Problem 3

a)
Thermal NO formation mechanism:

$$N_2 + O \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} NO + N \qquad E_{1f} = 318 \text{ kJ/mol}$$

$$N + O_2 \underset{k_{2r}}{\overset{k_{2f}}{\rightleftharpoons}} NO + O \qquad E_{2f} = 27 \text{ kJ/mol}$$

$$N + OH \underset{k_{3r}}{\overset{k_{3f}}{\rightleftharpoons}} NO + H \qquad E_{3f} = 0 \text{ kJ/mol}$$

Prompt NO formation mechanism:

$$N_2 + CH \underset{k_r}{\overset{k_f}{\rightleftharpoons}} HCN + N \qquad E_f = 75 \text{ kJ/mol}$$

$$HCN \xrightarrow{+O} NCO \xrightarrow{+H} NH \xrightarrow{+H} N \xrightarrow{+O_2, +OH} NO$$

The N_2O mechanism:

$$N_2 + O + M \rightleftharpoons N_2O + M$$

$$N_2O + O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} NO + NO \qquad E_f = 97 \text{ kJ/mol}$$
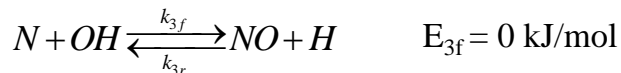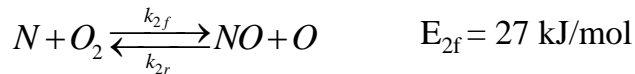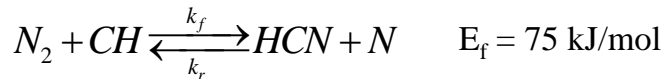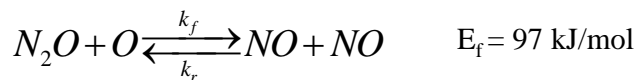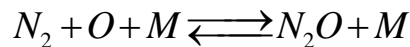
Influence of temperature:
Temperature influences NO formation directly through the temperature dependence of the reaction constants. A large (positive) activation energy in a reaction constant makes the exponential term in the reaction constant increasingly temperature sensitive. Comparing only the activation energies for the above mentioned NO formation mechanisms thermal NO formation is clearly most temperature sensitive due to the high activation energy of the first (initiating) reaction. This reaction therefore also becomes rate-limiting. Prompt NO formation is much less temperature sensitive when only considering the activation energy of the initiating reaction. The same is the case for the NO producing reaction in the N_2O mechanism. However, great care should be taken when analysing the relative importance of NO formation mechanisms as a function of temperature, since several other parameters than the activation energy are involved. Some of these parameters are indirectly temperature dependent, e.g. radical concentrations.

Influence of pressure:
The reaction constant of a true elemental reaction is not pressure dependent, but the reaction rate is influenced by pressure through changing reactant concentrations, which speed up the reaction rate for increasing pressure. Looking at the NO formation mechanisms, the reaction constants in the thermal NO and prompt NO formation reactions are not pressure dependent, while the reaction constant in the initiating reaction

in the N_2O mechanism is, since it is a third body reaction needing a "collision between three molecules" to form two molecules. This is not a true elemental reaction, but a series of reactions, where the reaction constant in the overall reaction becomes pressure dependent. In addition this reaction will be heavily influenced by pressure through its relative influence on reactant and product concentrations.

Influence of residence time:
Residence time influences NO formation heavily for the thermal NO formation mechanism, since the reaction rate in general is low due to its heavy temperature dependence, i.e. slow reactions need a longer residence time to reach equilibrium.

Influence of flame type:
The flame type influences the relative importance of the NO formation mechanisms. Basically the flame type influences the temperature levels where NO is formed (non-premixed flame, premixed flame, lean flames, staged flames, etc.) through changes in residence time at high temperatures and radical concentrations. Hence, only considering the activation energy or the temperature dependence of the reaction constant is in many cases a great simplification. Also the availability of key radicals such as O, OH and CH are very much important, often resulting in a considerable degree of temperature dependence also for the prompt NO mechanism.

b)

$$N_2 + O \underset{k_{1r}}{\overset{k_{1f}}{\rightleftarrows}} NO + N$$

$$N + O_2 \underset{k_{2r}}{\overset{k_{2f}}{\rightleftarrows}} NO + O$$
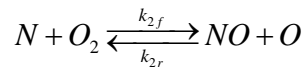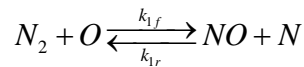
$$\frac{d[NO]}{dt} = k_{1f}[N_2][O] + k_{2f}[N][O_2]$$

$$\frac{d[N]}{dt} = k_{1f}[N_2][O] - k_{2f}[N][O_2]$$

Quasi-steady state: $\dfrac{d[N]}{dt} = 0$

$$\Rightarrow \frac{d[NO]}{dt} = \underline{\underline{2k_{1f}[N_2][O]}}$$

Assumptions that has to be made:
- the reaction rate of the reverse reactions is negligible
- steady state conditions for [N]

c)
We eliminate [O] through our equilibrium assumption

$$K_p = \frac{\left(\dfrac{p_O}{p^0}\right)^2}{\dfrac{p_{O_2}}{p^0}} = \frac{p_O{}^2}{p_{O_2}p^0} = \frac{([O]R_uT)^2}{[O_2]R_uTp^0} = \frac{[O]^2R_uT}{[O_2]p^0}$$

or

$$[O] = \left([O_2]\frac{K_p p^0}{R_uT}\right)^{\frac{1}{2}}$$

Thus

$$\frac{d[NO]}{dt} = 2k_{1f}[N_2]\left([O_2]\frac{K_p p^0}{R_uT}\right)^{\frac{1}{2}} = 2k_{1f}\left(\frac{K_p p^0}{R_uT}\right)^{\frac{1}{2}}[N_2][O_2]^{\frac{1}{2}}$$

where we assume that the volume fractions of N_2 and O_2 in air are
$$X_{N_2} \cong X_{N_2,i} = 0.79 \quad and \quad X_{O_2,e} \cong X_{O_2,i} = 0.21$$
since X_{NO} and X_O are both likely to be quite small.
We can convert the mol fractions to molar concentrations

$$[N_2] = X_{N_2}\frac{p}{R_uT} = 0.79\cdot\frac{3\cdot101325}{8315\cdot2500} = 1.155\cdot10^{-2}\ \frac{kmol}{m^3}$$

$$[O_2] = X_{O_2}\frac{p}{R_uT} = 0.21\cdot\frac{3\cdot101325}{8315\cdot2500} = 3.071\cdot10^{-3}\ \frac{kmol}{m^3}$$

and evaluate the rate coefficient

$$k_{1f,2500K} = 1.82\cdot10^{14}\exp\left(\frac{-38370}{2500}\right) = 3.93\cdot10^7\ \frac{cm^3}{mol\cdot s} = 3.93\cdot10^4\ \frac{m^3}{kmol\cdot s}$$

Assuming equilibrium between O_2 and O gives the equilibrium constant

$$K_p(T) = \frac{p_O{}^2}{p_{O_2}p^0} = \exp\left(\frac{-\Delta G_T^0}{R_uT}\right)$$

where

$$\Delta G_{2500K}^0 = \left[2\overline{g}_{f,O}^0 - \overline{g}_{f,O_2}^0\right]_{2500K}$$
$$= 2\cdot88203 - 0 = 176406\ kJ/kmol$$

$$K_{p,2500K} = \exp\left(\frac{-176406}{8.315\cdot2500}\right) = 2.063\cdot10^{-4}$$

We can now numerically evaluate d[NO]/dt

$$\frac{d[NO]}{dt} = 2\cdot3.93\cdot10^4\left(\frac{2.063\cdot10^{-4}\cdot101325}{8315\cdot2500}\right)^{\frac{1}{2}}[1.155\cdot10^{-2}][3.071\cdot10^{-3}]^{\frac{1}{2}} = 0.0505\ \frac{kmol}{m^3\cdot s}$$

If we assume that the N_2 and O_2 concentrations do not change with time and that the reverse reactions are unimportant over the 0.25 ms interval, we can simply integrate d[NO]/dt:

$$\int_0^{[NO]} d[NO] = \int_0^t k_G[N_2][O_2]^{\frac{1}{2}} dt$$

so

$$[NO] = k_G[N_2][O_2]^{\frac{1}{2}}t = 0.0505 \cdot 0.25 \cdot 10^{-3} = 1.263 \cdot 10^{-5} \frac{kmol}{m^3}$$

or

$$X_{NO} = [NO]\frac{R_uT}{p} = 1.263 \cdot 10^{-5} \cdot \frac{8315 \cdot 2500}{3 \cdot 101325} = 8.64 \cdot 10^{-4} \frac{kmol}{kmol} = \underline{\underline{864 \ ppm}}$$

This result is far from the result using detailed chemical kinetics, i.e. 9.46 ppm NO.

Assumptions that were made:
Equilibrium between O_2 and O: this assumption can be checked by comparing the equilibrium concentration O with [O] calculated using detailed chemical kinetics, and then we see that the equilibrium concentration overestimates [O]. By using an average [O] from the detailed chemical kinetics calculation we can use equation (2) to calculate the NO level, i.e. 9.49 ppm NO, which is very close to the detailed chemical kinetics result.

$$[O] = X_O \frac{p}{R_uT} = \frac{83.57 \cdot 10^{-6}}{2} \cdot \frac{3 \cdot 101325}{8315 \cdot 2500} = 6.110 \cdot 10^{-7} \frac{kmol}{m^3}$$

$$\frac{d[NO]}{dt} = 2k_{1f}[N_2][O] = 2 \cdot 3.931 \cdot 10^4 \cdot 1.155 \cdot 10^{-2} \cdot 6.110 \cdot 10^{-7} = 5.548 \cdot 10^{-4} \frac{kmol}{m^3 \cdot s}$$

$$[NO] = 2k_{1f}[N_2][O]t = 5.548 \cdot 10^{-4} \cdot 0.25 \cdot 10^{-3} = 1.387 \cdot 10^{-7} \frac{kmol}{m^3}$$

or

$$X_{NO} = [NO]\frac{R_uT}{p} = 1.387 \cdot 10^{-7} \cdot \frac{8315 \cdot 2500}{3 \cdot 101325} = 9.49 \cdot 10^{-6} \frac{kmol}{kmol} = \underline{\underline{9.49 \ ppm}}$$

Steady state for [N] was assumed, but [N] increase continuously up to our residence time of 0.25 ms. This means that the steady state assumption is not entirely correct, but [N] is very small, and the influence of a deviation from the steady state assumption therefore becomes small.
We have assumed that the **reversible reactions can be neglected**, which is a valid assumption at such a high temperature.

In general one should be very careful with using equilibrium assumptions in combustion modelling, and especially in connection with modelling of NO formation. The assumption of equilibrium between O_2 and O in our case very much over predicted [O],

while in a flame front [O] can be greatly under predicted using the same equilibrium assumption. Equilibrium assumptions become increasingly incorrect for decreasing residence times and temperatures. In our case the residence time is too short to achieve equilibrium between O_2 and O even if the temperature is very high, and much too short to reach equilibrium [NO]. Even if equilibrium between O_2 and O is reached, the history towards this equilibrium is important when calculating [NO]. In our case [O] increased almost linearly as a function of residence time, i.e. using an arithmetic average [O] in the calculation of [NO] is a good simplification, together with assuming constant [N_2], since in our case we are not dealing with a combustion case, where also [N_2] may vary.

Problem 4

a)
The principle of sensitivity analysis:
Sensitivity analysis means an analysis of how sensitive a specific result is subject to changes in the input causing the result. Sensitivity analysis of detailed chemical kinetics reaction mechanism may for example be a study of how sensitive [NO] is to changes in the reaction rate constants, as shown below:

The dependence of the solution c_i on the parameters k_r is called *sensitivity*. Absolute and relative sensitivities can be defined as

$$E_{i,r} = \frac{\partial c_i}{\partial k_r} \qquad \text{and} \qquad E_{i,r}^{\text{rel}} = \frac{k_r}{c_i}\frac{\partial c_i}{\partial k_r} = \frac{\partial \ln c_i}{\partial \ln k_r} . \qquad (7.16)$$

The individual sensitivities are then compared to each other, usually in a plot, and conclusions can be drawn regarding the relative importance of the single reactions, and the accuracy need of the single reaction constants, for [NO].

The principle of reaction path analysis:
Reaction path analysis means an analysis of the percentage of the contributions of different reactions to the formation (or consumption) of the different species in a reaction mechanism. Reaction path (flow) diagrams, either local or integral reaction flow diagrams, are usually constructed to visualise the flow of e.g. nitrogen in the air to NO. Hence, instantaneous reaction rates at a specific set of conditions are either compared directly (at a certain time or a certain location in a flame) or average reaction rates are calculated and compared (for the total reaction time or a selected time period, or for the whole flame or a selected flame region).

Usefulness of sensitivity- and reaction path analysis:
Both sensitivity analysis and reaction path analysis are very useful in analysis of reaction mechanisms. Sensitivity analysis can directly point out e.g. the reaction constants (reactions) that control the formation of e.g. NO at a specific set of conditions. A high level of accuracy in these reaction constants is therefore needed, and as such sensitivity

analysis can be used to suggest where efforts should be directed with regards to finding the most accurate reaction constant.

A reaction path analysis show the actual flow of elements through the reaction mechanism, and points out the most important reaction paths and reactions for the formation of e.g. NO.

Both analysis methods reveal different types of information, and they complement each other in the analysis of reaction mechanisms. However, reaction path analysis is the method to choose if you want to study the details behind the formation of e.g. NO using a given reaction mechanism.

b)

The structure of soot is difficult to characterize, because there is not a clear transition from gas to liquid, or liquid to solid phase. Freshly formed soot seems to consist of polycycles with side chains, having a molar H/C ratio of about 1. Aging, caused by heating, leads to compounds with a higher carbon content, similar to graphite. Physically, soot appears as grape-like clusters of small spheres (spherules). The single spherules typically reach 20-50 mm in diameter, depending on the combustion conditions.

Soot is formed by further growth of PAH through conglomeration of molecules. The PAH again are high molecular weight molecules formed from low molecular weight molecules in a series of process steps. Subsequently, the particles grow by surface growth by addition of mainly C_2H_2, and by coagulation. See figure below.
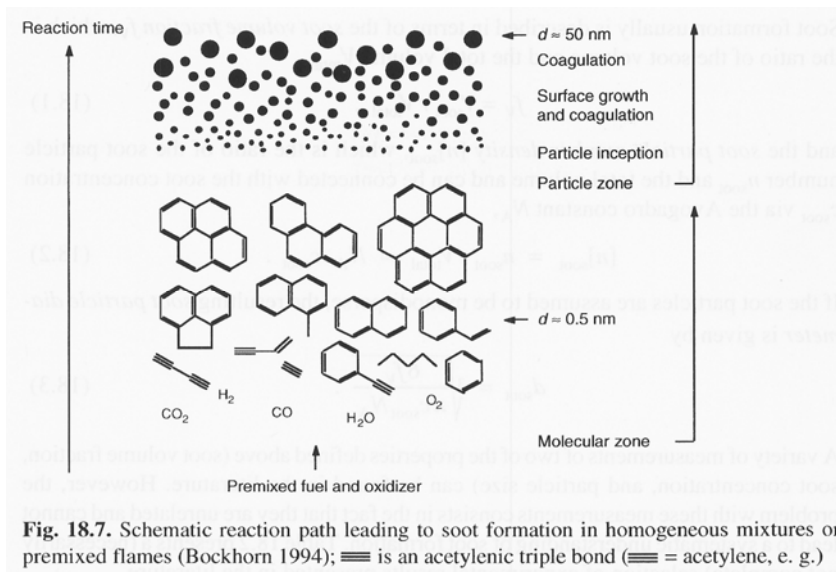

Fig. 18.7. Schematic reaction path leading to soot formation in homogeneous mixtures or premixed flames (Bockhorn 1994); ≡ is an acetylenic triple bond (≡ = acetylene, e. g.)

c)

Combustion of a small particle progresses sequential in the sense that major processes as drying, devolatilisation (pyrolysis) and char burnout happens in a quite distinct sequence:
- drying occurs first, and the drying front precedes devolatilisation and combustion. As long as water exist at a specific location, devolatilisation and combustion does not take place as all the heat is used to evaporate the water

- as the drying front moves into the small particle, devolatilisation takes place due to continuous heat transfer from the surroundings to the particle. Devolatilisation takes place first at the particle surface, and the devolatilisation front then moves into the particle, following the drying front
- char (mainly fixed carbon) remains after the devolatilisation front has passed, and this is combusted in a heterogeneous process where oxygen is diffusing in to the char surface and products are diffusing out from the surface

Dependent on a number of conditions the small particle may follow a quite distinct shrinking core or shrinking sphere behaviour or combinations of these. For shrinking core behaviour there is an unreacted particle core that shrinks as the devolatilisation front moves inwards, while no combustion takes place at the particle surface at the same time. Water vapour and devolatilisation products will flow outwards continuously and the surrounding oxygen will not react with the char surface. For shrinking sphere behaviour the combustion occurs on the outer particle surface as soon as the drying and devolatilisation has happened, so the particle diameter decreases continuously, leaving the particle core intact.

Shrinking core behaviour is favoured when the temperature is low.
Shrinking particle behaviour is favoured when the temperature is high.
A combination of shrinking core and shrinking sphere occur at moderate temperatures.
The particle combustion behaviour is a results of the influence of temperature on the main controlling factors, diffusion and reaction rates.
See figure below.

THREE ZONES COMBUSTION(III)
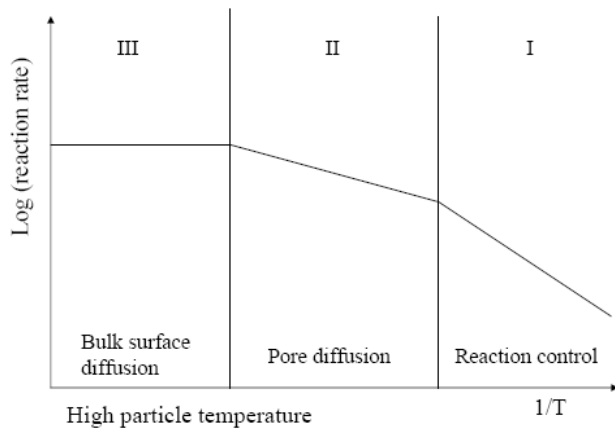
Combustion of a wood log, a large particle, progresses also as a sequential process, but there is in general considerably more overlap between the processes, and the total reaction time of a wood log is much longer than for a small particle.