

**Ben Gurion University of the Negev  
Faculty of Engineering**

**Lectures for a postgraduate course**

***Chemistry of Combustion and Pollution from  
Vehicles***

**Given by Prof. G. St. Cholakov in the summer semester of 2002.**

**Sofia – Beer Sheva,**

**2002**

## SUMMARY

Combustion phenomena and control of pollution from vehicles are a major multidisciplinary field for implementation of the expert knowledge of the modern chemical, mechanical and environmental engineers. The course focuses on the combustion reactions of the fuel constituents and the formation of pollutants, the multiengineering approach towards vehicles and the modern methods for control of their pollution. It introduces the students to the philosophy and practice of the delicate balance between fundamental civilisation needs and preserving the environment, as embodied in the concept of sustainable development and to future environmentally compatible vehicles. The course builds upon previously studied engineering principles, and shows how they are implemented in the real world of protecting the environment. The horarium of the course is 32 hours.

**To whom the course is oriented:** To graduate students (MSc and PhD alike) in chemical engineering, mechanical engineering, environmental engineering, etc. who, upon completing their education want to face the challenges of creating cleaner fuels and vehicles, and preserving the environment at the plant, community, national and/or international level.

### Topics covered by the course:

**1. Introduction to combustion phenomena, fuels and lubricants.** Related terms. Classification of pollutants. Overview of the environmental impact of pollution from vehicles. Composition of engine fuels and lubricants.

4 h

**2. Combustion reactions of the fuel constituents.** The  $H_2 - O_2$  system and the radical chain mechanism. Experimental observations, fundamentals of Semenov's theory for ignition and combustion, and its developments. Thermodynamic and chemical interpretation of ignition phenomena. Ignition and combustion of the main hydrocarbon groups, and relevant oxygen containing compounds. Formation of the major pollutants ( $CO_x$ ,  $NO_x$ ,  $SO_x$ , polycyclic hydrocarbons and particulate matter) and specific pollutants.

12 h

**3. Environmental classification of heat engines and fuels.** Combustion phenomena in SI and CI engines. Chemical interpretation of detonation, deflagration, auto-ignition and knocking, typical pollutants. Energy balance of ignition and minimum required ignition energy. Combustion phenomena in jet engines. Steady flow combustion in a constant volume chamber, typical pollutants. Evaporative emissions from vehicles.

3 h

**4. Control of pollution from heat engines.** Engine modifications. Catalytic and non-catalytic devices for post combustion control. Engine fuels, lubricants and additives. Biodegradable alternatives. Experimental testing of emissions. Estimation with emission factors, specialised software, inspection and maintenance (I/M), on-board diagnostics.

10 h

**5. Zero emission vehicles of the future.** Principles of electric and solar propulsion, entropy engines. Hybrid vehicles, principles of fuel cell propulsion. The zero emission vehicles concept and the challenge for new fuels and lubricants.

3 h

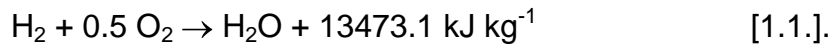
# LECTURES

## **Topic 1. Introduction to combustion phenomena, fuels and lubricants (4 h).**

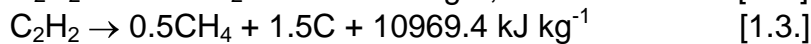
The purpose of this first topic is to outline the main processes taking place in combustion and the chemical compounds taking part directly in the formation of the pollution from vehicles and /or indirectly influencing that pollution. Combustion phenomena and environmental pollution are studied in one form or another in undergraduate and specialised postgraduate engineering courses. Because of that, the purpose of this topic in many cases will be only to activate old knowledge and/or to provide a different perspective to thermodynamic and chemical principles as applied in combustion science. References for further reading are recommended to students who want to brush up their knowledge with detailed derivations of formula, further explanations, experimental accessing of parameters, and solved illustrative examples.

### **1. Introduction to combustion phenomena.**

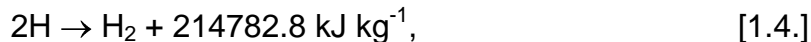
*Combustion* is a set of complex phenomena, involving predominantly interaction between substances, which are oxidised (fuels) and substances, which are reduced (oxidants), which results in the transformation of the potential chemical energy of the fuels into thermal and potential mechanical energy. The total energy in combustion is obtained predominantly from oxidation processes, i. e.



However, the dissociation energy of endothermic compounds, i. e.



and the association energy of some atoms into molecules, i. e.



may be also important contributions.

#### **1.1. Combustion and Ignition.**

Combustion is typically studied in order to understand the intrinsic mechanisms involved in controlled and uncontrolled combustion phenomena. Uncontrolled combustion is important because of fires and controlled combustion in heat installations provides around 90 % of the world energy support.

In order combustion to be realised, the fuel first has to be ignited. *Ignition* may be the result of the contact between the fuel and the oxidant in the absence of energy from an external source. In that case, it is usually called *selfignition*, or *spontaneous ignition*. A fuel-oxidiser mixture may also be ignited by an external energy source (i. e. a spark), and then the terms *forced ignition*, or if a spark is applied – *spark ignition* (SI), are used.

If ignition results in an instant release of energy in a small confined volume, it is usually described as *explosion*, and the other terms, relevant to ignition, i. e. *spontaneous explosion*, are also used.

As any state of the matter the combustion phenomena also require a particular combination of the values of the main state variables – temperature, pressure and concentration. Thus, the probability of a fuel – oxidiser mixture to be ignited is defined by *temperature, pressure and concentration ignition boundaries*, which are interrelated individual parameters for a given fuel-oxidiser combination.

Selfignition may be arrived at by a *thermal mechanism*, a *chain mechanism* or most often – a *thermal-chain mechanism*.

*Thermal selfignition* is the result of the release of heat from exothermic chemical reactions in a fuel - oxidiser mixture, for instance in a combustion chamber. If the amount of the released heat is greater than the amount of the heat lost through the walls of the chamber, at specific values of the parameters of state, selfignition will take place.

*Chain ignition* follows from the chain-radical mechanism of pre-ignition in which free radicals, atoms or energy enriched molecules are the active intermediate centers of chain branching, chain propagating and chain scissoring chemical reactions. If chain branching dominates over chain scissoring the number of reacted molecules within a short time period reaches the total number of fuel molecules, which is adequate to ignition.

*Chain-thermal ignition* is the most typical form of ignition at atmospheric or higher pressure, while a purely chain ignition may be observed only at low pressures and only for particular fuel – oxidiser systems. Chain thermal ignition will be further discussed in this course from thermodynamic and from chemical point of view. At low temperature and constant pressure pre-ignition reactions typically start by a chain mechanism, which is characterised by low effective activation energy and slow branching reactions. As the chain pre-ignition processes are developing, at some point the relatively high effective activation energy necessary for the start of the fast highly exothermic reactions is reached, and very soon the system ignites by a typical thermal mechanism.

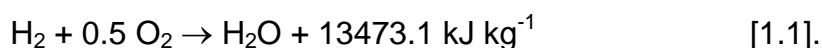
## 1.2. Combustion fundamentals.

### 1.2. a. Related chemical terms and definitions.

For many years combustion has been studied as a fluid mechanics phenomenon, which includes global heat release by chemical reaction. The heat release has often been described by thermodynamics and simplified by assuming infinitely fast chemical reactions. This approach is not sufficient for treating transition processes like ignition and quenching, but also for understanding pollutant formation.

Combustion is a complex phenomenon. Its understanding, among other things, requires knowledge of combustion specific topics of chemistry (oxidation of fuel species, chemical reactions, which lead to the formation of the major pollutants, multiple reaction mechanisms and their simplification, etc.). These should be applied together with combustion specific knowledge of fluid mechanics (turbulent flow with density change by heat release, potential generation of turbulence by heat release, etc.). Since, this course is focused on the chemistry of combustion and formation of pollutants hereunder some fundamental principles relevant to combustion chemistry will be reviewed. Combustion related topics of fluid mechanics, general thermodynamics, etc., which are typically very well covered in undergraduate courses, will only be outlined.

A *chemical reaction* is the exchange or rearrangement of atoms between colliding molecules, i. e. in the chemical reaction



the atoms are conserved while the reactant molecules are transformed into product molecules with simultaneous release of heat. The primary interest of combustion engineering is usually concentrated on the amount of heat, which would be released in a chemical reaction. Alternatively, environmental engineering and environmental combustion chemistry are concerned mainly with the properties of the reaction products, which may pollute the environment and how they can be monitored and controlled – within and/or out of the combustion process. Typical combustion related molecules are presented in Table 1.1.

Table 1.1. Typical combustion related molecules.



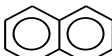
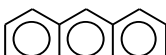
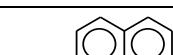


Chemical group name	Specific example	IUPAC name	Common name	General formula	Specific features
<i>n</i> -Alkanes	CH <sub>3</sub> -CH <sub>3</sub>	Ethane	Ethane	C <sub>n</sub> H <sub>2n+2</sub> RH	C-H bonds C-C bonds
<i>iso</i> -Alkanes*	CH(CH <sub>3</sub> ) <sub>3</sub>	Trimethyl methane	Isobutane	C <sub>4</sub> H <sub>10</sub> As above	As above
Alkenes	CH <sub>2</sub> =CH <sub>2</sub>	Ethene	Ethylene	C <sub>n</sub> H <sub>2n</sub> RCH=CH <sub>2</sub> RCH=CHR <sub>1</sub> (R) <sub>2</sub> C=CHR <sub>1</sub> (R) <sub>2</sub> C=C(R <sub>1</sub> ) <sub>2</sub>	>C=C<
Alkynes	HC≡CH	Ethyne	Acetylene	C <sub>n</sub> H <sub>2n-2</sub> RC≡CH RC≡CR <sub>1</sub>	-C≡C-
Cyclo alkanes		Cyclohexane	Cyclohexane	C <sub>n</sub> H <sub>2n</sub> NfH	Cycloalkane ring
Monoarenes		Benzene	Benzene	C <sub>n</sub> H <sub>n</sub> ArH, ArR	Arene ring
Bicyclic arenes		Naphthalene	Naphthalene	C <sub>10</sub> H <sub>8</sub> C <sub>n</sub> H <sub>n-2</sub>	Two fused arene rings
Tricyclic arenes		Anthracene	Anthracene	C <sub>14</sub> H <sub>10</sub> C <sub>n</sub> H <sub>n-4</sub>	Three fused arene rings
Polycyclic arenes, i.e.		1,2-[a]-benzopyrene	Benzo pyrene	C <sub>20</sub> H <sub>12</sub> C <sub>n</sub> H <sub>n-8</sub>	Five fused arene rings
Hybrid hydro carbons, i. e.		1,2,3,4-tetrahydronaphthalene	Tetrahydro naphthalene	C <sub>10</sub> H <sub>12</sub> C <sub>n</sub> H <sub>n+2</sub>	Arene, cyclohexane fused rings
Haloalkanes	CH <sub>3</sub> CH <sub>2</sub> Cl	Chloro ethane	Ethylchloride	RCI RX	C-X
Alcohols	CH <sub>3</sub> CH <sub>2</sub> OH	Ethanol	Ethyl alcohol	ROH	C-OH
Ethers	CH <sub>3</sub> OCH <sub>3</sub>	Methoxy methane	Methyl ether	C <sub>2</sub> H <sub>6</sub> O ROR	C-O-C
Amines	CH <sub>3</sub> NH <sub>2</sub>	Methylamine	Methylamine	RNH <sub>2</sub> , R <sub>2</sub> NH R <sub>3</sub> N	C-N
Aldehydes	CH <sub>3</sub> C(H)=O	Methanal	Formaldehyde	RC(H)=O	-C(H)=O
Ketones	CH <sub>3</sub> C(O)CH <sub>3</sub>	Propanone	Acetone	RC(O)CR <sub>1</sub>	>C=O
Carboxylic acids	CH <sub>3</sub> C(O)OH	Ethanoic acid	Acetic acid	CH <sub>3</sub> COOH RC(O)OH	-C(O)-OH
Thiols	CH <sub>3</sub> SH	Methylthiol	Methyl mercaptan	RSH	>CH-SH

Table 1.1. Typical combustion related molecules (continued).

Chemical group name	Specific example	IUPAC name	Common name	General formula	Specific features
Dialkyl sulphides	C <sub>2</sub> H <sub>5</sub> -S-C <sub>2</sub> H <sub>5</sub>	Diethyl sulphide	Ethyl sulphide	C <sub>4</sub> H <sub>10</sub> S RSR <sub>1</sub>	-CH <sub>2</sub> -S-CH <sub>2</sub> -
Dialkyl disulphides	C <sub>4</sub> H <sub>9</sub> -S-S-C <sub>4</sub> H <sub>9</sub>	Dibutyl disulphide	-	C <sub>8</sub> H <sub>18</sub> S <sub>2</sub> RSSR <sub>1</sub>	-CH <sub>2</sub> -S-S-CH <sub>2</sub> -
Alkyl benzo thiophenes	-	Benzo thiophene	-	C <sub>8</sub> H <sub>6</sub> S R-C <sub>8</sub> H <sub>5</sub> S	Fused Ar and thiophene rings
Alkyl pyridines		Pyridine	Alkyl pyridine	C <sub>5</sub> H <sub>5</sub> N R-C <sub>5</sub> H <sub>4</sub> N	Arene ring with N
Alkylquinolines	-	Quinoline	-	C <sub>9</sub> H <sub>7</sub> N R-C <sub>9</sub> H <sub>6</sub> N	Naphthalene with N

\* - Positional isomerism, typical for all organic compounds with more than 3 C atoms. Different forms of isomerism are described in detail in Organic Chemistry textbooks.

The amount of substance in chemistry is quantified usually as *number of moles*, ( $n$ , SI unit: kmol), *mass* ( $m$ , SI unit: kg) or *volume* ( $v$ , SI unit: m<sup>3</sup>). 1 mol of a compound contains – Avogadro's number - 6.02 10<sup>23</sup> particles (atoms, molecules). The molar mass of *species* is the mass of 1 mol, i. e. 1 kmol of CH<sub>4</sub> is 16 kg mol<sup>-1</sup>. Concentrations can be expressed as mole fractions,  $x_i = n_i / \sum n_i$ , mass fractions,  $m_i = m_i / \sum m_i$  or volume fractions,  $v_i = v_i / \sum v_i$ . Densities are intensive properties (do not depend on the size of the system), and are defined as the ratio of the corresponding extensive properties (which depend on the size of the system) and the system volume, i. e.

$$\text{Mass density (density): } \rho = m/V \text{ (i. e., in kg m}^{-3}\text{)} \quad [1.5.]$$

$$\text{Molar density (molar concentration): } c = n/V \text{ (i. e., in mol m}^{-3}\text{)} \quad (1.6.)$$

Molar concentrations are usually denoted in chemistry by the species symbol in square brackets (e. g.,  $c_{\text{H}_2\text{O}} = [\text{H}_2\text{O}]$ ).

For gases and gas mixtures an *equation of state* relates temperature, pressure and density of the gas. For many cases in combustion the *ideal gas equation of state* can be applied with allowable precision:

$$pV = nRT \quad (1.7.),$$

where  $p$  is pressure,  $V$  – volume,  $T$  – temperature and  $R$  is the *universal gas constant* (if all quantities are in SI units,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). For combustion temperatures near or less than the critical temperatures or combustion pressures near or above the critical pressures of the involved species, the concentration or density is not adequately predicted and the system is better approximated as a real gas. *Real gas equations of state* are applied in that case. An example of these is the van der Waals real gas equation of state.

### 1.2. b. Classification of combustion systems and basic flame types.

In combustion fuel and oxidiser are mixed and burnt. They may be *premixed* and ignited and burnt later or igniting, combustion and mixing occur simultaneously in *non premixed* fuel and oxidiser. Each of these combustion categories can be further subdivided, depending on the type of the fluid flow as *laminar* or *turbulent* (Table 1.2.).

Table 1.2.Types of combustion.

Mixture	Fluid flow	Examples
Premixed	Turbulent	SI gasoline engine, Low NOx stationary gas turbine
	Laminar	Flat flame, Bunsen flame (fuel lean)
Non premixed	Turbulent	Aircraft turbine Diesel engine H2/O2 rocket engine
	Laminar	Wood fire Radiant burners

In *laminar premixed flames*, the mixture is premixed and the fluid flow is laminar. A premixed flame is said to be *stoichiometric*, if fuel and oxidiser are consumed completely. If fuel is in excess, it is not completely consumed, and the system is called *fuel-rich*. If oxidiser is in excess, the system is *fuel-lean*, e. g.



Often the combustion reactions are written for 1 mol of fuel, e. g.



The fuel mole fraction,  $x_{fuel, stoich}$ , in that case is easily calculated as

$$x_{fuel, stoich} = \frac{1}{1 + \nu} \quad [1.12.]$$

from the number of moles of the oxidiser,  $\nu$ . For reaction [1.11.],  $\nu = 0.5$ ,  $x_{fuel, stoich} = 2/3$ .

If air is the oxidiser, when calculating stoichiometric quantities, the fact that dry air contains about 21 % oxygen (78 % nitrogen, 1 % noble gases) has to be taken into account.

Pre-mixtures of fuel and air (nitrogen has to be added) are characterised by the air equivalence ratio (air number),  $\lambda$

$$\lambda = (x_{air}/x_{fuel}) / (x_{air,stoich}/x_{fuel,stoich}) \quad (1.13.)$$

or by the reciprocal value, the fuel equivalence ratio,  $\phi$  ( $\phi = 1/\lambda$ ). Accordingly, premixed combustion processes are defined as:

rich combustion	$\phi > 1, \lambda < 1,$
stoichiometric combustion	$\phi = 1, \lambda = 1,$ and
lean combustion	$\phi < 1, \lambda > 1.$

In *turbulent premixed flames* the flame fronts burn and propagate into a turbulent fluid flow. If the turbulence is not too high, curved laminar premixed flame fronts are formed and the turbulent flame can be viewed as an ensemble of many laminar premixed flames (*flamelet concept*).

The advantage of premixed combustion is the greater possibility for control of combustion. By premixing at lean conditions, high temperature can be avoided and the production of thermal NO<sub>x</sub> diminished.

*Laminar non premixed flames* include more complex chemistry than the premixed ones, because the equivalence ratio can not be sustained. The flow is laminar, fuel and oxidiser are mixed, while burning and rich combustion occurs at the fuel side, and lean – on the oxidiser side.

*Turbulent non premixed flames* burn in turbulence, and at low turbulence intensities the flamelet concept may be applied.

*Hybrid premixed – non-premixed laminar flames* are typical for home and water heating devices burning natural gas.

## 1.2. c. Thermodynamics of combustion processes.

### Thermodynamic presentation of chemical equilibrium.

The *three fundamental laws of thermodynamics* have wide spread application in understanding and modelling combustion processes. For instance, they are used to obtain the thermodynamic properties of the species in the combustion process – e. g., enthalpy (H), entropy (S) and heat capacities as a function of temperature and pressure.

If a chemical system is at equilibrium, e. g.



then a combination of the 1<sup>st</sup> and the 2<sup>nd</sup> laws of thermodynamics gives the equilibrium condition

$$dU + pdV - TdS = 0 \quad [1.15.]$$

or

$$(dU)_{V,S} = 0 \quad [1.16.]$$

where **U** is the internal energy of the system, **p** is pressure, **V** – volume, **T** – temperature and **S** – the entropy, and the variables shown as subscripts in [1.16.] are held constant.

The *Le Chatelier principle* is used for characterising the influence of changes in reversible reactions. It follows from the above presentations ([1.14.] – [1.16.]), and states that addition of an infinitesimal quantity of a reagent to the left side of the reaction shifts the equilibrium to the right hand side, while taking away an infinitesimal quantity of a reagent, shifts the equilibrium to the left hand side.

The equilibrium condition [1.16.] is not convenient for practice, because, S = const is difficult to achieve (entropy can not be measured directly).



A more convenient presentation of the equilibrium state

$$d(U - TS) + pdV + SdT = 0 \quad [1.17.]$$

employs the *free Helmholtz energy*,  $A$  ( $A = U - TS$ ) to define equilibrium as

$$(dA)_{V,T} = 0 \quad [1.18.]$$

and

$$d(U - TS + pV) - Vdp + SdT = 0 \quad [1.19.]$$

introduces the *free enthalpy or Gibbs energy*,  $G$  ( $G = A + pV = H - TS$ ) and provides another useful formulation of *chemical equilibrium*

$$(dG)_{p,T} = 0 \quad [1.20.]$$

The chemical potential  $\mu_i$  of a compound "i" in a mixture is defined as the partial derivative of the Gibbs energy with respect to the amount of that substance (moles,  $n_i$ ):

$$\mu_i = \left( \frac{dG}{dn_i} \right)_{p,T,n_j} \quad [1.21.]$$

This expression for the chemical potential can be used for derivation of two very important thermodynamic relations for *the equilibrium constants* of the chemical reaction, which are introduced in the form

$$K_p = \prod_i \left( \frac{p_i}{p^0} \right)^{\nu_i} \quad \text{and} \quad K_c = \prod_i \left( \frac{c_i}{c^0} \right)^{\nu_i} \quad [1.22.]$$

where  $p$  and  $c$  are pressure and concentration,  $\nu_i$  is the stoichiometric number of moles for compound  $i$ , and the index "0" denotes a standard state. A derivation following from [1.21.] and [1.22.], presented in detail in ref. 1, leads to

$$K_p = \exp(-\Delta_R \bar{G}^0 / RT) \quad \text{and} \quad K_c = \exp(-\Delta_R \bar{A}^0 / RT), \dots [1.22'.]$$

where  $\Delta_R$  stands for summation of the products of the molar concentrations and standard functions of species,  $\bar{G}^0$  is the Gibbs energy at standard pressure,  $\bar{A}^0$  = free energy corresponding to  $\bar{G}$ . From [1.22'.] the calculation of the equilibrium constants (and gas composition) from thermodynamic data is possible.

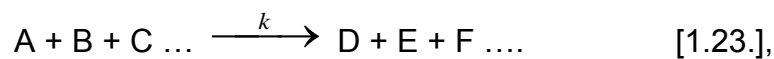
#### Practical determination of the equilibrium composition in gases.

The *practical determination of the equilibrium composition* in gases involves first the determination of the number of different compounds in the reaction system,  $S$  (to be distinguished from the same symbol, when used for entropy). Each mixture of  $S$  compounds has a number of **K components** (e. g., chemical elements) which are conserved and not changed by chemical reactions. The set of chemical reactions taking place in the system is described by  $R = S - K$  linearly independent equations. For a given temperature (i. e., the adiabatic flame temperature,  $T_b$ ) and total pressure, a system of  $S$  linear equations, looking for  $S$  partial pressures, can be derived from the equilibrium of the  $R$  chemical equations,  $K - 1$  constant ratios between the components and the summation of partial pressures. The solution of this system provides the values of the equilibrium partial pressures (concentrations) of the species for the given conditions.

*Transport phenomena* in combustion include several transport processes. Diffusion is the mass transport caused by concentration gradients, viscosity is the momentum transport resulting from velocity gradients, heat conduction is transport of energy, caused by temperature gradients. These phenomena are generally termed “molecular transport processes”, since the respective physical properties are transported by the movement of the molecules in the gas. Other phenomena like mass transport, caused by temperature gradients (thermal diffusion) and the transport of small amounts of energy by concentration gradients are also typical.

#### 1.2.d. Chemical kinetics in combustion processes.

A chemical reaction can be generalised by the equation



where **A**, **B**, **C**, ... are the different initial species participating in the reaction, **D + E + F ...** are the products, **k** is the rate coefficient of the reaction. The reaction rate for the consumption of species **A** is given by

$$\frac{d[A]}{dt} = -k [A]^a [B]^b [C]^c \dots \quad [1.24.]$$

where the exponents are the *reaction orders for the respective species*, and the sum of the exponents is the *overall reaction order*.

In combustion frequently some species are in excess and their concentrations change negligibly. If species **A** is consumed effectively, and the concentrations of the rest of the species can be assumed constant, an effective rate coefficient **k<sub>exp</sub>** can be defined from

$$k_{\text{exp}} = k [B]^b [C]^c \dots, ([B]^b [C]^c \dots \approx \text{const}) \quad [1.25.] \text{ and}$$

$$\frac{d[A]}{dt} \approx k_{\text{exp}} [A]^a \quad [1.26.]$$

The temporal change of the concentration of species **A** can be calculated by integration of [1.26.], e. g. for first order reactions (a = 1) integration gives

$$\ln \frac{[A]_t}{[A]_o} = -k_{\text{exp}} (t - t_o) \quad [1.27.]$$

where **[A]<sub>o</sub>** and **[A]<sub>t</sub>** are the concentrations of species **A** at time **t<sub>o</sub>** and **t**, respectively. The effective rate coefficient **k<sub>exp</sub>** can be determined graphically if the concentrations **[A]<sub>o</sub>** and **[A]<sub>t</sub>** are measured.

For a *reversible reaction in chemical equilibrium*

$$k^{(f)} [A]^a [B]^b [C]^c \dots = + k^{(r)} [D]^d [E]^e [F]^f \dots \quad [1.28]$$

and

$$\frac{[D]^d [E]^e [F]^f \dots}{[A]^a [B]^b [C]^c \dots} = \frac{k^{(f)}}{k^{(r)}} \quad [1.29]$$

$$K_c = \frac{k^{(f)}}{k^{(r)}} \quad [1.30.]$$

where  $k^{(f)}$  and  $k^{(r)}$  are the rate coefficients of the forward and the reverse reactions and  $K_c$  is the equilibrium constant expressed with concentrations.

#### Elementary and net reactions.

An *elementary reaction* is a reaction, which on a molecular level occurs exactly as described by the reaction equation, e. g.



What [1.31.] says is that due to the molecular motion in the gas, hydroxyl radicals collide with hydrogen molecules. If the collision energy is low the molecules bounce apart, but in reactive collisions, the left hand side molecules produce  $\text{H}_2\text{O}$  and  $\text{H}$ . However, the reaction



is not an elementary reaction, but water is produced by a complex sequence of 38 elementary reversible reactions, involving intermediates like  $\text{H}$ ,  $\text{O}$  and  $\text{OH}$ . Reactions like [1.32.] are called *net reactions* or *overall reactions*. Net reactions have very complicated rate laws: the reaction orders ( $a$ ,  $b$ ,  $c$ ...) are usually not integers, can be negative, depend on time and reaction conditions. Because of all that, they are usually assessed through elementary reactions.

Using elementary reactions has the advantage that the reaction order of an elementary reaction is always constant (independent of time and experimental conditions) and can be determined easily. The key point is to determine the *molecularity of the reaction* – the number of species that form the reaction complex in the transition state between reactants and products. In practice, reaction molecularity can take three possible values.

#### Determination of molecularity.

*Unimolecular reactions* describe rearrangement or dissociation of a molecule, have first order time behaviour and if the initial concentration is doubled, the reaction rate is also doubled



*Bimolecular reactions* are most typical in combustion

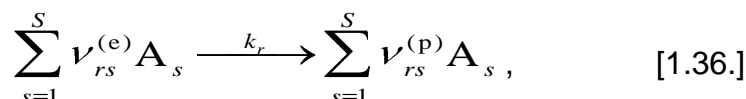


They have always a second order rate law and if the initial concentration of each reaction partner is doubled, the reaction rate is quadrupled. For gas phase reactions doubling the pressure increases four times the reaction rate.

*Trimolecular reactions* are usually recombination reactions and obey third order rate law, e. g.



In general for elementary reactions, molecularity equals the reaction order. If the equation of an elementary reaction,  $r$ , is given by



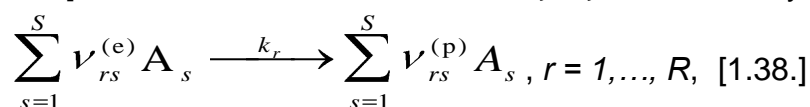
then the rate law for the formation of the species  $i$  in the reaction  $r$  is

$$\left( \frac{dc_i}{dt} \right)_{chem,r} = k_r (\nu_{ri}^{(p)} - (\nu_{ri}^{(e)})) \prod_{s=1}^S c_s^{\nu_{ri}^{(e)}}, \quad [1.37.]$$

where  $\nu_{rs}^{(e)}$  and  $\nu_{rs}^{(p)}$  are the stoichiometric coefficients of the reactants and the products, respectively,  $S$  is the number of species, as defined before,  $k_r$  is the reaction rate coefficient, and  $c_s$  are the concentrations of the  $S$  different species.

If the *reaction mechanism* includes all possible elementary reactions in the system (*complete mechanism*), which is rarely the case, it is valid for all conditions.

A reaction mechanism involving  $S$  species in  $R$  monomolecular reactions can be represented by [1.36.], but it has to be written for  $r = 1, \dots, R$  elementary reactions, i. e.



The rate of formation of a species  $i$  is then given by [1.37.] but  $r$  is not a constant, and the summation is done over the rate equations of all reactions

$$\left( \frac{dc_i}{dt} \right)_{chem} = k_r (\nu_{ri}^{(p)} - (\nu_{ri}^{(e)})) \prod_{s=1}^S c_s^{\nu_{ri}^{(e)}}, \quad i = 1, \dots, S \text{ and } r = 1, \dots, R \quad [1.39.]$$

#### Temperature and pressure dependence of rate coefficients.

The *temperature dependence of rate coefficients* is usually described in an *Arrhenius form*

$$k = A' \exp \left( -\frac{E'_a}{RT} \right), \quad [1.40.]$$

or if the relatively small temperature dependence of the pre-exponential factor  $A'$  is significant, eq. [1.41.] in which  $b$  is an empirical parameter, is preferred

$$k = A T^b \exp \left( -\frac{E_a}{RT} \right). \quad [1.41.]$$

The *activation energy*  $E_a$  is the energy barrier of the reaction. In dissociation reactions the activation energy is approximately the energy of the bond being split, but in

general, if new bonds are formed along the breaking of old bonds,  $E_a$  can be much smaller than the bond splitting energy.

For very small (vanishing) activation energies, or for very high temperatures the exponential term in the Arrhenius equation becomes close to zero, and *the pre-exponential factor* determines the rate coefficient. The physical meaning of the pre-exponential factor is different for mono-, bi- and trimolecular reactions. In monomolecular reactions it is related to the mean lifetime of an activated molecule and is approximately twice the frequency of the bond being split for dissociation ( $A' \approx 10^{14} - 10^{15} \text{ s}^{-1}$ ). For bimolecular reactions  $A'$  corresponds to a product of reaction rate and probability of reaction. The calculated from the kinetic theory of gases values of  $A'$  are in the range of  $10^{13}$  to  $10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

Trimolecular reactions are usually presented with sequential bimolecular reactions, which have a wide range of pre-exponential factors and small or negative activation energies.

*The apparent pressure dependence of rate coefficients* is considered usually for dissociation (unimolecular) and recombination (trimolecular) reactions. Two extreme cases – for low and for high pressures are typically distinguished. Often parameters of pressure dependent reactions are fitted in Arrhenius type equations.

#### Surface reactions.

*Surface reactions* are important in combustion, e. g. in wall recombination, soot and coke formation and oxidation, catalytic ignition and combustion, etc. A main feature of surface reactions (as compared to gas phase reactions) is the participation of surface sites and adsorbed species into the description of reaction rates. *Surface concentrations of species* (in  $\text{mol cm}^{-2}$ ) depend on surface and species type, concentration of available surface sites, thermodynamic parameters, etc. There may be more than one rate coefficient for the same material, since surface sites with different adsorption energies are treated as different species. An example of  $\text{H}_2$  surface oxidation reaction mechanism on Pt is illustrated in Fig. 1.1.

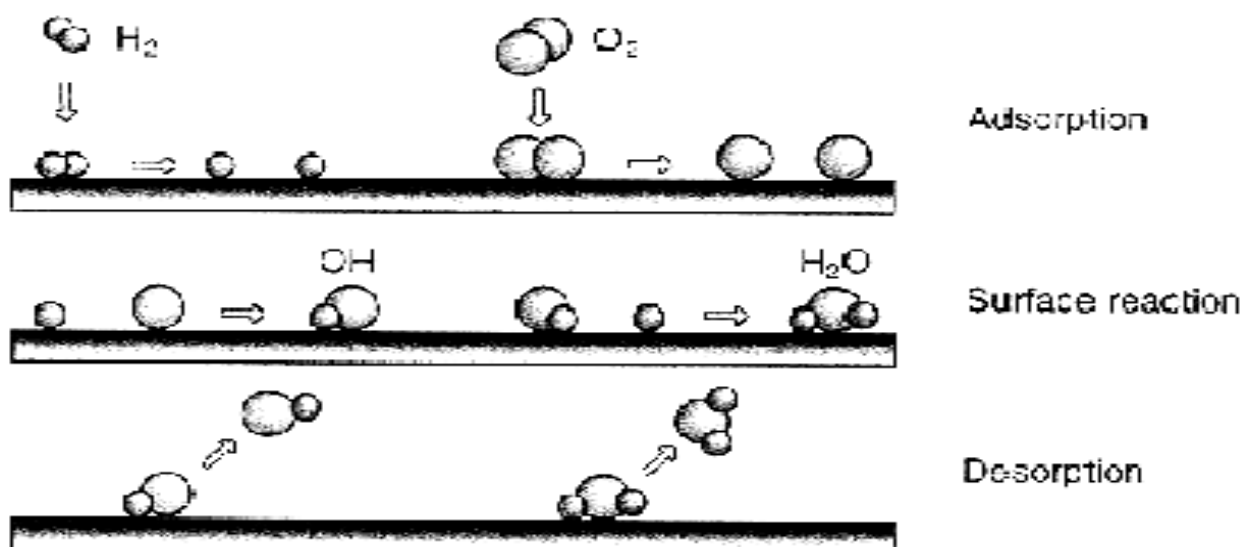


Figure 1.1. Surface reaction mechanism of hydrogen oxidation (schematic).

(Warnatz, J. Combustion: physical and chemical fundamentals, modeling and simulation, experiments, pollutant formation, 2nd ed., Berlin, - New York, Springer, 2001.)

The mechanism, shown in Fig. 1.1. consists of *dissociative adsorption* of  $\text{H}_2$  and  $\text{O}_2$  molecules, collision of the adsorbed atoms without detaching from the surface, formation

of OH and then H<sub>2</sub>O in surface reactions, and *desorption* of the H<sub>2</sub>O molecules into the gas phase.

The adsorption rate,  $k_{\text{ads}}$  is

$$k_{\text{ads}} = S \cdot k_{\text{max}}, \quad [1.42.], \quad \text{and}$$

$$k_{\text{max}} = c \cdot \bar{v} / 4 \quad [1.43.]$$

where  $S$  is the sticking coefficient – the probability that a molecule sticks, while colliding on the surface;  $k_{\text{max}}$  is the maximum adsorption rate, calculated from simple hard sphere gas kinetics,  $c$  is concentration,  $\bar{v}$  - average velocity.

The reaction rate for the surface reaction between sticking molecules, hopping on the surface, and having surface particle density  $[n]$  each,  $k_{\text{sr}}$  is

$$k_{\text{sr}} = A_{\text{surf}} e^{(-E/kT)} \cdot [n] \cdot [n] \quad [1.44.]$$

where the product of the pre-exponential factor,  $A_{\text{surf}}$ , and the particle densities gives the total number of collisions, and the exponent – the probability for collisions with sufficient energy for reaction.

The desorption rate of molecules having sufficient energy to overcome the bond strength between the surface and the adsorbed species,  $k_{\text{des}}$  is

$$k_{\text{des}} = A_{\text{des}} \exp(-E_{\text{des}}/kT) \quad [1.45.]$$

### Simplification of reaction mechanisms.

The possibility for *simplification of reaction mechanisms* follows from the fact that irrelevant of the specific problems, each mechanism has characteristic properties. Some reactions are very fast, others – comparatively slow, while physical phenomena are within a narrow time scale, etc., and thus certain steps may be ignored for particular tasks and conditions. Fig. 1.2. illustrates typical time scales of the main combustion phenomena.

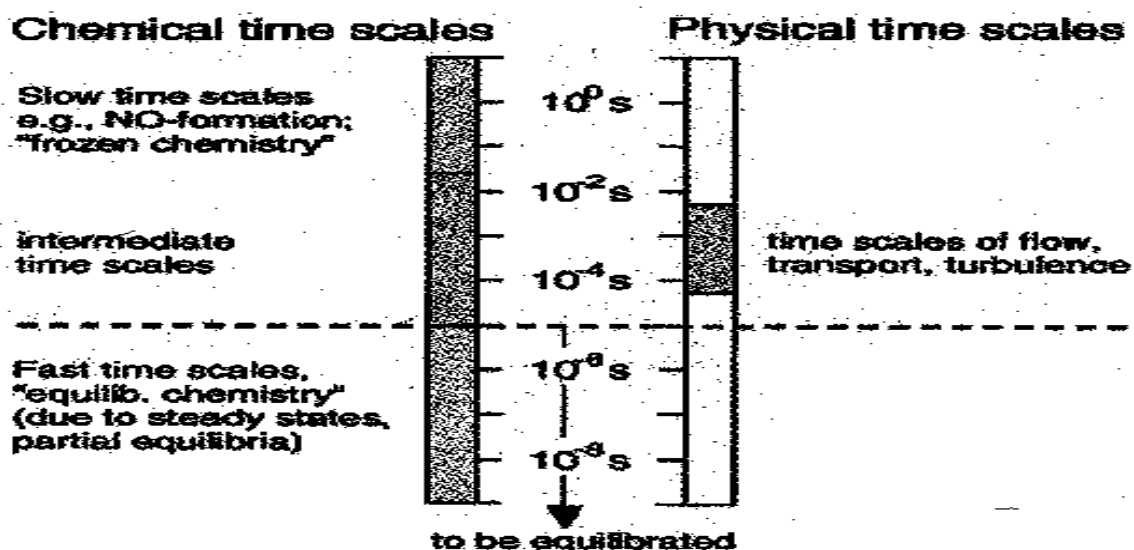
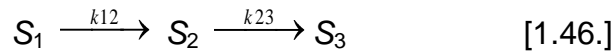


Figure 1.2. Classification of time scales in a chemically reactive flow.

(Warnatz, J. Combustion: physical and chemical fundamentals, modeling and simulation, experiments, pollutant formation, 2nd ed., Berlin - New York, Springer, 2001.)

Two typical simplification approaches are the concepts of *quasi-steady states* and *partial equilibria*. Both simplifications involve time behaviour and the existing of reactions, which are much faster than others.

If a simple reaction chain of two elementary steps is considered, e. g.



The reaction mechanism of [1.46.] may be simplified by steady state approximation if  $S_2$  can be assumed to be a very reactive species and its rates of formation and consumption are approximately equal. The quasi-state assumption gives

$$\frac{d[S_2]}{dt} = k_{12} [S_1] - k_{23} [S_2] \approx 0 \quad [1.47.]$$

and

$$[S_1] = [S_1]_0 \exp(-k_{12} t) \quad [1.48.]$$

The rate of formation of  $S_3$  can be estimated also only from the initial concentration of  $S_1$  and the rate coefficient  $k_{12}$ , i. e.

$$[S_3] = [S_1]_0 [1 - \exp(-k_{12} t)] \quad [1.49.]$$

The quasi-steady state approximation uses the existence of fast forward intermediate elementary reactions. *The partial equilibrium approximation* is based on the existence of forward and backward elementary reactions, which are so fast that allow for the assumption that the rates of the forward and the backward reactions constituting the reaction mechanism are approximately equal and the system may be considered in partial equilibrium.

Complete reaction mechanisms for hydrocarbon fuels may consist of thousands of elementary reactions. Several methods can be used to eliminate negligible reactions for a particular task. *Sensitivity analyses* identify the limiting reaction steps, while *reaction flow analyses* determine characteristic reaction paths. *Eigenvector analyses* determine the characteristic time scales and directions of the chemical reactions.

Thus, by a combination of different methods of analysis, unimportant information can be identified and neglected, and a simplified mechanism can be generated. Fig. 1.3. illustrates the mechanism of ignition and combustion of methane, in which more significant pathways are given with thicker arrows.

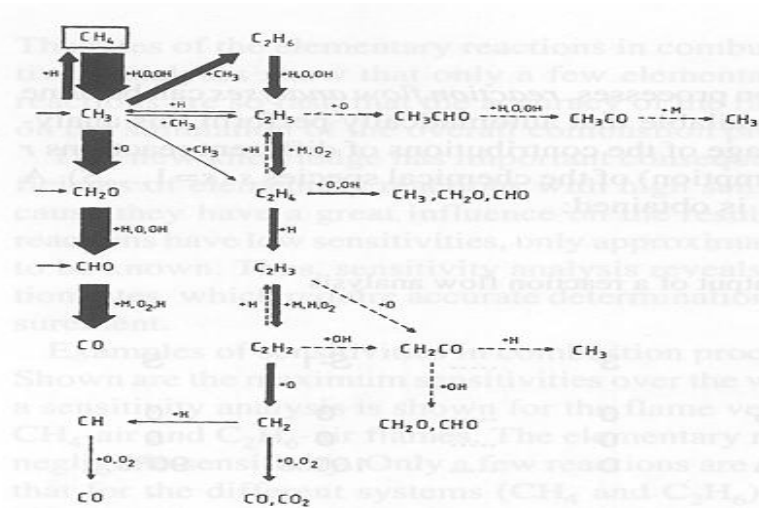


Fig. 1.3. Ignition and combustion of methane. (Warnatz, J. Combustion: physical and chemical fundamentals, modeling and simulation, experiments, pollutant formation, 2nd ed., Berlin - New York, Springer, 2001.)

## 2. Classification of polluting sources and pollutants.

*Environmental pollution* is a combined result of *natural and man-made (anthropogenic) contributions*. The natural pollutants result from the processes in the biosphere related to the bacterial transformations of matter, volcanic and geothermal activity, photosynthesis, the life of animals, fires, etc. The anthropogenic contribution is mainly the result of man's activity for production and use of energy, exploration for and production of raw materials, the industrial transformation of raw materials into useful products, and so on:

$$\text{Total Anthrop. Emissions} = \text{Population} \sum (\text{Activity/person}) * (\text{Spec. Emissions/Activity})$$

So, in the case of vehicles the total amount of emissions (i. e. for Beer Sheva) is a function of the total number of population involved, the type and the specific use of vehicles (e. g. cars, helicopters, etc.) in the region.

*Primary sources* of emissions are those, which generate directly particular pollutant flows. If pollutants from primary sources react (i. e. in the atmosphere) a *secondary source* producing *secondary pollutants* is created. Sources of *emissions* of pollutants created from outside the region may also be classified as secondary sources.

Air pollution is usually treated in terms of the creation, monitoring and control, etc. of the so called *major pollutants* - CO<sub>x</sub>, SO<sub>x</sub>, NO<sub>x</sub>, particulates, hydrocarbons, and - in connection with the pollution from gasoline engines - lead compounds. Other pollutants – *specific pollutants*, such as halogenated hydrocarbons, other metal aerosols, aldehydes, ketones and carboxylic acids, etc., are discussed in specialized studies.

It has to be underlined, however, that the overall environmental impact of different pollutants has to be estimated on the basis of their "*aggressiveness*" towards the environmental species. It includes not only their potential concentration in the environment, but also their ability to create even more dangerous secondary pollutants, their mobility, the hazard for a sudden increase of their concentration under unusual circumstances, etc. From this point of view, pollutants, which today have only minor significance, in case of unpredicted development of the society, might eventually become of primary concern. That is why, the evolution of any particular pollutant should be closely monitored, so that solutions of unexpected problems might be developed without delay, if needed.

## 3. Overview of the environmental impact of pollution from vehicles.

Fig. 1.4. illustrates the contribution of transportation to the total amount of emitted major pollutants in Europe.

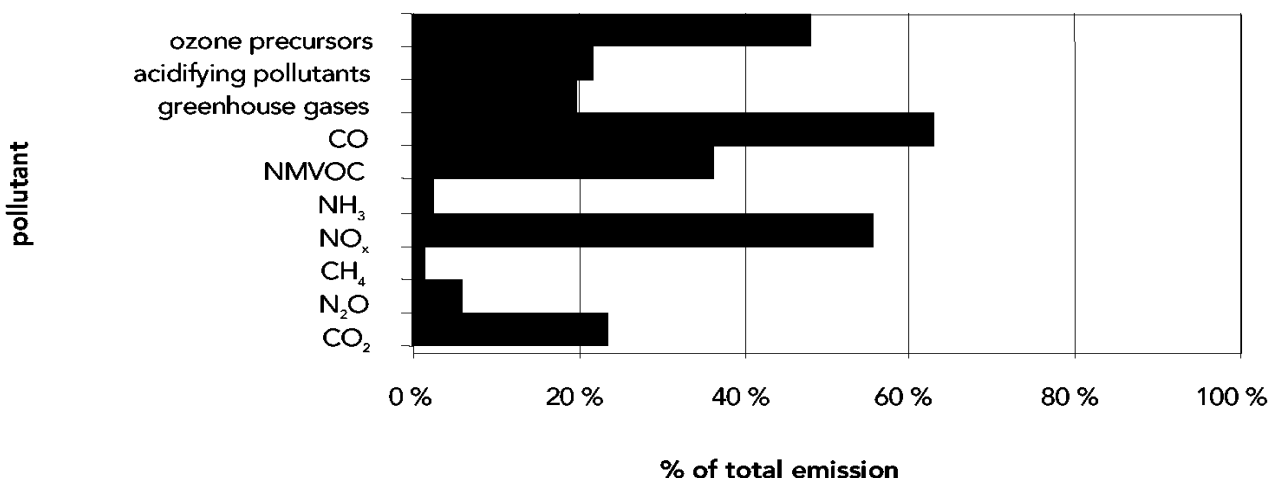


Figure 1. 4. Contribution of the transport sector to the total emission of pollutants in Europe. (S. Eggleston et al. Emissions of atmospheric pollutants in Europe, 1980-1996, EEA, Report No 9/2000).



It is evident from Fig. 1.4. that emissions from mobile sources constitute a major negative anthropogenic influence on environment. Data for USA also confirm that conclusion. In 1997, transportation contribution in the US was roughly 30, 4, and 67 per cent of the generated CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O, respectively. Total emissions of nitrogen oxides (NO<sub>x</sub>) from mobile sources represented 49 per cent of national emissions, while CO, NMVOC and SO<sub>2</sub> emissions contributed approximately 81, 40 and 7 per cent, respectively. Emissions of particulate matter from vehicles in the USA for the same year are reported as particulate matter smaller than 10 microns (PM10) – 2 569 Gg and total particulate matter (PT) – 5 489 Gg. Table 3.1. illustrates the relative participation of major vehicles groups to the total air pollution from mobile sources in the US in 1997.

Table 3.1. Contribution of US Internal Combustion Engine Vehicles to air pollution in 1997 (Compiled and adapted from Inventory of U.S. Greenhouse Gas Emissions and Sinks:1990 – 1997 (1999). EPA 236-R-99-003, US Environmental Protection Agency, NC, USA.)

Fuel/Vehicle type	Air Pollutants				
	CO	NO <sub>x</sub>	NMVOC	CH <sub>4</sub>	N <sub>2</sub> O
Gasoline Highway, Gg	44 225	4629	4528	211	191
- Passenger Cars, %	55.1	56.1	54.5	47.4	56.0
- Light Duty Trucks, %	37.6	37.2	39.4	43.1	41.9
- Heavy Duty Vehicles, %	6.9	6.5	5.4	7.6	2.1
- Motorcycles, %	0.4	0.2	0.7	1.9	+
Diesel Highway, Gg	1368	1753	217	12	7
- Passenger Cars, %	2.0	1.8	5.1	+	+
- Light Duty Trucks, %	0.7	0.6	2.3	+	+
- Heavy Duty Vehicles, %	97.3	97.6	92.6	91.7	100
Non Highway, Gg	15 201	4137	2205	20	9
- Ships and Boats, %	11.2	6.6	21.2	15.0	11.1
- Locomotives, %	0.7	20.8	2.0	10.0	11.1
- Farm Equipment, %	2.0	23.2	5.3	30.0	11.1
- Construction Equipment, %	7.1	27.2	9.9	5.0	+
- Aircraft <sup>a</sup> , %	6.0	3.9	7.8	35.0	66.7
- Other <sup>b</sup> , %	73.0	18.3	53.8	5.0	+
Total, Gg	60 794	10 519	6949	242	207

<sup>a</sup> – Air craft estimates for CO, NO<sub>x</sub> and NMVOC do not include altitude emissions.

<sup>b</sup> – For CO, NO<sub>x</sub> and NMVOC. “Other” includes: gasoline or diesel powered recreational, industrial, lawn and garden, light commercial, airport service, etc. equipment. For N<sub>2</sub>O and CH<sub>4</sub> “Other” includes: snowmobiles, small gasoline powered utility equipment, heavy-duty gasoline powered equipment, and heavy-duty diesel powered equipment.

+ - Does not exceed 0.5 Gg.

The above data show that even in countries, leading in pollution control and efficiency, vehicles with internal combustion engines (ICE) contribute significantly to pollution.

Leaded gasoline was banned in the US in 1995. Still, one source cited more than 1270 tons of lead emissions from vehicles in that country in 1994. Brazil and Japan eliminated leaded gasoline in the 1980s. The first European country, which prohibited leaded gasoline (in 1993), was Austria. Most of the countries in Central and Eastern Europe are also banning leaded gasoline. Still around one third of the gasoline consumed worldwide is leaded. In some countries manganese compounds are permitted as substitutes for tetra ethyl lead.

Toxic air pollutants from ICE include benzene, butadiene, aldehydes and lately – ethers (i.e. methyl t-butyl ether – MTBE), methanol, etc. The contribution of vehicles to these emissions in the USA in 1990 was estimated as benzene – 45 per cent, butadiene – 41 per cent, formaldehyde – 37 per cent. There are indications that the presence of MTBE in gasoline decreases benzene and butadiene emissions, but emissions of aldehydes are increased. Noise pollution is predominantly attributed to heavy-duty diesel vehicles and aircraft. It is concentrated at cities of increased transportation activities – highways, ports and stations, etc.

Environmental pollution from internal combustion engine vehicles (ICEV) is not limited only to combustion and air pollution. If all activities related to transportation are considered, many other pollution sources have to be added. Pollutants are emitted in vehicle production and maintenance, in construction and maintenance of roads, stations and ports, from cargo in normal transportation and in accident, from liquidation of old vehicles and obsolete transportation infrastructure, storage of fuels and so on.

For instance, highway pollution of water only from exploitation and maintenance includes that with fugitive dust, with chemicals used for deicing, with leaks of fuels and lubricants, from lead batteries, leaks from air conditioners, spills from cargo, etc. Solid wastes contribution will include hazardous material spilled from accidents, miscellaneous spent vehicle parts, sand used for deicing, broken asphalt pieces and so on. It should be noted that more than 60 per cent of all hazardous material in a country like the US is road transported.

These contributions are not at all insignificant. Only fugitive dust from US highways, for instance, constituted 29.0 Gg of PM<sub>10</sub> released into the air in 1994. Figure 3 presents the major sources of highway pollution.

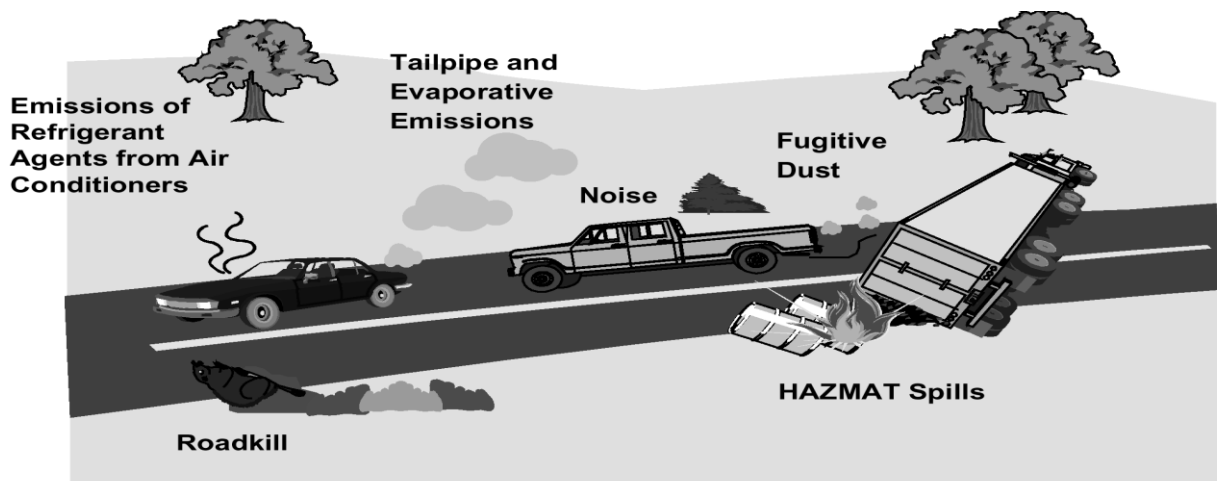


Figure 1.5. Highway pollution. (Indicators of the Environmental Impacts of Transportation (1996). Document EPA 230-R-96-009, US EPA.)

In 1994, 71 000 tons of the chlorofluorocarbon CFC-12 – then widely used in air conditioning were released in the USA. Twenty five percent of it was attributed to vehicle air conditioners. Following the Montreal protocol, this greenhouse gas is not produced in the US since 1996. Hydrofluorocarbons became the standard automobile air conditioner refrigerant in 1994. Their emissions grow rapidly as chlorine-containing chemicals disappear from the automobile fleet. The hydrofluorocarbons are unambiguously greenhouse gases but are still not harmless to global warming.

The relative proportions of the major pollutants in exhaust emissions depend mainly on the specific organization and parameters of the ignition and combustion processes in the ICE. Fuels are usually matched to engines although the full utilization of the advantages of some alternative fuels requires modification of the engine or the development of a new type of engine.

#### 4. Composition of engine fuels and lubricants.

##### 4.1. Composition of engine fuels.

The *traditional fuels and lubricants* used in vehicles nowadays are the fuels derived from the processing of petroleum. They are *additive products*, consisting predominantly of a base hydrocarbon mixture (*base fuel*) and a smaller amount (typically less than 0.5 %<sub>v</sub> each) synthesized compounds, called *additives*. The designed combination of all additives not only in gasoline, but also in any finished refinery product (incl. lubricants) is typically called “*the additive package*”. Modern gasolines have also a varying amount (up to 15 %<sub>v</sub>) of *oxygen containing components* (i. e., ethers, low molecular mass alcohols).

In 1999 the world, without the former Soviet bloc countries, consumed 3 280.3 million tons of crude oil, from which the gasoline fractions were 726.4 mln tonnes, the middle distillates – 775.9 mln tons, fuel oil – 253.2, and other fuels – 415.8 mln tons. The former Soviet bloc (in time of low industrial activity) consumed around 240 mln tons of crude, from which a similar portion of fuels were obtained. Most of these were burned in vehicles.

Several types of fuels are used in transportation, and their properties are selected so that they suit best the particular type of engine.

The typical fuel for SI engines, *gasoline*, should evaporate at relatively low temperatures to form vapors, which are ignited by the spark. Because of that, gasoline is produced from crude oil fractions boiling between 30 and 200° C. Gasoline is a mixture of up to 300 individual hydrocarbons, generally in the C5 – C12 range. The typical hydrocarbons in gasolines are aliphatic alkanes and alkenes, monocyclic arenes, and lesser amounts of monocyclic alkanes and alkenes. The presence of two types of hydrocarbons is limited in gasoline specifications – alkenes and arenes. The control of alkenes (typically below 10 %<sub>v</sub>) in gasoline reduces the emissions of 1, 3 – butadiene and the ozone reactivity of emissions. The control of arenes (30 – 50 %<sub>v</sub> arenes, between 1 and 5 % per cent benzene) in gasoline reduces not only the emission of arenes, but also of butadiene.

The oxygen content of gasolines depends on the amount of oxygenates used and is typically below 2.7 %<sub>v</sub>. Sulphur is in the form sulphur containing organic compounds (i. e. higher thiols, sulphides, thiophenes) and is currently limited to below 1000 ppm (0.1 %) in USA and 500 ppm in Europe. Lead content in most countries is at a very low level, and from the end of 2003 will not be permitted at all. In some countries manganese antiknock additives are allowed but their content is controlled at a low level. Nitrogen, potassium and

boron in very small quantities may be present in gasolines as incorporated in organic additive compounds.

In compression ignition (CI) engines, the fuel - air mixture is sprayed in compressed air at high temperatures (500 – 600° C). That is why *diesel fuels* are usually produced from distillate crude oil fractions boiling at normal pressure between 150 and 380 ° C. Hydrocarbons are typically with between 11 to 20 carbon atoms. All main homologous series are present in different proportions. It should be underlined that the identification of individual hydrocarbons in gas oils and heavier crude oil fractions is a complex task and there are no specification requirements outlining a particular mandatory composition. The upper content limits of n-alkanes, alkenes and arenes are controlled indirectly by low temperature, storage stability and ecological properties, respectively. For instance, contemporary diesel fuels may contain up to 30 % arenes, although attempts are underway for limiting their total content down to 10 % (i. e. in California) with not more than 1 % of three ring compounds. However, decreasing arenes (i. e. by severe hydrogenation) leads to impaired lubricity and high costs.

Sulphur content of diesel fuels is presently between 0.2 and 0.3 %, but in most industrialised countries there are already specifications for fuels with less than 0.5 % sulphur, which will become mandatory from 2004 onwards. Further decreasing of sulphur is been planned for the years after 2008 (i. e. down to 0.002 % in Sweden).

Nitrogen and small amounts of metal containing organic compounds may also be found in diesel fuels. Vanadium is typically limited, because of corrosion problems.

Additives for diesel fuels typically contribute relatively low amounts of nitrogen and polymeric compounds. Oxygen containing compounds may also be used as additives and/or components (i. e. esters of fatty acids, known as biodiesel additives). Some metal containing compounds (i. e. Cu, Ce, Fe, etc.) which are used to improve ecological compatibility of diesel fuel will be discussed later.

*Aviation gas turbine fuels (jet fuels)* work in conditions, which require distillate crude oil fractions boiling between 140 and 280 ° C (for supersonic aircraft up to 315 ° C) for their production. Their hydrocarbon portion includes the higher boiling compounds typical for gasolines and the lower boiling compounds of diesel fuels. Typically isoalkanes and alkyl cyclic alkanes are preferred in jet fuel. Normal alkanes are limited by low temperature properties, arenes – by ecological compatibility, and alkenes – by polymerisation and gum-forming problems. Metals are excluded from jet fuels because of the increased wear of turbine blades. Glycol ethers are the typical antifreeze additives, N, N' – disalicylidene 1,2 – propanediamine is the permitted metal deactivator, hindered alkylphenols are usually the antioxidants. Ashless derivatives of dimeric acids are used as corrosion inhibitors. Antistatic additives for jet fuels should also be metal free.

Gas turbines used for transportation of ships, trains, etc. usually utilise heavier and cheaper crude oil fractions, which usually have vacuum stripped components with end boiling points above 360 ° C.

*Residual fuel oils* with initial boiling points above 360° C find application in some heavy-duty marine engines.

Rockets and some of the very specialised air and space vehicles, may use not only petroleum fractions but - more often - alcohol, ammonia, liquid hydrogen, etc., and as oxidants - liquid oxygen, hydrogen peroxide, nitric acid and so on.

It should be emphasised that all fuels except the jet fuels contain some small amount of water, incorporated during storage.

Alternative fuels (i. e., gaseous fuels, alcohols, etc.) will be discussed later in detail as options for controlling vehicle emissions.

#### 4.2. Composition of engine lubricants.

Lubricants have indirect and direct influence on pollution from vehicles. They are typical additive products consisting of a base oil blend of components, and a mixture of additives (*additive package*).

The traditional *petroleum lubricating oils* are produced from crude oil fractions, *synthetic lubricating oils* are mixtures of synthesised chemical compounds and *semi-synthetic oils* are usually combinations of petroleum and synthetic components in different proportions. *Biodegradable lubricating oils and components* are increasingly being introduced on the market. They are usually vegetable oils or produced from vegetable oils by a suitable chemical modification of the glyceride esters of fatty acids.

*Petroleum (mineral) base oils* are compounded from refined distillate fractions boiling between 350 and 500° C and residual components boiling above 500° C. The hydrocarbons are typically with more than 20 C atoms, with small amounts spanning in some cases up to the 50 – 60 C range. Isoalkanes and hybrid cyclic structures with long side chains usually prevail in well-refined base oils. Hydrotreated base oils may have less than 1 % arenes, and hydroisomerised oils - more than 75 % isoalkanes.

Sulphur is typically in benzothiophene structures, and controlled amount of these compounds is considered beneficial for oxidation stability. Severely hydrotreated oils do not contain sulphur, but in solvent extracted oils sulphur may reach 1 % for the distillate and even to 3 % in residual components.

Nitrogen compounds in petroleum base oils are typically in the form of alkyl pyridines and alkylquinolines. They are pro-oxidants and ecologically incompatible. Their content varies from zero in hydroisomerisates up to 500 ppm in viscous distillates and more than 1000 ppm – in vacuum resid oils.

Synthetic base oils used in vehicles typically consist of hydrocarbons (i. e. polyalphaolefines) or esters. *Hydrocarbon synthetic oils* are narrow boiling fractions obtained by polymerisation and hydrogenation of low molecular alkenes. *Ester synthetic oils* are either esters of dicarboxylic acids with monovalent alcohols or esters of monocarboxylic acids with polyvalent alcohols. Such ester oils are typically used in aircraft applications. Ester oils based on natural fatty acids, which are biodegradable, find increasing application as hydraulic fluids in vehicles, when high level of ecological compatibility is required. Spacecraft lubrication requires very low volatility, which is achieved with *fluorine containing synthetic oils*. *Semi-synthetic oils* are mixtures of mineral and synthetic oils.

The finished lubricating oil contains also a mixture of additives (*an additive package*). Crankcase oils may have more than 20 per cent different additives, which contribute sulfur, nitrogen, oxygen, phosphorus, boron, different metals, etc. to vehicle pollution. Table 1.4. presents the types of additives used in lubricating oils for vehicles. They perform different functions as seen from their names, shown in the table. While these functions may be essential for the lubricant's performance, they may evoke adverse effects in the overall environmental compatibility of the vehicle. That is why, not only fuels, but also lubricants will be within the focus of this course, as one of the possibilities to improve or compromise the different options for control of the pollution from vehicles.

Table 1.4. Lubricant additives.

Additive /Application	Oxi-dation inhibitor	Corro-sion inhibitor	AW/EP	Disper-sant	Deter-gent	Friction modifier	Depre-sant	Foam inhibitor	Visco-sity modifier	Other*
Gasoline engine oils	X	X	X	X	X	X	X	X	X	
Diesel engine oils	X	X	X	X	X		X	X	X	
Aviation engine oils	X	X	X	X			X			
Two stroke engine oils	X	X	X	X	X					X
Automotive gear oils	X	X	X			X	X	X	X	
Automatic transmission fluids	X	X	X	X	X	X	X	X	X	X
Tractor hydraulic oils	X	X	X		X	X	X	X	X	X
Greases	X	X	X							X

\* - Seal-swell agents, couplers, dyes, diluents, emulsifiers, demulsifiers, etc.

Lubricants contribute to vehicle pollution directly with lubricant components burnt in the combustion chamber, with leaks and with products of thermal and oxidative lubricant degradation emitted in the air. Indirectly through friction energy losses lubricants control and facilitate the quick start of the engine, thus influencing the amount of fuel and pollutants being emitted in the environment.

In summary, this first topic should be viewed as a pivotal step in the course on chemistry of combustion and pollution from vehicles, which provides the basic definitions, formula, reactions, typical compounds involved, etc. Some of these will be revisited in the next lectures. But even if they are not directly used in the present course, it is believed that this first lecture lays out the necessary foundations for future individual activity of the graduates in relevant scientific fields.

#### References for further reading.

1. Warnatz, J. Combustion: physical and chemical fundamentals, modeling and simulation, experiments, pollutant formation, 2nd ed. ,Berlin - New York, Springer, 2001.
2. Turns, St. R. An introduction to combustion : concepts and applications, 2nd ed., Boston ; London : McGraw-Hill, 2000.
3. Glassman, I., *Combustion*, 3<sup>rd</sup> ed., Academic Press, Inc., London, UK., 1996.
4. Handbook of air pollution from internal combustion engines. Ed. E. Sher, Academic press, USA, 1998.
5. Modern petroleum technology. Vol. 2. Downstream. Ed. A. G. Lucas, 6th ed., Wiley & Sons, Chichester, U. K., 2000

**Ben Gurion University of the Negev  
Faculty of Engineering**

**Lectures for a postgraduate course**

***Chemistry of Combustion and Pollution from  
Vehicles***

**Given by Prof. G. St. Cholakov in the summer semester of 2002.**

**Sofia – Beer Sheva,**

**2002**

## Topic 2. Combustion reactions of the fuel constituents.

The purpose of this topic is to present the main chemical reactions taking place in the ignition and combustion of the fuel constituents, outlined in the previous topic.

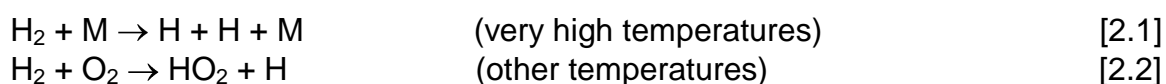
The emphasis is on the identification of the pathways, which lead to the formation of the major pollutants.

The topic starts with the characterisation of the  $H_2 - O_2$  system and then continues with the modern theoretical understanding of the general chemical reactions taking place in the ignition and combustion of hydrocarbons. Most of the reactions can be considered elementary only in first approximation.

### 2.1. The $H_2 - O_2$ system and the radical chain mechanism.

Hydrogen, as shall be seen later, is one of the most perspective fuels for cleaner environment. The system  $H_2 - O_2$  already has its own application in spacecraft propulsion. Moreover, this system is very important in the oxidation of hydrocarbons. Hereunder, follow the main reactions involved in the oxidation of hydrogen. Hereunder, and throughout this course for easier notation the traditional dots above radicals will be omitted. In some cases a boldface presentation of the atom or chain with unpaired electrons will be used in order to denote a radical.

#### Initiation



#### Chain propagation and branching



#### Chain termination



The above mechanism is not completely outlined, but before continuing, several important comments have to be made.

In the above reactions a symbol "M" is introduced. M denotes the so-called "third body", which influences a particular reaction. The third body substantiates the increased probability of species to exchange energy and may be "any molecule" with which the reactants exchange energy. Implicitly, M is also a symbol for high temperature and pressure, when the probability that the reacting species receive energy from other species is much higher. Furthermore, by definition the third body is written on both sides of the reaction in order to emphasise its indifference in the described chemical transformations.

Reactions above illustrate a typical sequence of *chain branching radical reactions*. *Chain reactions* are reactions in which a radical species is produced, and that



subsequently reacts to produce a new radical species, which produces another species and so on.

The chain starts with an initiation reaction between two molecules or between a molecule and M. Initiation reactions are typically slow because the reactants are whole molecules. However, the radical concentrations increase and *the chain is propagated*. In the same time radicals may meet and recombine into stable molecules or long lived radical configurations which are not that active. Radicals may also exchange energy with the wall of the vessel in which the chain reaction takes place, and also transform into stable species. Thus, the chain process should be viewed in its dynamic development, and when recombination of radicals prevails over production of radicals, the process is terminated.

Figure 2.1. shows the explosion limits for a stoichiometric  $H_2 - O_2$  mixture in a spherical vessel.

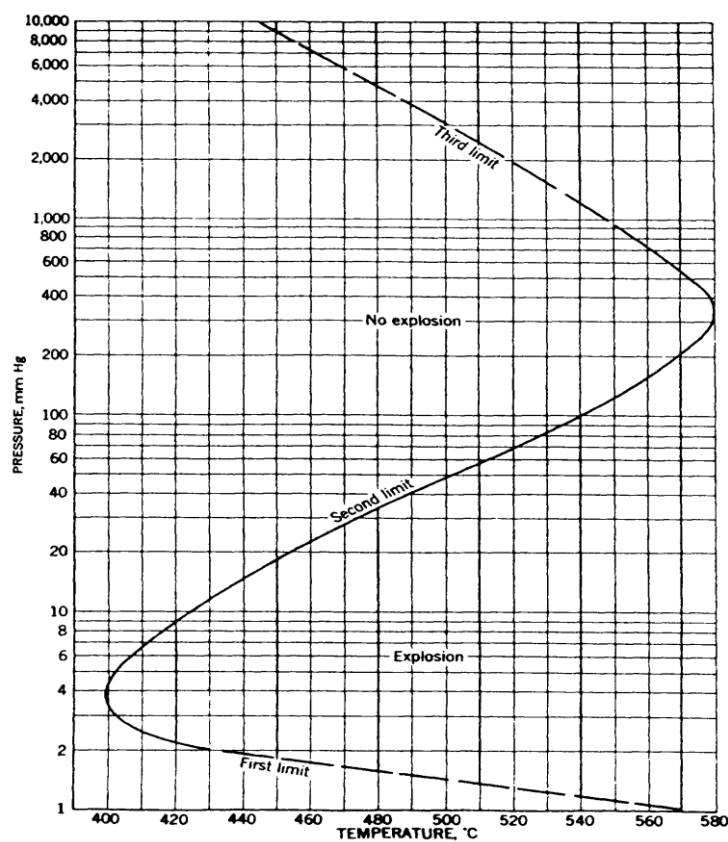


Figure 2. 1. Explosion limits for a stoichiometric  $H_2 - O_2$  mixture in a spherical vessel (from Ref. 6).

It may be seen that the  $H_2 - O_2$  system is characterised by three explosion limits. There are regions on the P - T diagram, of relatively high temperature and pressure, in which the system will not explode. They may be understood qualitatively by following up a vertical line at constant temperature, i. e. of  $500^\circ C$  in Fig. 2.1. At low pressure up until about 1.5 mm Hg there is no explosion, although the pre-ignition reactions are taking place, because at low pressure (and gas densities), the free radicals produced in reactions [2.2] to [2.6] easily diffuse to the wall and recombine. The first spontaneous ignition is registered only when pressure has reached a particular value, at which the rate of free radical production becomes higher than the rate of radical recombination. Because the recombination reactions are surface reactions, which compete with the production

reactions in the gas phase, the material and the dimensions of the vessel participate considerably in the parameters of the phenomena, e. g. one and the same system will have different explosion limits in different vessels.

Above the first explosion limit the competition for production and recombination of the free radicals is lead by the same production reactions, but the recombination takes place also in the gas phase and is governed by the three-body reactions [7] to [10]. A new recombination reaction [11], which at these relatively low temperatures competes effectively for H-radicals with the main production reaction [3.], has to be introduced, together with its closely related reactions, which describe the fate of peroxide ion HO<sub>2</sub>:



Since, at relatively low pressure the peroxide ion, playing the major role in [2.11] to [2.20] is relatively stable, it will diffuse to the walls to be destroyed, and reaction [2.11] will effectively become the most important recombination reaction between the first and the second explosion limit. Continuing the journey up above the first explosion limit it should be noted that increasing pressure would increase the rate of the production binary reaction [2.3] linearly, while the rate of the competing trimolecular reaction [2.11] will increase exponentially. So, when the second explosion limit is reached, radical recombination will start prevailing over radical production, and the system will be again non-explosive.

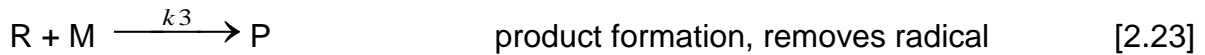
The third explosion limit is often called the *thermal explosion limit* of the H<sub>2</sub> – O<sub>2</sub> system, because with increasing the pressure, the heat production from the chemical reactions increases. There is more available heat, the rate of the transformation of HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> in branching reactions (i. e. [2.12] and [2.20]) is increased in comparison to the recombination reactions (i. e., [2.11]) which favour lower energy conditions. Thus, the rate of production of free radicals once again becomes higher than the rate of their recombination, so the system becomes explosive.

The reaction mechanism of the H<sub>2</sub> – O<sub>2</sub> system is often called “the ping – pong” mechanism, because of the incessant passing of electrons from one species to another and back. The radicals produced in this system (H, O, OH, etc.) are also forming in any hydrocarbon – oxidiser system, and because of that – it is fundamental for hydrocarbon combustion. These radicals usually are denoted as the primary members of the so-called “**X**” *pool*. The “X” pool for a given combustion system is the pool of the most energy-rich and active radicals. In addition to the primary members, the “X” pool of hydrocarbon combustion systems contains other species, active under particular circumstances (i. e., HO<sub>2</sub>) and the most active hydrocarbon radicals – CH<sub>3</sub>, CH<sub>2</sub>, CH, etc. From a chemical point of view a definition of combustion as a process ruled by members of the “X” pool of the particular system can also be found in the literature. It should be noted, however, that

the particular activity and importance even of the members of the “X” pool depends on the particular conditions and development of the combustion system.

The mechanism of oxidation of H<sub>2</sub> provides an opportunity for definition of branching reactions, *the multiplication factor,  $\alpha$*  and *the criterion for explosion,  $\alpha_{crit}$* .

A general branched chain reaction system may be written as:



chain termination.



where **M** is a molecule (not to be confused with the previously defined third body), **R** – a radical, and **P** is a product. A reaction is defined as branching when it produces more radicals than it consumes, and for a branching reaction  $\alpha > 1$ .

If a quasi-steady state is assumed, the explosive condition is determined by the rate of formation of the product,

$$d(P)/dt = k_3 (R) (M). \quad [2.26]$$

From the reaction system above, the steady state condition for the production of radicals is

$$d(R)/dt = 0 = k_1 (M) + k_2 (\alpha - 1) (R) (M) - k_3 (R)(M) - k_4 (R) - k_5 (R) \quad [2.27]$$

Solving for (R) and substituting into the equation for the rate of formation of P gives:

$$d(P)/dt = k_1 k_3 (M)_2 / \{k_3 (M) + k_4 + k_5 - k_2 ((\alpha - 1) (M))\} \quad [2.28]$$

The rate of formation of the product becomes infinite and the system – explosive when the denominator becomes zero. Expressing  $\alpha$  for the zero value of the denominator, and denoting the specific value as  $\alpha_{crit}$ , the following is obtained:

$$\alpha_{crit} = 1 + \frac{k_3(M) + k_4 + k_5}{k_2(M)} = \left( 1 + \frac{k_3}{k_2} \right) + \frac{k_4 + k_5}{k_2(M)} \quad [2.29]$$

For a given reaction mechanism the multiplication factor,  $\alpha_{react}$  may be calculated and if  $\alpha_{react} > \alpha_{crit}$  the system is explosive, if not – the products form by slow reactions. In many cases (M) is proportional to the total pressure, so the pressure effect just described for the H<sub>2</sub> – O<sub>2</sub> system, can be understood.

## 2. 2. Experimental observations, fundamentals of Semenov's theory for ignition and combustion, and its developments. Thermodynamic and chemical interpretation of ignition phenomena.

### 2. 2. 1. Experimental observations for the ignition and combustion of hydrocarbons.

The mixtures of hydrocarbons and  $O_2$  react very slowly at temperatures below  $200^\circ C$ . If the temperature is increased, different oxygen containing compounds are formed.  $CO$  and  $H_2O$  are predominant at first, but then formaldehyde,  $HCHO$ ,  $H_2O_2$  and other compounds begin to appear. In the  $300 - 400^\circ C$  interval a faint light is often observed. The light may be followed by blue flames and eventually – by an explosion.

The experimentally observed combustion characteristics of hydrocarbons may be summarised as follows:

1. The ignition of hydrocarbons starts with an induction period followed by a very rapid reaction development. Below  $300^\circ C$  induction periods are of the order of 1 min, but around  $400^\circ C$  last less than a second.
2. The reaction rate is strongly decreased in larger vessels, which is an indication of the importance of free radicals in the reaction mechanism.
3. Aldehydes form and if they are added artificially to the hydrocarbon - oxidiser mixture, they extremely accelerate the reactions and significantly shorten the induction period. Formaldehyde is the most efficient aldehyde in that respect.
4. Except for methane and ethane, "cool" flames, during which the reaction rate is decreasing although the temperature is increasing and ignition can not be realised, are observed. Figure 2. 2. illustrates the zone of cool flames, as well as the two stage ignition (registered as flash and ignition temperature) when the temperature is increased slowly at constant pressure.

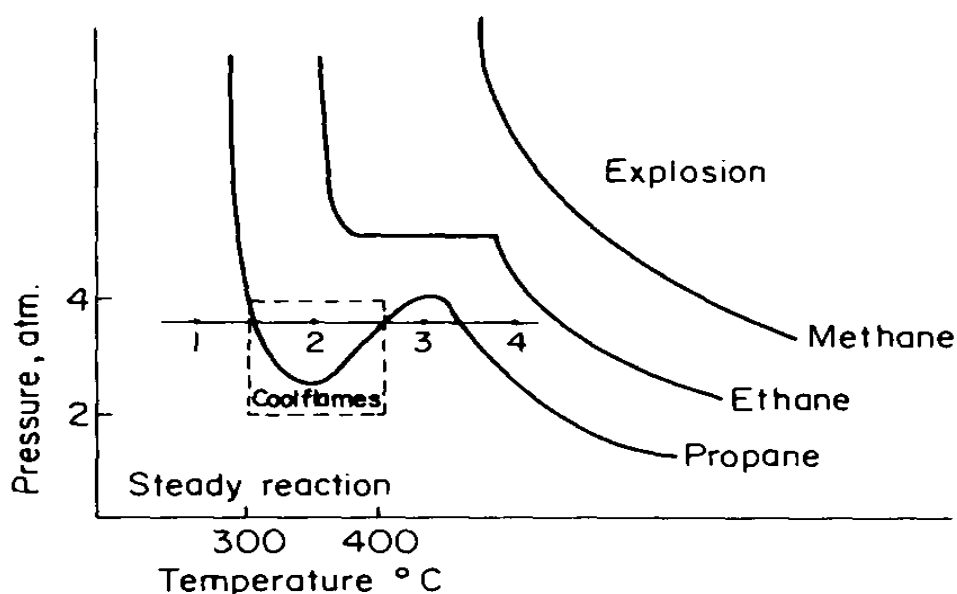


Figure 2. 2. General explosion limit characteristics of hydrocarbon – air mixtures. (from Ref. 3)

5. With the increase of the number of C-atoms, the curves of the hydrocarbons move left and downwards in Fig. 2. 2. to lower temperatures and pressures, thus showing that heavier hydrocarbons are more easily ignited.
6. For hydrocarbons multiple ignition limits when increasing pressure at constant temperature can be observed, as illustrated in Figure 2. 3. The first two explosion limits of hydrocarbons are explained with the phenomena already described for the  $H_2 - O_2$  system. The explanation of the multiplicity of cool flame in the region of the thermal explosion limit of hydrocarbons is more difficult and will be discussed later.

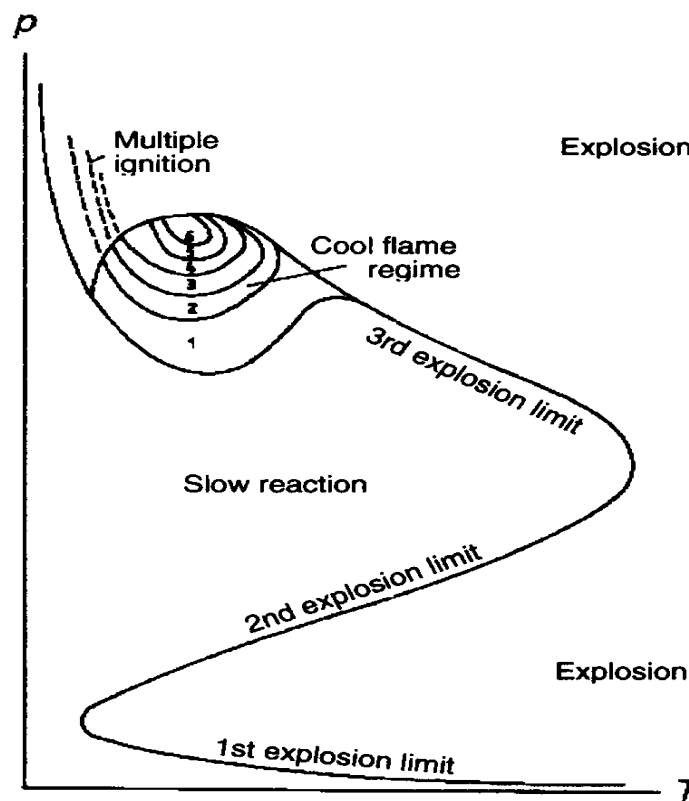


Figure 2. 3. Ignition limits for hydrocarbons (from Ref. 5).

7. From propane on, the explosions are not accompanied by self-heating and usually at constant pressure follow the  $1 \rightarrow 2$  root, shown in Figure 2. 2. Explosions may occur also in other regions and conditions, but they are then so fast that it can not be ascertained if there is self-heating.

Attempts to explain the above behaviour have been made by different scientists. Semenov was the first to give a widely accepted hypothesis of the low temperature behaviour of hydrocarbons from the point of view of thermodynamics and chemical kinetics in 1930, and then – from a chemical point of view – in 1958. Hereunder, a brief description of Semenov's theory is given. The recommended literature provides further detail and insight. It should be noted, however, that Semenov's radical chain mechanism is interpreted in almost every book on combustion. However, because of the different context in different books, and the constant development of the combustion field, some of the explanations may be confusing. That is why, the original work of Semenov is also included in the recommended literature.

2. 2. 2. Fundamentals of Semenov's theory for ignition and combustion, and its developments. Thermodynamic and chemical interpretation of ignition phenomena.

Low temperature oxidation (below approx. 900 K at 1 bar).

Semenov explained induction periods with the existence of unstable, but long-lived particles,  $M^*$  (N. B.:  $M$  is not a third body, but a radical). These particles may form intermediates with different fate, depending on the amount of available energy in the system. Two routes (reactions of the type "fuel – products") for the development of the system, after the formation of the unstable  $M^*$ , are postulated. These are shown below.

**Reaction Route I: No branching and stable molecules.**



**Reaction Route II: Chain branching and free radicals.**

The above presentation will be interpreted together with Fig. 2. 2. and the following Fig. 2. 4. We shall also refer to a virtual experimental determination of flash points, rather than to the classical combustion experiment with propane heated with a constant temperature bath.

Flash and ignition temperatures (points) are fuel characteristics, required by specifications of jet and heavier fuels, and lubricating oils. In a typical flash/ignition point determination the product is heated with a prescribed low rate in a open or closed cup apparatus. When the expected flash point is approached, an outside flame source with specified characteristics is passed over the surface of the fluid for a prescribed short time (5 s). When the flash temperature is reached, a blueish flame is initiated by the outside source. The flame, which from the point of view of the combustion theory is a typical "cool flame", is accompanied by a characteristic sound, but would not ignite the fuel. When the fuel is ignited and the flame is sustained, the ignition temperature is registered. Then the cup is closed in order to prevent an accident in the laboratory. It should be also underlined that the described set-up is not applicable to gasolines and lower molecular fuels.

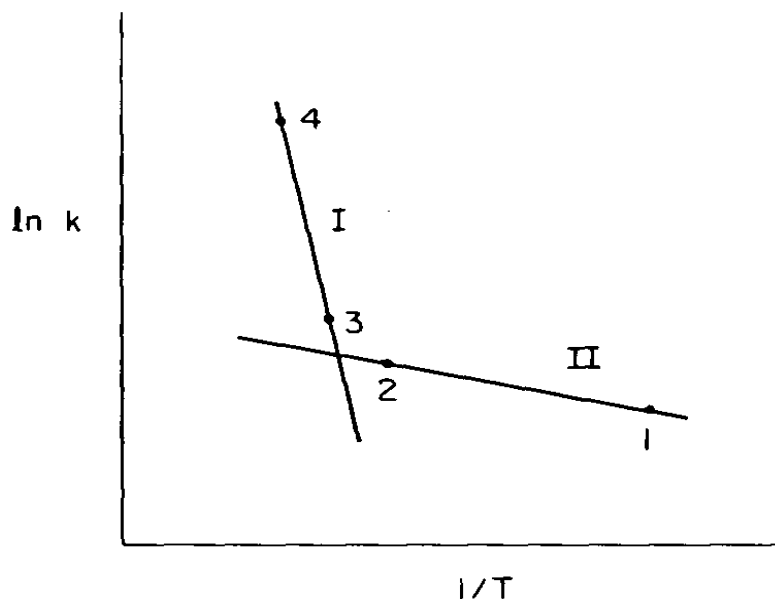


Figure 2. 4. An Arrhenius plot of Semenov's steps in hydrocarbon oxidation. Points 1 – 4 correspond to the same points in Fig. 2. 2. (from Ref. 1).

Fig. 2. 4. shows the changes of the respective reaction rates of the two routes of Semenov with temperature.

If the initial hydrocarbon – oxidiser mixture is heated slowly at constant pressure the system will start developing along **Route II**, which has a lower  $E_a$ . Free radicals will be formed and when moving from point **1** to point **2**, the cross point with the P-T curve in Fig. 2. 2. is reached, the system will become explosive. The outside ignition source in the determination of the flash temperature initiates a cool flame, but the amount of excessive heat is small (as prescribed for the determination of flash points), so the system only moves from point **2** to point **3**, becomes non-explosive, and the cool flame is not sustained. Negative changes of the reaction rate, although the temperature is rising, are registered (Fig. 2. 4.), if the system does not receive more energy from outside. However, if the system is heated further up, it passes from point **3** to point **4**, at the cross point with the P-T curve the activation energy of **Route I** is reached and the faster exothermic reactions leading to stable molecules are turned on. The system becomes explosive again, and along **Route I** the ignition temperature can be reached and registered.

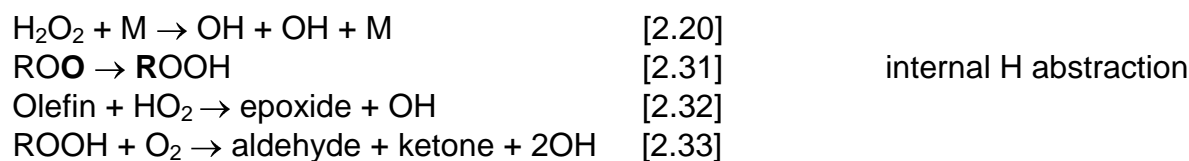
A similar behaviour will be observed without an outside source, if the system is heated slowly in an isothermal liquid bath. In that case the development along **Route II** will be initiated at the hotter walls of the vessel. Cool flames will move from the walls to the cooler center. However, ignition would not be realised, because the system moves to point **3** and becomes non-explosive.

The understanding of the low temperature is very important from a general engineering point of view, because it is related not only to ignition at specific conditions, but also to the processes of oxidation decay of the properties of organic products.

The chemical reaction mechanism of low temperature oxidation of hydrocarbon suggested by Semenov is outlined below (with the addition of some reactions contributed later by Benson and other authors). The reactions of Semenov are denoted with the symbol "S", and the radical symbol (atom in bold) is used only in reaction [S.8.] to emphasise the formation of two radicals from aldehydes.

$RH + O_2 \rightarrow R + HO_2$	[S.1.]	<b>chain initiation</b>
$R + O_2 \rightarrow RO_2$	[S.2.]	<b>chain propagation</b>
$R + O_2 (+M) \rightarrow \text{olefin} + HO_2 (+M)$	[S.3.]	
$RO_2 + RH \rightarrow ROOH + R$	[S.4.]	
$RO_2 \rightarrow R'CHO + R''O$	[S.5.]	
$HO_2 + RH \rightarrow H_2O_2 + R$	[S.6.]	
$ROOH \rightarrow RO + OH$	[S.7.]	<b>degenerate</b>
<b>branching</b>		
$R'CHO + O_2 \rightarrow R'CO + HO_2$	[S.8.]	
$RO_2 \rightarrow \text{wall destruction}$	[S.9.]	<b>chain termination</b>
$H_2O_2 \rightarrow \text{wall destruction}$	[10]	
$RH + X \rightarrow R + XH$ , X = radical from the "X" pool,	[S.11.]	<b>secondary chain initiation reactions</b>
i. e. $RH + OH \rightarrow R + HOH$	[S.11.a.]	

The following additional reactions are important at the higher temperature boundary and for hydrocarbons with more than 5 atoms (atoms with free valences are given in bold):



The above scheme describes the low temperature gas phase oxidation and ignition of hydrocarbons and was originally developed for hydrocarbons with less than 5 carbon atoms. Semenov calls reactions [S.7.] and [S.8.] “degenerate” branching, because branching does not occur right away (i. e., as with the  $\text{H}_2 - \text{O}_2$  system), but only after some induction period, needed for passing through the previous reactions.

The relative importance of the different reactions depends on the molecular mass and structure of the particular hydrocarbon (s) and the values of the parameters, determining the state of the system. Because of that, reactions [20] and [31] to [33] have to be added to the original Semenov’s scheme in order to reflect the behaviour of heavier molecules and provide a bridge to intermediate temperature reactions. It should be noted also that at least some of the reactions in Semenov’s scheme are not elementary reactions.

It may be seen that in Semenov’s scheme reactions [S.2] and [S.3.] have the same left hand side and define two alternative routes for development of the system, namely:

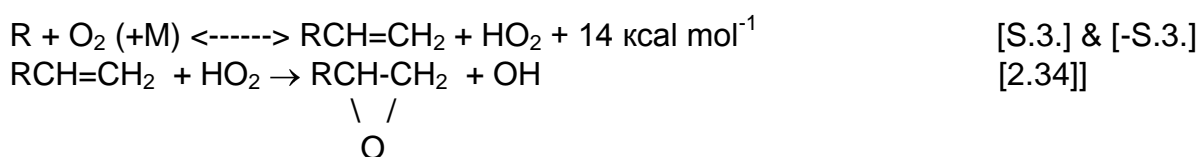
**Route I:** [S.3.]  $\rightarrow$  [S.6.]  $\rightarrow$  **straight chain (steady reaction);**

**Route II:** [S.2.]  $\rightarrow$  [S.4.]  $\rightarrow$  [S.5.]  $\rightarrow$  [S.7.]  $\rightarrow$  [S.8.]  $\rightarrow$  **degenerate chain branching.**

These two routes clearly correspond to the two routes defined before. The two key reactions may have the following continuation (not shown above), which can influence equilibria:



and



Reaction [S.2.] is with lower activation energy and at low temperatures is several times faster than [S.3.]. However, with increasing the temperature, the reverse reaction [-S.2.] starts quickly to dominate, while the equilibrium of reaction [S.3.] moves to the right hand side because  $\text{HO}_2$  becomes more reactive, reaction [2.34] becomes effectively irreversible, which accelerates the **Route I** (Fig. 1 and Fig. 3) development.

Thus, the system starts moving along **Route II** from **1** to point **2** with reaction [S.3.] and by chain branching becomes eventually explosive. If as described above, a flame is passed over the vessel quickly, a cool flame at the flash temperature is registered. The cool flame, however, can not be sustained (i. e., in point **3**), because **Route I** is turned on at temperature above the arbitrary temperature for reversing [S.2.]. Within the relevant



time scales chain branching stops and the system becomes non-explosive. Moving the system further to point 4 makes the system explosive again, because secondary initiation reactions (i. e., [S.11.a.]) and reactions [2.33] to [2.35] increase their impact on chain branching at the higher temperatures involved.

The reactions start in the shown order, but when the scheme is well developed typically all reactions run in the same time, although some of them have a significant and others – a negligible influence.

The initiation reaction [S.1.] is typically slow and with relatively high activation energy. The abstraction of the H-atom will be realised at low temperatures from the weakest C-H bond. The C-H bond scission energies differ by several kcal mol<sup>-1</sup> and diminish from CH<sub>4</sub> to CH.

The two routes in Semenov's scheme, however, are interrelated and the system goes to ignition by a combination of chain branching and self-heating. At temperatures around 300° C, and higher, reaction [S.5.] becomes the main chain propagating reaction, and [S.8.] is the main chain branching reaction, instead of [S.7.]. This statement is considered controversial by authors, related to combustion engineering rather than to combustion theory. The formation [S.4.] and chain branching through hydroperoxides [S.7] appears to fit more readily in the explanation of detonation in spark ignition (SI) engines.

It may be noted also that [S.5.] is effectively an oxidation pyrolysis reaction, because a C-C bond is effectively broken and both products have shorter hydrocarbon chains than the parent peroxide. Thus it accounts for C – C scissoring and the production of lower molecular mass products even at low temperatures.

The boundary between low temperature and intermediate temperature oxidation is usually defined by the termination of the cool flames and the “negative temperature coefficients” (NTC) regime. Thus the specific value of the arbitrary temperature, above which the two routes are changed is an important parameter. This temperature has been at first determined to be around 200° C. However, it depends on what R means in the above general mechanisms. Moreover, computer modeling of induction periods indicates that the particular value and hence – the turnover temperature might be pressure sensitive. Fig. 2. 5. Illustrates the modeling results.

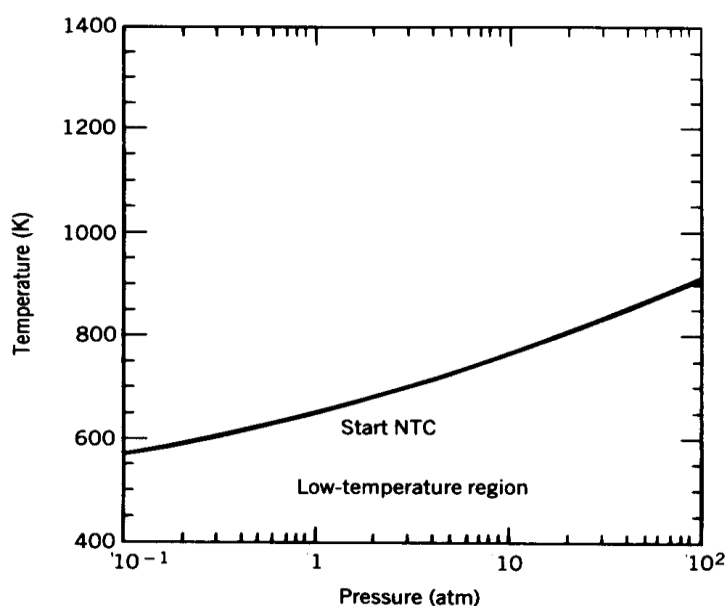


Figure 2. 5. “Turnover” temperature as a function of reaction pressure for a stoichiometric mixture of n-butane and air (From Ref. 4).

Figure 2.5. is important because in practical applications, combustion systems and especially engines work at much higher pressures than atmospheric. Higher “turnover” temperature means that hydroperoxides (ROOH) continue to be produced (by reaction [S. 4.] and other reactions which are going to be considered below) to a significantly higher temperature than 200° C. This may play a very significant role when trying to understand knocking phenomena observed in engines.

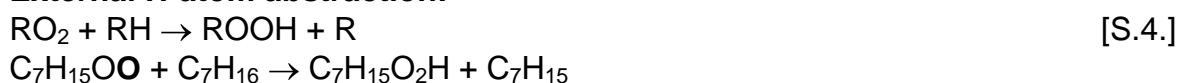
With the approaching of the “turnover” temperature for hydrocarbons with more than 6 carbon atoms (for n-alkanes - even with four C-atoms), an important internal isomerisation by internal H- atom abstraction of peroxy-hydroperoxy biradicals may take place. Because different presentations may be found in combustion chemistry publications for this significant and fairly recent development of Semenov’s original work, Ref. 5 and the original publication (Ref. 7) are the recommended sources for further reading.

In Semenov’s scheme only one direct attack of molecular oxygen on radicals is described. For clarity, hereunder, first it will be repeated, with the example of an important component of gasolines (n-heptane) used for illustration. Please note, that the reversibility of the reactions is explicitly shown here, important sites are shown with a down pointing arrow, and boldface is used to show atoms with unpaired electron, where an emphasis on that is needed.):

**First O<sub>2</sub> addition:**



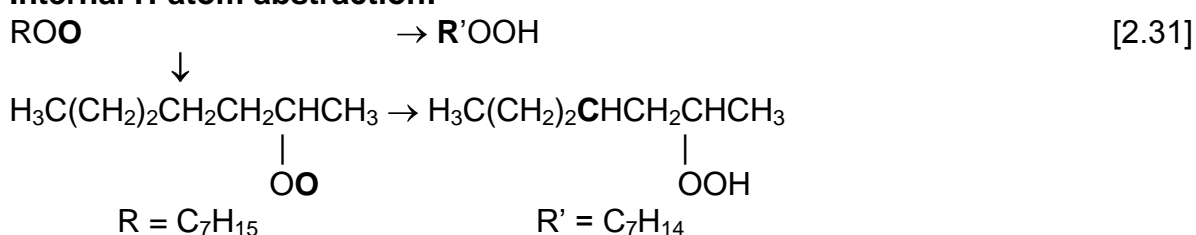
**External H-atom abstraction:**



**Chain branching:**



**Internal H-atom abstraction:**



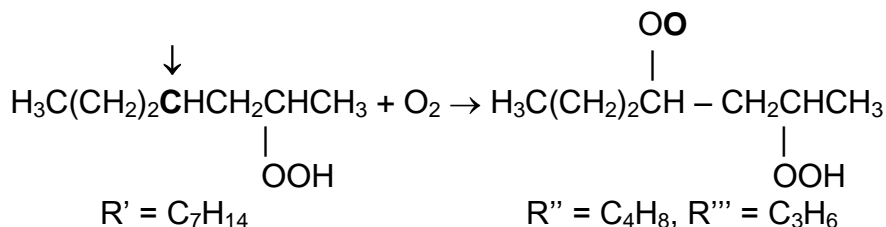
**Chain propagation:**



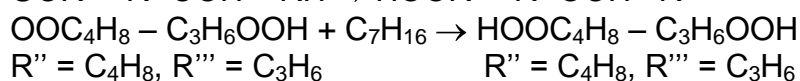
The above opportunities given by Semenov’s scheme, postulate that external H-atom abstraction leads to pronounced chain branching, whereas internal H-atom abstraction (typically via a ring mechanism), leads only to chain propagation. However, external H-atom abstraction is much slower than the internal and calculations show that no

distinct acceleration of ignition (and thus moving towards autoignition) can be expected. In order to explain why experimental systems autoignite, a second attack by molecular oxygen is postulated:

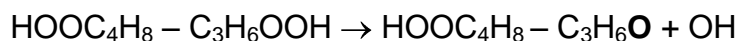
**Second oxidation at the new radical site:**



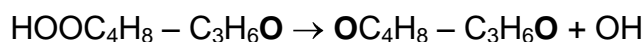
**External H-atom abstraction:**



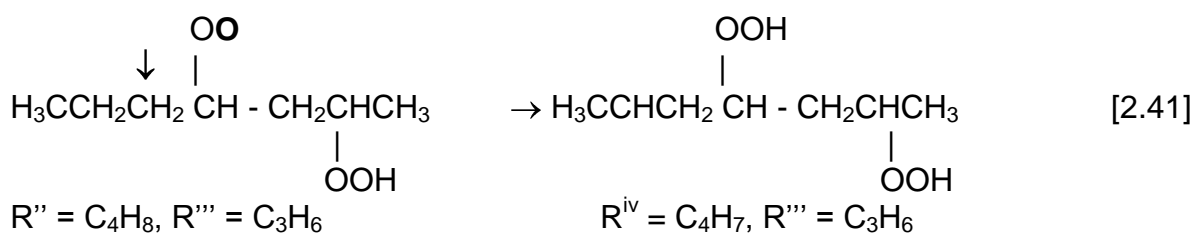
**Chain branching**



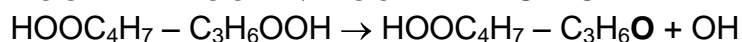
**Chain propagation:**



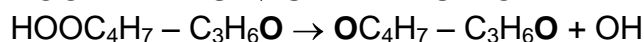
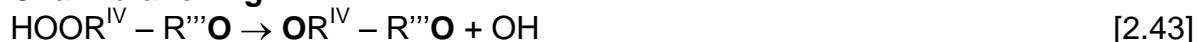
**Internal H-atom abstraction:**



**Chain propagation:**



**Chain branching:**



The above development of Semenov's scheme explains the existence of two stage autoignition in stoichiometric n-heptane – air mixtures, which is illustrated in Fig. 2. 6 and Figure 2. 7.

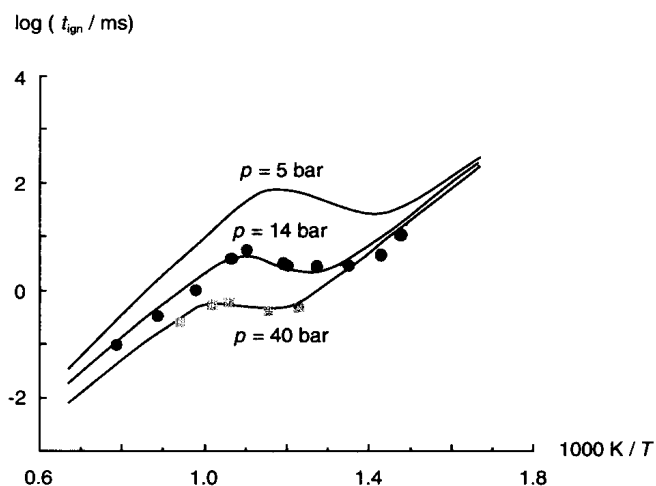


Figure 2.6. Ignition delay times in stoichiometric heptane – air mixtures, negative temperature coefficients occur just below 1000 K (From Ref. 7).

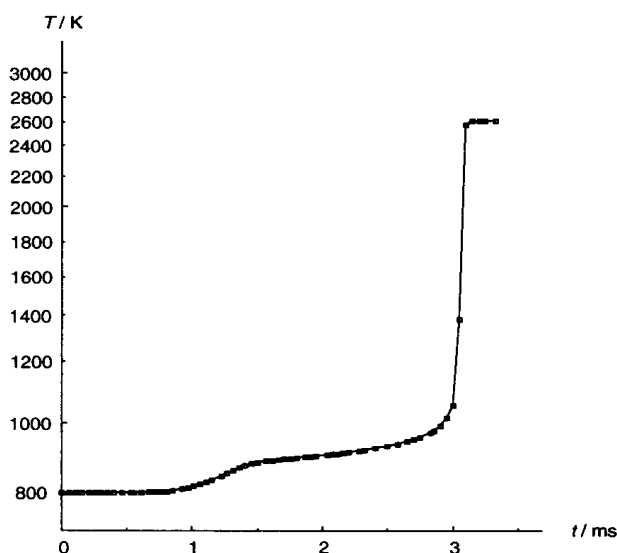
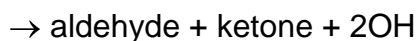
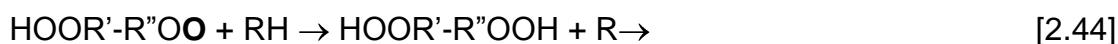
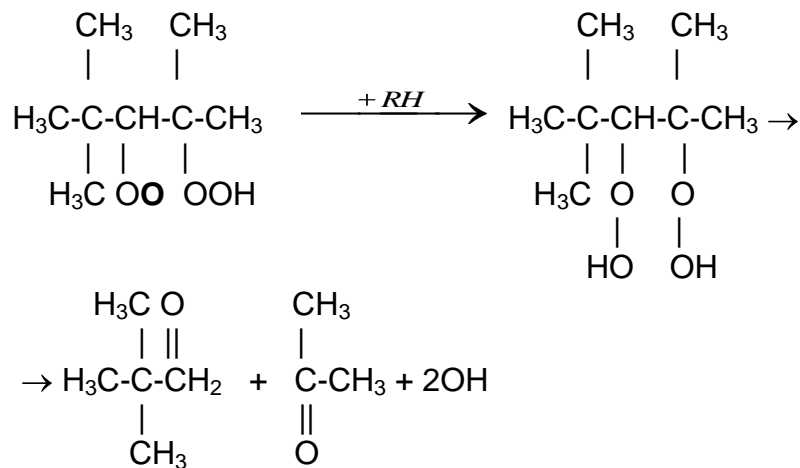


Figure 2.7. Calculated time behaviour of the temperature (log plot) during two stage autoignition of the system from Fig. 2. 6  $T_o = 800$  K,  $p = 15$  bar (From Ref. 5)

The two figures complement the pressure sensitivity of the turnover temperature, presented in the previous Fig. 5. The addition to the Semenov's scheme, suggested above explains the ignition time behaviour with the stability of the peroxides, which control chain branching but tend to decompose back to the initial reactants (i. e., reversing [S. 2.]) at high temperature. This explains also the multiple cool flames, observed in some regions of the P – T curves of hydrocarbons (Fig. 2.3.).

There is also a third possibility for the fate of the hydroperoxides (the other two are reaction [S.7.] and the repeating of the isomerisation steps – reactions [36] to [43]). Within the isomerisation steps the biradicals (i. e.,  $\text{HOOR}'\text{-R}''\text{OO}\cdot$ ) after external abstraction may produce an aldehyde and a ketone. For instance, for 2,2,4-trimethylpentane (*iso*-octane):





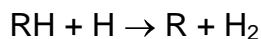
The same decomposition is feasible at some stage for *n*-heptane as well. However, because the time scales of the three possibilities are structure dependent, some authors relate the differences in the antidetonation behaviour of straight and branched structures to these possibilities and their relevance to the delay of the decomposition of the hydroperoxides to higher temperatures and pressures.

#### Intermediate temperature oxidation (900 – 1100 K at 1 bar).

As already mentioned the boundary between low and temperature oxidation is defined by the completion of the “negative temperature coefficients” (NCT) regime. As shown above, in particular circumstances (i. e., high pressure) this boundary may be extended to relatively high temperatures.

Within a limited frame of time and space it is not possible to describe in detail all processes and chemical reactions which hydrocarbons of different structure and molecular mass undergo in combustion. The low temperature regime was discussed in some detail because of the important phenomena involved (i. e., cool flames, degenerate branching, ignition, etc.) and the fact that many pollutants and/or their precursors are generated in this regime. Hereunder, some of the main features of the intermediate temperature oxidation will be summarised:

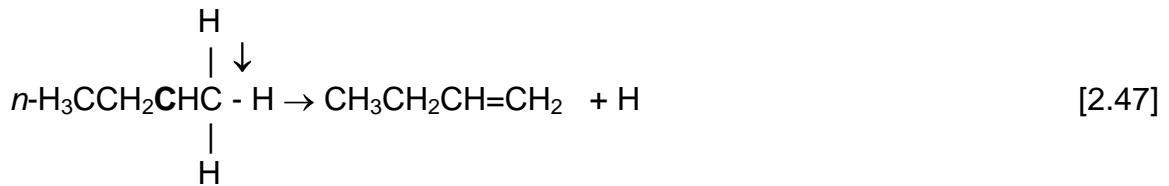
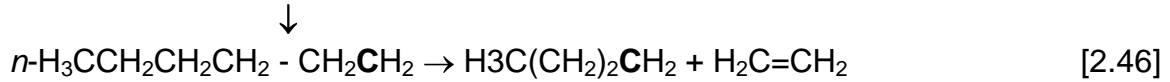
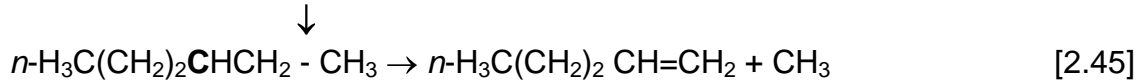
- At higher temperatures the RH molecules are attacked by radicals (predominantly from the X pool, but also other energy rich radicals – i. e., biradicals) rather than by the molecular oxygen. The relatively small differences between the scission energies of C-H bonds become negligible.
- At higher temperatures and/or in fuel rich mixtures and zones of non-premixed flames, H radicals increase their role in the attack of the fuel molecules, i. e.:



[S.11.]

- The importance of the reactions which produce hydroperoxide ions is increased (i. e., reactions [S. 3.] and [S. 6.]), because the H<sub>2</sub>O<sub>2</sub> starts to decompose, by reaction [20] and becomes the main source of OH radicals which attack the remaining whole molecules at these temperatures [i. e. by [S.11.]]. The OH radicals are a primary member of the X pool and facilitate the “ping - pong” mechanism.

- Scissoring of C-C bonds begins directly both in whole molecules and in radicals, especially for alkyl chains with more than 3 C-atoms. The scissoring of the C-C and C—H bonds in radicals, follows the so called “β-scissoring” rule, i. e., the bond being broken is one bond away from the carbon with unpaired electrons:

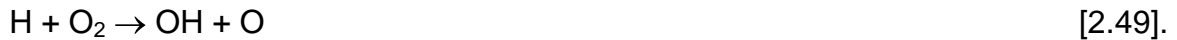


- Methyl radicals start synthetic flame reactions, like



### 2. 2. 3. High temperature oxidation (above 1100 K at 1 bar).

The transition boundary between the intermediate and high temperature regimes of oxidation is usually defined by the importance of reaction [2.49]:



When [2.49] starts to dominate in the competition for the consumption of the H-atoms over the two reactions governing this process in the intermediate regime,



the high temperature regime is on, and the primary members of the “X” pool are reproduced directly by the “ping – pong” scheme (i. e., by [2.49]). Fig. 2. 8. illustrates the transition to the high temperature oxidation regime.

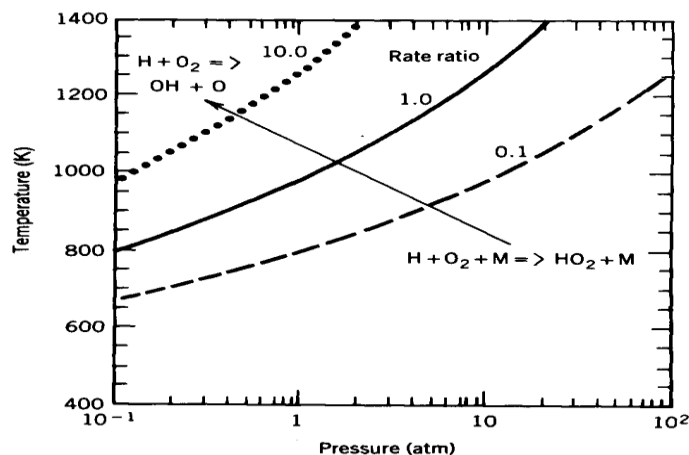


Figure 2. 8. Temperature for a constant ratio of H-atom addition to O<sub>2</sub> and ratios of

reactions [2.49] and [2.50] as functions of pressure (From Ref. 4).

It may be seen that the temperature above which reaction [2.49] will start to dominate over [2.50] depends significantly on the pressure involved and is around 1000 K at atmospheric pressure, but increases steeply when the pressure is increased.

As may be expected, initiation reactions involving direct cleavage of C-H and C-C bonds, i. e.



increase their role in the high temperature regime, because more energy is available. The original initiation reaction of Semenov's scheme becomes:



The attack of the members of the X pool on the whole molecules (i. e., [S11.] and radicals lead typically to abstraction products, but for smaller molecules and radicals (i. e., small olefins – ethene, propene, acetylene) addition products may be observed as well.

The scheme, suggested by Semenov and completed by the achievements of many other scientists, allows for the explanation of the experimental observations, outlined in the beginning of this chapter.

We may now summarise what we learned:

- The  $\text{H}_2 - \text{O}_2$  is very important in combustion, because hydrogen is a clean fuel on which we are going to rely, but also because this system is part of the mechanism of the combustion of most fuels.
- The low temperature regime is the most interesting from the point of view of the aims of this course. The ignition processes in this regime are fuel specific, to a great extent it covers the conditions typical for ignition in engines and most of the pollutants are formed in this regime.
- Multiple cool flames and negative temperature coefficients are an important characteristic of the low temperature ignition of fuels. In order to explain them, Semenov's scheme has to be expanded.
- The processes in the intermediate temperature regime are governed by reactions involving the hydroperoxide ion ([i. e., S.6.] and [20]), which are the main producer of the primary X pool members. Its boundaries are determined by the end of cool flames and the negative temperature dependence of rate coefficients on the one hand, and the high temperature regime, which is governed by the primary members of the X pool – on the other.
- The high temperature regime is governed directly by the ping – pong mechanism, which provides the members of the X pool. It is responsible for the completion of the combustion reactions and for the formation of some of the pollutants.

The above presentation is based mainly on model reactions derived from experimental work and modeling of the ignition and combustion of individual pure compounds. It can be seen that the particular reactions strongly depend on the state parameters of the systems and on the molecular structure of the hydrocarbon molecule. Figures 2.9. and 1. 3. show the effect of the fuel – oxidiser ratio on the main pathways in stoichiometric and rich combustion of methane.

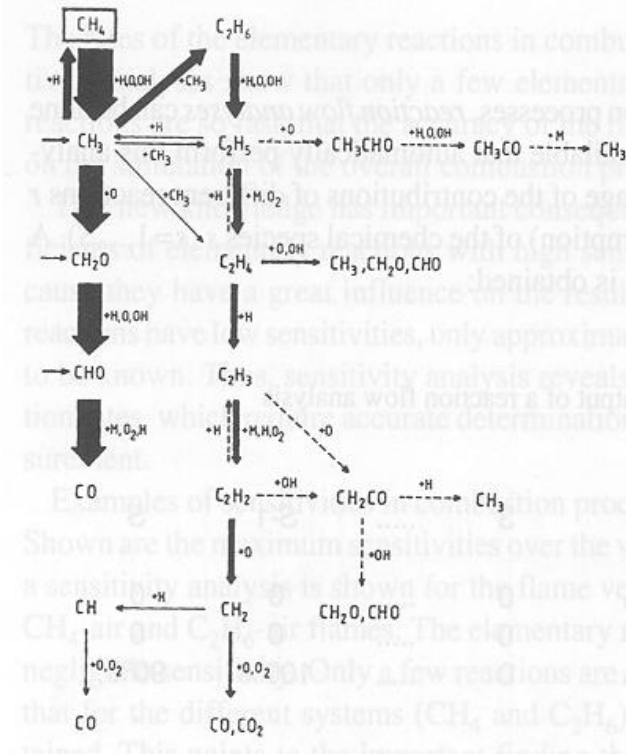


Figure 1.3. Main pathways in a premixed stoichiometric  $\text{CH}_4$  – air flame,  $p = 1$  bar,  $T_0 = 298$  K. (From Ref. 5)

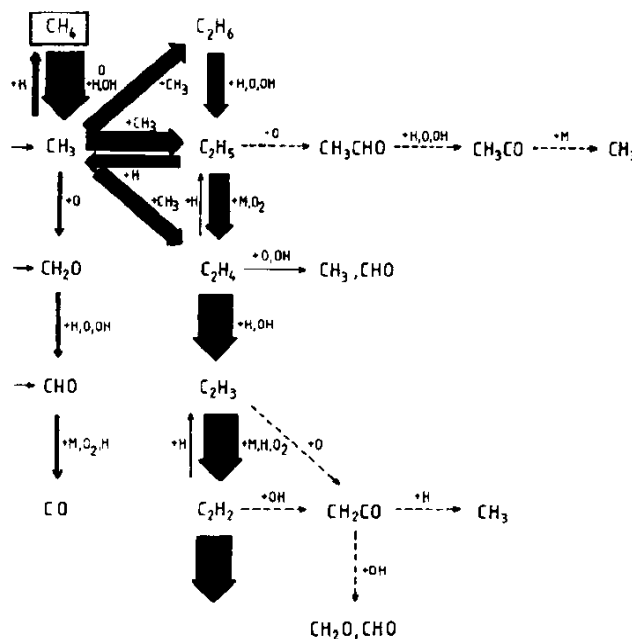


Figure 2.9. Main pathways in a premixed rich  $\text{CH}_4$  – air flame,  $p = 1$  bar,  $T_0 = 298$  K. (From Ref. 5)



It is believed that the above presentation clearly and comprehensively outlines the theoretical chemical fundamentals of hydrocarbon oxidation.

However, it should be emphasised, that with the increasing of the number of atoms in the fuel molecule, the number of species and possible reactions increase tremendously. For instance, the oxidation mechanism of n-cetane ( $n\text{-C}_{16}\text{H}_{34}$ ) – one of the typical hydrocarbons in diesel and jet fuels, involves around 2000 species participating in 6000 reactions. Having in mind the composition of gasolines, which may contain up to 300 hydrocarbons, and the main features of the composition of the heavier fuels, discussed in the first topic, it becomes obvious that the understanding of combustion chemistry is a very difficult task. Moreover, attempts for generalisation and direct application of the above model reactions to real life combustion, without understanding the underlying chemistry, might be dangerous.

#### References for further reading.

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