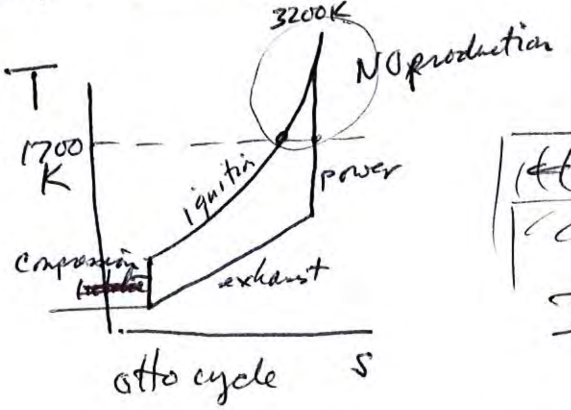
note - at the equilibrium limit - there would be forward + backward reactions $O + N_2 \rightleftarrows NO + N$

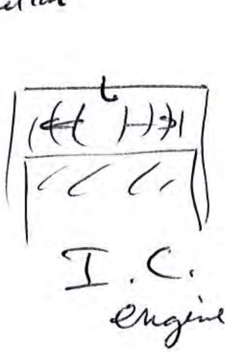
↑ important when there is a lot of NO

NO_x control = limit residence time at high T>1700K

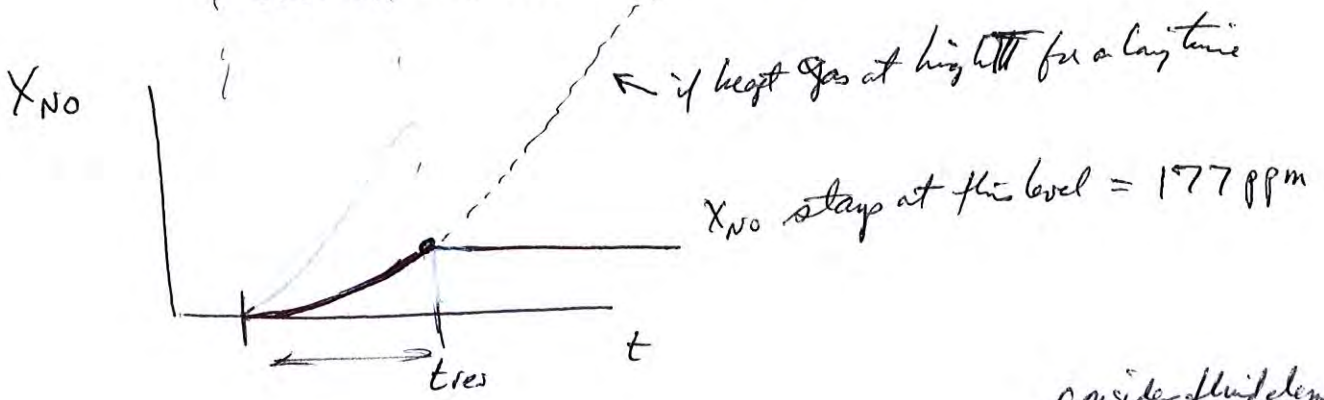


residence time at T > 1700K



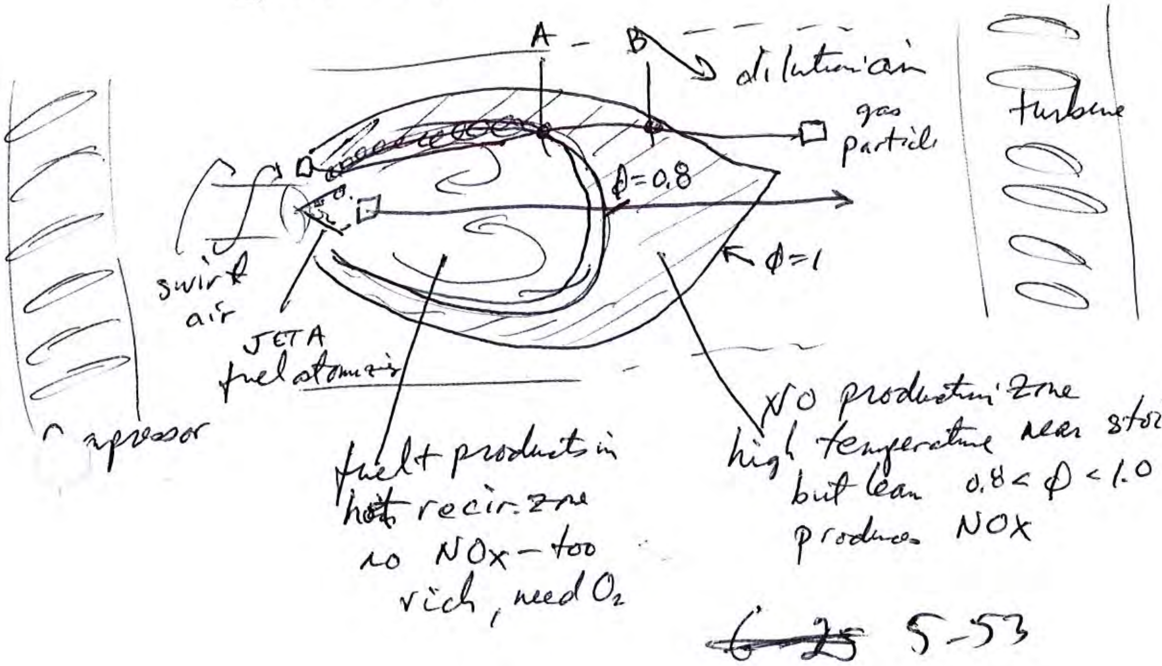


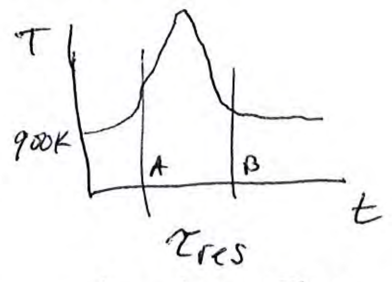
equil 41,000 ppm



consider fluid element on CL
gas particle sees

Jet engine is similar





τres

to reduce τres

reduce the size of the NO production zone, increase speed of gas going through it!

Low NO_x strategies for jet engine

- minimize residence time in hot, lean gases ($T > 1700K$, $\phi < 1$)

a) $\boxed{LPP}$ = lean premixed, prevaporized (G.E.)

$\phi < 0.7$ so $T_{max} < 1800 K$

$$\frac{d[NO]}{dt} = 2 k_1 \left(\frac{K_P P_0}{R_u T}\right)^{1/2} [N_2][O_2]^{1/2}$$ (Turns p. 131)

↑ idea - keep k_1 small

- port fuel injection IC engine
- HCCI engine
- lean Premix. gas turbine (TAPS)

b) $\boxed{RQL}$ - "rich burn, quick quench, lean combustion P. + W.

$\boxed{\text{"Staged combustion"}}$

see Turns

- burn slightly rich, so all O_2 used up $[O_2] = 0$ in products, T_{rich} less than T_{stoich}, k_1 small
- add air to rich products but accelerate them + ~~dilute~~ quickly so residence time of stoich. reactions is small

- stratified charge Mitzubishi GDI engine
- direct injection engine (rich near fuel spray)

c) $\boxed{\text{Catalytic converter}}$ platinum lowers activation energy for the reaction to remove NO_x in exhaust

$NO + NO + \overset{\text{platinum}}{\text{catalyst}} \rightarrow N_2 + O_2$

d) $\boxed{EGR}$ Turns p. 563 - add inert after cooling them - extract their heat energy + burn cooler or add water

d) $\boxed{\text{Reburn}}$ see

$CH + NO \rightarrow HCN + O$

$HCN + NO \rightarrow N_2 + HCO$

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e) $\boxed{\text{Ammonia } \overset{\text{advanced}}{\text{reburn}}}$ addition,

$NH_3 \rightarrow NH + H_2$ $NH + CH_2 \rightarrow HCN + H_2 \rightarrow HCN + NO \rightarrow N_2 + HCO$

a 5-54

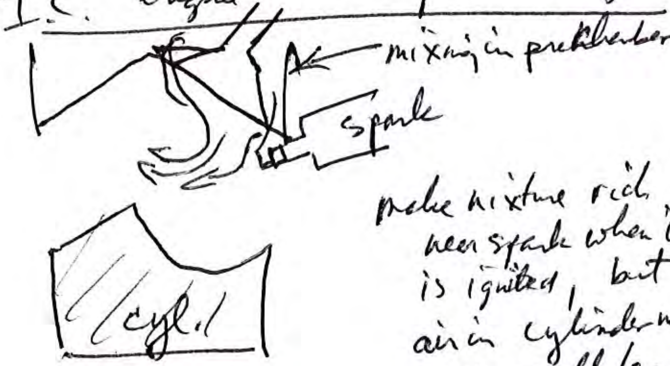
Low NOx strategies

#1 Burn very lean + premixed {flame blowout or flashback - stabilize. (do not burn stoich or slightly lean)

#2 Burn rich + premixed - how to burn up excess fuel?

#3 ~~S~~Since non-premixed combustion cannot be avoided, wherever near-stoichiometric combustion occurs - minimize the residence time there

1) I.C. engine - stratified charge or direct-injected stratified charge



make mixture rich near spark when it is ignited, but air in cylinder mixes + is overall lean

Mitsubishi GDI
reduces NOx

2) I.C. Homogeneous Charge Compression Engine (Assanis)

- want premixed + lean
- want no spark - compress to very large CR - as in diesel

∴ premixed diesel (no spark)

add to p. 26

5-55
~~4-300~~ ~~6-266~~

Shvab - Zeldovich Formulation   Kuo p. 332

Through a premixed flame we have separate ODE's

for $\frac{dY_{H2}}{dx} = \ldots$, $\frac{dY_{O2}}{dx} = \ldots$, $\frac{dY_{H2O}}{dx} = \ldots$ and $\frac{dT}{dx} = \ldots$

we can simplify all four of these ODE's to a single ODE

if we assume: $Le = 1$ so $\alpha = D$

all species have same diffusivity $D_i = D$

---

ex:

(i) $\rho_0 S_L \frac{dY_{H2}}{dx} - \rho D_{H2} \frac{d^2 Y_{H2}}{dx^2} = \dot{\omega}_{H2}$ ← kg/sec/vol H_2 created = -

(ii) $\rho_0 S_L \frac{dY_{O2}}{dx} - \rho D_{O2} \frac{d^2 Y_{O2}}{dx^2} = \dot{\omega}_{O2}$

(iii) $\rho_0 S_L \frac{dY_{H2O}}{dx} - \rho D_{H2O} \frac{d^2 Y_{H2O}}{dx^2} = \dot{\omega}_{H2O}$

Consider a stoichiometric $H_2 - O_2$ flame

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ then

$\dot{\omega}_{O2} = \frac{16}{2} \dot{\omega}_{H2}$ and

$\dot{\omega}_{H2O} = -\frac{18}{2} \dot{\omega}_{H2}$

→ Equations (i), (ii), (iii) are directly proportional to each other if $D_{H2} = D_{O2} = D_{H2O}$ ⇒ solve only one!

Zeldovich theory of premixed laminar flame (p. 451)

- better than Mallard theory – we solve for $T(x)$
- must solve two ODEs → $\frac{dY_r}{dx} = \ldots$ and $\frac{dT}{dx} = \ldots$
- still only approximate, we assume:
  - $D_i = D$ all species same diffusivity
  - $Le = 1$ $\alpha = D$
  - $\rho D = \lambda / c_p$ = const in x
  - steady, laminar, 1-D, P = const

---

solve:

(a) $$(\rho u)\frac{dY_r}{dx} - (\rho D)\frac{d^2 Y_r}{dx^2} = \dot{\omega}_r$$

$\dot{\omega}_r$ = neg
dY_r/dx = neg

(b) $$(\rho u)\, c_p \frac{dT}{dx} - \lambda \frac{d^2 T}{dx^2} = |\dot{\omega}_r|\, q_R$$

RHS = +
dT/dx = +

assume $\dot{\omega}_r$ is proportional to $A\exp(-E_a/R_u T)$ $\dot{\omega}_r$ not function of Y_r!
zeroth order reaction

Kuo defines: a = number density of reactant molecules (molecules/cm^3) $= \frac{Y_r N_A \rho}{MW_r}$

Y_r = mass fraction reactants

N_A = Avogadro's Number

ρ = mixture density

mW_r = molec. wt of reactants

and $$\rho_r \equiv \text{density of reactants} = Y_r \cdot \rho$$

$$\dot{\omega} = \frac{\text{molecules/sec of reactants consumed}}{\text{vol}} = \frac{|\dot{\omega}_r|\, N_A}{mW_r}$$

$$Q = \frac{|\text{heat of reaction}|}{\text{molecule of reactants}} = \frac{|\dot{\omega}_r|\, q_R}{\dot{\omega}}$$

q_R = kJ liberated / kg reactant

$$\Theta = \begin{matrix}\text{non dim.}\\ \text{temperature}\end{matrix} = \frac{T - T_0}{(Q/c_p)}$$

$$\alpha = \begin{matrix}\text{new (dimensional)}\\ \text{molecules / kg of}\\ \text{reactant}\end{matrix} = \left(\frac{a_0}{\rho_0} - \frac{a}{\rho}\right)$$

insert into (a) + (b) to get:

(c) $$(\rho u)\frac{d\Theta}{dx} - \left(\frac{\lambda}{c_p}\right)\frac{d^2\Theta}{dx^2} = \dot{\omega}$$

(d) $$(\rho u)\frac{d\alpha}{dx} - (\rho D)\frac{d^2\alpha}{dx} = \dot{\omega}$$

For our assumptions the solution is

(e) $$\boxed{\Theta(x) = \alpha(x)}$$ because

because θ and α obey same ODE
and b.c.s for $\theta + \alpha$ are same (see Kuo)
we still have to solve for $\theta(x)$ by solving Eqn (c)
but we can use (e) to find $\alpha(x)$, which
leads to $Y_r(x)$ and $Y_p(x) = 1 - Y_r(x)$

<u>Solution to Eq. (c):</u>

- break up flame into two zones (preheat + reaction zones)
- integrate in each region
- assume $\lambda \left.\frac{dT}{dx}\right|_{x=0^-} = \lambda \left.\frac{dT}{dx}\right|_{x=0^+}$ at boundary of regions
- do <u>not</u> make the assumptions in reaction zone that we did for Mallard theory

preheat zone – do same as Mallard theory }

$$(\rho_0 S_L)\, c_p \frac{dT}{dx} = \lambda \frac{d^2T}{dx^2}$$

integrate to get eqn (f) as we did for Mallard theory

$$(\rho_0 S_L)(T_i - T_0) = \left(\frac{c_p}{\lambda}\right) \left.\frac{dT}{dx}\right|_{x=0^-} \qquad (f)$$

reaction zone (Kuo p. 455)

do <u>not</u> define $\overline{\dot{\omega}}_r$ as we did in Mallard theory

in new notation

Kuo 5-25

$$\frac{d^2T}{dx^2} + \frac{\dot{\omega}\,Q}{\lambda} = 0$$

mult. by $2\frac{dT}{dx}$ to get:

$$\underbrace{2\frac{dT}{dx}\frac{d^2T}{dx^2}} = -2\frac{dT}{dx}\frac{\dot{\omega}Q}{\lambda}$$

mult by dx

$$\int_{x=0^+}^{x=\infty} \frac{d}{\cancel{dx}}\left(\frac{dT}{dx}\right)^2 \cancel{dx} = -2\int \frac{\dot{\omega}\,Q}{\lambda}\,\frac{dT}{\cancel{dx}}\,\cancel{dx}$$

$$\left(\cancelto{0}{\left.\frac{dT}{dx}\right|_{\infty}} - \left[\frac{dT}{dx}\right]_{0^+}\right)^2 = -2\,\frac{Q}{\lambda}\int_{0^+}^{\infty}\dot{\omega}\,dT$$

$$\Downarrow$$

so $$\left|\frac{dT}{dx}\right|_{0^-}^2 = 2\,\frac{Q}{\lambda}\int_{0^+}^{\infty}\dot{\omega}\,dT \qquad (n)$$

Combine eqns (f) and (n) to get:

$$(\rho_0 S_L)^2 (T_i - T_0)^2 = 2\,\frac{Q}{\lambda} \int_{\substack{x=0^+ \\ T=T_i}}^{\substack{T=T_f \\ x=\infty}} \dot{\omega}\, dT \qquad (0)$$

so

$$\boxed{S_L = \sqrt{\frac{\lambda}{\rho_0 c_p}\,\frac{2}{(T_f - T_0)}\,\frac{1}{a_0}\int_{T_i}^{T_f} \dot{\omega}\, dT}}$$

Eqn. 5-29
p. 456

zero th order reaction

$Le = 1$, $D_i = D$

better at saying $S_L \sim \sqrt{\alpha \cdot RR}$

now we can compute RR with the integral

but best way → use Chemkin!

(a) Initial value problem:

$$\frac{d^2T}{dx^2} + 100\,\text{m}^{-2}\,T = 0$$

with b.c.'s: $x = 0 \quad T = 0$

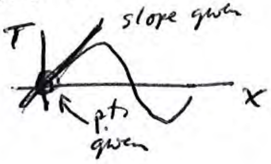
$x = 0 \quad \frac{dT}{dx} = 50\,\text{K/m}$

$\Rightarrow$ solution is:

$$T = A\sin(10\,\text{m}^{-1}x) + B\cos(10\,\text{m}^{-1}x)$$

first b.c. gives $B = 0$

second b.c. gives: $\left.\frac{dT}{dx}\right|_0 = A\,10\,\text{m}^{-1}\cancelto{1}{\cos(10\,\text{m}^{-1}\,0)} = 50\,\frac{\text{K}}{\text{m}}$ so $A = 5\,\text{K}$



answer: $\boxed{T(x) = 5\,\text{K}\cdot\sin(10\,\text{m}^{-1}x)}$ ✓

(b) overspecified initial value problem (eigenvalue problem)

$$\frac{d^2T}{dx^2} + kT = 0$$

b.c.: $\begin{cases} x = 0 & T = 0 \\ x = 0 & \frac{dT}{dx} = 50\,\text{m}^{-1}\,\text{K} \\ x = \frac{\pi}{2}\text{m} & T = 50\,\text{K} \end{cases}$

$T = A\sin(\sqrt{k}\,x) + B\cos(\sqrt{k}\,x)$

first bc: $\rightarrow B = 0$

second bc: $\rightarrow A\sqrt{k}\,\cancelto{1}{\cos(\sqrt{k}\,x)}\Big|_{x=0} = 50\,\text{m}^{-1}\,\text{K}$

so $A = \frac{50\,\text{m}^{-1}\,\text{K}}{\sqrt{k}}$

third b.c. $\rightarrow$ $T = 50\,\text{K} = \frac{50\,\text{m}^{-1}}{\sqrt{k}}\sin\left(\sqrt{k}\,\frac{\pi}{2}\text{m}\right)$

solution is $k = 1\,\text{m}^{-2}$

solution: $\boxed{T = (50\,\text{K})\sin\left[(1\,\text{m}^{-1})\,x\right]}$

$\therefore$ Adding a third b.c. forces k to be a certain value $(1\,\text{m}^{-2})$

(c) Boundary Value problem #1

$$\frac{d^2T}{dx^2} + kT = 0$$

b.c.'s: $\begin{cases} x = 0 & T = 0 \\ x = 10\,\text{m} & T = 0 \end{cases}$ $\Rightarrow$

$T = A\sin(\sqrt{k}\,x) + B\cos(\sqrt{k}\,x)$

1st b.c: $B = 0$

2nd bc: $0 = \sin(\sqrt{k}\,10\,\text{m})$

$\therefore (\sqrt{k}\cdot 10\,\text{m}) = n\pi$ so $\boxed{k = \left(\frac{n\pi}{10\,\text{m}}\right)^2}$ only way to have a non zero solution!

for $n = 1$ $k = \left(\frac{\pi}{10\,\text{m}}\right)^2$ solution is $\boxed{T = A\sin\left(\frac{\pi}{10\,\text{m}}x\right)}$

need one more b.c. to find A!

add bc. that

at $x = 5m$ $\quad T = 100K \quad A = ?$

$$100K = A \overset{1}{\cancel{\sin\left(\frac{\pi\, 5m}{10m\, 2}\right)}} \qquad A = 100K$$

so soln is $\boxed{T = (100K)\sin\left(\frac{\pi x}{10m}\right)}$ if $k = \left(\frac{n\pi}{10m}\right)^2$

$\boxed{T = \text{no solution}}$ if $k \neq \left(\frac{n\pi}{10m}\right)^2$

Conclude: to specify a unique solution we need three b.c.s, such as:

$$\begin{cases} x = 0 & T = 0 \\ x = 10m & T = 0 \\ x = 5m & T = 100K \end{cases}$$

eigenvalue k is uniquely determined by the boundary conditions

$$k = \left(\frac{\pi}{10m}\right)^2$$

if k is not equal to this value, then no solution exists

(d) boundary value problem #2 – more like a flame

equation is: $\frac{d^2 (T-1000K)}{dx^2} + k\,(T-1000K) = 0$

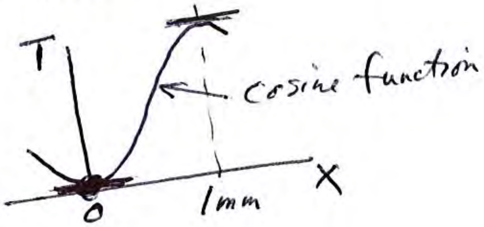
3 b.c.'s are: at $\begin{cases} x=0 & \frac{dT}{dx}=0 \\ x=0 & T=0 \end{cases}$ + at $x = 1mm$ $\frac{dT}{dX}=0$

---

solution is: $(T-1000K) = A\sin(\sqrt{k}\,x) + B\cos(\sqrt{k}\,x)$

1st b.c says $x=0, \frac{dT}{dx}=0$ so $\frac{dT}{dx} = A\sqrt{k}\cos(\sqrt{k}x) - B\sqrt{k}\sin(\sqrt{k}x)$
$= 0$ if $x=0$

so if $x=0$ $\sin \to 0$, $\cos \to 1$ $\therefore 0 = A\sqrt{k}\,(1)$ $\therefore A=0$



next bc. says at $x = 1mm$ $\frac{dT}{dx}=0$
we see that our solution must look like graph at right:

$\frac{dT}{dX} = -B\sqrt{k}\sin(\sqrt{k}x) = 0$ when $x = 1mm$
this only can occur if $\sqrt{k}\,x = \frac{\pi}{2}$ so $\sqrt{k} = \left(\frac{\pi}{2mm}\right)$ eigenvalue

third b.c. $x=0$ when $T=0$

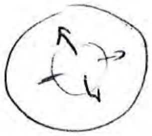
$(T-1000) = B\cos\left(\frac{\pi \overset{x=0}{x}}{2mm}\right) \Longrightarrow (-1000) = B \cdot (1)$
at $T=0$

solution is: $T = 1000 + -1000\cos\left(\frac{\pi x}{2mm}\right)$

or $\boxed{T = 1000K\left(1 - \cos\frac{\pi x}{2mm}\right)}$ see graph above

Measure laminar burning velocity S_L

a) bunsen burner $S_L = U_0 \sin\alpha$



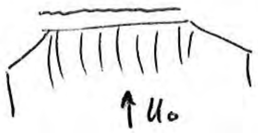
b) constant volume chamber (HW problem)

$$S_L = \frac{dr}{dt} - \frac{R^3 - r^3}{3p\gamma_u r^2}\frac{dp}{dt}$$ Kuo p. 396

problems -
nonuniform pipe flow
buoyancy forces
non adiabatic chamber
buoyancy prevents flame from being spherical

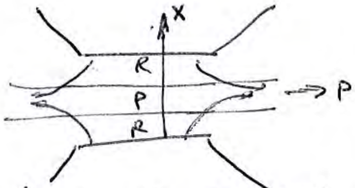
c) flat flame burner

heat transfer to burner



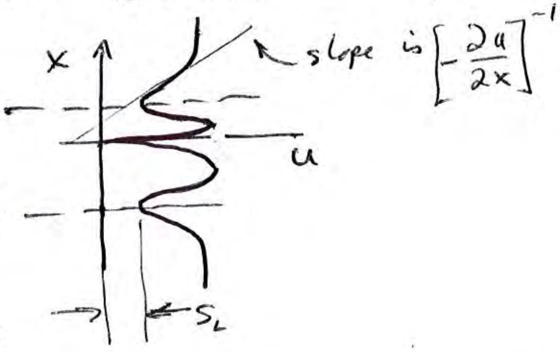
$U_0 = S_L$

d) best - counterflow twin flame



~~Zhu~~, Egolfopoulos, Cho Law Combust Flame 76, 375-391, 1989.

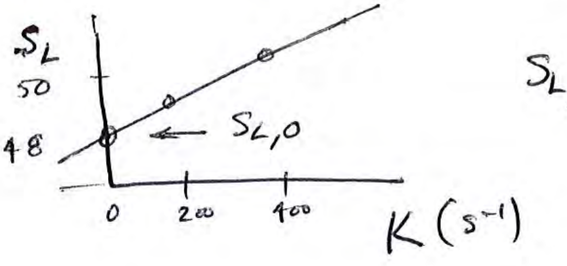
stretch rate $K = -\frac{du}{dx}\Big|_{\text{unburned}}$



= stretched burn. vel.

S_L = min. velocity ahead of flame, as shown

so plot



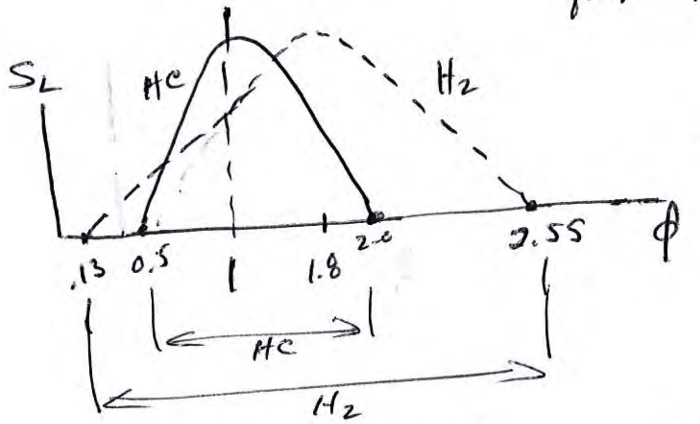
$S_{L,0}$ = unstretched laminar burning vel.
= extrapolated value as $K \to 0$

- measure $u(x)$ → LDV

Equivalence Ratio, Pressure and temperature dependences of S_L

$S_L = f(\phi, P_i, T_i)$ $\phi, P, T =$ unburned gas for given fuel type

	ϕ flammability limits
HC	~0.5 to ~2.0
H_2	0.13 to 2.55



flammability limits — Kuo p. 511

fuel	$S_L (\phi = 1)$ $\frac{cm}{s}$	
air - methane CH_4	40	Kuo
air - propane C_3H_8	46	"
air - acetylene C_2H_2	90	"
air - etylene C_2H_4	80	"
hydrogen-air H_2	260	Lewis Von Elbe
hydrogen - O_2 H_2	900	"
CO - air CO	46	"

Effect of pressure on S_L — for second order reaction

$C_{C3H8} = X_{C3H8} \frac{P}{R_u T}$

$$S_L \sim \sqrt{\alpha \cdot \overline{RR}}$$

$\frac{dX_{C3H8}}{dt} = \frac{dC_{C3H8}}{dt}$

$$\alpha = \frac{k}{\rho c_p} \sim \frac{k/c_p}{P/R_uT} \sim P^{-1}$$

$A + B \rightarrow C + D \quad dC_A/dt \sim C_A \cdot C_B \sim P^2$ see last page

we showed second order reaction

$$\boxed{\boxed{\overline{RR} \sim \underset{(s^{-1})}{\frac{dX_{C3H8}}{dt}}} \cancel{\frac{1}{C_{C3H8}} \frac{dC_{C3H8}}{dt}} \sim P^{-1}\, P^{2} \sim P^{+1}}$$

$$C_{C3H8} \sim X_{C3H8} \frac{P}{R_uT} \sim P$$

for propane → $\frac{dC_{C3H8}}{dt} \sim C_F^{0.1} C_{O_2}^{1.65} \cancel{ek} + \ldots \sim C_i^2 \sim P^2$

so $\boxed{S_L = \sqrt{\alpha \overline{RR}} \sim \sqrt{P^{-1} \cdot P^{+1}} = P^0}$

most HC reactions overall second order

so $\underline{S_L \text{ indep of } P.}$

Effect of Temperature on S_L (see Turns p. 274)

T_u = unburned T

T_b = burned T

$\overline{T} = \frac{T_b + T_u}{2}$

which T to use?

Turns uses empirical reasoning - what gives best fit to experiment!

Effect of temperature on S_L - see Turns p. 274

$$S_L \cong \sqrt{\alpha\, \overline{RR} \left(\frac{T_f - T_i}{T_i - T_0}\right)} \qquad (a)$$

expts show $(T_f - T_i)/(T_i - T_0) \simeq$ const.

where we define

T_u = unburned gas T

T_f = final product T

$\bar{T} = (T_f + T_u)/2$

E_A = activation energy Turns p. 156 (handout)

$(E_A/R_u = 15{,}098\text{ K}$ for propane)

N = overall order of reaction: $N = 0.1 + 1.65 = 1.75$

(for one-step propane-air rate - approx second order)

we said (Turns p. 156)

one-step propane

$$\frac{d C_{C_3H_8}}{dt} = -(8.6\times10^{11})\left[\exp\left(-\frac{15098\text{K}}{T}\right)\right] C_{C_3H_8}^{0.1}\, C_{O_2}^{1.65}$$

so

$$\left.\begin{aligned} \lambda &\sim \bar{T}^{0.85} \\ c_p &\sim \bar{T}^{0.10} \\ \rho_u &\sim P/T_u \end{aligned}\right\} \text{from expt.} \therefore \quad \alpha = \frac{\lambda}{\rho_u c_p} \approx \frac{\bar{T}^{0.85}}{(P/T_u)\,\bar{T}^{0.1}} = \frac{T_u \bar{T}^{0.75}}{P} \qquad (b)$$

$$\overline{RR} \approx \frac{1}{C_{C_3H_8}} \frac{d C_{C_3H_8}}{dt}$$

now assume X_i mole fraction do not change with T, P

$$\overline{RR} \sim \left(\frac{P}{R_u \underset{\uparrow}{T_u}}\right)^{-1} \left(\exp \frac{-E_A}{R_u \underset{\uparrow}{T_f}}\right) \left(\frac{P}{R_u \underset{\uparrow}{T_f}}\right)^{N} \qquad (C)$$

Turns $\left\{ \begin{array}{l} \text{assume } T = T_u \text{ here} \\ \underline{\underline{\text{assume}}}\ T = T_f \text{ for exponential term and for } \overline{RR} \text{ term} \\ \text{Combine (a) + (b) + (C) :} \end{array} \right.$

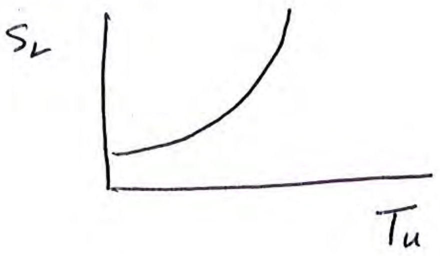
$$\boxed{S_L \underset{\substack{\uparrow \\ \text{prop.to}}}{\propto} \left(\bar{T}^{\,0.375}\, T_u\, T_f^{-N/2}\right)\left(\exp\left(\frac{-E_A}{R_u T_f}\right)\right) P^{\frac{N-2}{2}}}$$

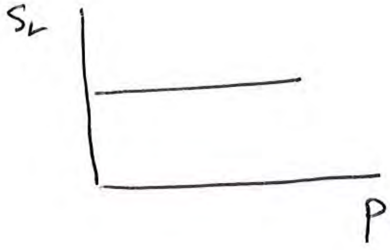
Turns p.275 is a good fit to data

recall $T_f \sim T_u$

$\bar{T} \sim T_u$ so $S_L \sim T_u^{\,0.375} \exp\left(\frac{-E_A}{R_u T_u}\right) \cdot P^{0}$

$N \approx 2$





preheat reactant - flame goes faster - basis for flame <u>stabilization</u>

other correlation by Metghalchi + Keck:

$$S_L = S_{L,ref} \left(\frac{T_u}{298K}\right)^{\gamma} \left(\frac{P}{1atm}\right)^{\beta}$$

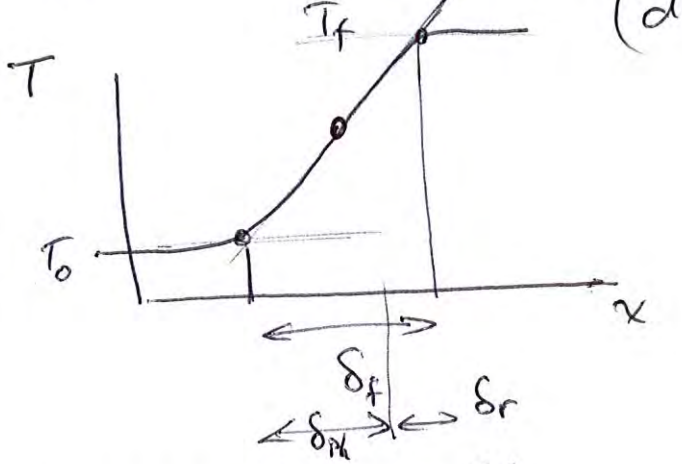
see Turns p. 280,

flame thickness $\quad \delta \sim \sqrt{\dfrac{\alpha}{\overline{RR}}} \quad \Rightarrow$ use above formulas for α and $\overline{RR}$

low pressure flames are <u>thick</u>

Thickness of laminar premixed flame

δ_f = flame thickness $\equiv \dfrac{T_f - T_0}{(dT/dx)_{max}}$



$\delta_f = \delta_{ph} + \delta_r$

Mallard theory said:

$$S_L = \frac{\alpha_0}{\delta_r}\left(\frac{T_f - T_i}{T_i - T_0}\right)$$

assume as you change P, ϕ $\left(\dfrac{T_f - T_i}{T_i - T_0}\right) \approx const = C_1$

$$\therefore \quad \delta_r = \frac{\alpha}{S_L} \cdot C_1$$

assume $\delta_{ph} = c_2 \cdot \delta_r$

$$\delta_f = \delta_{ph} + \delta_r = (c_2 + 1)\,\delta_r = (c_2 + 1)\, c_1 \frac{\alpha}{S_L}$$

define $C_3 = (c_2 + 1) \cdot c_1$

6-41 $\boxed{\delta_f = c_3 \dfrac{\alpha_0}{S_L}}$ $\Rightarrow$

S_L → from expt's or CHEMKIN
$C_3 = 7.8$ from expt.
$\alpha_0 = 0.15\ cm^2/s$ 298K

but $S_L = \sqrt{\alpha_0 RR} \cdot \text{const}$

so $$\delta_f = \frac{C_3\, \alpha_0}{\text{const}\sqrt{\alpha_0}\,\sqrt{RR}} = \boxed{\frac{C_3}{\text{const}}\sqrt{\frac{\alpha_0}{RR}}}$$ another way to write flame thickness

how does flame thickness δ_f depend on ~~p~~ pressure?

~const with pressure

$$\delta_f = C_3\,\frac{\alpha_0}{S_L} = \frac{C_3\,(\lambda/c_p)}{\underset{\sim P}{\rho}\; S_L}$$

$$\boxed{\delta_f \sim P^{-1}}$$

high pressure flames are thin
low pressure flames are thick (easier to resolve by probes for expts)

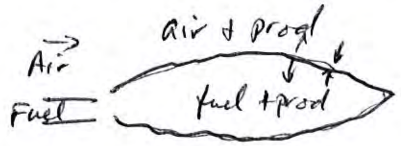
Read 6.1 - 6.3 Kuo

Laminar Jet Diffusion Flames

(Read Ch 9 Turns)

- called "nonpremixed" flames - fuel + air injected separately
- fuel + air must mix before combustion = mixing rate limited
- nonpremixed flames cannot propagate - do not have a "burning velocity"
  - must exist near boundary of fuel and oxidizer, not a "wave"

ex:



nonpremixed - kinetics not so important
- diffusion important
- not a wave
- mixing limited

premixed

flame goes where it wants to go - speed determined by kinetics + diffusion $S_L = \sqrt{\alpha RR}$

flame = wave

Conserved Scalar

= scalar quantity that is neither created nor destroyed by chemical reactions, but varies in space due to convection + diffusion terms in conservation eqns.

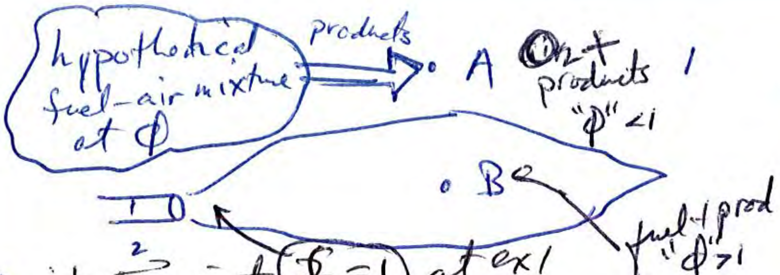
- conservation eqn for a conserved scalar has no source term due to chemical reactions

Z_H = mass fraction of H atoms present, independent of whatever molecule they are attached to

ex (2 moles =) $(H_2 + H_2O)$

$$Z_H = \frac{\text{mass of H atoms}}{\text{total mass}} = \frac{2g + 2g}{2g + 18g}$$

$Z_H = 0.2$



Read Cpt 6 Kuo

$$\boxed{f \equiv \frac{Z_H - Z_{H,2}}{Z_{H,1} - Z_{H,2}}}$$

mixture fraction

p. 241

mixture fraction is a conserved scalar

A.) exit inner jet $\boxed{f = 1}$ at exit
exit outer flow $f = 0$

at A = air + products

B = fuel + products

fuel + air had to mix to some ϕ, burn, then then products mix with, fuel, air or other products

define ϕ = fuel-air equiv. ratio of a "hypothetical" premixed mixture that would ~~give the~~ have products same as gas mixture at A

at point A above

ex $\underbrace{CH_4 + 4O_2 + 4\overset{79/21}{(3.76)}N_2}_{\phi = 1/2 \text{ for hypothetical f-a mixture}} \rightarrow \underbrace{CO_2 + 2H_2O + 2O_2 + 4\overset{79/21}{(3.76)}N_2}$

O_2 + "products" are gas that really exists at A

for the "real gas = RHS"

$$Z_H = \frac{4g}{(44 + 36 + 64 + 421)_g} = .0071$$

$$Z_{H,1} = \frac{4g}{16g} = 0,25 \qquad Z_{H,2} = 0$$

$$f(\text{at } A) = \frac{Z_H - \cancel{Z_{H2}}}{Z_{H,1} - \cancel{Z_{H2}}} \cong 0.028$$

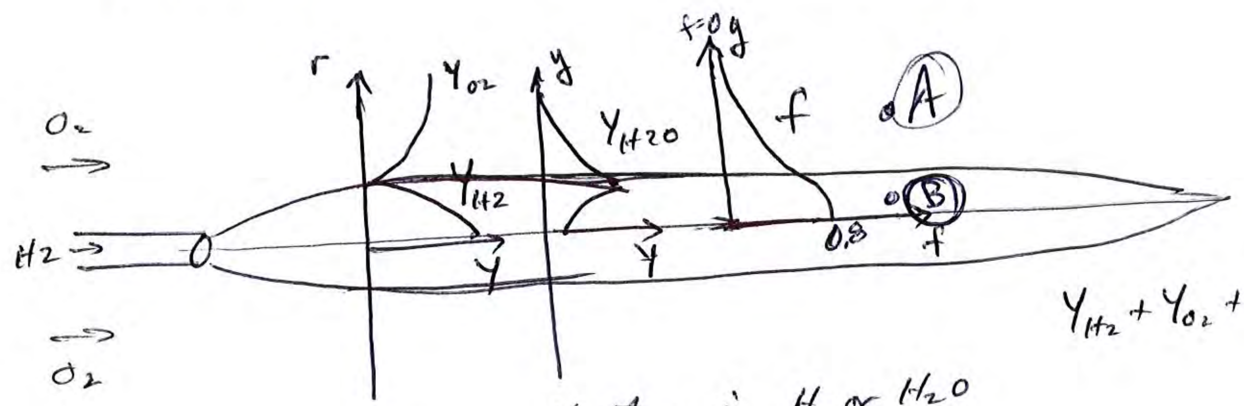
$Z_{H,2} = 0$

$$Y_{CO2}(\text{at } A) = \frac{44}{44 + 2(18) + 2(32) + 4\frac{79}{21}(28)} =$$

6-2 → if you knew f you could determine ϕ + Y_{CO2}

example laminar jet flame

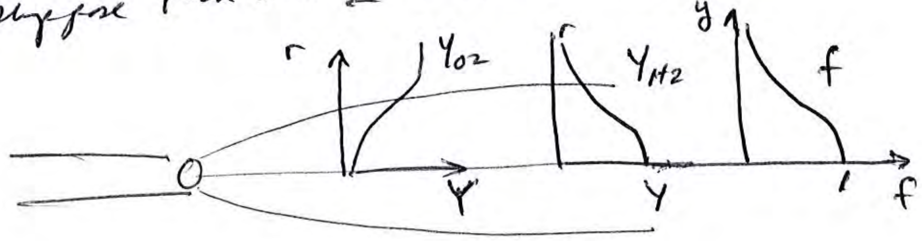
what do we expect mixture fraction (f) profiles to look like?



$Y_{H_2} + Y_{O_2} + Y_{H_2O} = 1$

f ~ mass fraction of H atoms, in H_2 or H_2O

suppose there was no reaction - just a H_2 jet into O_2



$Y_{O_2} + Y_{H_2} = 1$

mixture fraction profile f (r,x) looks ~~about the~~ not ~~the~~ quite the same ~~whether~~ when there is reaction ~~or not~~ but not too different (~~assuming all species diffuse at same rate~~)

f = 1 ⇒ pure (inner) fluid = H_2

f = 0 ⇒ pure outer fluid = O_2

(B.) enthalpy/mass (h) is a conserved scalar

$$h \equiv \sum_i Y_i \left(h_{f_i}^{\circ} + \int_{298}^{T} c_{p_i}\, dT\right)$$

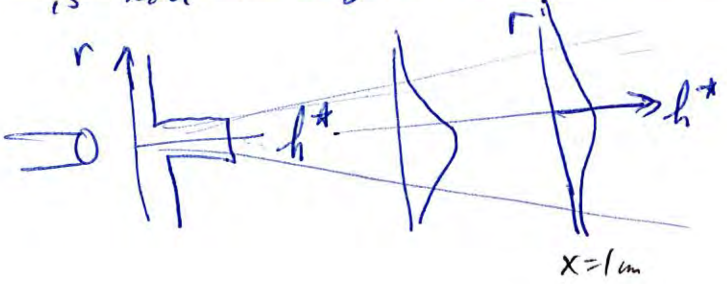
no bars = (kJ/kg)

$$h^* = \frac{h - h_2}{h_1 - h_2}$$

normalized enthalpy/mass

h^* will vary in space due to convection + diffusion, but is not changed due to chemical reaction, just like f

no source term in the conservation eqn for h^*



$h^* = 1$ pure inner fluid

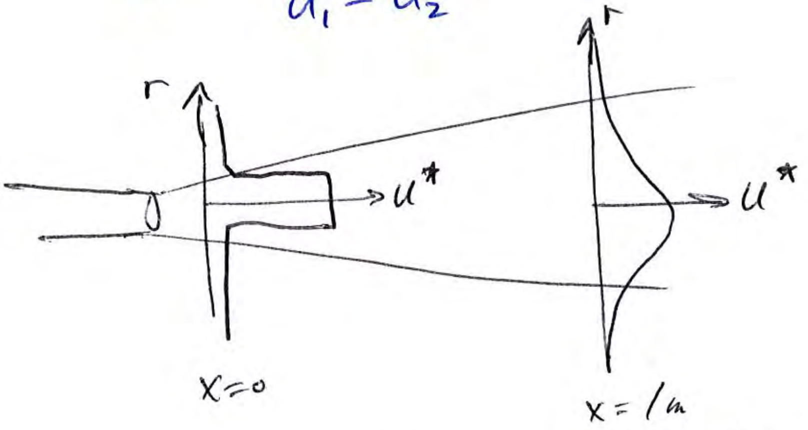
$h^* = 0$ pure outer fluid

(C.) Axial velocity (u) is a conserved scalar if the pressure field is constant everywhere

$$\frac{\partial P}{\partial x} = 0$$

$$\frac{\partial P}{\partial y} = 0$$

$$u^* = \frac{u - u_2}{u_1 - u_2}$$

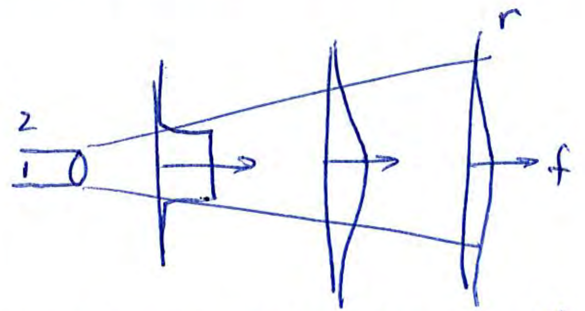


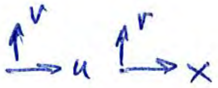
$u^* = 1$ pure inner fluid

$= 0$ pure outer fluid

Concept: we will prove that $f = h^* = u^*$ at every point (x, r) in a jet – just have to solve one PDE for $f(x,r)$

Laminar jet flame (Kuo p. 557)





∞ fast chemistry

assume: fuel in jet (~~al~~ also could be in stream 2), air in stream 2

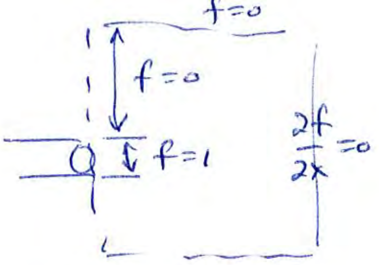
laminar, steady, p = constant (no recir.), neglect buoyancy

$Sc = Pr = Le = 1$, neglect diffusion in x

ρD = constant $\qquad u_0$ = jet exit velocity ($= u_1$)

conservation eqns: $\qquad h^* = \frac{h - h_2}{h_1 - h_2}$

$$\boxed{\begin{aligned}
&\frac{\partial}{\partial x}(\rho u r) + \frac{\partial}{\partial r}(\rho v r) = 0 \\
&\frac{\partial}{\partial x}\left(\rho u r \frac{u}{u_0}\right) + \frac{\partial}{\partial r}\left(\rho v r \frac{u}{u_0}\right) = \frac{\partial}{\partial r}\left(\rho\left(\frac{\mu}{\rho}\right) r \frac{\partial u/u_0}{\partial r}\right) \\
&\frac{\partial}{\partial x}(\rho u r f) + \frac{\partial}{\partial r}(\rho v r f) = \frac{\partial}{\partial r}\left(\rho D r \frac{\partial f}{\partial r}\right) \\
&\frac{\partial}{\partial x}(\rho u r h^*) + \frac{\partial}{\partial r}(\rho v r h^*) = \frac{\partial}{\partial r}\left(\rho \alpha r \frac{\partial h^*}{\partial r}\right)
\end{aligned}}$$



now $\frac{\mu}{\rho} = \nu = D = \alpha$

b.c. for $\frac{u}{u_0}$, f, h^* are identical

equations for $\underbrace{\qquad\qquad}$ are identical

$$\therefore \boxed{\frac{u}{u_0} = f = h^* \text{ at all locations } (x, r)} \qquad 6.62$$

laminar jet flame solution   Kuo p. 553   Schlichting

$$\boxed{f = \frac{u}{u_0} = \frac{h - h_2}{h_1 - h_2} = \frac{3}{32}\left(\frac{Re\, d_0}{x}\right)\left(1 + \frac{\xi^2}{4}\right)^{-2}}$$

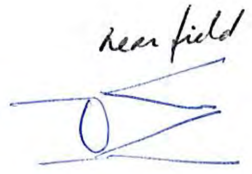
valid for $x/d_0 > 10$ (far field) (6-56a p. 553)

$Re \equiv \frac{u_0 d_0}{\nu_0}$ d_0 = jet diameter

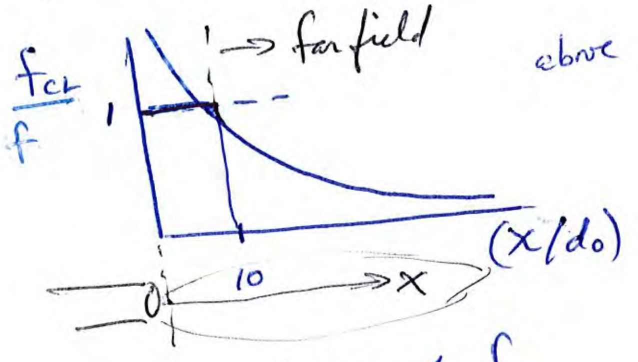
$$\boxed{\xi = \text{nondim. radial location} = \frac{\sqrt{3}}{8}\left(\frac{r}{d_0}\right)\left(\frac{Re\, d_0}{x}\right)}$$

on jet centerline $r = 0$, $\xi = 0$

$$\boxed{f_{CL} = \frac{u_{CL}}{u_0} = h^*_{CL} = \frac{3}{32} Re\left(\frac{d_0}{x}\right)}$$



let's plot these eqns:



above solution not valid for $x/d_0 < 10$

for $x/d_0 < 10$ $f = \frac{u}{u_0} = h^* = 1$

jet "core" shear layers not yet formed

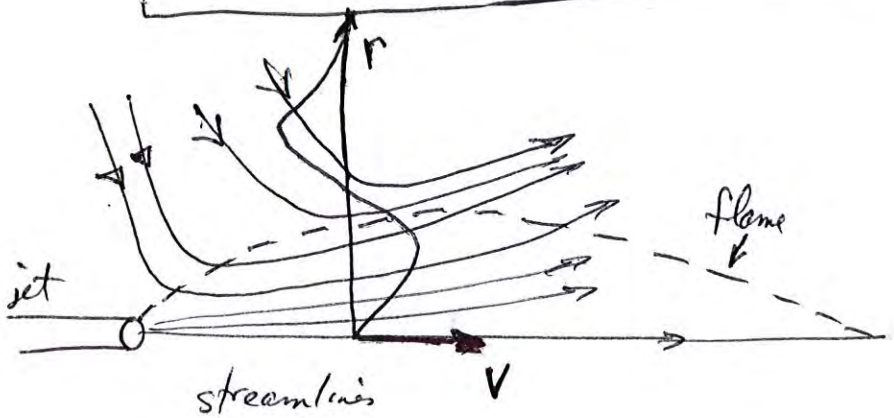
radial variation of f

$\partial f/\partial r = 0$ on CL, at $r = \infty$ too

Radial velocity (v)

$$\boxed{v = u_0 \left(\frac{3}{64}\right)^{1/2} \left(\frac{x}{d_0}\right)^{-1} \left(\xi - \frac{\xi^3}{4}\right) \left(1 + \frac{\xi^2}{4}\right)^{-2}}$$

Kuo 6-57
p. 554



for small r: $v \sim \xi$ since we ignore ξ^3 and ξ^2 terms
near centerline – radial velocity <u>out</u>ward

for large r: $v \sim -\dfrac{\xi^3}{4}\left(\dfrac{\xi^2}{4}\right)^{-2}$

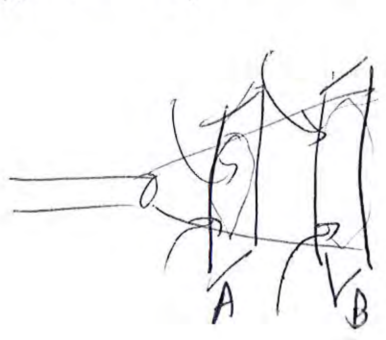
far from CL, radial velocity is <u>in</u>ward but drops off as you go far away from CL

mass/second entrained

$\dot m$ through a plane ⊥ to jet axis increases in the x direction

$$\frac{d\dot m}{dx} = 8\pi\mu \quad \text{so} \quad \dot m = 8\pi\mu x + \dot m_0$$

$$\frac{d\dot m}{dx} = \frac{\left(\text{mass/sec through } B - \text{mass/sec through } A\right)}{\Delta x}$$



$$= \frac{d}{dx}\int_0^\infty \rho u \, 2\pi r \, dr \quad 6\text{-}\cancel{10}7$$

Flame shape

flame is where $f = f_s$ ~~$= 0.2$ for methane-oxygen~~

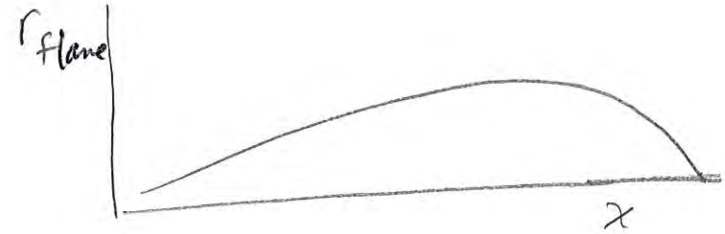
- set $f = f_s$ ~~$= 0.2$ in above eqn $f = f(x, r)$~~
- solve for ~~$r_{flame} = r(x)$~~ $r = r_{flame}$

$$f_s^{1/2} = \frac{(I_f/x)^{1/2}(3/4)^{1/2}}{1 + c_1\left(\frac{x}{r_f}\right)^2} \qquad \cancel{1+} c_1\left(\frac{x}{r_f}\right)^2 = \frac{I_f^{1/2}(3/4)^{1/2}}{f_s^{1/2}}\frac{1}{x^{1/2}} - 1$$

$$\boxed{\frac{r_{flame}}{x} = \frac{16}{\sqrt{3}\,Re}\left(\sqrt{\frac{3}{32}\frac{Re}{f_s}\frac{d_0}{x}} - 1\right)^{1/2}}$$

flame radius
$r_f(x)$

$Re = \frac{u_0 d_0}{\nu}$



flame shape

Flame length

set $r_f = 0$, solve for $x = x_f$ = flame length

$$\boxed{x_{flame} = \frac{3}{32\pi}\frac{1}{f_s}\frac{(\pi d_0^2 u_0)}{\nu}}$$

← ( ) = fuel volumetric flowrate

$\nu \approx D$ for $Sc = 1$

laminar jet flame

flame length

larger d_0 or u_0 → longer flame
larger f_s or ν → shorter flame

note: $L_f \sim \frac{Q_1}{D} = \frac{\text{volume/sec fuel}}{\text{diffusivity}} = \frac{m^3/s}{m^2/s}$

$r^2 \sim D t_D \sim d_1^2$ ← solve for t $t = d_1^2/D$

$X_f \sim V_{x,1} \cdot t_c$ ← plug in $\rightarrow L_f \sim \frac{V_{1x} d_1^2}{D}$

explanation

$t_D = t_c$

diffusion time convection time

6-9a

~~6-19 6-27~~

Flame length (laminar)

$X_{Flame} = L =$ x location where $f = f_s$, $\xi = 0$

$$f_s = \frac{3}{32} \frac{Re\, d_0}{X_{Flame}}$$

$$\boxed{X_{\underset{\text{laminar}}{Flame}} = \frac{3}{32} \frac{Re\, d_0}{f_s}}$$ Kuo 6-92

6-9b

~~6-27~~

mixture "state relations"   Kuo. p. 558

= formulas that relate, at each point

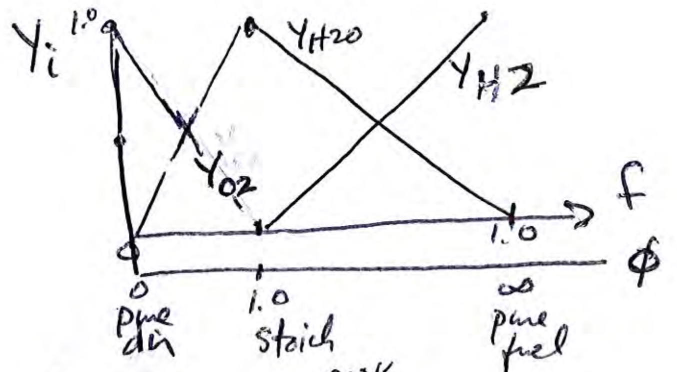
mixture fraction f ⟺ Y_i mass fractions, T temp., "ϕ" hypothetical equiv. ratio

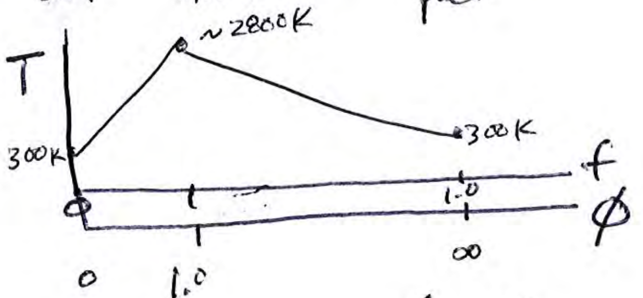
called "lookup tables"

idea: solve governing mixture fraction (f) eqn. for f
use state relations to get Y_i, T for each f

assume:
- equilibrium (fast) chemistry, so fuel and O_2 cannot co-exist
- all species diffuse at same rate

Plots of "state relations":   hydrogen – O_2
$f_s = 0.111$





a) what are the state relations ?

ex. H_2 fuel, O_2 oxidizer in rocket

$f_s = 0.111$

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

$Z_H(\text{product}) = \frac{2}{18} = 0.111$

$Z_{H,1} = 1 \qquad Z_{H,2} = 0$

inside flame (fuel + products)

state relation $\phi > 1$

$$\boxed{Y_{H_2} = \frac{f - f_s}{1 - f_s}, \quad Y_{O_2} = 0, \quad Y_{H_2O} = \frac{1-f}{1-f_s}}$$

outside flame

$$\boxed{Y_{H_2} = 0 \quad Y_{O_2} = 1 - \frac{f}{f_s}, \quad Y_{H_2O} = \frac{f}{f_s}}$$

these are straight lines – see plot on previous page

b) how to derive these state relations for any fuel?

Step #1 write down a balanced chemical equation for rich conditions $\phi > 1$

ex. $H_2 - O_2$:

$$\underbrace{H_2 + \frac{1}{2\phi} O_2}_{\text{hypothetical reactants}} \rightarrow \underbrace{\left(1 - \frac{1}{\phi}\right) H_2 + \frac{1}{\phi} H_2O}_{\text{ACTUAL MIXTURE inside flame}}$$

Step #2 Calculate f as function of ϕ

basis = 1 mole H_2

$$f = \frac{Z_H - \overset{0}{\cancel{Z_{H,2}}}}{\underset{1}{\cancel{Z_{H,1}}} - \underset{0}{\cancel{Z_{H,2}}}} = \frac{\left(1-\frac{1}{\phi}\right)(2\text{ grams}) + \frac{1}{\phi}(2\text{ gram})}{\left(1-\frac{1}{\phi}\right)2 + \frac{1}{\phi}\,18}$$

mult by $\frac{\phi}{2}$

$$f = \frac{\phi - 1 + 1}{(\phi-1)+9} \qquad f = \frac{\phi}{\phi+8} \quad \text{rich side}$$

Step#3: compute Y_{H_2}, Y_{O_2}, Y_{H_2O}, as fcns of ϕ

use ★: $$Y_{H_2} = \frac{\text{mass } H_2}{\text{total mass}} = \frac{\left(1-\frac{1}{\phi}\right)2}{\left(1-\frac{1}{\phi}\right)2 + \frac{1}{\phi}18}$$

$$Y_{H_2} = \frac{\phi-1}{\phi-1+9} = \boxed{\frac{\phi-1}{\phi+8}}$$

$$Y_{H_2O} = \frac{\frac{1}{\phi}\cdot 18}{\left(1-\frac{1}{\phi}\right)2 + \frac{1}{\phi}18} = \frac{9}{(\phi-1)+9} = \boxed{\frac{9}{\phi+8}}$$

$$Y_{O_2} = 0$$

note $Y_{H_2} + Y_{O_2} + Y_{H_2O} = 1$ ✓

Step # 4 Use enthalpy equation (OR USE CEC code) to get temperature T for each ϕ on rich side

or assume $T = af + b$ $\quad T = T(\phi=1)$ at $f = f_s$, $\quad T = 300K$ at $f = 0,1$

step # 5 Now eliminate ϕ and replace it with mixture fraction f

from step 2 : $$f = \frac{\phi}{\phi+8} \qquad \therefore \cancel{f\phi} + 8f = \phi(1-f$$

$$\therefore \phi = 8f/(1-f)$$

$$\therefore Y_{H_2} = \frac{\phi-1}{\phi+8} = \frac{\frac{8f}{\cancel{1-f}} - \frac{1-f}{\cancel{1-f}}}{\frac{8f}{\cancel{1-f}} + \frac{8-8f}{\cancel{1-f}}} = \boxed{\frac{(9f-1)}{8}}$$

$$Y_{H_2O} = \frac{9}{\phi+8} = \frac{\frac{9-9f}{\cancel{1-f}}}{\frac{\cancel{8f}}{\cancel{1-f}} + \frac{8-\cancel{8f}}{\cancel{1-f}}} = \boxed{\frac{(9-9f)}{8}}$$

what is f_s? $\quad H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

$$f_s = \frac{Z_{H,s}}{Z_{H,1}} = \frac{\left(\frac{2\cancel{g}}{18\cancel{g}}\right)}{\left(\frac{2\cancel{g}}{2\cancel{g}}\right)} = \frac{1}{9}$$

$$\text{so } Y_{H_2} = \frac{9f-1}{8} = \frac{f - 1/9}{8/9} = \boxed{\frac{f-f_s}{1-f_s}} \checkmark$$

inside flame (fuel + products)

$$Y_{H_2O} = Y_P = \frac{9-9f}{8} = \frac{1-f}{8/9} = \boxed{\frac{1-f}{1-f_s}} \checkmark$$

$$Y_{O_2} = 0$$

Step # 6 now write <u>lean</u> conditions chemistry

$$\underbrace{H_2 + \frac{1}{2\phi} O_2}_{\text{cannot coexist}} \rightarrow \underset{\text{actual gas mixture}}{\boxed{\frac{1}{2}\left(\frac{1}{\phi}-1\right) O_2 + H_2O}} \quad ☆☆$$

and repeat :

$$f = \frac{2}{\frac{1}{2}\left(\frac{1}{\phi}-1\right)32 + 18} = \frac{\cancel{2}\phi}{(1-\phi)\cancel{16}^{8} + \cancel{18}^{9}\phi} = \frac{\phi}{\phi+8}$$

$$☆☆ \quad Y_{O_2} = \frac{\left(\frac{1}{\phi}-1\right)16}{16\left(\frac{1}{\phi}-1\right)+18} = \frac{(1-\phi)\cancel{16}^{8}}{(1-\phi)\cancel{16}_{8} + \cancel{18}_{9}\phi} = \frac{8-8\phi}{8+\phi} = \frac{8-8\phi}{\phi+8}$$

$$Y_{H_2O} = \frac{\cancel{18}\,9\phi}{\cancel{16}_{8}\left(\frac{1}{\cancel{\phi}}-\phi\right) + \cancel{18}\,9\phi} = \frac{9\phi}{\phi+8}$$

note $Y_{H_2} + Y_{O_2} + Y_{H_2O} = \frac{8+\phi}{\phi+8} = 1$ ✓

$$Y_{H_2} = 0$$

so $\cancel{f\phi} + 8f = \phi(1-f) \rightarrow \phi = 8f/(1-f)$ $f_s = 1/9$ so

$$\text{so} \quad Y_{O_2} = \frac{1-\phi}{\frac{\phi}{8}+1} = \frac{\frac{1-f}{\cancel{1-f}} - \frac{8f}{\cancel{1-f}}}{\frac{\cancel{f}}{\cancel{1-f}} + \frac{1-\cancel{f}}{\cancel{1-f}}} = \underset{\text{outside flame}}{1-9f} = \boxed{1-\frac{f}{f_s}} \; ✓$$

$$Y_{H_2O} = \frac{\phi}{\frac{\phi}{9}+\frac{8}{9}} = \frac{\frac{8f}{\cancel{1-f}}}{\frac{\cancel{\frac{8f}{9}}}{\cancel{(1-f)}} + \frac{8/9 - \cancel{\frac{8}{9}f}}{\cancel{(1-f)}}} = 9f = \boxed{f/f_s} \; ✓$$

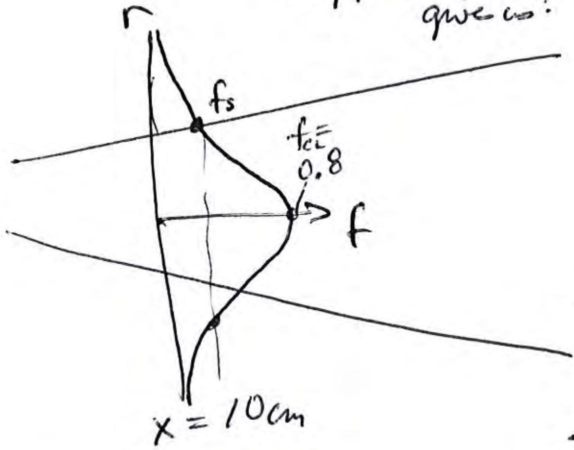
$Y_{O_2} + Y_{H_2O} + Y_{H_2} = 1$ ✓

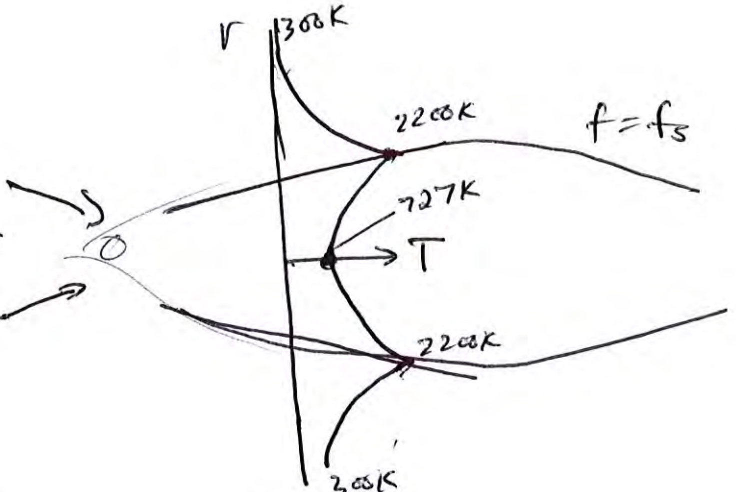
$Y_F = Y_{H_2} = 0$

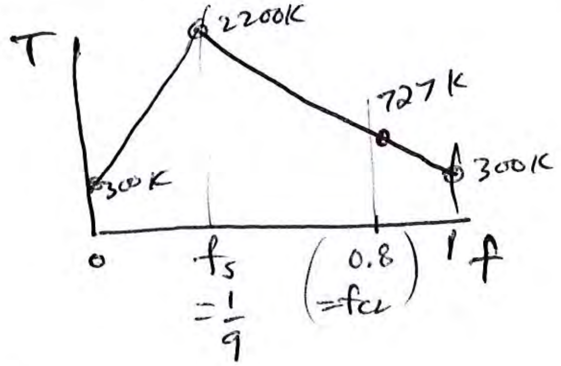
Proof!

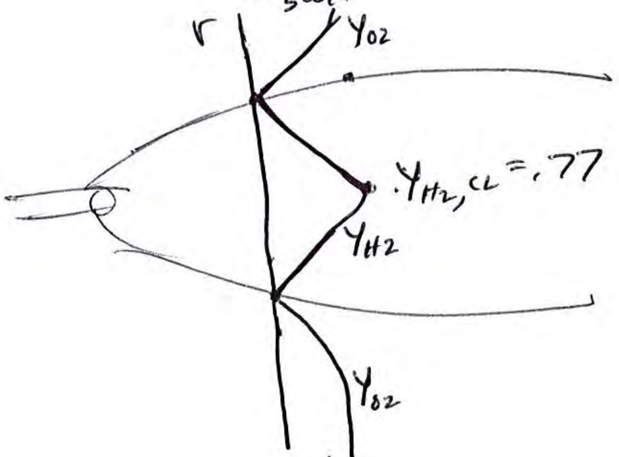
Now we can "map" scalers (other than f)

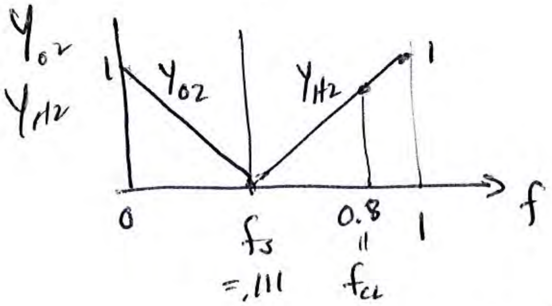
suppose our eqn for f(r,x) gives us:





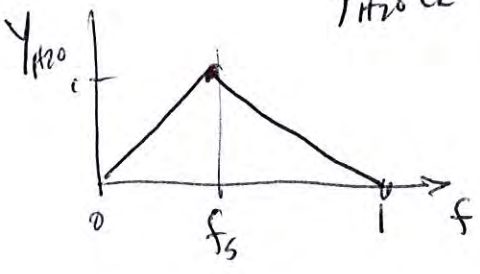


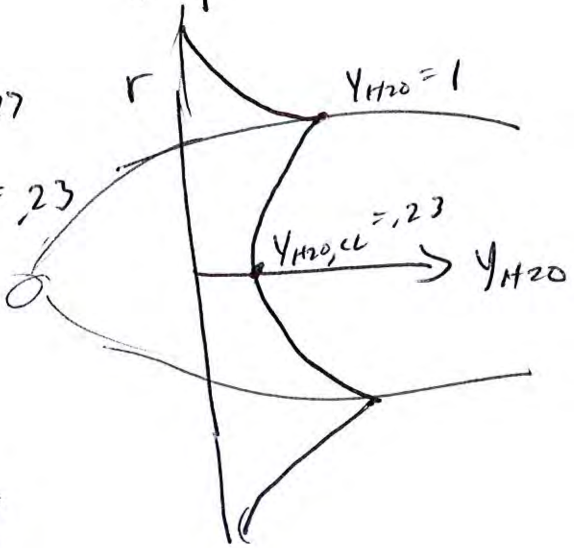




$\therefore Y_{H_2,CL} = .8(1-.111) = 0.77$

$Y_{H_2O\,CL} = 1 - Y_{H_2,CL} = .23$





Methane - oxygen state relations (example)

rich: $CH_4 + \frac{2}{\phi} O_2 \rightarrow \frac{1}{\phi} CO_2 + \frac{2}{\phi} H_2O + \frac{\phi-1}{\phi} CH_4$

lean $CH_4 + \frac{2}{\phi} O_2 \rightarrow CO_2 + 2H_2O + \left(\frac{2}{\phi}-2\right) O_2$

rich (use RHS)

$$f = \frac{\left.\dfrac{\left(\dfrac{2\cdot(2\ \text{g/mole})}{\phi} + \dfrac{\phi-1}{\phi}\,4\right)}{\left(\dfrac{44}{\phi}+\dfrac{36}{\phi}+\dfrac{\phi-1}{\phi}\cdot 16\right)}\right\} z_H}{\left.\left(\dfrac{4}{16}\right)\right\} z_{H,1}\ (\text{for } CH_4)} = \frac{\phi}{\phi+4}$$

so $\phi = \frac{4f}{1-f}$

lean

$$f = \frac{\left(\dfrac{4}{44+36+\left(\frac{2}{\phi}-2\right)32}\right)}{(4/16)} = \frac{\phi}{4+\phi}, \quad \phi = \frac{4f}{1-f}$$

so

rich

$$Y_{CH4} = \frac{\frac{\phi-1}{\phi}16}{\frac{44}{\phi}+\frac{36}{\phi}+\frac{\phi-1}{\phi}16} = \frac{\phi-1}{\phi+4}$$

plug in $\phi(f) = \frac{4f}{1-f}$

$\boxed{Y_{CH4} = 1.25f - 0.25}$ (rich)

$\boxed{Y_{CH4} = 0 \quad (\text{lean})}$

lean

$$Y_{O2} = \frac{\left(\frac{2}{\phi}-2\right)32}{44+36+\left(\frac{2}{\phi}-2\right)32} = \frac{4-4\phi}{4+\phi}$$

plug in $\phi(f) = \frac{4f}{1-f}$

$\boxed{Y_{O2} = 1-5f}$ (for $f \leq 0.2$) lean

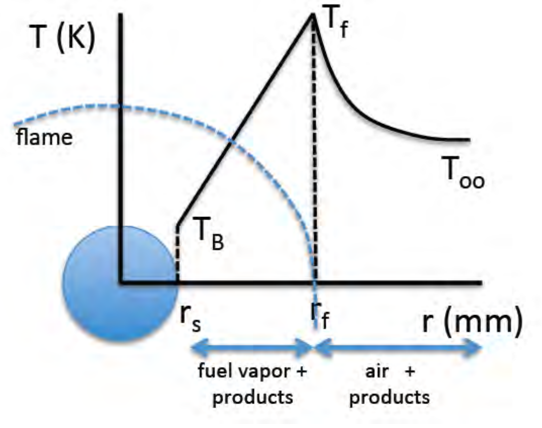
$\boxed{Y_{O2} = 0, \text{ rich}}$

16-16

Droplet evaporation and combustion theory (simplified version)

(For exact theory see Kuo, K., *Principles of Combustion*)

Consider a single drop of Jet-A fuel surrounded by hot air issued from the compressor



r_s = drop radius, r_f = flame radius

T_B = boiling temperature of Jet-A = 169° C = 442 K

T_f = adiabatic flame temperature = 2200 K

T_{oo} = surrounding air temperature from compressor = 650 K

λ_g = fuel vapor (gas) thermal conductivity

Δh_v = heat of vaporization of Jet-A fuel = 2,200 kJ/kg

$\dot{m}_{evap}$ = mass/sec of fuel evaporated

Kuo's text explains that the First Law of Thermodynamics at the drop surface is:

$$\lambda_g \quad \left[\frac{dT}{dr}\right]_{r=r_s} \quad (4\,\pi\, r_s^2) \;=\; \dot{m}_{evap} \quad \Delta h_v$$

kJ/sec heat conducted from hot gas near drop into liquid drop	mass/sec liquid fuel evaporating (solve for this)	heat of evaporation kJ/kg

Assume a linear temperature profile near drop, so that

$$\left[\frac{dT}{dr}\right]_{r=r_s} = \frac{T_f - T_B}{r_f - r_s}$$

Define $\Delta T_c = T_f - T_{oo}$ so $T_f = \Delta T_c + T_{oo}$

Assume that: $r_f = 2\, r_s$ so that $r_f - r_s = r_s$

Then $$\left[\frac{dT}{dr}\right]_{r=r_s} = \frac{\Delta T_c + T_{oo} - T_B}{r_s}$$

Insert into equation on last page and solve to get

$$\dot{m}_{evap} = (\lambda_g/c_p)\ (4\,\pi\, r_s)\, B$$

where $$B = \frac{c_p\ (\Delta T_c + T_{oo} - T_B)}{\Delta h_v}$$

Now apply conservation of mass to the droplet, which has a mass M:

$$\dot{m}_{evap} = \frac{-\,dM}{dt} = -\,\frac{d}{dt}\left(\rho_L\,\frac{4}{3}\ \pi\ r_s^3\right) = -\rho_L\,\frac{4}{3}\ \pi\ 3\,r_s^2\,\frac{dr_s}{dt}$$

Combine this with the previous two equations to get:

$$(\lambda_g/c_p)\ (4\,\pi\, r_s)\ B = -\rho_L\,\frac{4}{3}\ \pi\ 3\,r_s^2\,\frac{dr_s}{dt}$$

Now multiply by dt, divide by r_s to separate variables, then integrate from time $t = 0$ to $t = t_{evap}$ and from $r_s = d_0/2$ to $r_s = 0$, where:

d_0 = initial drop diameter and the result is:

****

evaporation time = $$t_{evap} = \frac{d_0^2}{\beta}$$ called the d-squared law, where

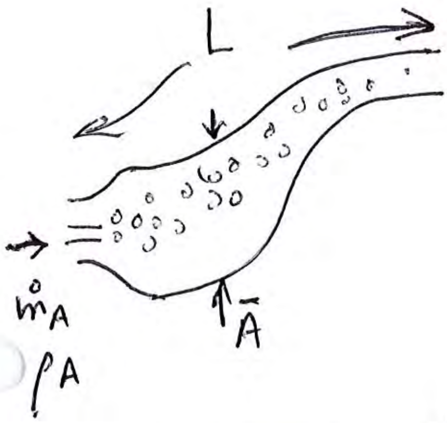
$$\beta = \frac{8\,\lambda_g\,B}{\rho_L\,c_p} \qquad \text{and} \qquad B = \frac{c_p\ (\Delta T_c + T_{oo} - T_B)}{\Delta h_v}$$

evaporation coefficient "B-number"

****

Droplet Combustion Theory   Kuo p. 569 – 583

motivation: liquid fuel atomizers can produce drop sizes (d_0) of either 30 μm, 50 μm, 100 μm etc. how small must d_0 be to burn the drops within the given combustor length L ?



$\bar{u}$ = mean velocity of gas in combustor $= \dfrac{\dot{m}_A}{\rho_A \bar{A}}$

$\bar{A}$ = avg. area of combustor

answer: droplets burn according to the d^2 law

t_{life} = drop lifetime $= \dfrac{d_0^2}{\beta_v}$

β_v = evaporation coefficient

ex. Jet-A fuel $\beta_v = 3 \times 10^{-7}\ m^2/s$

combustor $\bar{u} = 30\ m/s$

initial drop diameter $d_0 = 30\ \mu m$

combustor length $L = \bar{u} \cdot t_{life} = \dfrac{\bar{u}\, d_0^2}{\beta_v} = 9\,cm = 3.5''$

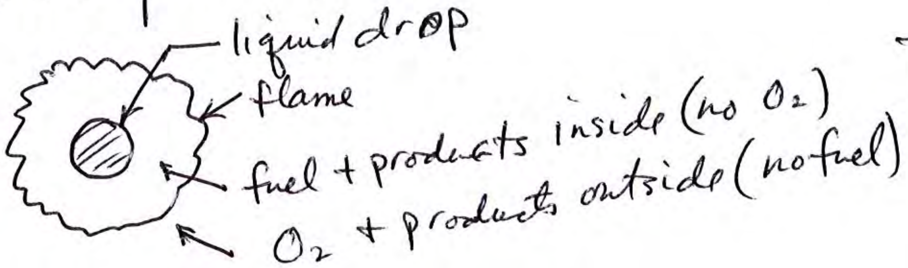
theory - prove droplet d^2-law

derive equation for β_v = evaporation coefficient

what does β_v depend upon?

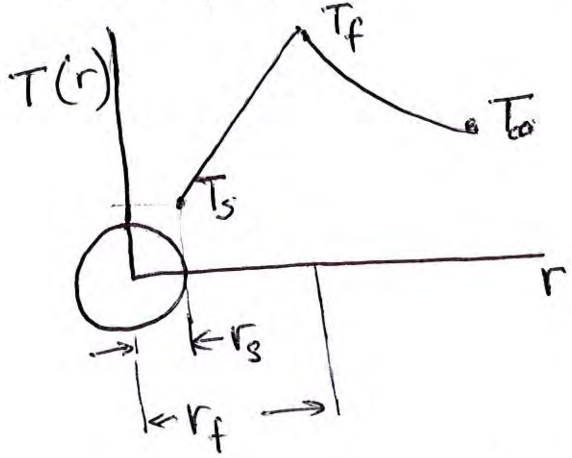
solve for profiles of $T(r)$, $Y_F(r)$, $Y_{O_2}(r)$.

spherical fuel drop will be surrounded by spherical flame



non-premixed just like our jet flame!

what profiles do we expect?



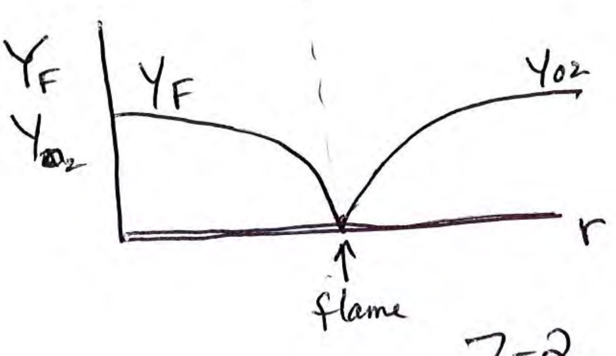
T_s = drop surface temperature

$T_s = T_B$ = boiling temperature of the liquid fuel
$\simeq 169°C$ Jet A
(Mattingly textbook)

T_∞ = surrounding air temperature $\doteq 650K$
from compressor in jet engine

T_f = flame temperature

r_f = flame radius



assume: drop is spherical – moving slowly, no buoyancy

boiling temperature of liquid fuel (T_B) is known

flame radius: $r_f = c_1 r_s$ $\quad c_1 =$ some constant

$\lambda / c_p =$ constant in r direction $= \lambda_\infty / c_{p\infty}$

$Le = 1$ so $\frac{\alpha}{D} = 1$ so $\frac{\lambda}{\rho c_p} = D$ or $\frac{\lambda}{c_p} = \rho D$

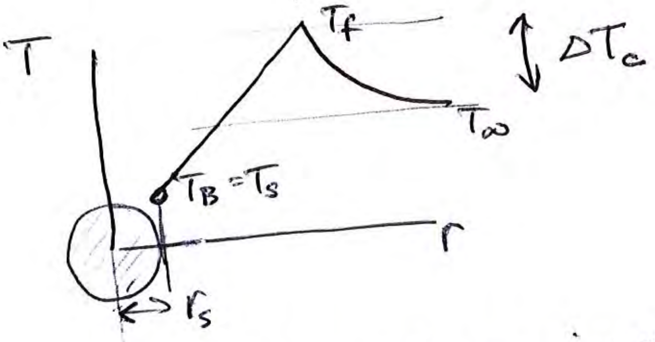
$\therefore \rho D =$ const in r direction $= \rho_\infty D_\infty$ $\quad D =$ mass diffusivity

T(r) is linear between drop and flame, as above

(for our simple analysis; Kuo does not assume it)

define $\Delta T_c \equiv T_f - T_\infty \approx (2200K - 650K)$

$\Delta T_c =$ temperature added by the combustion to raise gas temperature from T_∞ to T_f



$h_v =$ heat of vaporization of Jet A fuel

$= 2{,}200$ kJ/kg

to evaporate 1kg fuel, need 2200 kJ

$r_s(t) =$ drop radius as function of time drop combustion theory - First law cons. energy

Kuo 6-122 p.575

① $$\boxed{\dot{m}_F \;\Delta h_v = \lambda \left.\frac{dT}{dr}\right|_{r=r_s} \cdot 4\pi r_s^2}$$

$$\underbrace{\underset{\text{mass/sec fuel evaporating}}{\dot{m}_F}\quad\underset{\text{heat of vaporization }\left(\frac{kJ}{kg}\right)}{\Delta h_v}}_{\text{kJ/sec causing phase change inside droplet}} \qquad \underbrace{\underset{\text{kJ/sec/area conducted into droplet Fourier's law}}{\lambda \left.\frac{dT}{dr}\right|_{r=r_s}} \quad \underset{\text{area of droplet}}{4\pi r_s^2}}_{\text{kJ/sec conducted into drop}}$$

② $$\left.\frac{dT}{dr}\right|_{r=r_s} \approx \frac{T_f - T_B}{r_f} = \frac{(T_\infty + \Delta T_c) - T_B}{c_1 \; r_s}$$

based on two assumptions - prev. page

Kuo 6-147c

③ define (non-dim) $$B \equiv \frac{c_p\left(T_\infty + \Delta T_c - T_B\right)}{\Delta h_v}$$

combine 1-3:

④ $$\dot{m}_F = \frac{4\pi r_s}{c_1}\left(\frac{\lambda}{c_p}\right) \cdot B$$

now apply cons. of mass for fuel drop:

⑤ $$\dot{m}_F = -\frac{d\, M_{drop}}{dt} = -\frac{d}{dt}\left[\rho_L \frac{4}{3}\pi r_s^3\right]$$

ρ_L = liquid fuel density ≈ 800 kg/m^3
(water is 1000 kg/m^3)

combine ④ + ⑤, integrate

$$\frac{4\pi \cancel{r_s}}{c_1}\left(\frac{\lambda}{c_p}\right) B = -\rho_L \frac{4\pi}{\cancel{3}}\left(\cancel{3} r_s^{\cancel{2}}\right)\frac{dr_s}{dt}$$

$$\frac{4\pi}{c_1}\left(\frac{\lambda}{c_p}\right) B \int_0^{t_{life}} dt = -\rho_L 4\pi \int_{d_0/2}^{0} r_s \, dr_s$$

$$\boxed{t_{life} = \text{drop lifetime} = \frac{d_0^2}{\beta_v}}$$ where

$$\boxed{\begin{aligned} \beta_v &= \text{evaporation coeff} = \frac{8\lambda(B/c_1)}{\rho_L c_p} \\ B &= \frac{c_p\left(T_\infty + \Delta T_c - T_B\right)}{\Delta h_v} \end{aligned}}$$

how to make drops burn faster

inspect result: if evap coeff $\beta_v \uparrow$ drops burn faster

what makes $\beta_v \uparrow$? faster burning

if $T_\infty \uparrow$ of surrounding hot air

if $T_o \uparrow$ more heat from combustion into drop

if $T_B \downarrow$ lower boiling T, easier to evap

if $\Delta h_v \downarrow$ less heat needed to evap

if $d_o \downarrow$ small drops burn faster

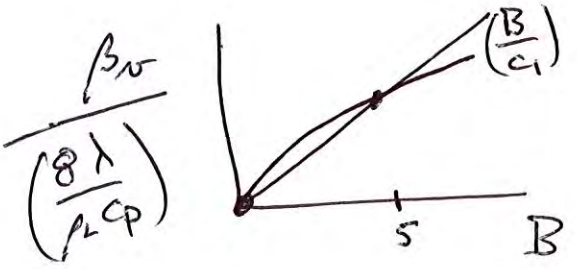
if $\lambda \uparrow$ more heat to drop, faster burn

Exact Theory of Kuo (p. 573)

- do not assume $T(r)$ is linear between drop + flame
- prove that $r_f = c_1 r_s$ and determine c_1
- final answer is same as ours : $t_{life} = \frac{d_0^2}{\beta_v}$

except we said $\beta_v = \frac{8\lambda}{\rho_L c_p} \cdot \left(\frac{B}{c_1}\right)$

Kuo finds $\beta_v = \frac{8\lambda}{\rho_L c_p} \cdot \ln(1+B)$ 6-135 p.577

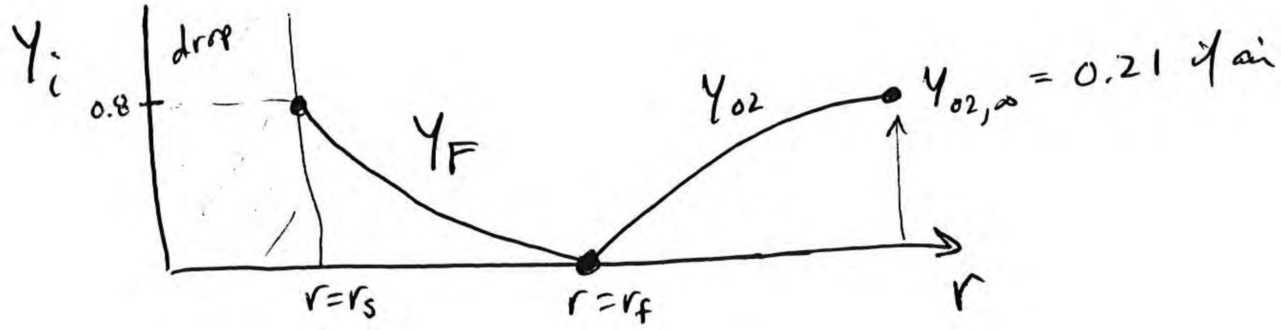


what should c_1 be to agree with Kuo for $B=5$?
($B=5$ typical for jet fuel) (p. 581)

$\frac{5}{c_1} = \ln 6 \qquad c_1 = 2.8$

- Kuo does not assume $T_s = T_B$ = given
  he applies complex Clausius eqn for phase change at drop surface

therefore if we combine ① and ③



to plot this we must know:

✓ $b_s = \frac{Y_{F,s}}{Y_{Fs}-1}$ $Y_{F,s}$ = given from vapor equil

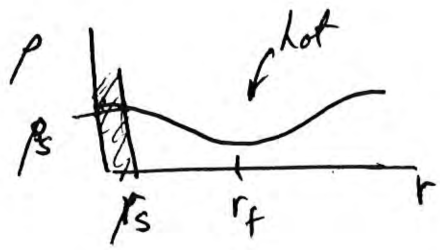
✓ $b_\infty = -\frac{Y_{O2,\infty}(F/O_2)_{ST}}{Y_{Fs}-1}$ $Y_{O2\infty} = 0.21$ given

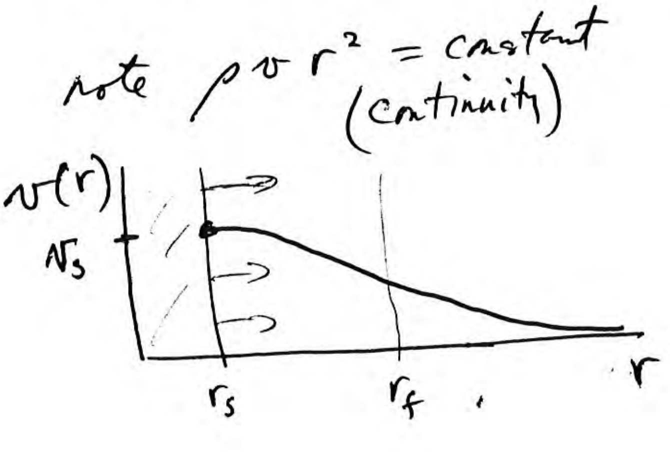
✓ $\rho_\infty D_\infty$ = for air faraway = given

✓ r_s = drop radius = given

but $(\rho_s v_s)$ appears in Eq. 1 = unknown

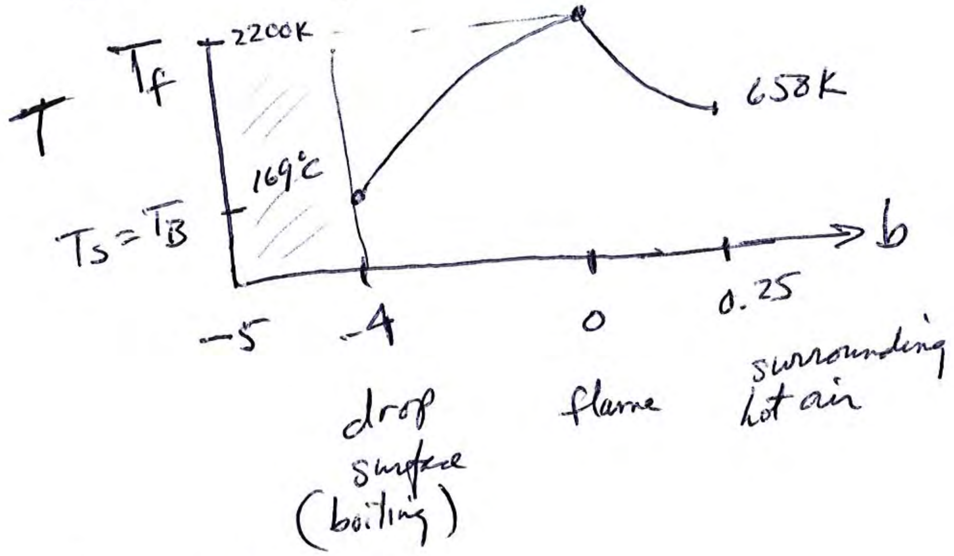
note $\rho v r^2$ = constant (continuity)



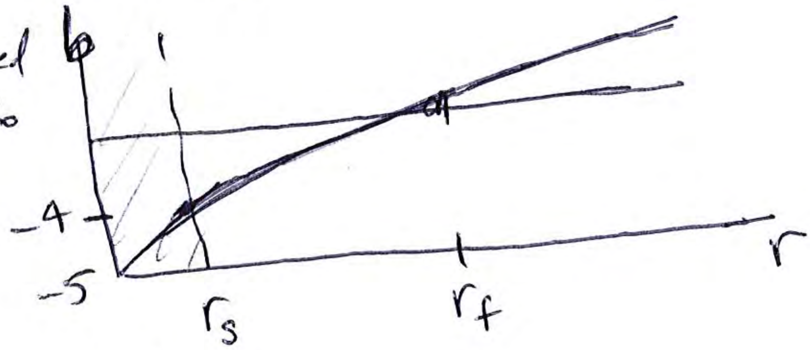


radial velocity of gas decreases in r direction given that $b(r)$ = conserved scalar

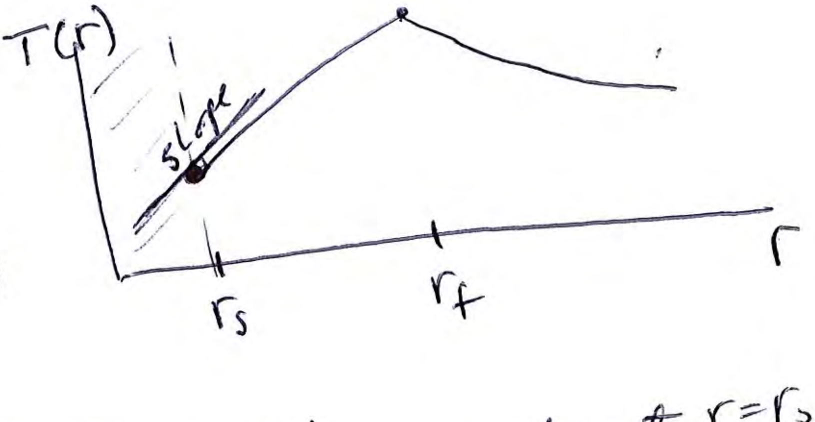
we can compute state relations as we did for jet flame



since we solved b eqn to get



we can combine to get T(r)



from this curve we get $\left.\frac{dT}{dr}\right|_{r=r_s}$ = slope at $r=r_s$

from T(r) curve on previous page we get:

$$\left.\frac{dT}{dr}\right|_{r=r_s} = \frac{\Delta h_v}{c_p r_s} \ln(1+B) \qquad (a)$$

where B, as before, was:

$$B = \frac{c_p\left(T_\infty + \Delta T_c - T_B\right)}{\Delta h_v}$$

we started with First Law at drop surface:

$$\dot{m}_F \, \Delta h_v = \lambda \left.\frac{dT}{dr}\right|_{r=r_s} 4\pi r_s^2 \qquad (b)$$

ⓐ + ⓑ give

$$\dot{m}_F \cancel{\Delta h_v} = \lambda \frac{\cancel{\Delta h_v}}{c_p \cancel{r_s}} \ln(1+B)\, 4\pi r_s^{\cancel{2}}$$

$$\boxed{\dot{m}_F = 4\pi r_s \left(\frac{\lambda}{c_p}\right) \ln(1+B)}$$

Drop life time — consider the unsteady change in drop radius $r_s(t)$

lifetime = time for r_s to drop from $(d_0/2)$ to zero

(i) $$\dot{m}_F = \frac{d}{dt}\left(\rho_L \frac{4}{3}\pi r_s^3\right)$$ cons of mass for liquid
ρ_L = liquid density

we said

(ii) $$\dot{m}_F = \frac{\lambda_g}{\Delta h_v} \left.\frac{dT}{dr}\right|_s 4\pi r_s^2$$

show that (see Kuo) $$\frac{\lambda_g}{\Delta h_v}\left(\frac{dT}{dr}\right)_s = \frac{\rho_\infty D_\infty}{r_s} \ln(1+B)$$
(iii)
where B = Spalding transfer number = 5.82
n-heptane

Combine (i)-(iii):

$$\rho_\infty D_\infty \ln\left(1+B\right) 4\pi r_s = \frac{d}{dt}\left(\rho_L \frac{4}{3}\pi r_s^3\right)$$

everything is constant except $r_s(t)$.

$$\int \rho_\infty D_\infty \ln(1+B)\,\cancel{4\pi}\,\cancel{r_s}\,dt = \rho_L \cancel{\tfrac{4}{3}\pi} \int_0^{r_s} \cancel{3} r_s^{\cancel{2}} \frac{dr_s}{\cancel{dt}}$$

$$\frac{\rho_\infty D_\infty}{\rho_L} \ln(1+B) \cdot t = \frac{r_s^2 - r_{s,0}^2}{2}$$

define $d = r_s \cdot 2$

$$\therefore \quad \boxed{d^2(t) = d_0^2 - \beta_v t}$$

"d^2 law"

$$\boxed{\beta_v = \frac{8 \rho_\infty D_\infty}{\rho_L} \ln(1+B)}$$

$B = 5.82$
n-heptane

Ex. $\rho_\infty = 5 \text{ kg/m}^3$ (compressed)

$D_\infty = 1 \times 10^{-5} \text{ m}^2/\text{s}$

$\rho_L = 700 \text{ kg/m}^3$

$\ln(1+B) = \ln(6.82) = 1.91$

$\therefore \beta_v = 1.1 \times 10^{-6} \text{ m}^2/\text{s}$

if $d_0 = 30 \, \mu\text{m} =$

$$\boxed{t_{evap} = \frac{d_0^2}{\beta_v}} = \frac{(30 \, 10^{-6})^2 \text{ m}^2}{1.1 \, 10^{-6} \frac{\text{m}^2}{\text{s}}} = \underline{\underline{0.8 \text{ msec}}}$$

Exact Droplet Combustion Theory of Kuo (p. 569)

start with same basic equation – 1st Law at drop

$$\boxed{\dot{m}_F \, \Delta h_v = \lambda \left.\frac{dT}{dr}\right|_{r=r_s} 4\pi r_s^2}$$

Kuo 6-122
p. 575

kJ/sec causing phase change = kJ/sec from gas into drop

now: {what are profiles $Y_F(r)$, $Y_{O_2}(r)$, $T(r)$?
do not assume T = linear
do not assume $r_f = c_1 r_s$

$r_F(t)$ = flame radius
$r_s(t)$ = drop radius (at surface)

must solve conservation equations to get $T(r)$, $Y_F(r)$, $Y_{O_2}(r)$

$$\frac{\partial}{\partial r}\left(\rho v r^2\right) = 0$$

$$\left(r^2 \rho v\right) \frac{dY_F}{dr} = \frac{d}{dr}\left(r^2 (\rho D) \frac{dY_F}{dr}\right) + r^2 \dot{\omega}_F$$

$$\left(r^2 \rho v\right) \frac{dY_{O_2}}{dr} = \frac{d}{dr}\left(r^2 (\rho D) \frac{dY_{O_2}}{dr}\right) + r^2 \dot{\omega}_{O_2}$$

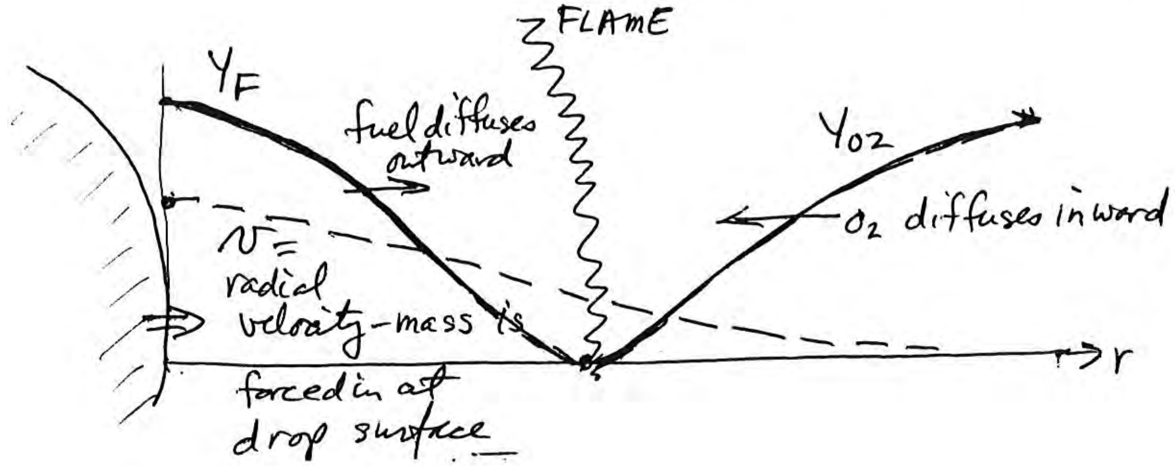
$$\underbrace{\left(r^2 \rho v\right)}_{\substack{\text{constant} \\ \text{in } r \\ \text{direction}}} \frac{dh}{dr} = \frac{d}{dr}\left(r^2 \underbrace{(\rho D)}_{\substack{\rho D = \\ \text{constant}}} \frac{dh}{dr}\right) + 0$$

also $p = \rho R T$ = constant

$$h = \sum_{i=1}^{N} \left(h^{o}_{f_i} + \Delta h_i\right) Y_i \qquad \text{chemical enthalpy} + \text{sensible enthalpy (thermal)}$$

$$\dot{\omega}_F = \dot{\omega}_{O_2} \left(\frac{F}{O_2}\right)_{st} \qquad \left(\frac{F}{O_2}\right)_{st} = \left(\frac{\text{mass fuel}}{\text{mass } O_2}\right)_{\text{stoichiometric}}$$

for methane (CH_4) + O_2 → = 0.25



solution to governing eqns

$$\text{define } \boxed{b(r) = \text{conserved scalar based on fuel} + O_2 \text{ mass fractions} = \frac{Y_F - \left(\frac{F}{O_2}\right)_{st} Y_{O_2}}{(Y_{FS} - 1)}}$$

$Y_F(r)$ = fuel mass fraction

$Y_{O_2}(r)$ = O_2 mass fraction

$Y_F + Y_{O_2} + Y_{N_2} + Y_{CO_2} + Y_{H_2O} = 1$

Y_{FS} = fuel mass fraction at drop surface

$Y_{FS} \simeq 0.8$ 80% fuel vapor evaporating out of liquid
20% products (N_2, CO_2, H_2O) diffusing inward away from flame

→ assume Y_{FS} = given for now

assume T_B = drop boiling temperature given for now

Note: we can solve for Y_{FS} + T_B using liquid-vapo equilibrium (Clasius - Clapeyron relation)

$$\boxed{\underbrace{(\rho v r^2)}_{\text{constant from continuity eqn}} \frac{db}{dr} = \frac{d}{dr}\left(r^2 \underbrace{(\rho D)}_{\text{constant}} \frac{db}{dr}\right)}$$

6-110 Kuo

integrate this ODE!, mult. by dr:

$$(\rho v r^2)\int db = \int d\left(r^2 (\rho D)\frac{db}{dr}\right)$$

$$(\rho v r^2)(b + \text{const}) = r^2 (\rho D)\frac{db}{dr}$$

separate variables all b's on right

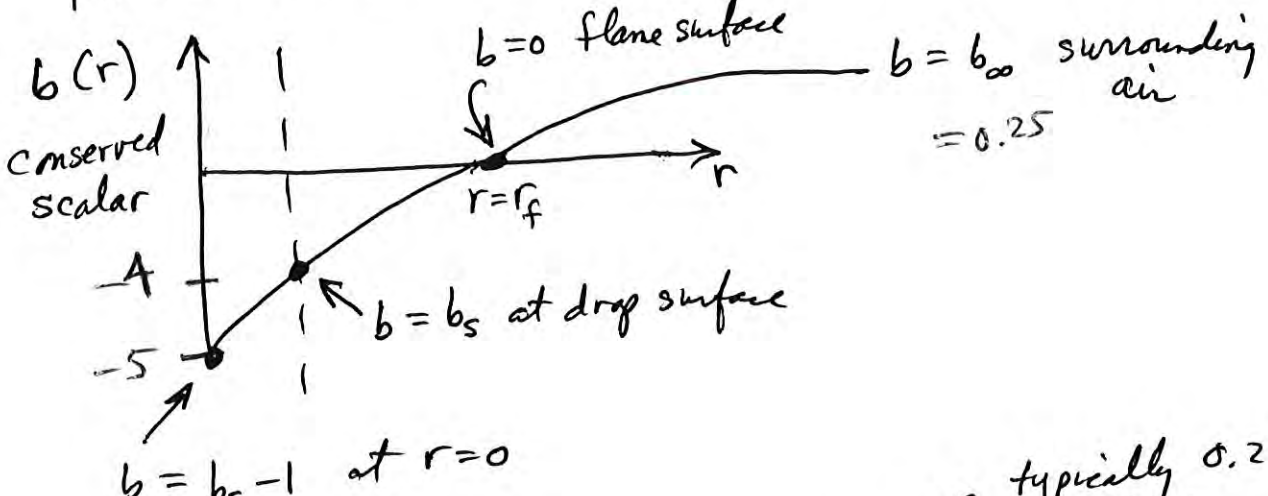
$$\underbrace{\left(\frac{\rho v r^2}{\rho D}\right)}_{\text{constant}}\int \frac{dr}{r^2} = \int \frac{db}{(b + \text{const})}$$

①

$$\therefore \quad \boxed{b(r) = (b_s - 1) + (b_\infty - b_s + 1)\exp\left(\frac{-\rho_s v_s r_s^2}{\rho_\infty D_\infty r}\right)}$$

s = surface, ∞ = r = ∞

plot our solution



$$b \equiv \frac{Y_F - Y_{O2}\left(\frac{F}{O_2}\right)_{st}}{Y_{Fs} - 1} \quad ②$$

recall that ↖ typically 0.25 given

ex. $\begin{cases} Y_{Fs} = 0.8 \\ b_s = \frac{0.8 - 0}{0.8 - 1} = -4 \\ b_\infty = \frac{0 - 0.21(.25)}{-0.20} = 0.25 \end{cases}$ ↖ typically 0.8 = given

fast chemistry assumption = fuel + O_2 cannot coexist

∴ inside flame → fuel + products (no O_2) $Y_{O2} = 0$

outside flame → O_2 + products (no fuel) $Y_F = 0$

$$③ \begin{cases} \text{inside flame:} \quad b = \frac{Y_F}{(Y_{Fs} - 1)} = \frac{Y_F}{(-0.2)} \quad \text{for this example} \\ \text{outside flame} \quad b = \frac{-Y_{O2}\left(\frac{F}{O_2}\right)_{st}}{(Y_{Fs} - 1)} = \frac{+Y_{O2}(0.25)}{(+0.2)} \end{cases}$$

at flame $Y_F = 0$, $Y_{O2} = 0$ only products exist ∴ $b = 0$

what is gas velocity (v_s) at drop surface?

determines how fast droplet burns!

need heat transfer boundary condition at drop surface

more heat transferred to drop $\Rightarrow$ more liquid fuel is evaporated $\Rightarrow$ drop burns faster

(i)
$$\boxed{\underset{\text{kJ/sec in}}{\dot{Q}_{in}} = \underbrace{\dot{m}_{liq\,evap}}_{\text{mass/sec liquid evaporated}} \cdot \underset{\text{heat of vaporization}\left(\frac{kJ}{kg}\right)}{\Delta h_v}}$$

Heat transfer b.c.

(ii)
$$\dot{m}_{liq\,evap} = \dot{m}_{\substack{fuel\\ vapor\ out}} = \rho_s v_s 4\pi r_s^2 = \dot{m}$$

(iii)
$$\dot{Q}_{in} = \lambda_g \frac{dT}{dr}\bigg|_{s,g} \cdot 4\pi r_s^2$$

s = at surface
g = in gas
Fourier's Law

combine (i)-(iii)

$$(\rho_s v_s) = \frac{\lambda_g}{\Delta h_v} \frac{dT}{dr}\bigg|_s$$

more heat transfer to drop - larger gas velocity v_s away from drop

plug into (ii)

$$\dot{m}_F = \frac{\lambda_g}{\Delta h_v} \frac{dT}{dr}\bigg|_s 4\pi r_s^2$$

Droplet Combustion

summary of equations

We define a conserved scalar "b" = $b_{F,O}$ to be:

$$b_{F,O} \equiv \frac{Y_F - Y_O(F/O)_{st}}{(Y_{Fs}-1)+Y_{Os}(F/O)_{st}} \qquad \text{(6-141a)}$$

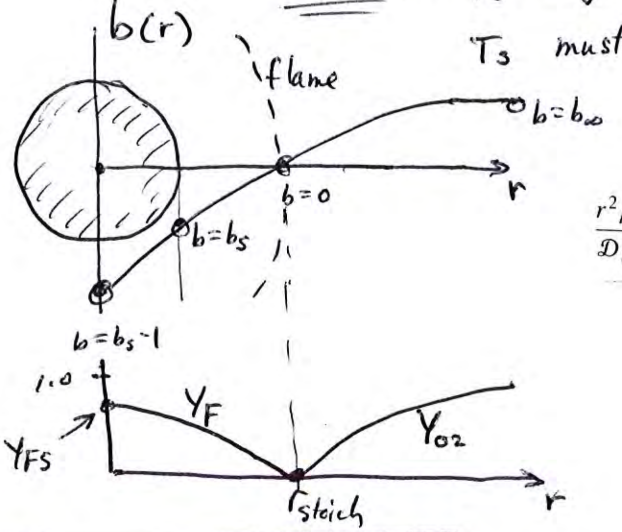
assuming: $\rho_s D_s = \rho_\infty D_\infty$ = known $Le = 1$

r_s = drop radius = known

T_s = drop liquid surface temperature = boiling temperature

either: T_s = given OR

T_s must be computed using Clapteyron equation



solution for b(r) is:

$$\frac{r^2\rho v}{\mathcal{D}\rho r} = \ln\left(\frac{b_\infty - b_s + 1}{b - b_s + 1}\right) \qquad \text{(6-145)}$$

$\boxed{\text{? How to get } Y_{FS} \text{ ?}}$ (fuel mass fraction at drop surface)

Method A: if drop boiling temperature T_s is given, use:

$$B_T = \frac{C_p(T_\infty - T_s)}{\Delta h_v} = \frac{Y_{F\infty}-Y_{Fs}}{Y_{Fs}-1} = B_M = B \qquad \text{(6-129)}$$

for no combustion – evaporation only,

or

$$\frac{Y_{O\infty}(F/O)_{st}+Y_{Fs}}{1-Y_{Fs}} = \frac{\Delta h_{r,F}(F/O)_{st}Y_{O\infty}+C_p(T_\infty - T_s)}{\Delta h_v} \qquad \text{(6-148)}$$

with combustion

solve this for Y_{FS}, given all other quantities in the equation

Method B: to get Y_{FS} if T_s not given: solve 3 eqns:

6-129 or 6-148 on last page

\+

$$\boxed{\ln \frac{p_{Fs}}{p_{Fs,\text{ref}}} = \frac{\Delta h_v}{R}\left(\frac{1}{T_{s,\text{ref}}} - \frac{1}{T_s}\right)} \qquad (6\text{-}132)$$

$$Y_F = \frac{\rho_F}{\rho} = \frac{n_F \mathrm{Mw}_F}{n\mathrm{Mw}} = \frac{p_F}{p}\frac{\mathrm{Mw}_F}{\mathrm{Mw}} \quad \text{or} \quad \boxed{Y_{Fs} = \frac{p_{Fs}}{p}\frac{\mathrm{Mw}_F}{\mathrm{Mw}}} \qquad (6\text{-}130)$$

example: water droplet surrounded by air at $P = \overset{2.9}{\cancel{3.6}}$ atm, $T_\infty = 1585$ K

no combustion, evaporation only

$C_{P\,H_2O} = 1.87$ kJ/kg K

$\Delta h_v = 2{,}229$ kJ/kg (Sonntag)

$P_{FS\,ref} = 1$ atm

$T_{s,ref} = 100°C = 373K$

$R = \dfrac{8.314}{mW_F} = 0.461 \dfrac{kJ}{kgK}$

* assume $MW = \dfrac{18+32}{2} = 25$ g/mol

6-129: $$\frac{1.87(1585 - T_s)}{2229} = \frac{0 - Y_{FS}}{Y_{FS} - 1}$$

6-130: $$\ln \frac{P_{FS}}{1\,atm} = \frac{2229 \frac{kJ}{kg}}{0.461 \frac{kJ}{kgK}}\left(\frac{1}{373K} - \frac{1}{T_s}\right)$$

$$Y_{FS} = \frac{P_{FS}}{2.9\,atm}\,\frac{18}{25}$$

3 eqns for T_s, Y_{FS} P_{FS}

answer is:
$$\begin{cases} Y_{FS} = 0.5 \\ T_s = 393K = 120°C \\ P_{FS} = 2.0\ atm \end{cases}$$

"water boils" at 120°C at 2.0 atm $= P_{FS}$

Table A.1.1 (Continued)
Saturated Steam: Temperature Table

Sonntag Thermodynamics

Temp. °C T	Press. MPa P	Specific Volume Sat. Liquid v_f	 Sat. Vapor v_g	Internal Energy Sat. Liquid u_f	 Evap. u_{fg}	 Sat. Vapor u_g	Enthalpy Sat. Liquid h_f	 Evap. h_{fg}
100	0.101 35	0.001 044	1.6729	418.94	2087.6	2506.5	419.04	2257.0
105	0.120 82	0.001 048	1.4194	440.02	2072.3	2512.4	440.15	2243.7
110	0.143 27	0.001 052	1.2102	461.14	2057.0	2518.1	461.30	2230.2
115	0.169 06	0.001 056	1.0366	482.30	2041.4	2523.7	482.48	2216.5
120	0.198 53	0.001 060	0.8919	503.50	2025.8	2529.3	503.71	2202.6
125	0.2321	0.001 065	0.7706	524.74	2009.9	2534.6	524.99	2188.5
130	0.2701	0.001 070	0.6685	546.02	1993.9	2539.9	546.31	2174.2
135	0.3130	0.001 075	0.5822	567.35	1977.7	2545.0	567.69	2159.6
140	0.3613	0.001 080	0.5089	588.74	1961.3	2550.0	589.13	2144.7
145	0.4154	0.001 085	0.4463	610.18	1944.7	2554.9	610.63	2129.6
150	0.4758	0.001 091	0.3928	631.68	1927.9	2559.5	632.20	2114.3

avg is 2229 $\dfrac{kJ}{kg}$

Spalding transfer number (B)

$$B \equiv b_\infty - b_s$$

$$B = B_{FO} = B_{FT} = B_{OT}$$

$$B_{F,O} = \underbrace{\frac{(Y_{F\infty} - Y_{Fs}) + (Y_{Os} - Y_{O\infty})(F/O)_{\text{st}}}{(Y_{Fs} - 1) + (F/O)_{\text{st}}(Y_O)_s}}_{\text{with or without combustion}} = \underbrace{\frac{(F/O)_{\text{st}} Y_{O\infty} + Y_{Fs}}{1 - Y_{Fs}}}_{\text{with combustion}} \tag{6-147a}$$

$$B_{F,T} = \underbrace{\frac{\Delta h_{r,F}(Y_{F\infty} - Y_{Fs}) + C_p(T_\infty - T_s)}{\Delta h_v + \Delta h_{r,F}(Y_{Fs} - 1)}}_{\text{with or without combustion}} = \underbrace{\frac{C_p(T_\infty - T_s) - Y_{Fs}\Delta h_{r,F}}{\Delta h_v + \Delta h_{r,F}(Y_{Fs} - 1)}}_{\text{with combustion}} \tag{6-147b}$$

$$B_{O,T} = \underbrace{\frac{(F/O)_{\text{st}}(Y_{O\infty} - Y_{Os})\Delta h_{r,F} + C_p(T_\infty - T_s)}{\Delta h_v + (F/O)_{\text{st}} Y_{Os}\Delta h_{r,F}}}_{\text{with or without combustion}}$$

$$= \underbrace{\frac{C_p(T_\infty - T_s) + Y_{O\infty}(F/O)_{\text{st}}\Delta h_{r,F}}{\Delta h_v}}_{\text{with combustion}} \tag{6-147c}$$

where for the combustion case $Y_{Os} = Y_{F\infty} = 0$. Because $B_{F,O} = B_{O,T}$, we have

velocity at drop surface V_s

$$r_s \rho_s v_s = \mathcal{D}_s \rho_s \ln[1 + (b_\infty - b_s)] = \mathcal{D}_s \rho_s \ln(1 + B)$$

$$d^2 = d_0^2 - \left[\frac{8\rho_s \alpha_s}{\rho_l} \ln(1 + B)\right] t$$

evaporation coefficient

$$G_F = \boxed{\frac{\dot m_F}{4\pi r_s^2} = \mathcal{D}_s \rho_s \frac{\ln(1 + B)}{r_s}}$$

Flame radius:

$$\frac{r_s^2 \rho_s v_s}{\mathcal{D}_s \rho_s r_{\text{stoich}}} = \ln[1 + (F/O)_{\text{st}} Y_{O\infty}] \tag{6-151}$$

Table 6.1 Values of the Transfer Number for Various Condensed Combustible Substances[8–10]

Combustible in Air	B
iso-Octane	6.41
Benzene	5.97
n-Heptane	5.82
Toluene	5.69
Aviation gasoline	≈5.5
Automobile gasoline	≈5.3
Kerosene	≈3.4
Gas oil	≈2.5
Light fuel oil	≈2.0
Heavy fuel oil	1.7
Carbon	0.12

Ex: an n-heptane C_7H_{16} drop has diameter 100μm determine its mass burning rate if it burns in air at $P = 1atm$, $T_\infty = 300K$, given that:

drop boiling temperature $T_s = 371.5\ K$

$c_p = 4.22$ kJ/kg K $\rho_s D_s = \rho_\infty D_\infty = (1.2 \frac{kg}{m^3})(.15 \times 10^{-4} m^2/s)$

$\Delta h_v = 316$ kJ/kg heat of vaporization

$\Delta h_{r,F} = 44,926$ kJ/kg lower heating value

$$C_7H_{16} + \underline{11}\,O_2 + \underline{11}\,\frac{79}{21}N_2 \rightarrow 7CO_2 + 8H_2O + \underline{11}\,\frac{79}{21}N_2$$

$$\left(\frac{F}{O_2}\right)_s = \frac{100}{352} = 0.284$$

B = ? Spalding transfer no.   use Eq 6-147c

$$\boxed{B = \frac{c_p(T_\infty - T_s) + Y_{O\infty}(F/O_2)_s \Delta h_{r,F}}{\Delta h_v}}$$

$$= \frac{4.22\overset{-302}{(300-371.5)} + 0.23(.284)\,44,926}{316}$$

$$B = 8.33$$

$$\dot m_F = 4\pi r_s^{\cancel{2}} \frac{(\rho_s D_s)}{\cancel{r_s}} \ln(1+B)$$

$$= 4\pi\,(50\ 10^{-6}\cancel{m})(1.2 \frac{kg}{\cancel{m^3}})(.15\ 10^{-4}\frac{m^2}{s}) \ln(\overset{2.23}{9.33})$$

$$\dot m_F = 2.5 \times 10^{-8}\ kg/s$$

boundary conditions at drop surface –

$T_s, \rho_s, b_s, Y_{Fs}, V_s = ?$

— we have our solutions for $Y_F(r)$, $Y_{O_2}(r)$, $Y_P(r)$, $T(r)$

— but we have above unknown constants

– step 1 – let's <u>not</u> consider V_s yet only:

⇒ at drop surface: T_s, $Y_{F,s}$ ρ_s and $P_{F,s}$ are related
fuel-product mixture at surface is saturated with fuel
by the Clausius Clapeyron vapor pressure relation
and by rate of heat transfer rate / vaporization rate balance

1) P_{FS} = partial pressure fuel at surface $= Y_{FS}\, P \left(\frac{MW_s}{MW_F}\right)$ 6-130

of fuel-prod. mixture –

2) $\rho_s = \frac{P \cdot MW_s}{R_u T_s}$

vapor pressure curve

3) $$\boxed{\ln \frac{P_{FS}}{P_{FS,ref}} = \frac{\Delta h_v}{R}\left(\frac{1}{T_{s,ref}} - \frac{1}{T_s}\right)}$$ 6-132

4) $$\cancel{\boxed{\lambda \left(\frac{dT}{dr}\right)_s = \rho_s V_s \Delta h_v}}$$ 6-122

~~$\frac{kg}{m^3}$ $\frac{m}{s}$ $\frac{kJ}{kg}$~~

~~heat conducted out of gas/sec/area~~

~~(λ = gas~~
~~$(dT/dr)_s$ in gas)~~

~~heat used to vaporize drop/sec/area of drop surface~~