Lectures on Combustion and heat transfer in practical systems

Combustion – 1

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Combustion related aspects

- Thermodynamic preliminaries
- Fuels – Liquid and Gaseous fuels and key characteristics
- Fuels – Stoichiometric and Equivalence Ratios and their relevance
- Heat release in Combustion Processes, Flame temperature and how to enhance the flame temperature
- Gaseous Flame Types – Diffusion and pre-mixed and their importance in practical combustion systems
- Ideas Laminar and Turbulent flows and flames
- Chemistry of Premixed and Diffusion flames both in steady state and Limiting mixture situations and the mechanisms of flash back and blow off
- Mixing Fuel Gas with air – techniques and implications in practical fuel systems
- An understanding of Liquid fuel spray systems
- Flameless modes of combustion

Preliminaries on mixture of gases

- Perfect gases, Idea of equilibrium
- Equation of state for perfect gases
- Gaseous mixtures
- Moles, partial pressures
- Volume fraction or mole fraction, mass fraction
- Equilibrium of liquid with vapor or gas
- LPG composition and its determination

Perfect gases

The assumption of ideal gas relation means -
- The gas particles take up negligible volume
- The intermolecular potential energy between particles is small
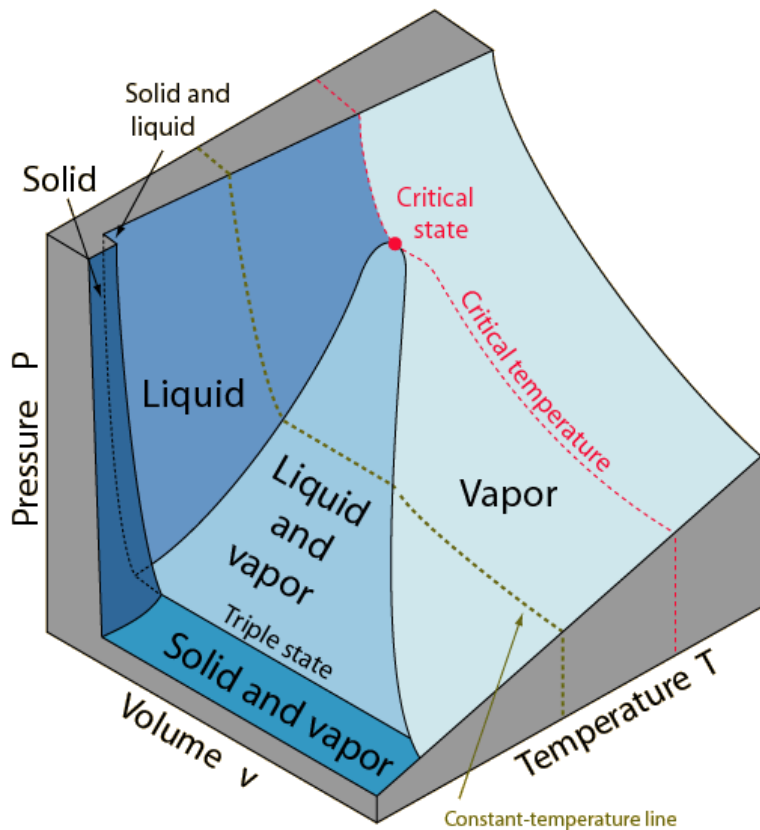
The <mark>equilibrium</mark> states of a simple, compressible substance can be specified in terms of its pressure, volume and temperature. If any two of these state variables is specified, the third is determined. The PvT surface above represents a substance which expands upon freezing. The vast majority ofsubstances contract upon freezing. The notable exception is water for which the expansion upon freezing has an enormous impact on the nature of the Earth

A point lying on a line between a single-phase and a two-phase region represents a "saturation state". The line between the liquid and the liquid-vapor regions is called the liquid-saturation line and any point on that line represents a saturated-liquid state. A point on the boundary between the vapor and the liquid-vapor regions is called a saturated-vapor state.
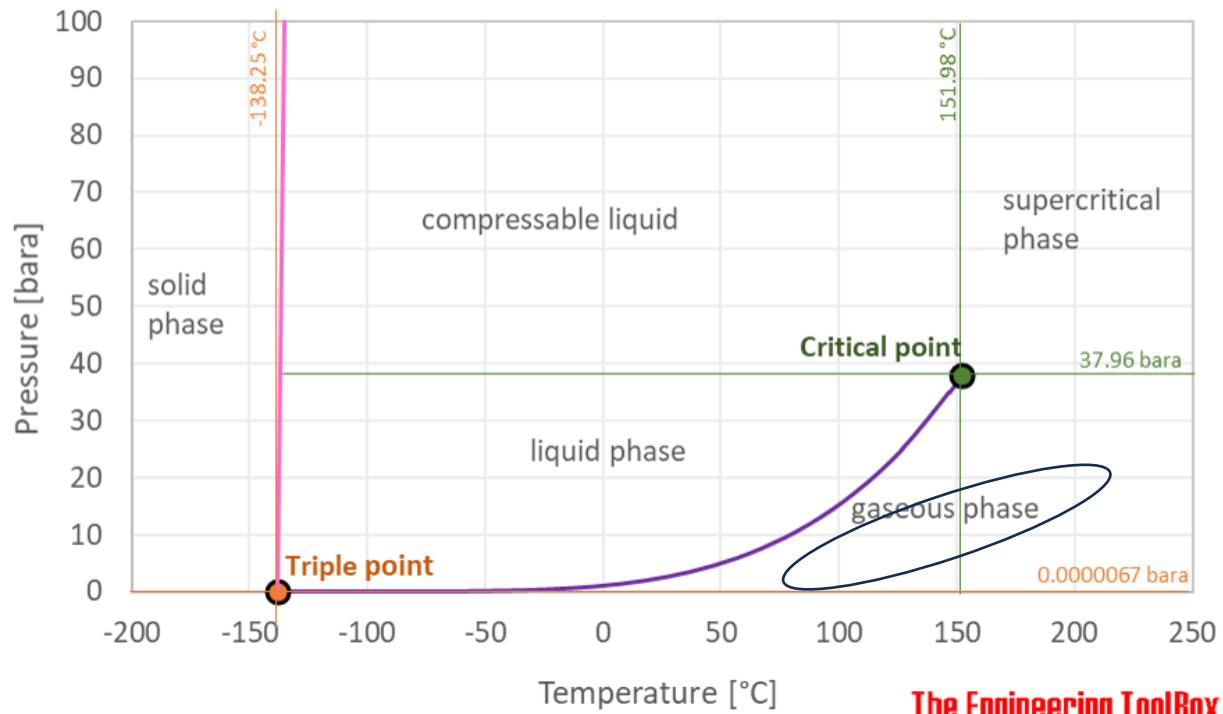
Note the critical state where the saturated-liquid and saturated-vapor lines meet. The state variables of this unique point are denoted by P_c, v_c and T_c. If a substance is above the critical temperature T_c, it cannot condense into a liquid, no matter how high the pressure. This merging of the liquid and vapor states above the critical temperature is a characteristic of all known substances. While a pure vapor state can exist at a pressure lower than P_c, at pressures above P_c it is constrained to be a vapor. States with pressures above P_c are described as "supercritical states".

The remarkable "triple state" of matter where solid, liquid and vapor are in equilibrium may be characterized by a temperature called the triple point. The triple state is represented by a line parallel to the p-v plane with a characteristic pressure for the substance but variable volume. The triple point temperature of water is assigned the value 273.16 K and the triple state of water is used as the reference for establishing the Kelvin temperature scale.
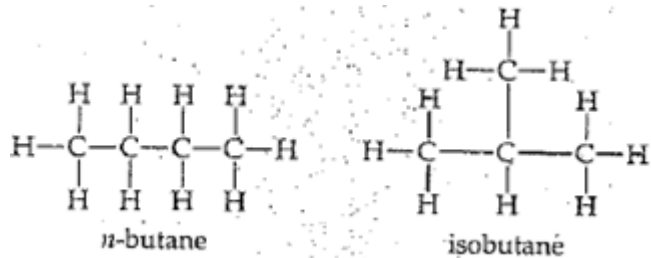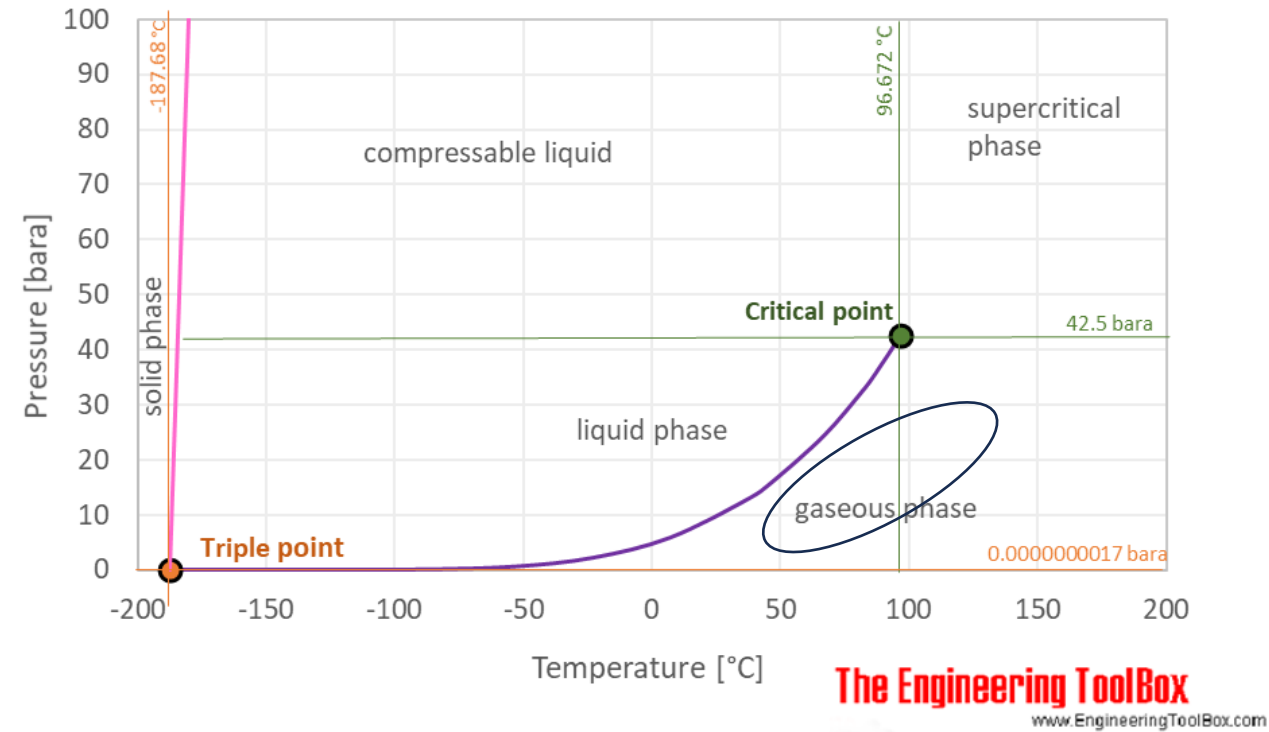
Equilibrium?

1. Equilibrium in the most rigorous sense is a state with no change in space or time = a basic "use-less" idea....however,

2. Equilibrium over appropriate special and temporal scales is what the idea of equilibrium is.

3. We state a temperature of this room, perhaps even a kitchen with a flame, temperature of a city (TV keeps showing this), of a country, of southern hemisphere vs northern hemisphere and of the earth itself (climate change issues). All these have embedded in them the idea of local equilibrium – a kind of mean through a day, over a season, over an year – stated again – over appropriate temporal and special scales

4. Local equilibrium – No changes in space or time of relevance – Temperature of the earth, Temperatures over northern and southern hemispheres, Temperatures in cities, Temperatures in kitchen and other rooms in a house – Idea is that temperature is not in equilibrium over some distance, but is at equilibrium over a much shorter distance, Example: temperature varies over a flame of 2 mm thickness from say 300 K to 2300 K, but does not change over a special region of 0.001 mm (1 micron)

5. Temperature is defined as the 0th law! (When a body, 'A', is in thermal equilibrium with another body, 'b', and also separately in thermal equilibrium with a body ', C', then body, 'B' and 'C', will also be in thermal equilibrium with each other. This statement defines the zeroth law of thermodynamics.)

6. Chemical equilibrium is when the reactant species and product species at a specific temperature and pressure react and produce each other keeping the actual measured values over practical time scales the same.....(we will talk more later)
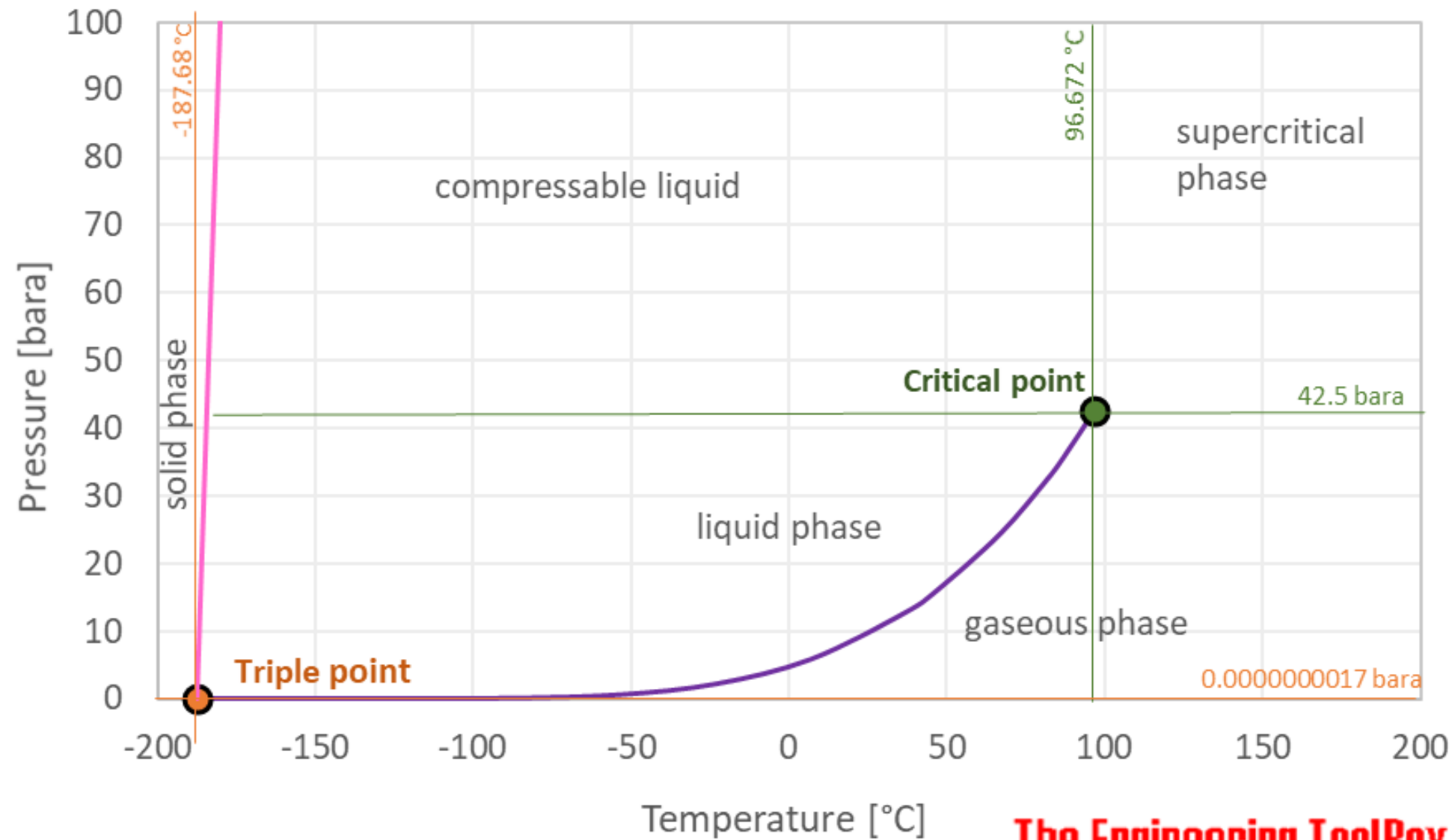
Butane phase diagram

- solid phase
- compressable liquid
- supercritical phase
- liquid phase
- gaseous phase
- **Critical point** — 37.96 bara
- **Triple point** — 0.0000067 bara
- -138.25 °C
- 151.98 °C

Pressure [bara] vs Temperature [°C]

Propane phase diagram

- solid phase
- compressable liquid
- supercritical phase
- liquid phase
- gaseous phase
- **Critical point** — 42.5 bara
- **Triple point** — 0.0000000017 bara
- -187.68 °C
- 96.672 °C

Pressure [bara] vs Temperature [°C]

n-butane   isobutane

Species	P_c atm	T_c K	ρ_c kg/m^3
CH_4	46.0	190	163
C_3H_8	42.4	369	220
n-C_4H_{10}	38.0	425	227

Propane phase diagram

Propane phase diagram showing Pressure [bara] versus Temperature [°C], with the solid phase, compressable liquid, liquid phase, gaseous phase, and supercritical phase regions. The Triple point is at -187.68 °C and 0.0000000017 bara, and the Critical point is at 96.672 °C and 42.5 bara.

Compressibility Factor – an extension of ideal equation of state

- Particles act independent of one another However, real gases deviate from ideal gas behavior.
- This deviation at given temperature and pressure can be accurately accounted for by introduction of a correction factor called the compressibility factor Z.

$$Z = pV/RT, \text{ or } PV = ZRT, \quad \text{Obviously, Z = 1 for ideal gases.}$$

- Gases behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures.

$$p_R = p/p_{cr} \text{ and } T_R = T / T_{CR}$$

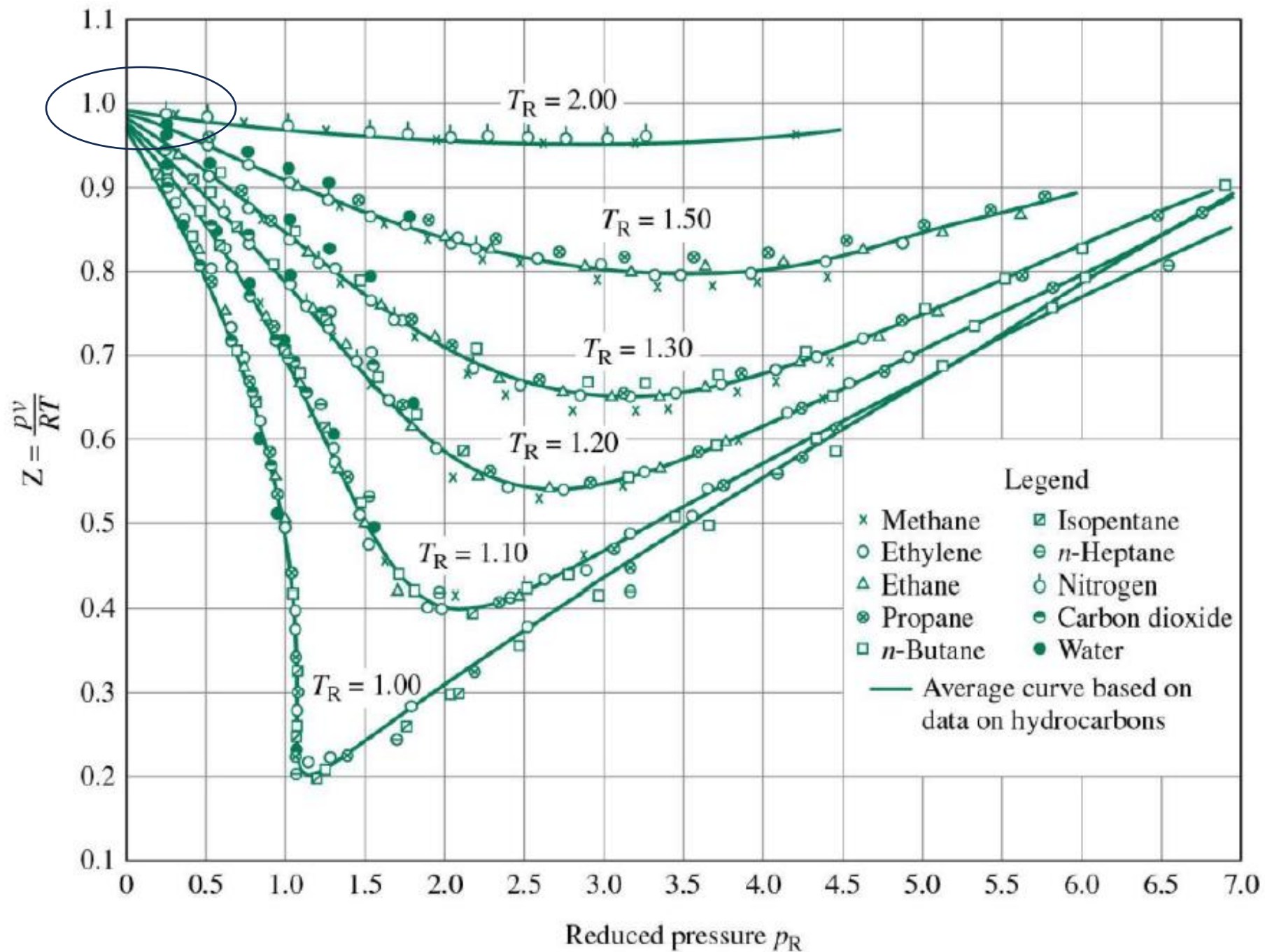p_R and T_R are called the reduced pressure and temperature, respectively.

- By curve-fitting all the data, the general compressibility chart is obtained which can be used for all gases.........

The zone of our interest – low pressures compared to critical pressure and higher temperatures more Than the critical temperature

Another equation of state

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

$$a = \frac{27R^2 T_{cr}^2}{64 P_{cr}} \quad and \quad b = \frac{RT_{cr}}{8 P_{cr}}$$

Legend

x Methane	⊠ Isopentane
o Ethylene	⊖ n-Heptane
▵ Ethane	◊ Nitrogen
⊗ Propane	⊕ Carbon dioxide
□ n-Butane	● Water
—— Average curve based on data on hydrocarbons	

$T_R = 2.00$
$T_R = 1.50$
$T_R = 1.30$
$T_R = 1.20$
$T_R = 1.10$
$T_R = 1.00$

$Z = \frac{pv}{RT}$

Reduced pressure p_R

Perfect gas and some useful results.

The equation connecting p, V, m and T is the equation of state

$$pV = m\,RT, \quad p = \rho RT, \quad R = \text{Specific gas constant}$$
$$pV = (m/Ṃ)\,Ɍ\,T = p\,n\,ɌT, \quad Ɍ = \text{Universal gas constant}, \quad Ṃ = \text{Molecular weight}$$

If there is a mixture of gases, according to Dalton's law of partial pressures,

$$p = \Sigma p_i, \qquad p_i V = (m_i/Ṃ_i)\,Ɍ\,T = n_i\,ɌT\,Ṃ$$

$$X_i = \text{molar fraction} = n_i/n = p_i/p = m i/m\ Ṃ/\,Ṃ_i = Yi\ Ṃ/\,Ṃ_i, \quad Y_i = \text{mass fraction}$$

Therefore, $$X_i\,Ṃ_i = Yi\,Ṃ.$$

Summing up gives $Ṃ = \Sigma X_i\,Ṃ_i$, the average molecular weight. If we know only mass fractions,

we take a sum on Xi to get $1/\,Ṃ = \Sigma Y_i/\,Ṃ_i$ or $Ṃ = 1/\,\Sigma Y_i/\,Ṃ_i$. These two relationships are useful

$$p_i v = m_i \mathscr{R}_i T = m_i \mathscr{R} T / \mathscr{M}_i \qquad (4.7)$$

where p_i is the partial pressure of species i and m_i is the mass of the species i.

If we express the total pressure by $pv = m\mathscr{R}T = mRT/\mathscr{M}$, we can state the Dalton's Law as,

$$p = \Sigma p_i \qquad (4.8)$$

In combustion literature, one uses molar units, one mole implying mass equivalent to molecular weight. Thus we have

$$n_i = m_i / \mathscr{M}_i \qquad (4.9)$$

and $p_i v = n_i RT$, $pv = nRT$. The ratio n_i/n equals X_i called the mole fraction.

$$X_i = n_i/n = p_i/p \qquad (4.10)$$

In addition, one defines mass fraction as

$$Y_i = m_i/m \qquad (4.11)$$

the ratio of the mass of the species i to the total mass.

Equations (4.10) and (4.11) concerning X_i and Y_i can be used to write $Y_i = m_i/m = (n_i \mathscr{M}_i)/(n \mathscr{M})$ and we get

$$Y_i = X_i \mathscr{M}_i / \mathscr{M} \qquad (4.12)$$

or

$$Y_i/\mathscr{M}_i = X_i/\mathscr{M} \tag{4.13}$$

Summing up Eqn. (4.12) over all i, one gets

$$\mathscr{M}_i = \Sigma X_i \mathscr{M}_i, \tag{4.14}$$

the average molecular weight.

Summing up Eqn. (4.13) over all i gives an alternate but equivalent expression for $\mathscr{M}$

$$\mathscr{M} = [\Sigma(Y_i/\mathscr{M}_i)]^{-1} \tag{4.15}$$

Equilibrium in an LPG cylinder as a reaction process

The cylinder carriers a liquid with vapor above the liquid surface with the valve closed. The liquid is stated to be in equilibrium with the vapor above. This process and what happens in a reaction at equilibrium are very similar. The pressure inside is a function of temperature only.

Dynamic equilibrium

A reversible reaction is where products can, under appropriate conditions, turn back into reactants.

- There will be a range of conditions over which both the forward and backward reaction will take place, and this can lead to a state of balance with reactants and products present in unchanging amounts.
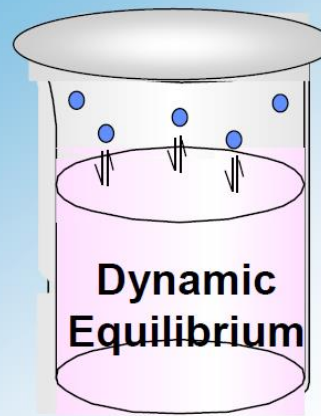
- This is called a dynamic equilibrium.

  A   B   ⇌   A B

  these combine   these decompose

Equilibrium

A state where the forward and reverse conditions occur at the same rate.

Dynamic process
Rate of forward Rxn = Rate of reverse Rxn

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$
(reactant)   (product)

Concentration of reactants and products remain constant over time.

Dynamic Equilibrium
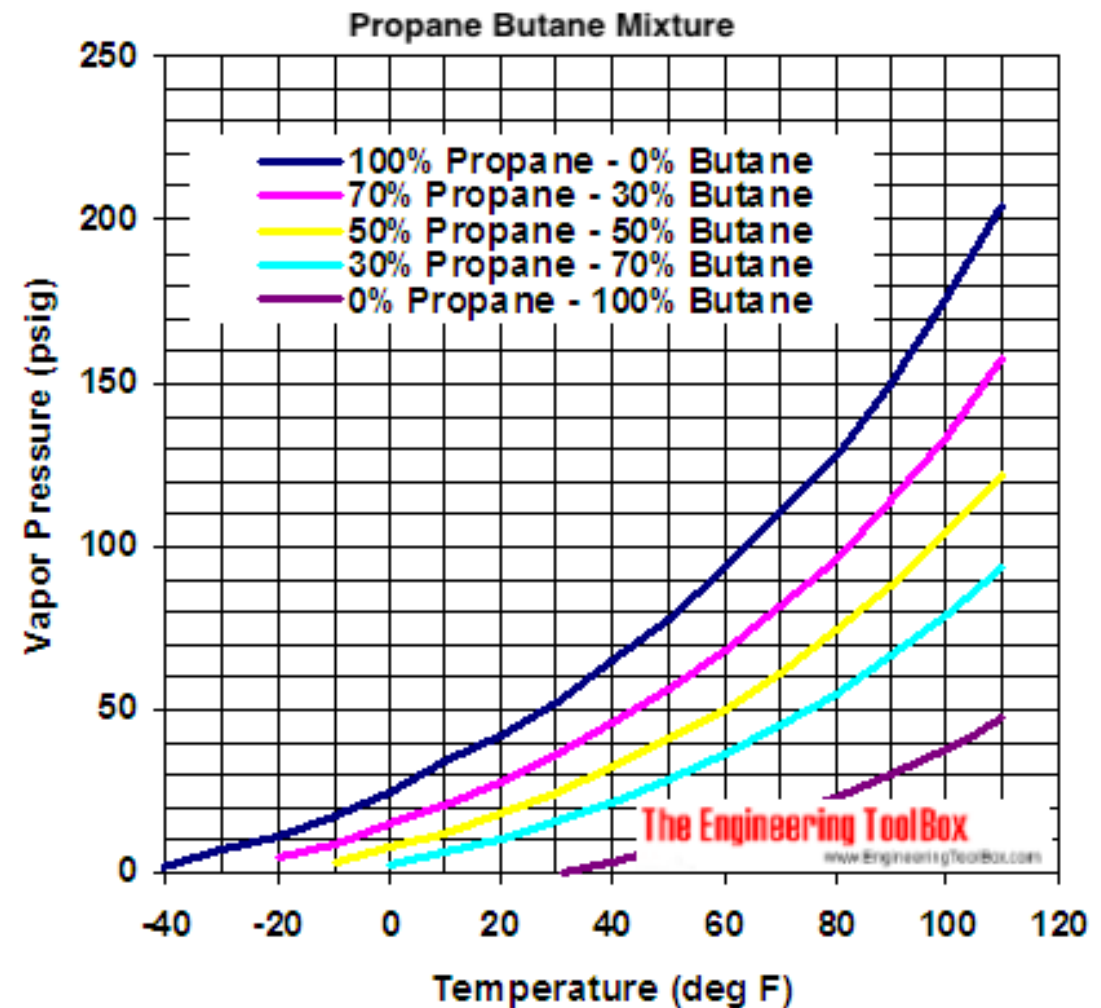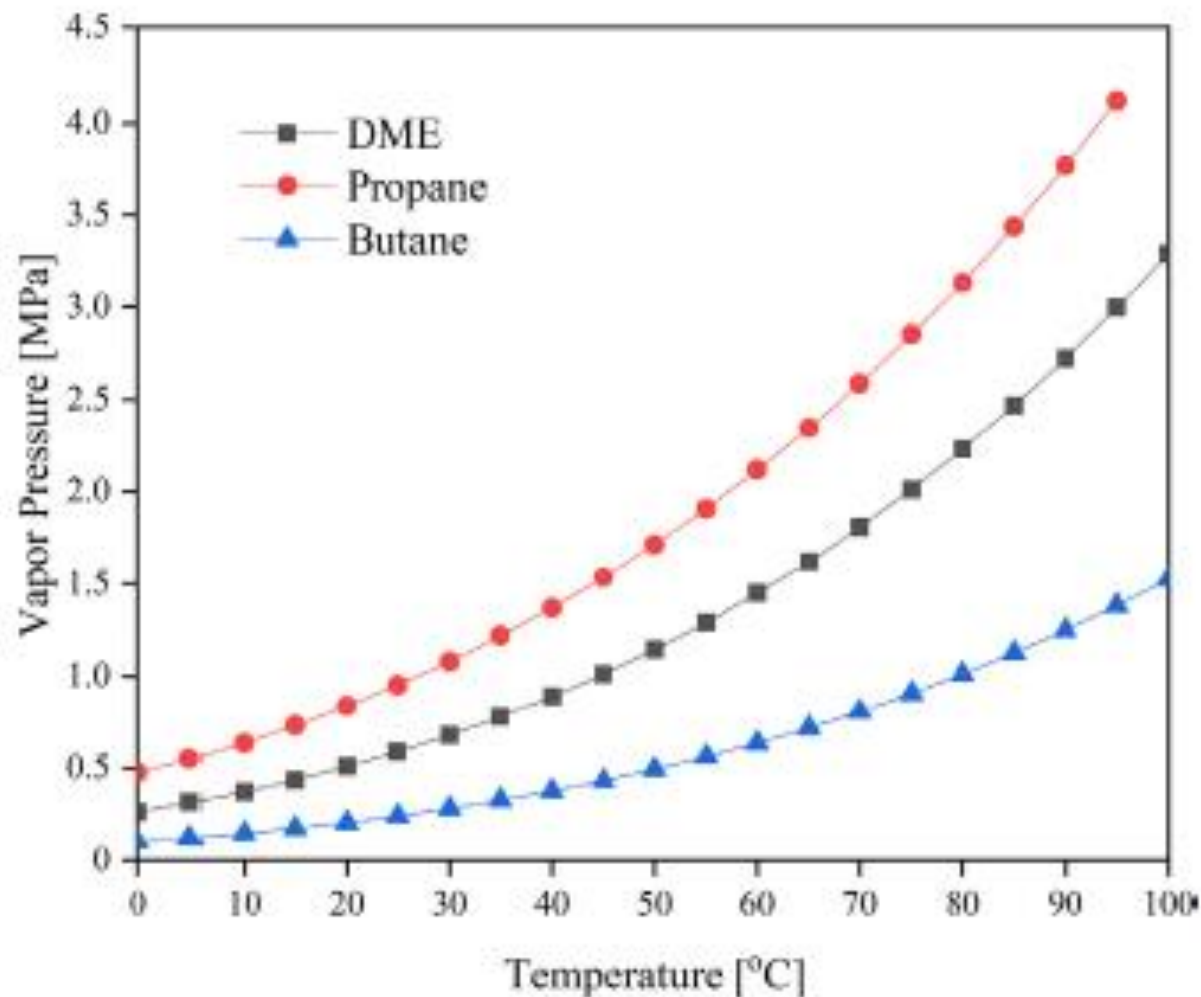
The above plots are the experimental data of the boiling points of the fuels at various pressures. Technically, these are the vapor pressures at various temperatures

p atm	Propane T, K		Butane	
1	230	1.00	273	1.00
2	246	1.90	293	1.99
3	256	2.72	307	3.05
4	266	3.80	317	4.05
5	272	4.59	327	5.28
10	300	9.99	355	10.24

Propane	Butane	p
100	0	12.77
90	10	11.82
80	20	10.88
70	30	9.94
60	40	8.99
50	50	8.05
40	60	7.10
30	70	6.16
20	80	5.22
10	90	4.27
0	100	3.33

Propane	Butane	310 K	300 K	290 K	280 K
100	0.00	12.77	10.00	7.71	5.83
90	10.00	11.82	9.25	7.12	5.37
80	20.00	10.88	8.50	6.53	4.92
70	30.00	9.94	7.74	5.94	4.46
60	40.00	8.99	6.99	5.35	4.01
50	50.00	8.05	6.24	4.76	3.56
40	60.00	7.10	5.49	4.17	3.10
30	70.00	6.16	4.73	3.58	2.65
20	80.00	5.22	3.98	2.99	2.19
10	90.00	4.27	3.23	2.39	1.74
0	100.00	3.33	2.48	1.80	1.29

$$p = X_{propane}\, e^{(2270*(1/230 - 1/T))} + X_{butane}\, e^{(2750*(1/273 - 1/T)}$$

$$X_{butane} = 1 - X_{propane}$$
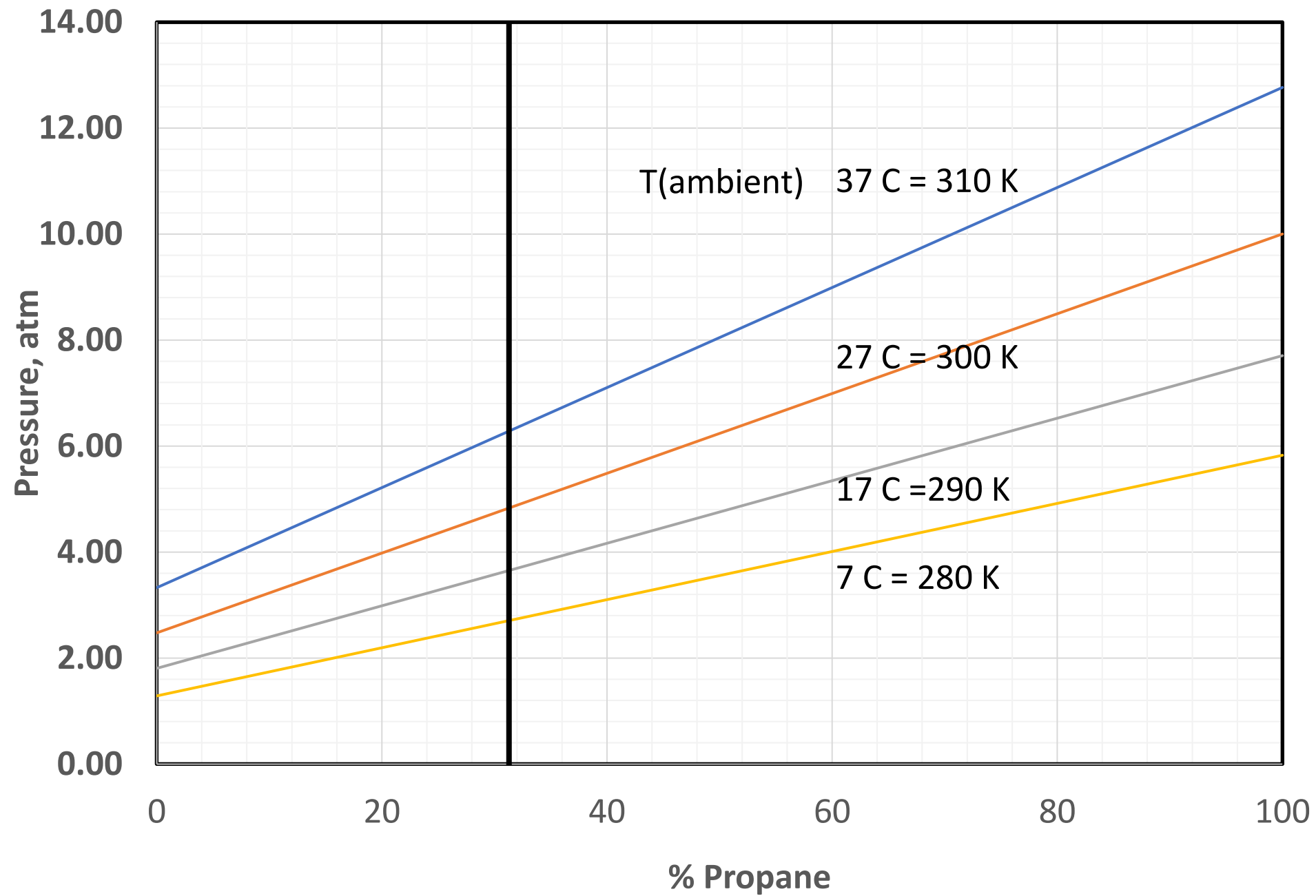
Fuels – Liquid and Gaseous fuels and key features

Gaseous fuels – Natural gas (> 65 % methane, other higher hydrocarbons), LPG (mix of propane and butane largely), Acetylene, Biogas (a mix of carbon dioxide and methane), Producer gas, coal gas (Carbon monoxide, hydrogen, carbon dioxide, nitrogen), Synthesis gas (Carbon monoxide, hydrogen, carbon dioxide),

Synthetic natural gas (SNG)

- all burn depending on the flow rate of fuel and oxidant (air/oxygen)

Liquid fuels – Gasoline, High speed diesel, Light Diesel oil, Marine diesel oil, Fuel oil -2 or Furnace oil (all are a mix of several hydrocarbons), Ethanol, Gasohol,

- all burn depending on the surface area provided and the heat flux to the surface, can be atomized to enable larger combustion rate

Solid fuels –Coal (mined), peat, biomass (renewable) (Camphor)

 - all burn depending on the surface area provided and the heat flux to the surface, can be pulverized to enable larger combustion rate

Liquefied Petroleum Gas (LPG) and properties

• Propane, butane and unsaturates, lighter C2 and heavier C5 fractions

• Hydrocarbons are gaseous at atmospheric pressure but can be condensed to liquid

• LPG vapor is denser than air. When released at height, it moves towards the ground

Fuel	Boiling Point, ºC	Density g/cm³	LCV MJ/kg	A/F, stoich (m)	A/F, stoich (v)	Flame Temp ºC	Burning vel, m/s
Natural Gas	~ -150	0.6	47	17	10	1954	0.36
Propane (C_3H_8)	-42	1.52	45	15	25	1967	0.38
Butane (C_4H_{10})	-1	2.0	45	15	32	1973	0.40

Comments: Natural gas is largely composed of methane (~ 95 %).
Density of methane is essentially obtained as 16/29 x density of air ~ 0.55 of air; <u>similarly,</u>
for propane and butane
Calorific value in mass terms is about the same, but will differ based on volume.
The air-to-fuel ratio for stoichiometry implies complete conversion to CO_2 and H_2O. Again
on mass basis it is about the same, but on volume basis is different.
Flame temperature is about the same. Burning velocity with air increases slightly towards
0.4 m/s

Synthetic Natural Gas (SNG)
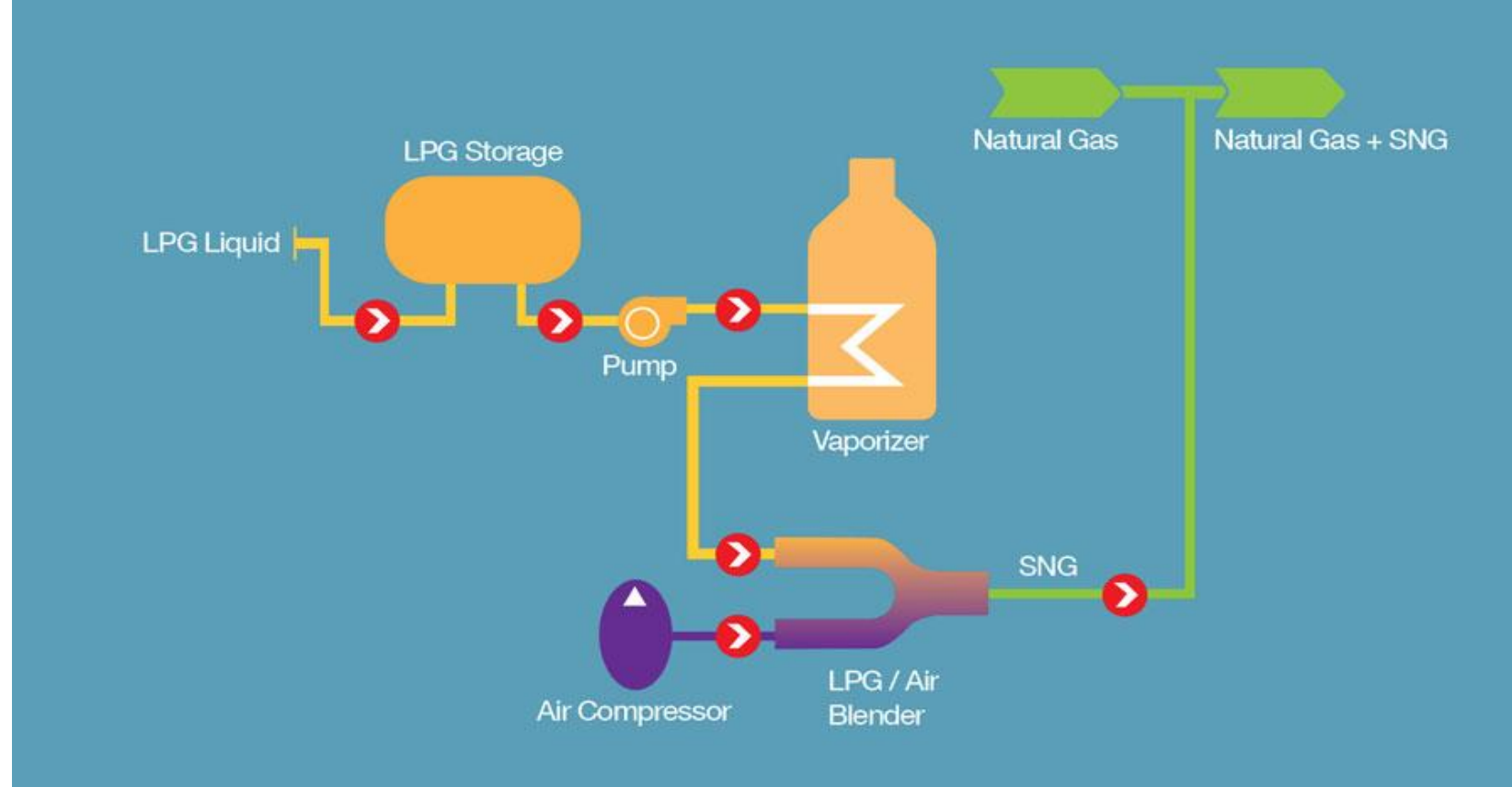
What is SNG? – It is blended LPG with air (usually) – Why is it done?

SNG systems provide for an gaseous fuel with combustion characteristics similar to Natural Gas. The claim is that In emerging economies where NG is in its infancy, SNG plants help local gas utility firms to "build up" a customer base during planning and construction of a natural gas transmission system. What it does is to eliminate re-condensation problems commonly associated with undiluted LPG vapor, as the "tempering" of the LPG with air suppresses the dew point. This enables piping the gas like NG. In so far as combustion properties are concerned, they are the same as in LPG. The air required for combustion has to factor the oxygen already present in the gas.

Wobbe index and density of gaseous fuels

The **Wobbe index** (WI) or **Wobbe number**[1] is an indicator of the interchangeability of gaseous fuels such as NG, LPG, and is defined in the specifications of gas supply and transport utilities.

It is defined as WI = HCV $(MJ/m^3)/\sqrt{(M/29)}$……Why square root of density?...because flow rates vary as $\sqrt{(\rho \Delta p)}$ and ρ is proportional to the molecular weight of the gases. 29 is the mol. weight. of air

Webbe index of LPG is 74 to 88 and of NG is 45 to 55. Higher index requires lower flow cross section if the flow rate is controlled by this dimension. Usually, with the margins available in the dimensions.

Very specifically, natural gas valves/piping have to account for about twice the sizes compared to LPG or at least must be verified to be adequate. On the other hand, those operating on NG will conveniently operate on LPG. Only the controller must be tuned appropriately.

Properties of liquid fuels

Name	Formula	S	ρ_f kg/m³	HCV MJ/kg	LCV MJ/kg
Gasoline	C_8H_{17}	14.9	700	47.6	44.2
Gasoline	C_8H_{17}	14.9	739	47.1	43.9
Kerosene	$C_{10}H_{22}$	15.0	825	45.9	43.0
Light diesel oil	$C_{12}H_{26}$	15.2	876	44.7	42.4
Med. Diesel oil	$C_{13}H_{28}$	15.2	920	44.4	41.9
Heavy diesel oil	$C_{14}H_{30}$	14.9	960	43.7	41.4

Mercaptan sulphur is present across the entire range of hydrocarbons: natural gas, liquefied petroleum gas, gasoline fraction, kerosene fraction, Diesel, etc

Mercaptans like CH$_3$SH, in liquefied petroleum gases have unpleasant odor to help detect leakage. COS is also there in some LPG streams. These on combustion lead to SO$_2$ that is considered acid generating pollutant (H_2SO_4 in the atmosphere)

For purposes of calculating the stochiometric ratio, S and chemical heat release aspects, it is fine to treat the composition as CH_n

LPG = $CH_{2.54}$
Diesel = $CH_{2.2}$
Gasoline = $CH_{2.1}$

LPG S = 150 ppm (mass) max
HSD S = 50 ppm (mass) max
FO S   = 4000 ppm (mass) max

Note that the H:C ratio increases as we move from furnace oil (FO), diesel, gasoline and LPG, and NG This is primarily responsible for greater emissions in fuels as it is more difficult to oxidize C than H

The combustion process

- Combustion is the exothermic reaction of fuel with oxidant – air generally.

- If it occurs without a formal supply of air – it is a stove; example – a biomass stove. Against this, one can have fan supplied air for combustion. It is a combustion device. Further, if you mix LPG with air by an aerodynamic principle, you have a combustion device. LPG combustion system (LPG stove is abit of misnomer)

- Air: 20.9% oxygen, 79.1% nitrogen and others

- Complete combustion: total oxidation of fuel (adequate supply of oxygen needed)

- Nitrogen: (a) moderates the temperature (b) forms NO_x at high temperatures (No_x is indicated like that because it is composed of NO_2 and NO in different proportions)

- Carbon forms CO_2 and CO due to high temperature decomposition/reaction of CO_2 and also mixing related problems leading to incomplete combustion

Fuels, Oxidizers and Uses

Fuels	Oxidizers	Uses

I. Gaseous fuels, Oxidiser

1. Liquified Petroleum Gas (LPG) — air $(0.209 \, O_2 + 0.791 \, N_2)$ — Domestic purposes, furnaces
2. Biogas — air — Domestic purposes, engines
3. Producer gas — air — Engines (Reciprocating),
4. Acetylene — Oxygen (O_2) — Gas welding/gas cutting
5. Basic fuel Species, CH_4, C_3H_8, C_4H_{10}, CO, H_2 — Oxidising Species, O_2 (N_2 inert) — All combustion

II. Liquid Fuels-Oxidiser

1. Gasoline — Air — Spark ignition engines, aircraft piston engines
2. High Speed Diesel (HSD) — Air — Compression ignition engines, Furnaces
3. Light Diesel Oil, furnace Oil — Air — Furnaces
4. Kerosene (wide cut) — Air — Domestic applications (wide cut) Aircraft gas turbines, ramjet,
5. Alcohols — Air — Engines
6. Hydrazine, UDMH, LH_2 — N_2O_4, RFNA, LO_2 — Liquid Rocket Engines,
7. LH_2, kerosene — Air — Scramjet

(LH$_2$ =Liquid hydrogen, LO_2 = Liquid oxygen, RFNA = Red fuming nitric acid

Stoichiometric and Equivalence Ratios and their relevance

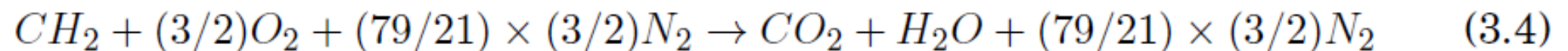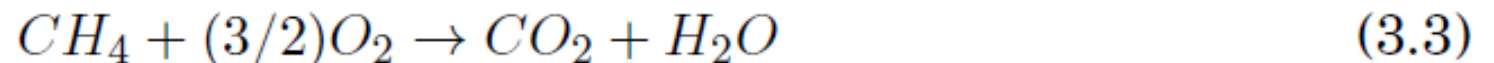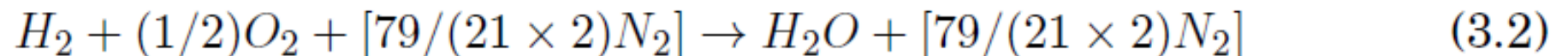Hydrocarbon, Alcohols, Coal, Biomass + oxygen (air) → CO_2 + H_2O + N_2 + Other species

CH_n, $CH_mO_pN_q$,   + a O_2 + b N_2 → CO_2 + H_2O + N_2 + Other species

n = 2 – 4,   m = 1.5 to 3, p = 0.7 – 1, q ~ 0.01

All composition is normalized to C = 1. Can this be done? Yes, for stoichiometry it is OK.

If the reaction has two constituents, the volumetric or mass ratio of one with respect to the other is stoichiometric ratio. Engineers usually use mass units. Chemists, volume units

In the present context, stoichiometric ratio is the amount of oxidant (oxygen or air) to lead to stable products – C going to carbon dioxide and hydrogen going to water (gas), nitrogen is treated as inert. It makes a difference to the ratio.

$$H_2 + (1/2)O_2 \rightarrow H_2O \tag{3.1}$$

$$H_2 + (1/2)O_2 + [79/(21 \times 2)N_2] \rightarrow H_2O + [79/(21 \times 2)N_2] \tag{3.2}$$

$$CH_4 + (3/2)O_2 \rightarrow CO_2 + H_2O \tag{3.3}$$

$$CH_2 + (3/2)O_2 + (79/21) \times (3/2)N_2 \rightarrow CO_2 + H_2O + (79/21) \times (3/2)N_2 \tag{3.4}$$

Stoichiometry

How much oxidizer is required to just completely react with unit mass of the given fuel.
This ratio is called the stoichiometric ratio.

Example: $2 H_2 + O_2 \rightarrow 2 H_2O$ 2 moles of H2 reacts with 1 mole of O2 to give 2 moles of H2O
This means that ther is a volume reduction.

This equation states that 4 grams of hydrogen react with 32 grams of oxygen to give 36 gms of H2O.
This means mass is the same. Also, the stoichiometric ratio, S is 32/4 = 8.

• For typical hydrocarbon fuel burning in air:

All hydrocarbons can be represented by for stoichiometry CH_n [C_3H_8 ~ $CH_{2.66}$, C_4H_{10} ~ $CH_{2.5}$, etc]

• $CH_n + (1+n/4)(O_2 + 79/21 N_2) \rightarrow CO_2 + n/2 H_2O + 79n/84 N_2$
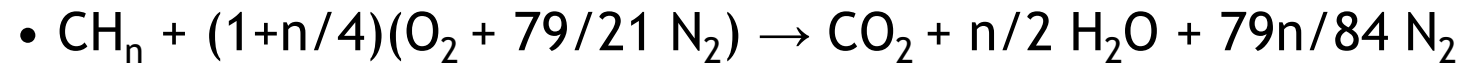
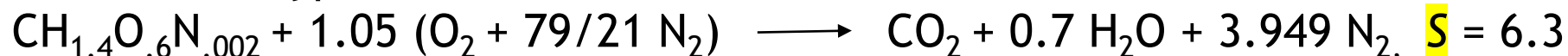$\boxed{S = (32+3.76 \times 28)(1+n/4)/(12+n)}$ For methane, n = 4, S = 17.1,
For propane, n = 2.66, S = 15.6

For Diesel/gasoline, n ≈ 1.8, S = 14.4

• If we take typical biomass combustion,
$CH_{1.4}O_{.6}N_{.002} + 1.05 (O_2 + 79/21 N_2) \longrightarrow CO_2 + 0.7 H_2O + 3.949 N_2,$ S = 6.3

More on Stoichiometry....

In general, $CH_nO_mN_p + (1+n/4-m/2)(O_2 + 79/21\ N_2) \longrightarrow CO_2 + n/2\ H_2O + [3.76\ (1+n/4-m/2)+p/2)]\ N_2$

$s = (32+3.76 \times 28)(1+n/4-m/2)/(12+n+16m+14p)$

- In an actual situation air provided for combustion may be more or less than the stoichiometric ratio.
- There are many ways of expressing the relative *richness or leanness* of the mixture.
- The ratio $(F/A)_{actual}/(F/A)_{stoichiometric}$ is termed the fuel equivalence ratio or simply equivalence ratio, denoted by ϕ.
- The inverse of this expression is also sometimes a definition used for equivalence ratio.
- $\phi = 1$ means stoichiometric mixture.
- Rich mixtures ($\phi > 1$) result in emission of CO and hydrocarbons.
- In most combustion systems designed for industrial applications, the mixture ratio is maintained slightly lean ($\phi < 1$).
- Excess air ratio is also another way of specifying the leanness of the mixture. This leads to the formation of oxides of nitrogen, a green house gas, particularly N_2O.

Stoichiometry

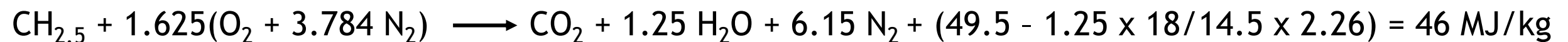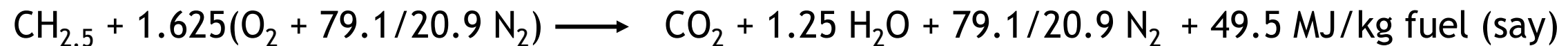## Table 3.2: Stoichiometric Ratio for Several Fuels

Fuel	Formula	Molecular Weight	$(O/F)_{stoi}$ with	
			Oxygen	Air
Hydrogen	H_2	2.0	8.00	34.50
Magnesium	Mg	24.0	1.66	7.10
Aluminium	Al	27.0	3.80	16.40
Methane	CH_4	16.0	4.00	17.20
Butane	C_4H_{10}	58.0	3.58	15.40
Carbon monoxide	CO	28.0	0.57	2.46
Kerosene	$CH_{1.8}$	13.8	3.36	14.50
Ethyl Alcohol	C_2H_5OH	46.0	2.09	9.00
Methyl Alcohol	CH_3OH	32.0	1.50	6.46
Hydrazine	N_2H_4	32.0	1.00	4.30

Energetics of Reactions

- The overall combustion reactions are *exothermic* - the reactions are accompanied by release of heat.

- The amount of heat energy released by burning unit mass of fuel is called the *calorific value* of the fuel.

- Higher calorific value (HCV) corresponds to water being condensed. Lower calorific value (LCV) is for water as gas.

- Bomb calorimeter (for liquid and solid fuels) and gas calorimeter (for gaseous fuels) measures the higher calorific value. How do we get LCV from HCV?

Let us take one of the components of LPG: Butane, C_4H_{10} = $CH_{2.5}$

$CH_{2.5} + 1.625(O_2 + 79.1/20.9\ N_2) \longrightarrow CO_2 + 1.25\ H_2O + 79.1/20.9\ N_2 + 49.5$ MJ/kg fuel (say)

$CH_{2.5} + 1.625(O_2 + 3.784\ N_2) \longrightarrow CO_2 + 1.25\ H_2O + 6.15\ N_2 + (49.5 - 1.25\ x\ 18/14.5\ x\ 2.26) = 46$ MJ/kg

Notice that if C_4H_{10} instead of $CH_{2.5}$ had been used, the result would be the same.

HHV and LHV

Let us take LPG of the composition: Butane, $C_4H_{10} = CH_{2.5}$

$CH_{2.5} + 1.625(O_2 + 79.1/20.9 \ N_2) \longrightarrow CO_2 + 1.25 \ H_2O + 1.625 \times 79.1/20.9 \ N_2 + 50.0 \ MJ/kg$ fuel (say)

1 kg fuel + 15.7 kg air = 16.7 products (3.03 kg CO2 + 1.57 kg H2O + 12.1 kg N2)

$X_{H2O} = 1.25/(1 + 1.25 + 6.15) = 0.15$, $Y_{H2O} = 1.25 \times 18 / (1 \times 44 + 1.25 \times 18 + 6.15 \times 28) = 0.094$

LHV = HHV – Heat not received because of steam condensation

$= 50.0 – 1.57 \times 2.3 = 46.4 \ MJ/kg$

There is heat in the gas phase species whose heat from ~ 2300 K is brought back to ambient conditions in the experiment. This amounts to 1.1 kJ/kg K x 200 K = 0.22 MJ/kg
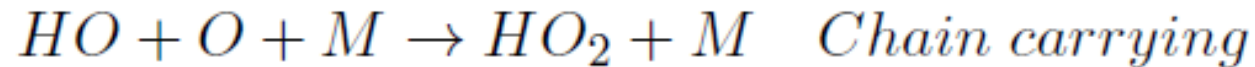We get then 46.4 – 0.2 = 46.2 MJ/kg.

Heats of combustion/kg fuel, product

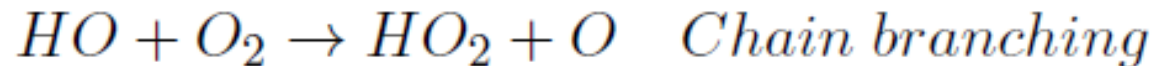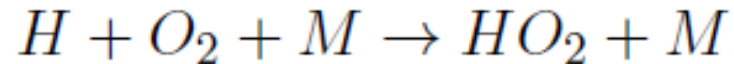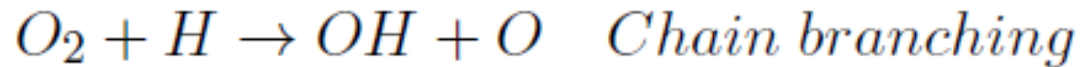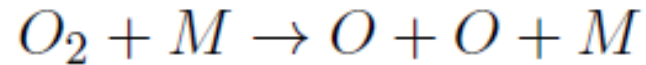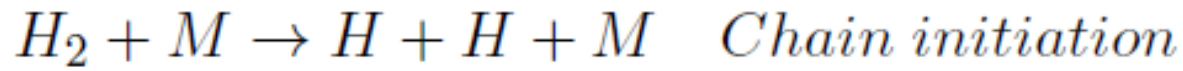Table 4.5: Heats of combustion H_c, fuel or propellant – v = by volume, w = by weight

System	H_c, MJ/kg	Hc/kg product
LPG [80 Butane, 20 Propane (v)] + Air	46.2 ~~44.0~~	46.2/16 = 2.9
Biogas + Air	32.0–36.0	32/6 = 5.3
Prod. gas $20CO + 20H_2 + 2CH_4 + 58N_2$ (v) + Air	4.6	4.6/2 = 2.3
Kerosene + Air	42.0	42/16 = 2.62
Wood (sun dry) + air	16	16/7 = 2.3
Bituminous coal + air	26	26/7 = 3.7
Indian coal (45 % ash) + air	14	
Solid Propellant		
50 NC + 50 NG (w)	5.4	
70 AP+20 Al+10 CTPB (w)	6.0	
Liquid Propellant		
50 N_2O_4 + 50 N_2H_4 (v)	6.0	
0.50 UDMH+0.50 N_2O_4 (v)	7.5	

How does the reaction proceed?

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \quad \text{(propane oxidation)}$$
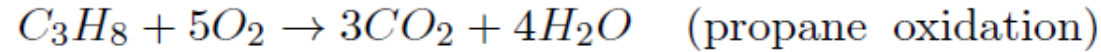
The reaction of propane does not proceed the way the stoichiometric reaction shows. It proceeds as a chain mechanism as follows.

$$RR = A_f X_1 X_2 p^2 e^{-E/RT}$$

$$H_2 + M \rightarrow H + H + M \quad \textit{Chain initiation}$$
$$O_2 + M \rightarrow O + O + M$$
$$H_2 + O \rightarrow OH + H \quad \textit{Chain branching}$$
$$O_2 + H \rightarrow OH + O \quad \textit{Chain branching}$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO + O_2 \rightarrow HO_2 + O \quad \textit{Chain branching}$$
$$HO + O + M \rightarrow HO_2 + M \quad \textit{Chain carrying}$$
$$HO + H + M \rightarrow H_2O + M \quad \textit{Chain termination}$$
$$H + O + M \rightarrow H_2O + M \quad \textit{Chain termination}$$
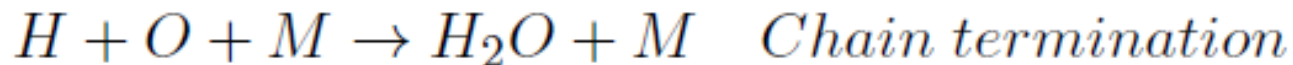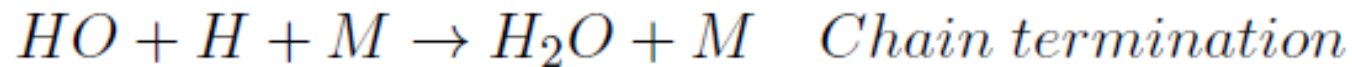
RR = Volumetric reaction rate, kg/m³s

X_1, X_2 = mole fractions of reactants

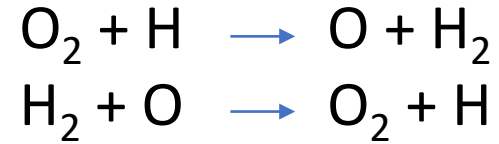p = pressure

T = Temperature

E = Activation energy

R = Universal gas constant

E/R = Activation temperature

Reaction rate depends very strongly on temperature

Reactions reaching equilibrium

$O_2 + H \longrightarrow O + H_2$

$H_2 + O \longrightarrow O_2 + H$

These two reactions can take place independently different rates

$O_2 + H \longleftrightarrow O + H_2$

When he rates are equal, it is inferred that they have reached equilibrium

In a large complex chemistry situation, they are treated as follows……………….

What does rate of reaction mean?

The speed of different chemical reactions varies.
Some reactions are very fast and others are very slow.
The speed of a reaction is called the **rate** of the reaction.
What is the rate of these reactions?

rusting

baking
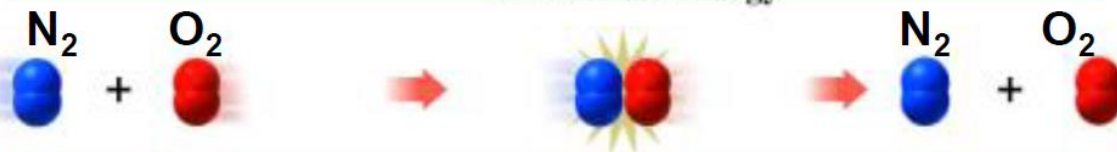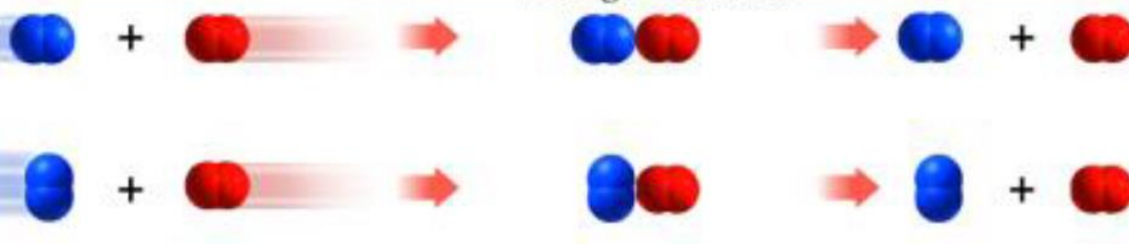

explosion

slow   **fast**   **very fast**

Effective collisions

A reaction won't happen if:

Insufficient energy to break bonds.

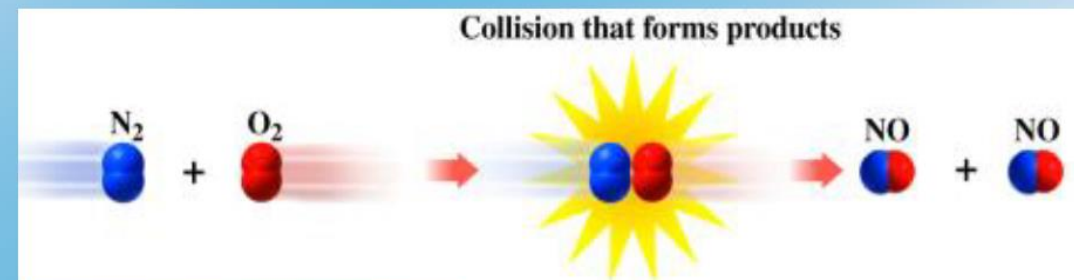N_2 O_2 N_2 O_2

Molecules are not aligned correctly.

Effective collisions

For reactants to make products:

1. Molecules must **collide**

2. They have to be **aligned** correctly.

3. They have to have enough E.

Collision that forms products

N_2 O_2 NO   NO

Reactions, particles and collisions

Reactions take place when particles collide with a certain amount of energy.

The minimum amount of energy needed for the particles to react is called the **activation energy**, and is different for each reaction.

The rate of a reaction depends on two things:

- the **frequency** of collisions between particles
- the **energy** with which particles collide.

If particles collide with less energy than the activation energy, they will not react. The particles will just bounce off each other.
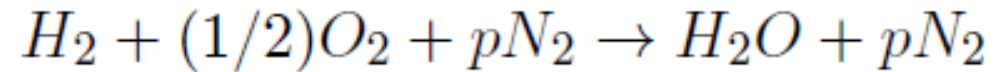
Reaction Rates

| 0 s	20 s	40 s
1.00 mol A 0 mol B	0.54 mol A 0.46 mol B	0.30 mol A 0.70 mol B
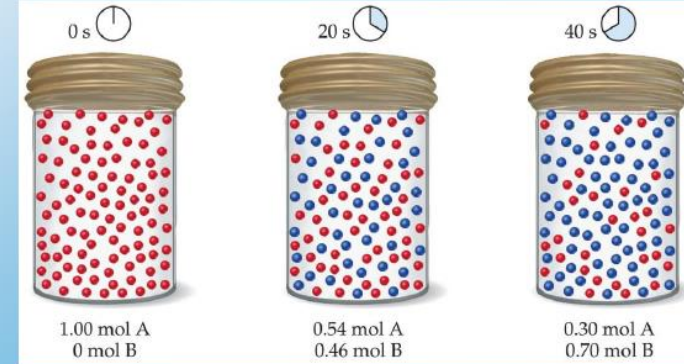
Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time.

How does reaction proceed? And why?

Take for instance: $$H_2 + (1/2)O_2 + pN_2 \rightarrow H_2O + pN_2$$

Will it proceed this way? The answer is No! Why? Molecules are moving around randomly and nothing much happens. But when ignition energy is deposited through a spark or a naked flame, this energy creates a number of reactive species like atoms and ions. These impinge on the molecules involved in the reaction and break "single" bonds or break and make other single bonds. Thus the reaction proceeds in steps of molecular events.

$$H_2 + H_2 \rightarrow H + H + H_2 \quad (1)$$
$$H_2 + O_2 \rightarrow H + H + O_2 \quad (2)$$
$$H_2 + M \rightarrow H + H + M \quad (3)$$
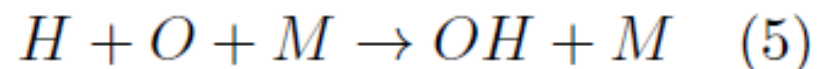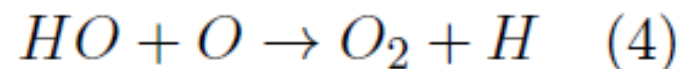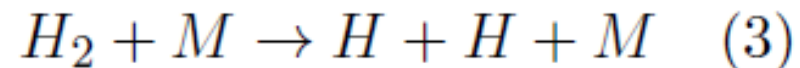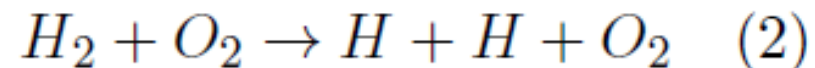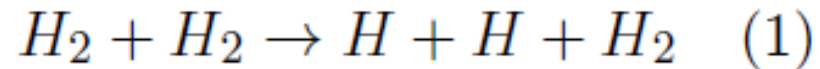
Breaking of a single bond

$$HO + O \rightarrow O_2 + H \quad (4)$$

Breaking and making of single bond

$$H + O + M \rightarrow OH + M \quad (5)$$

Making of a bond with excess energy to a random molecule

Dynamic equilibrium

A reversible reaction is where products can, under appropriate conditions, turn back into reactants.

- There will be a range of conditions over which both the forward and backward reaction will take place, and this can lead to a state of balance with reactants and products present in unchanging amounts.
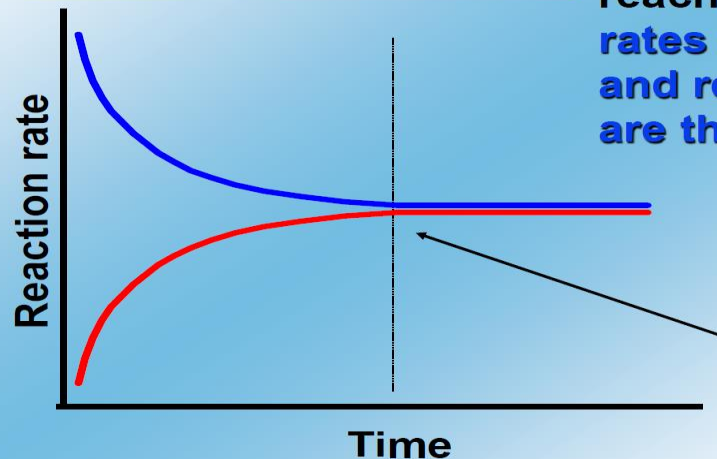
- This is called a dynamic equilibrium.

A   B $\rightleftharpoons$ A B

these combine   these decompose

Equilibrium and reaction rates

$H_2O_{(l)}$ $\rightleftharpoons$ $H_2O_{(g)}$
(reactant)   (product)

A point is ultimately reached where the **rates of the forward and reverse reactions are the same.**

Reaction rate vs Time
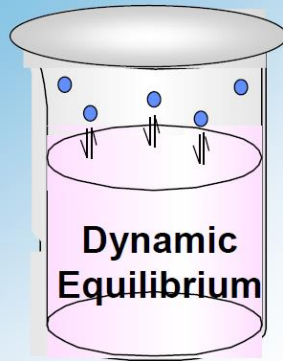
At this point, equilibrium is achieved.

Equilibrium

A state where the forward and reverse conditions occur at the same rate.

Dynamic process
Rate of forward Rxn = Rate of reverse Rxn

$H_2O_{(l)}$ $\rightleftharpoons$ $H_2O_{(g)}$
(reactant)   (product)

Dynamic Equilibrium

Concentration of reactants and products remain constant over time.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

At Equilibium

Concentration (mol/L)

N₂   O₂   Forward reaction   N₂   O₂   NO   Reverse reaction   NO

At equilibrium

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

$N_{2(g)}+O_{2(g)}$
Initially

$NO_{(g)}$
Initially

reserved.
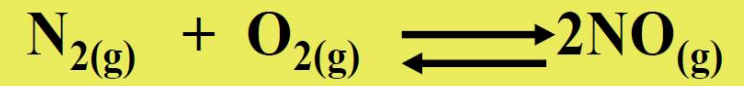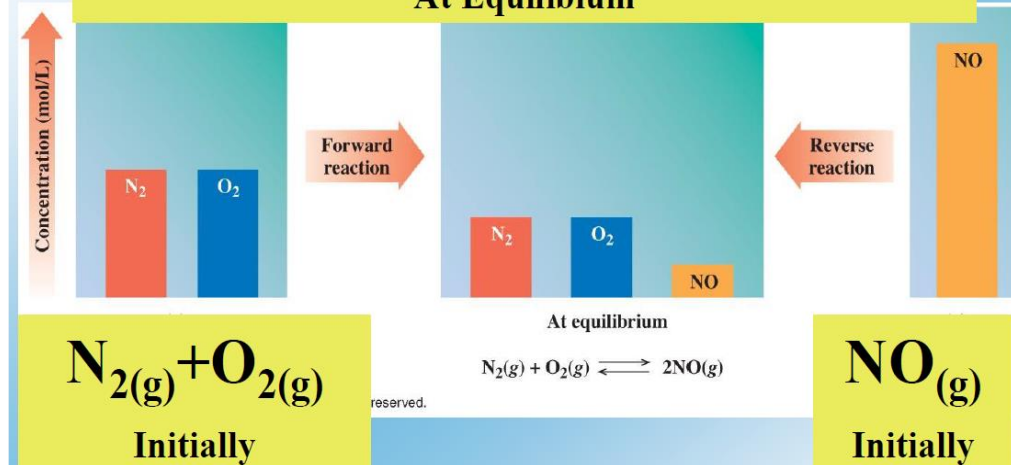
The Equilibrium Constant

Reversible reaction: $N_2O_{4\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$

Forward reaction: $N_2O_{4\,(g)} \longrightarrow 2\,NO_{2\,(g)}$

Rate law: $V_f = k_f\,[N_2O_4]$

Reverse reaction: $2\,NO_{2\,(g)} \longrightarrow N_2O_{4\,(g)}$

Rate law: $V_r = k_r\,[NO_2]^2$

The Equilibrium Constant

Therefore, at equilibrium

$$V_f = V_r$$

$$k_f\,[N_2O_4] = k_r\,[NO_2]^2$$

Rewriting this, it becomes

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

The Equilibrium Constant

The ratio of the rate constants is a constant at that temperature, and the expression becomes

$$K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

Equilibrium constant (K)

Equilibrium expression
(for any reaction at constant temperature)

$$aA + bB \rightleftharpoons cC + dD$$

reactants   products

$$K_{eq} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

coefficients

moles per liter

Generalised chemical kinetics

If the reverse reaction $\Sigma a_i A_i \rightleftharpoons \Sigma a_i' A_i$ is involved and if one uses equation of state and relationships between molar and mass fractions, one gets

$$\frac{dY_i}{dt} = \frac{\mathcal{M}}{\mathcal{M}_i} \frac{RT}{p} \left\{ k_f \times \Pi \left[\frac{Y_j \mathcal{M}_j}{\mathcal{M}} \frac{p}{RT} \right]^{a_j} - k_b \Pi \left[\frac{Y_j \mathcal{M}_j}{\mathcal{M}} \frac{p}{RT} \right]^{a_j'} \right\} \tag{5.4}$$

Where the first and second terms within the parenthesis sign are the rates of forward and backward reactions.

Now if steady state or equilibrium is attained, one gets $dY_i/dt = 0$ and so

$$\frac{k_f}{k_b} = \Pi \left(\frac{Y_j \mathcal{M}_j}{\mathcal{M}} \frac{p}{RT} \right)^{(a_j' - a_j)} = K_p = K_p(T) \tag{5.5}$$

Thus one can note that equilibrium constant is obtained in the limit of reaction rates in a reversible reaction going to zero. Equation 5.4 can be written as

$$\frac{dY_i}{dt} = \frac{\mathcal{M}}{\mathcal{M}_i} \frac{RT}{p} k_f \times \Pi \left[\frac{Y_j \mathcal{M}_j}{\mathcal{M}} \frac{p}{RT} \right]^{a_j} \left\{ 1 - \frac{1}{K_p(T)} \Pi \left[\frac{Y_j \mathcal{M}_j}{\mathcal{M}} \frac{p}{RT} \right]^{(a_j' - a_j)} \right\}$$

The unknown parameters of chemical rates are A_f and E in $k_f = A_f \exp(-E_i/RT)$.
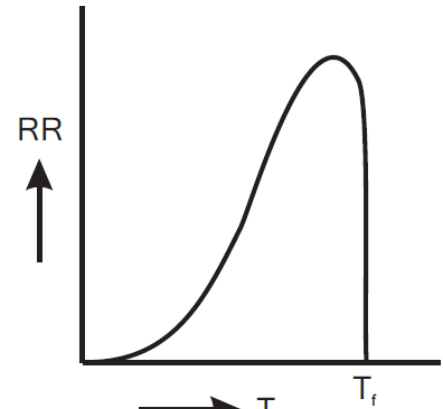
Activation Energy

The **activation energy** E_{act}

Is the minimum energy needed for a reaction to take place upon proper collision of reactants.
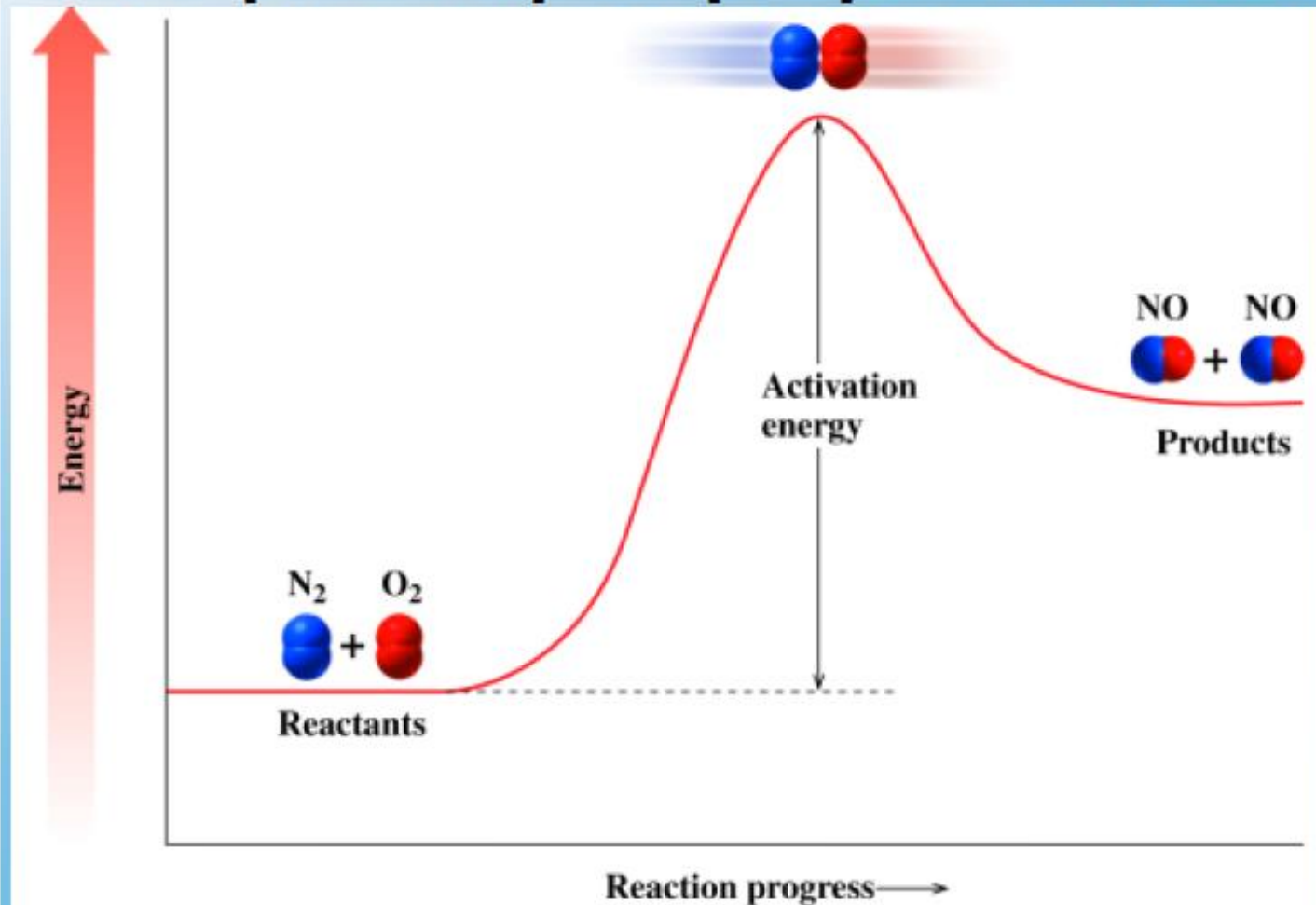
How to calculate composition and adiabatic flame temperature

$$K_p(T) = \Pi p_i^{a_i' - a_i} \qquad \Pi p_i^{(a_i' - a_i)} = \exp(-\Delta g^\circ / RT), \quad \Delta g^\circ = \Sigma(a_i' - a_i) g_i^\circ$$

Change in Free energy

Fundamental thermodynamic data will be used to obtain the free energy change for each of then equilibrium reactions and get the equilibrium constants and from them the composition and adiabatic flame temperature.

There is a NASA accessible online to give the results.
Just seek CEARUN and you can open the link and operate the code.

Energetics of Reactions

A measure of the energy release is the peak temperature of a stoichiometric fuel-air mixture.

Table 4.8: Flame temperature of some typical fuels

| Fuel	Oxidizer	Pressure MPa	Initial Temp K	Peak Temp K
Methane	Air	0.1	300	2210
Methane	Air	2.0	300	2270
Methane	Air	2.0	600	2500
Methane	Oxygen	0.1	300	3030
Methane	Oxygen	2.0	300	3460
Hydrogen	Air	0.1	300	2400
Hydrogen	Oxygen	0.1	300	3080
Acetylene	Air	0.1	300	2600
Acetylene	Oxygen	0.1	300	3400
Carbon monoxide	Air	0.1	300	2400
Butane	Air	0.1	300	2250
Kerosene	Air	0.1	300	2270
Producer gas	Air	0.1	300	1500
Wood (dry)	Air	0.1	300	1900
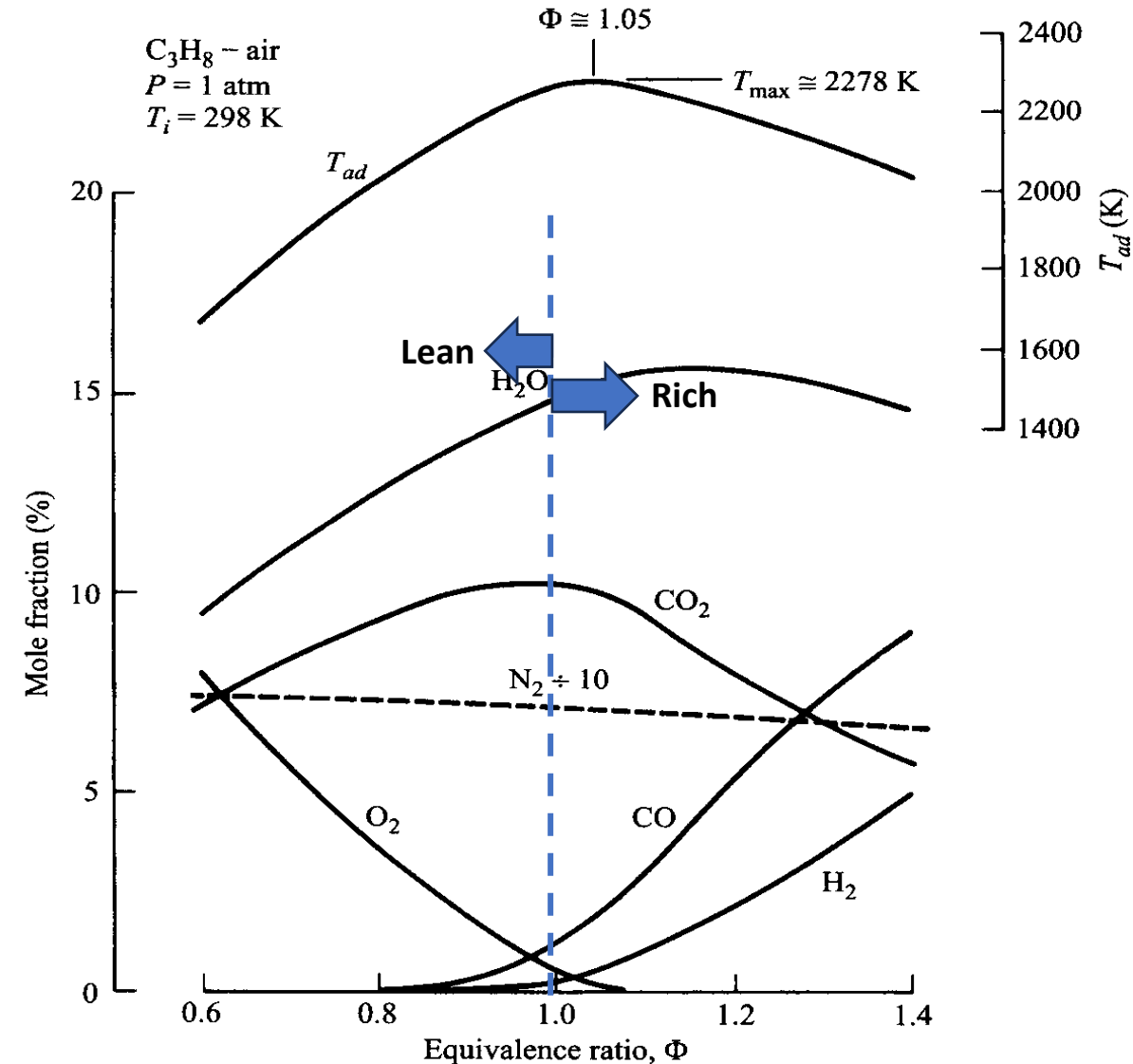
Composition and flame temperature - Typical HC -air

Kerosene: $CH_{1.942}$; $h_f(l) = -52.6\ kJ/mol$
Air: $O_{0.149}N_{1.56}C_{0.0003}$; $h_f(g) = -0.118\ kJ/mol$
Pressure: $= 0.1\ MPa$

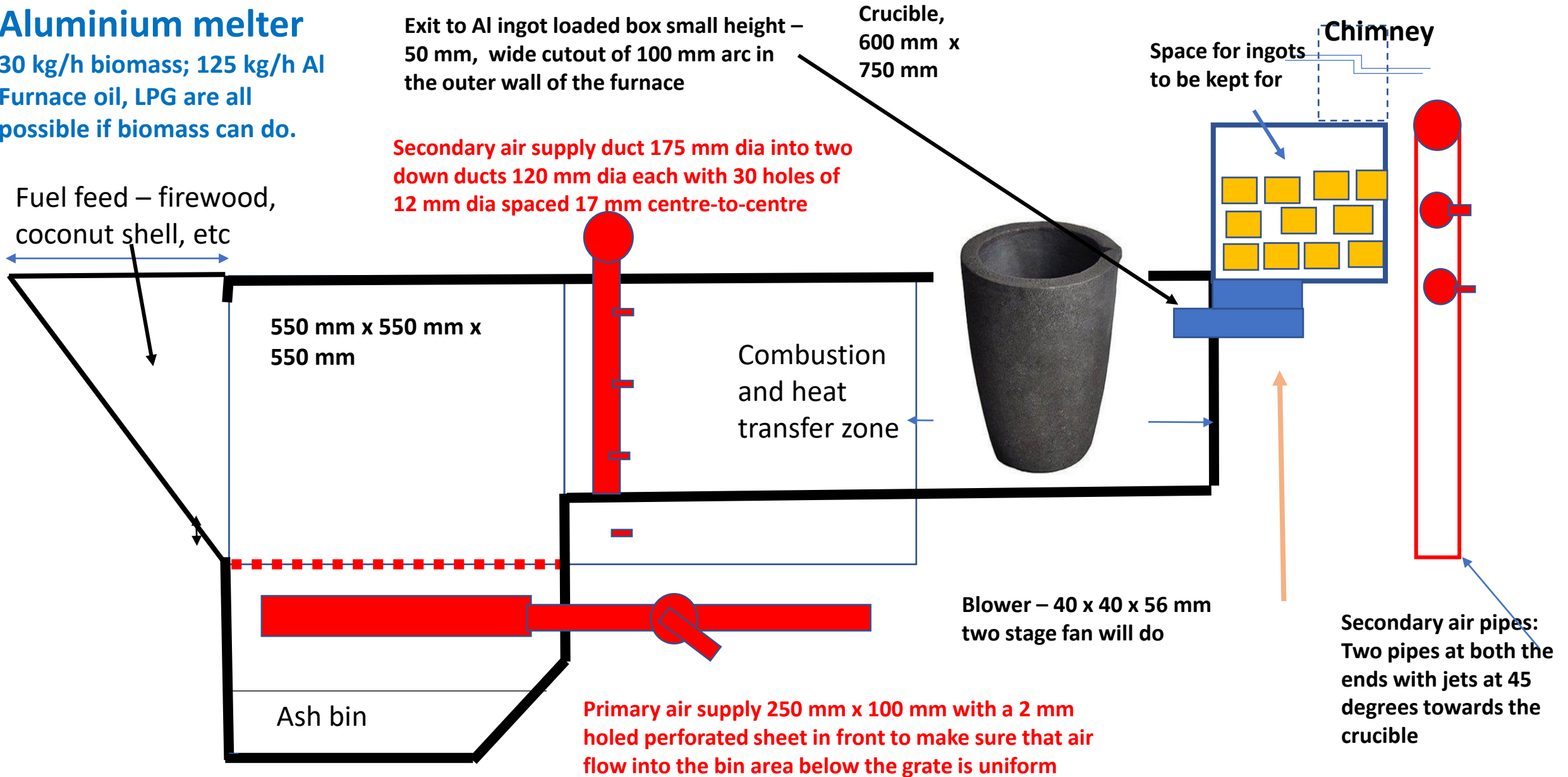|					
A/F	10.0	12.0	15.0	20.0	30.0
e.r	1.47	1.22	0.98	0.735	0.5
T, K	2007	2198	2266	1949	1493
X_i					
H_2O	0.117*	0.129	0.121	0.095	0.065
CO_2	0.058	0.088	0.117	0.098	0.067
CO	0.114	0.065	0.012	0.0004	-
N_2	0.650	0.69	0.724	0.741	0.755
H_2	0.0500	0.018	0.002	–	–
H	0.0004	0.0007	0.0004	–	–
OH	0.00009	0.0007	0.00316	0.001	–
O_2	–	–	0.0085	0.051	0.102
$\mathscr{M}$	26.5	27.7	28.7	28.9	28.9
c_p, (J/ mole K)	9.6	10.6	15.2	10.2	9.0
γ	1.26	1.24	1.17	1.24	1.28

*Mole fractions

How to raise the flame temperature beyond the normal adiabatic value
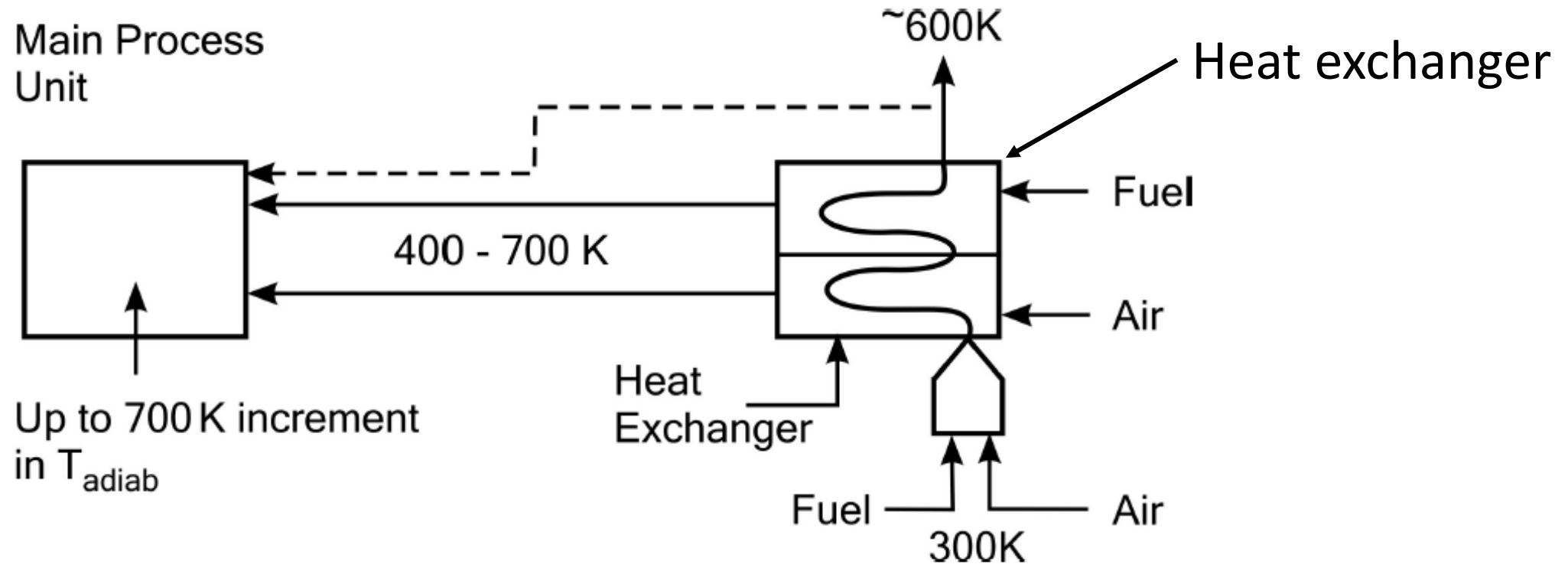
One can use arrangements to better use the exhaust heat...because heat extraction vis a solid is superior........

Aluminium melter

30 kg/h biomass; 125 kg/h Al Furnace oil, LPG are all possible if biomass can do.

Exit to Al ingot loaded box small height – 50 mm, wide cutout of 100 mm arc in the outer wall of the furnace

Crucible, 600 mm x 750 mm

Space for ingots to be kept for

Chimney

Fuel feed – firewood, coconut shell, etc

Secondary air supply duct 175 mm dia into two down ducts 120 mm dia each with 30 holes of 12 mm dia spaced 17 mm centre-to-centre

550 mm x 550 mm x 550 mm

Combustion and heat transfer zone

Blower – 40 x 40 x 56 mm two stage fan will do

Ash bin

Primary air supply 250 mm x 100 mm with a 2 mm holed perforated sheet in front to make sure that air flow into the bin area below the grate is uniform

Secondary air pipes: Two pipes at both the ends with jets at 45 degrees towards the crucible

Biomass –air combustion temperature ~ 1100°C, Temperature of Al melter ~ 750°C. Hence many fuels can be used

Summary

We have covered in this segment many aspects of

- Combustion related thermodynamics and thermo-chemistry briefly.

- Fuels – Liquid and Gaseous fuels and key characteristics

- Fuels – Stoichiometric and Equivalence Ratios and their relevance

- Heat release in Combustion Processes, Flame temperature and how to enhance the flame temperature

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