Eksamensoppgaver i Varme- og forbrenningsteknikk – Oppgaver - Engelsk

Problem 1

a) Describe the 3 most important NO formation mechanisms for NO formation from N_2 in air, with special focus on the chemistry involved, and how this is influenced by temperature, pressure residence time and flame type.

Solution:

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.

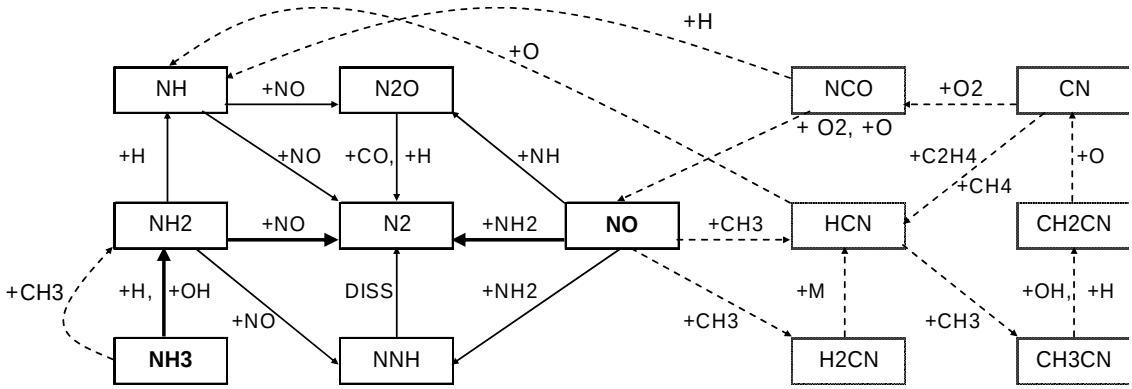
Influence of residence time:
Residence time influences NO formation heavily for the thermal NO formation mechanism, since the reaction rate in general is low due to its heavy temperature dependence, i.e. slow reactions need a longer residence time to reach equilibrium.

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) NO can also be formed from bound nitrogen in a solid fuel. How?
Staged air combustion is one method of NOx reduction in solid fuel combustion applications. Describe the principle.

Solution:
Nitrogen in a solid fuel is partly released in the pyrolysis phase, or remains in the char fraction. Nitrogen released in the pyrolysis phase is released mainly as NH3 and HCN, and these gas species will through a sequence of homogeneous reactions mainly form either NO or N2. The nitrogen remaining in the char fraction will be heterogeneously oxidised to also mainly either NO or N2.

The principle of staged air combustion is to add sufficient air in the primary air stage to ensure a maximum reduction of NO by reaction with mainly NH2 (formed from NH3), but not so much air that the NH2 instead is oxidised to NO. Hence, there exist and optimum primary excess air ratio that gives a maximum overall reduction of fuel-N to N2. This optimum depends on several factors, the primary excess air ratio being very important. Other influencing factors are temperature, fuel-N content, fuel-N speciation in the pyrolysis and the composition of the pyrolysis gas.



c) A pressure dependent reaction:

$$A + M \xrightarrow{k} P(roducts) + M$$

is not an elementary reaction, but a series of reactions:

$$A + M \xrightarrow{k_a} A^* + M \quad \text{(activation)}$$

$$A^* + M \xrightarrow{k_{-a}} A + M \quad \text{(deactivation)}$$

$$A^* \xrightarrow{k_u} P(roducts) \quad \text{(unimolecular reaction)}$$

Explain what happens.

Find an expression for d[P]/dt at very low pressure and at very high pressure.

Solution:
The reactant A needs to increase its energy level to be able to react to form P. This happens when A collides with a so-called third body species, which is not consumed in the reaction. Some of the A molecules with a higher energy level will be deactivated through reactions with a M again, but some may also react to form P.

Pressure dependence of rate coefficients

$$
\begin{array}{llll}
A + M & \xrightarrow{k_a} & A^* + M & \text{(activation)} \\
A^* + M & \xrightarrow{k_{-a}} & A + M & \text{(deactivation)} \\
A^* & \xrightarrow{k_u} & P(\text{roducts}) & \text{(unimolecular reaction)}\ .
\end{array}
\qquad (6.21)
$$

The rate equations for this case

$$
\frac{d[P]}{dt} = k_u[A^*] \quad \text{and} \quad \frac{d[A^*]}{dt} = k_a[A][M] - k_{-a}[A^*][M] - k_u[A^*]\ . \qquad (6.22)
$$

Assumption: the concentration of the reactive intermediate is in quasi-steady state

$$
\frac{d[A^*]}{dt} \approx 0\ , \qquad (6.23)
$$

Pressure dependence of rate coefficients

Solving for [A*] this gives

$$
[A^*] = \frac{k_a[A][M]}{k_{-a}[M] + k_u}
$$

and

$$
\frac{d[P]}{dt} = \frac{k_u k_a[A][M]}{k_{-a}[M] + k_u}\ . \qquad (6.24)
$$

Two extremes can be distinguished, i.e. reaction at very low and very high pressure

At very low pressure (low pressure range) the concentration of M is very small, with $k_{-a}[M] << k_u$, and you get an apparent second-order rate law

$$
\frac{d[P]}{dt} = \frac{\cancel{k_u} k_a[A][M]}{\cancel{k_{-a}[M]} + \cancel{k_u}}
$$

$$
\frac{d[P]}{dt} = k_a \cdot [A][M]\ . \qquad (6.25)
$$

Thus, the reaction rate is proportional to the concentration of A and M, because the activation reaction is slow (rate-limiting) at low pressures

Pressure dependence of rate coefficients

At very high pressure (high pressure range) the concentration of M is high and together with $k_{-a}[M] >> k_u$, one obtains the apparent first order rate law:

$$\frac{d[P]}{dt} = \frac{k_u k_a [A]\cancel{[M]}}{k_{-a}\cancel{[M]} + \cancel{k_u}}$$

$$\frac{d[P]}{dt} = \frac{k_u k_a}{k_{-a}}[A] = k_\infty \cdot [A] \,. \qquad (6.26)$$

Here the reaction rate does not depend on the concentrations of the collision partners, because at high pressures collision occurs very often and, thus, the decomposition of the activated molecule A* is rate limiting instead of the activation

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Problem 2

a) Combustion of solid fuels is a sequential process. Describe this sequential process for a small particle. Will the sequential process for a wood log be different compared to the small particle?

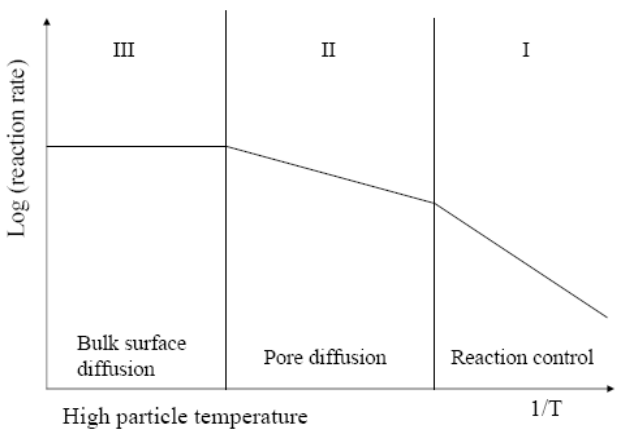
Solution:
Combustion of a small particle progresses sequential in the sense that major processes as drying, devolatilisation (pyrolysis) and char burnout happens in a quite distinct sequence:
- drying occurs first, and the drying front precedes devolatilisation and combustion. As long as water exist 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.

b) In pyrolysis of solid fuel samples in a ThermoGravimetric Analyser (TGA) we can find a reaction constant k, as a function of temperature, an amplitude factor A and an activation energy E. How, and which assumptions must be made? What kind of kinetics have we actually found?

Solution:
We treat the normalised mass loss rate as a negative rate of formation in a unimolecular reaction, where the rate of formation depends only on the fraction of the remaining sample mass and a temperature dependent reaction constant k. In principle the reaction order is n, while n=1 is the usual assumption. Hence, we have a first order reaction.

$$\frac{-d\left(\frac{m}{m_0}\right)}{dt} = k \cdot \left(\frac{m - m_{char}}{m_0}\right)^n \quad where \quad k = A \cdot \exp\left(\frac{-E}{R_u \cdot T}\right)$$

In a TGA experiment we record the rate loss as a function of time and temperature, and the only unknowns then are A and E. In principle we can find these values by selecting

only two temperature levels, i.e. getting two equations with two unknowns. However, in practice more points are selected, to minimize experimental uncertainties and get as accurate values as possible for A and E. If the fuel (e.g. wood) is treated as consisting of for example cellulose, hemicellulose and lignin, we have six unknowns and a data fitting procedure must be used to get A and E for the three corresponding first order reactions.

Assumptions:
- no transport limitations in the sample, e.g. the mass loss rate is only controlled by kinetics
- the fuel is regarded as a single zero-dimensional sample, consisting of one or a few chemical compounds/structures, and we do not, or cannot, take into account the thermal decomposition behaviour of the many chemical sub-structures in complex solid fuels
- we assume a first order reaction

The kinetics that we have found is global kinetics. Hence, we do not investigate the detailed chemistry. However, in this case we do not take into account which gas/tar species that are formed either.

c) A number of denominations are used when reporting emissions. How large is a NOx emissions level (reported as NO_2) in mg/kg fuel if 25 ppm (volume basis) NO is measured in a <u>dry</u> flue gas, at 15 vol% O_2, if the fuel is methane?

Solution:

Combustion of CnHm - Emission conversion

				n	1	m	4									
		Lambda	Stoichiometric													
1	CnHm +	3.2375	2	(O2 +	3.762	N2)	=	1	CO2 +	2	H2O +	4.475	O2 +	24.36	N2	31.83333 mol wet flue gas
								1				4.475		24.36		29.83333 mol dry flue gas
								3.141		6.283		14.06		76.52		100 vol% wet flue gas
								3.352				15.00		81.65		100 vol% dry flue gas

25	ppm NO
16.043	MCnHm (kg/kmol)
46.0055	MNO2 (kg/kmol)
29.8333	Ntot,dry (kmol flue gas / kmol fuel)
22.4136	VMol (Nm^3 gas / kmol gas)
41.6799	VFG (Nm^3 flue gas / kg fuel)

2138.78	mg NO2/kg CnHm	$mg\ NO_2 / kg\ fuel = ppm\ NO \cdot V_{FG} \cdot \frac{M_{NO_2}}{V_{Mol}}$
2138.78	mg NO2/kg CnHm	$mg\ NO_2 / kg\ fuel = ppm\ NO \cdot N_{tot,dry} \cdot \frac{M_{NO_2}}{M_{CnHm}}$

$$V_{FG,dry} = \frac{V_{Mol}}{M_{CnHm}} \cdot N_{tot,dry}$$