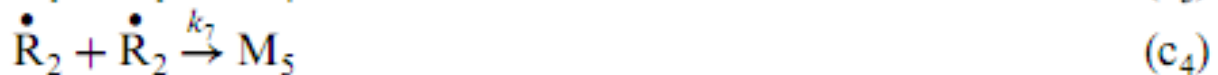# Module 1 Theoretical Background of Thermal Processes
Lecture 2. Thermodynamics and kinetics of thermal reactions of petroleum hydrocarbons.

The kinetic equations can be deduced on the basis of the reaction mechanism. For the thermal decomposition of a hydrocarbon, the chain mechanism may be represented by the generalized scheme:

Initiation	$M \xrightarrow{k_1} \dot{R}_1 + \dot{R}_2$	(a)
Propagation	$\dot{R}_1 + M \xrightarrow{k_2} R_1H + \dot{R}_3$	(b_1)
	$\dot{R}_2 + M \xrightarrow{k_2} R_1H + \dot{R}_3$	(b_2)
	$\dot{R}_3 \xrightarrow{k_3} \Sigma M_f + \dot{R}_1$	(b_3)
Interruption	$\dot{R}_1 + \dot{R}_3 \xrightarrow{k_4} M_2$	(b_4)
	$\dot{R}_2 + \dot{R}_3 \xrightarrow{k_5} M_3$	(b_5)
	$\dot{R}_1 + \dot{R}_1 \xrightarrow{k_6} M_4$	(c_3)
	$\dot{R}_2 + \dot{R}_2 \xrightarrow{k_7} M_5$	(c_4)
	$\dot{R}_3 + \dot{R}_3 \xrightarrow{k_8} M_6$	(c_5)
	$\dot{R}_1 + \dot{R}_2 \xrightarrow{k_9} M_7$	(c_6)

The initiation reaction results in the formation of two types of radicals: R1 - which can propagate the reaction chain and R2 - which cannot. Since the length of the kinetic chain is about 200 reactions, it results that the concentration of the R2 radicals is about 200 times lower than of the radicals R1 and R3. Considering that the rate constants are of the same order of magnitude, it results that the interruption reactions that involve the R2 radicals, i.e. (c2), (c4), and (c6) may be neglected.

From among the remaining reactions, reaction (c1) takes place between two different radicals, whereas the reactions (c3) and (c5) take place between two identical radicals.

Since again the rate constants may be considered to be equal, it is possible to deduce the condition required in order that the preferred (most probable) interaction be that among identical radicals.

If in an arbitrary volume, the number of radicals of different species is $n1$, $n2,..., ni,..., nk$, the probability of interaction between two identical radicals is proportional to n_i^2 and that for all the possible reactions are proportional to:

$$\left(\sum_1^k n_i\right)^2$$

The probability of interaction between different radicals will be proportional to the difference:

$$\left(\sum_1^k n_i \right)^2 - \sum_1^k n_i^2$$

Thus, the condition that the interaction between two identical radicals, for example of species 1, should be more probable than the interactions between different radicals will be given by the relation:

$$\left(\sum_1^k n_i \right)^2 - \sum_1^k n_i^2 < n_i^2$$

Using this relation one can compute that the interaction between two identical radicals (*ni*) is more probable only if their concentration is about 3 times larger than the sum of concentrations of the rest of the radicals.

It is obvious that this condition can not be fulfilled during the thermal reactions of higher hydrocarbon or petroleum fractions. Consequently, the only interruption reaction which needs to be taken into account is reaction (c1).

By applying the theorem of stationary states to the reactions of scheme (a)–(c1), one obtains:

$$\frac{d[\dot{R}_1]}{d\tau} = k_1[M] - k_2[\dot{R}_1][M] + k_3[\dot{R}_3] - k_4[\dot{R}_1][R_3] = 0 \tag{2.6}$$

$$\frac{d[\dot{R}_2]}{d\tau} = k_1[M] - k_2[\dot{R}_2][M] = 0 \tag{2.7}$$

$$\frac{d[\dot{R}_3]}{d\tau} = k_2[\dot{R}_1][M] + k_2[\dot{R}_2][M] - k_3[\dot{R}_3] - k_4[\dot{R}_1][\dot{R}_3] = 0 \tag{2.8}$$

From Eq. (2.7) it results 2.9:
$$[\dot{R}_2] = \frac{k_1}{k_2}$$

By substitution, reaction (2.8) becomes :

$$k_2[\dot{R}_1][M] + k_1[M] - k_3[\dot{R}_3] - k_2[\dot{R}_1][\dot{R}_3] = 0$$

By adding this to Eq. (2.6), it results:

$$[\dot{R}_3] = k_1 \frac{[M]}{k_4[\dot{R}_1]}$$

and by substitution in (2.6), after simplifications one obtains 2.10:

$$[\dot{R}_1] = \left(\frac{k_1 k_3}{k_2 k_4}\right)^{1/2}$$

The initial decomposition rate of the molecules M is given by the equation:

$$\frac{-d[\mathrm{M}]}{d\tau} = k_1[\mathrm{M}] + k_2[\dot{\mathrm{R}}_1][\mathrm{M}] + k_2[\dot{\mathrm{R}}_2][\mathrm{M}]$$

By substituting for $[\dot{\mathrm{R}}_1]$ and $[\dot{\mathrm{R}}_2]$ the expressions (2.9) and (2.10), it results:

$$\frac{-d[\mathrm{M}]}{d\tau} = \left\{ 2k_1 + \left(\frac{k_1 k_2 k_3}{k_4} \right)^{1/2} \right\}[\mathrm{M}]$$

which shows that the reaction is of first order in accordance with the experimental data.

This expression can be written as 2.11: $\quad \dfrac{d[\mathrm{M}]}{d\tau} = k[\mathrm{M}]$

where the overall rate constant is a function of the rate constants of the elementary reactions according to the relation 2.12:

$$k = 2k_1 + \left(\frac{k_1 k_2 k_3}{k_4} \right)^{1/2} = \left(\frac{k_1 k_2 k_3}{k_4} \right)^{1/2}$$

If in the simplified expression (2.12), one replaces the overall rate constant and the rate constants of the elementary reactions by expressions of the Arrhenius type, it results:

$$Ae^{-E/RT} = \left(\frac{A_1 A_2 A_3}{A_4}\right)^{1/2} e^{-\frac{1}{2RT}(E_1+E_2+E_3-E_4)}$$

from where: $E = \dfrac{1}{2}(E_1 + E_2 + E_3 - E_4)$

From the above discussion it results that the overall activation energy for the chain reaction is much lower than that of the initiation reaction, or of the decomposition following a molecular mechanism. Usually, this is expressed by: in thermal decompositions, the mechanism of chain reactions is "energetically more advantageous" than the molecular mechanism.

The general scheme discussed above represents a gross simplification of the actual mechanism of the thermal decomposition of hydrocarbons with high molecular mass, or of fractions of crude oil. It does not take into account the formation during the initiation reactions of different types of radicals depending on the position in the molecule of the C–C bond which is broken of the further decomposition of the radicals initially formed, or of the fact that the R3 radicals are of various types, depending on the position of the extracted hydrogen within the various molecules M.