Kinetic modeling of complex reaction networks

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Eurokin workshop, Villeurbanne

October 18, 2001

- Introduction / Scope
- Case: Hydrocracking
- Families of elementary reactions
- Adjustable parameters
- Network
- Conclusions

Scale-up

intrinsic kinetic
laboratory data

→

intrinsic chemical kinetics
based on elementary steps

→

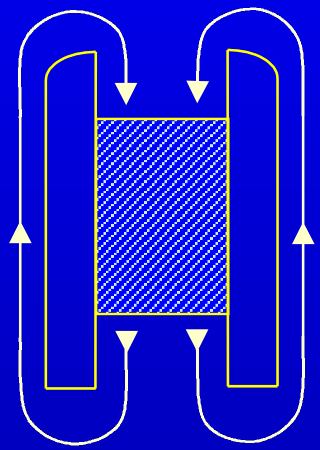
conservation laws, including
transport phenomena

→

industrial reactor
design & optimization

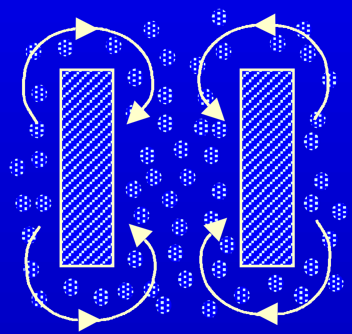
Reactors: laboratory versus industrial

BERTY



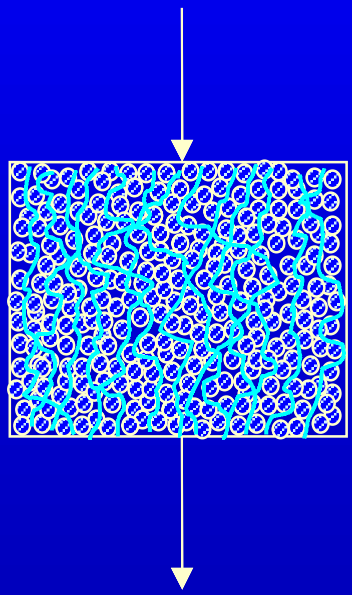
$1\ dm^3$

ROBINSON-
MAHONEY



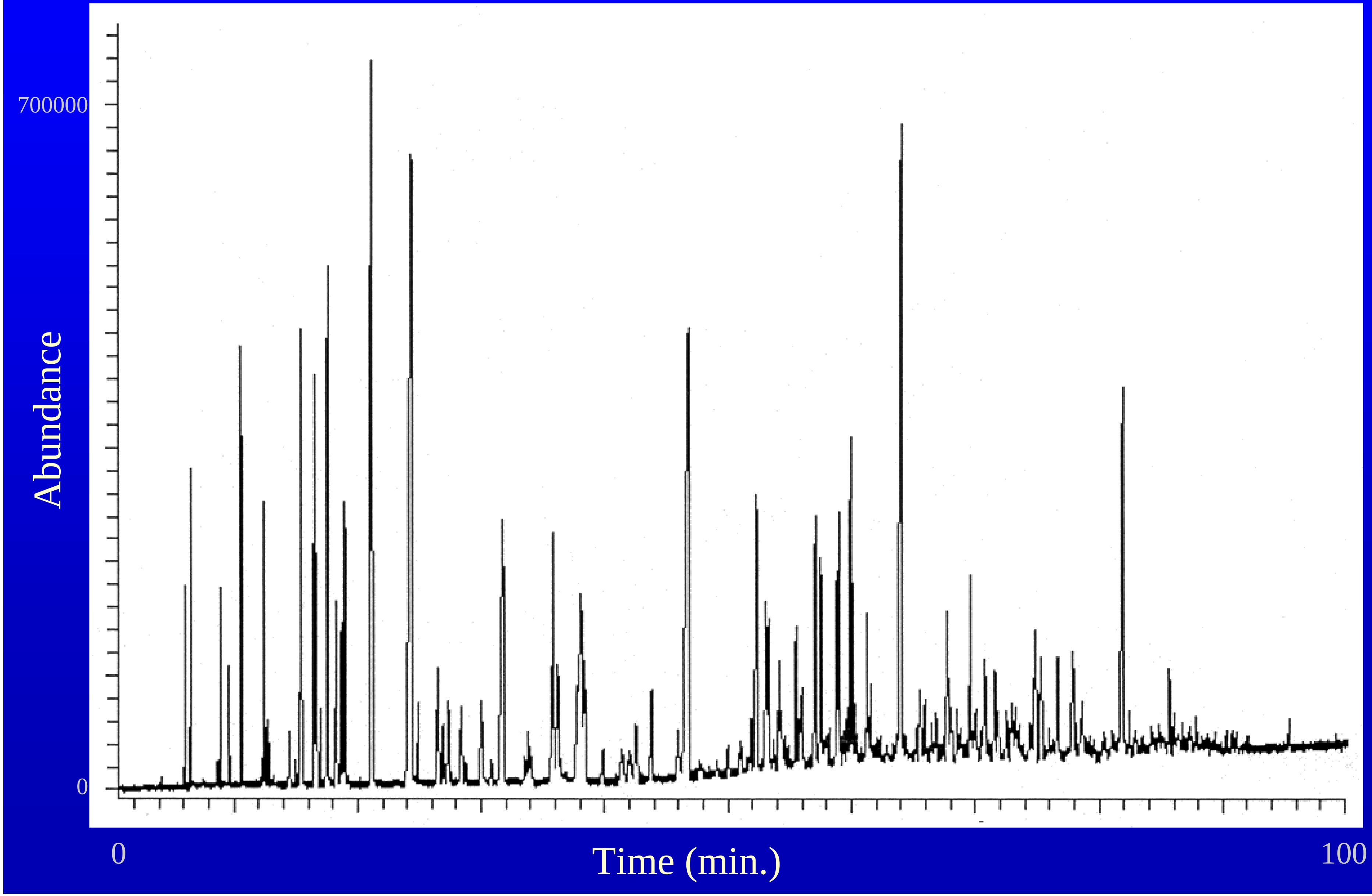
$1\ dm^3$

TRICKLE FLOW



$100\ m^3$

Complex mixtures



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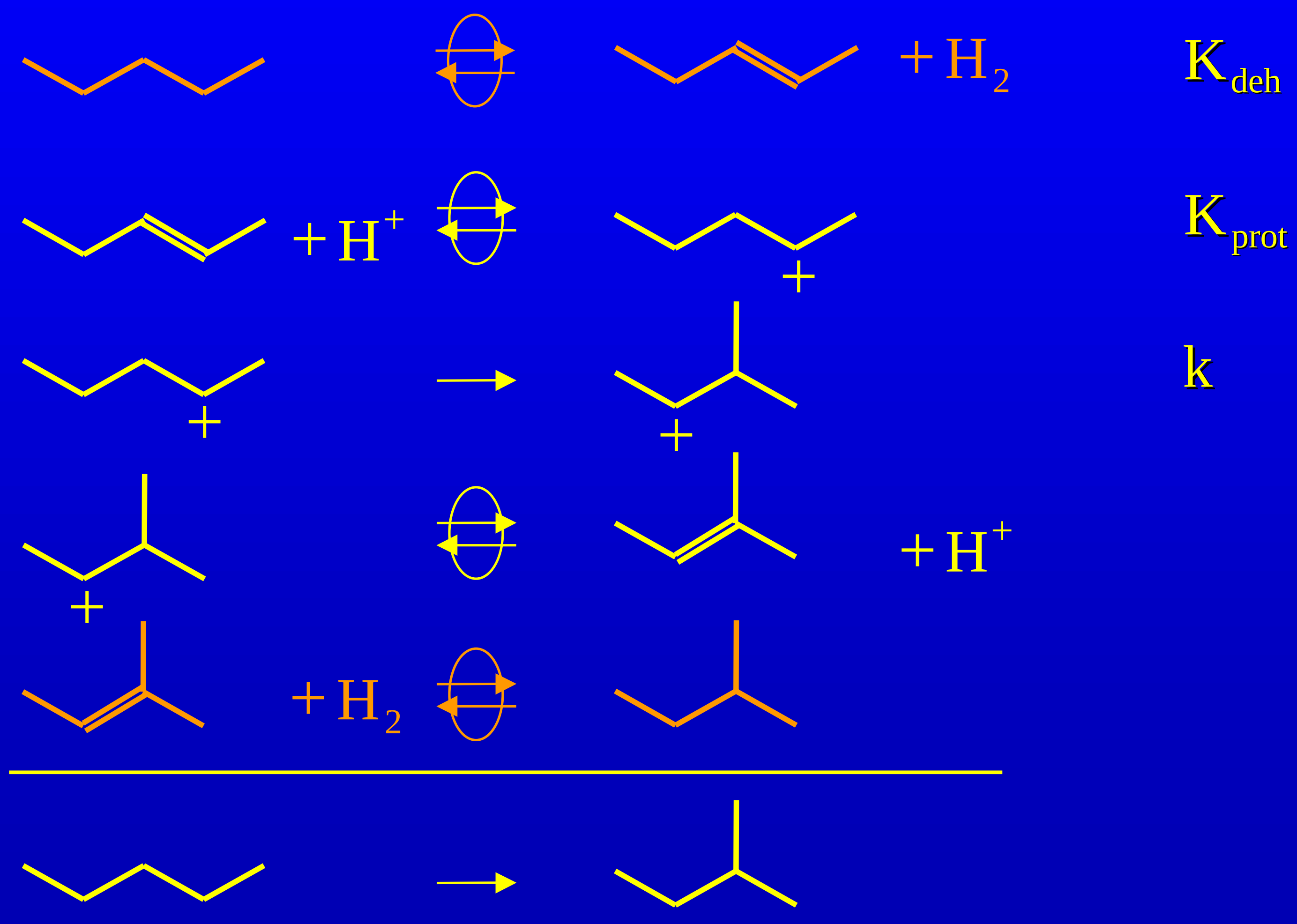
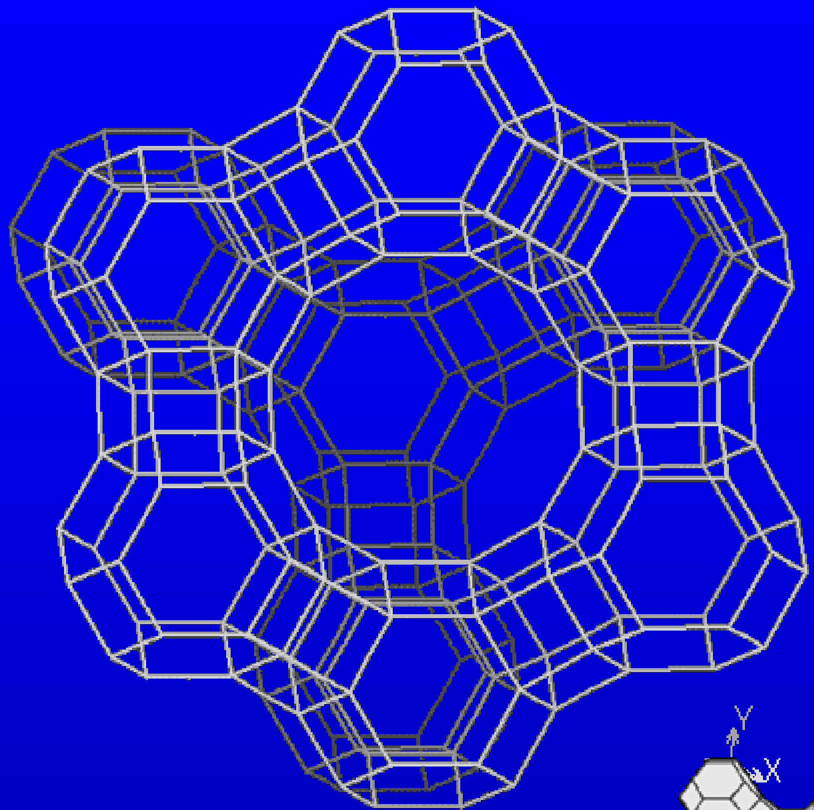
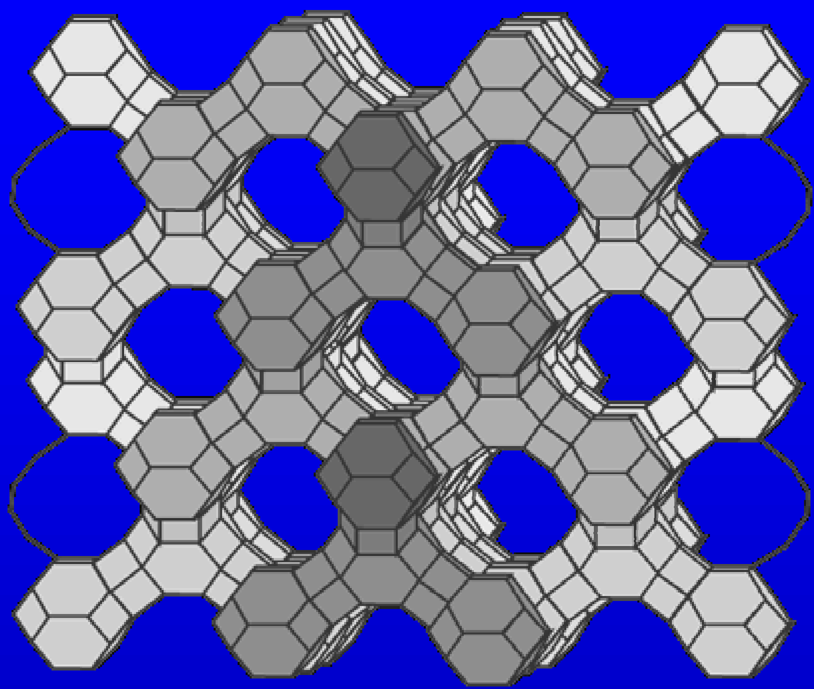
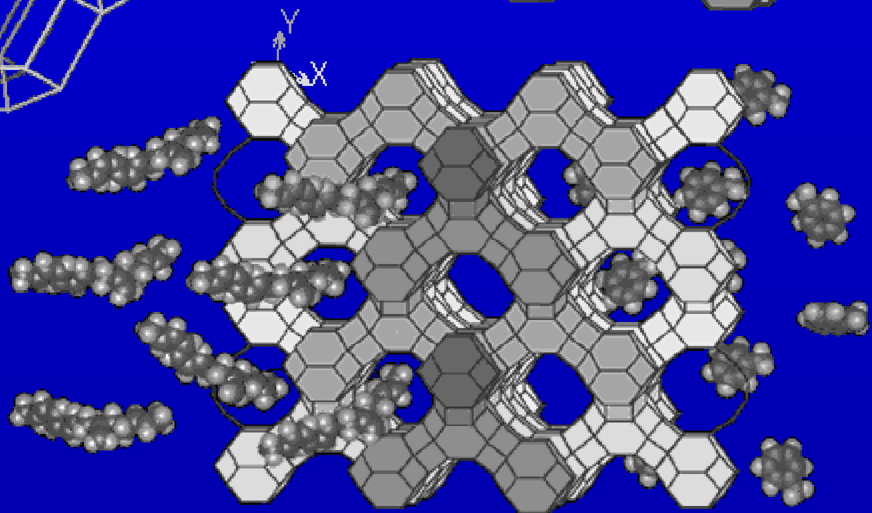
Hydroisomerization

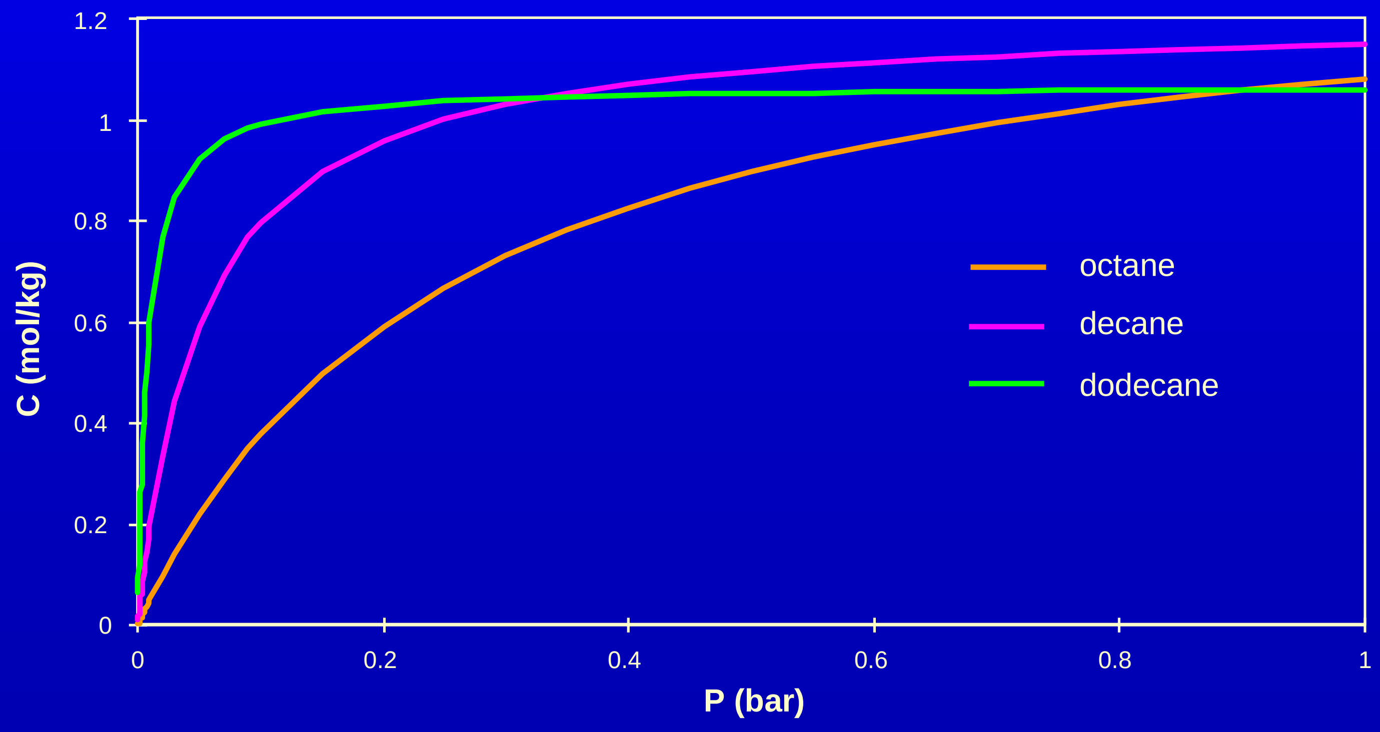


Hydrocracking: catalyst

Langmuir physisorption coefficients

$$K_L = \frac{H^0 e^{-(\Delta H_{ads}/RT)}}{C_{sat}}$$ with H^0 and ΔH_{ads} from Baron et al. (1998)



Hydrocracking: rate equations

alkylshift
PCP-branching
β-scission

$$r = k\, C_{R^+}$$

(de-)protonation

$$\mathrm{C}_{\mathrm{R}^+} = \frac{\mathrm{C_t K_{prot} C_O}}{1 + K_{prot} C_O} \cong \mathrm{C_t K_{prot} C_O}$$

(de-)hydrogenation

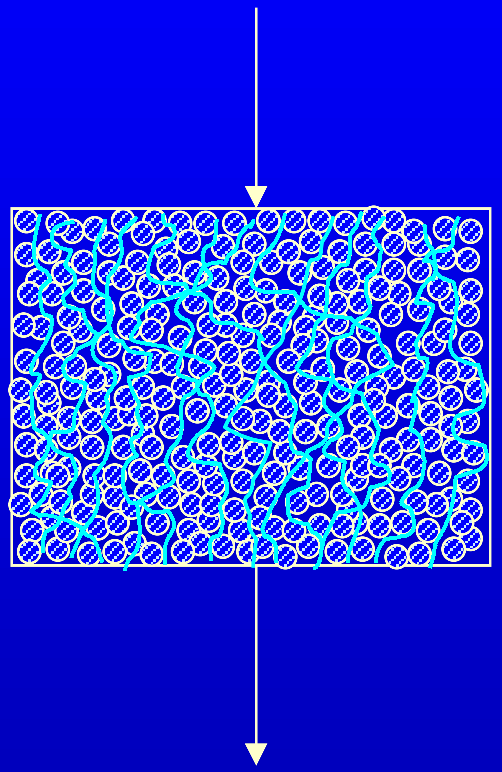
$$C_O = \frac{K_{deh} C_P}{p_{H_2}}$$

physisorption

$$C_P = \frac{C_{sat} K_L\, p_P}{1 + K_L\, p_P}$$

$$r = \frac{C_{sat}\, \mathrm{C_t}\; k\, K_{prot} K_{deh} K_L\, p_P\; p_{H_2}^{-1}}{1 + K_L p_P}$$

Hydrocracking: Industrial scale

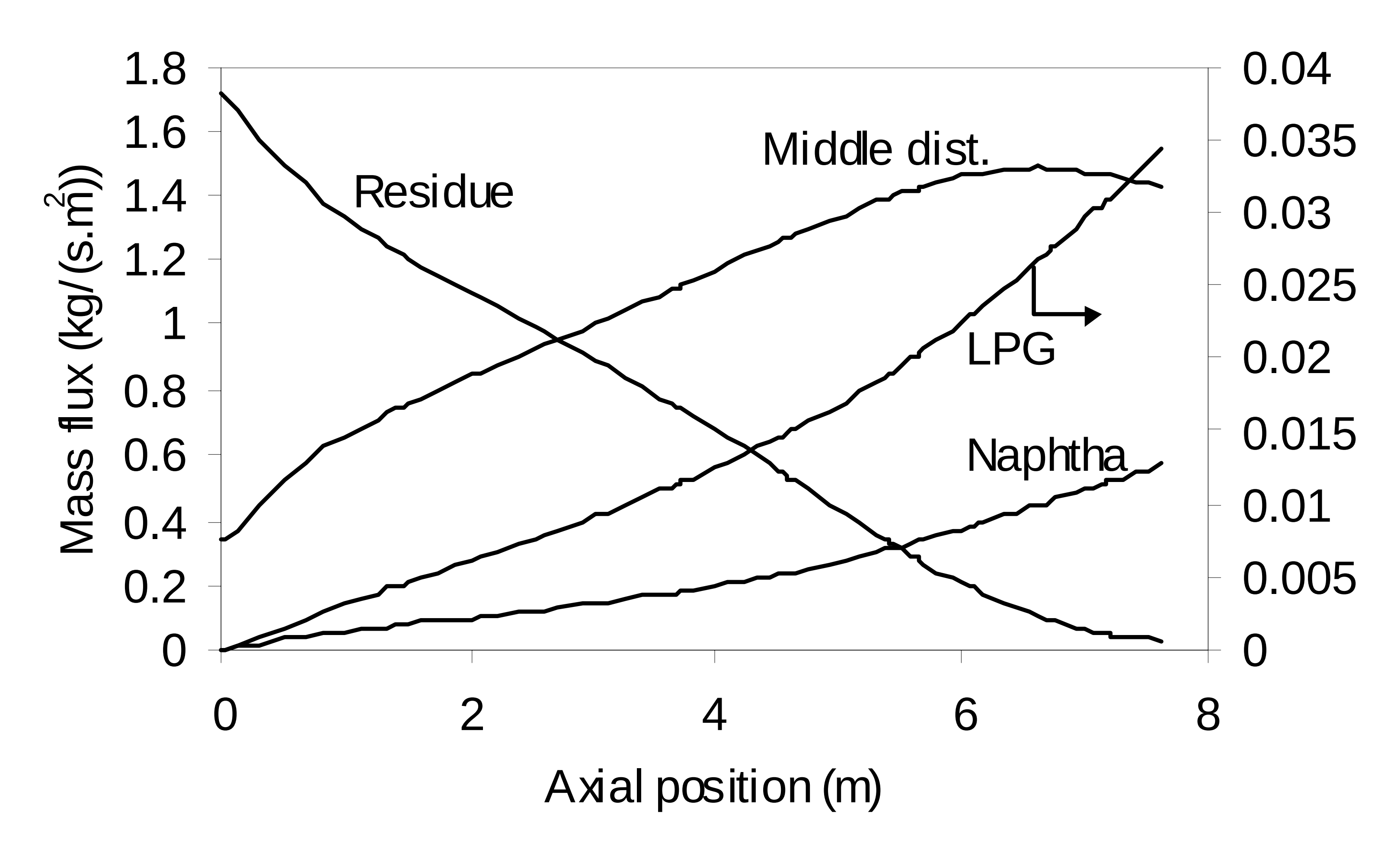


Reactor geometry	
reactor diameter, m	2.82
reactor length, m	7.625
Physical catalyst properties	
catalyst particle diameter, m	$1.3\ 10^{-3}$
porosity of catalyst, $m_f^3 m_p^{-3}$	0.65
bulk density of the bed, $kg_{cat} m_r^{-3}$	800
catalyst density, $kg_{cat} m_p^{-3}$	400
catalyst mass, kg_{cat}	19000
tortuosity	3.7
Conditions	
inlet temperature, K	540
inlet pressure, MPa	12
LHSV, $m_L^3 m_{cat}^{-3} h^{-1}$	3.8
Liquid flow rate, $m^3 day^{-1}$	2175
Gas flow rate, $Nm^3 day^{-1}$	1100 000

Hydrocracking: product streams

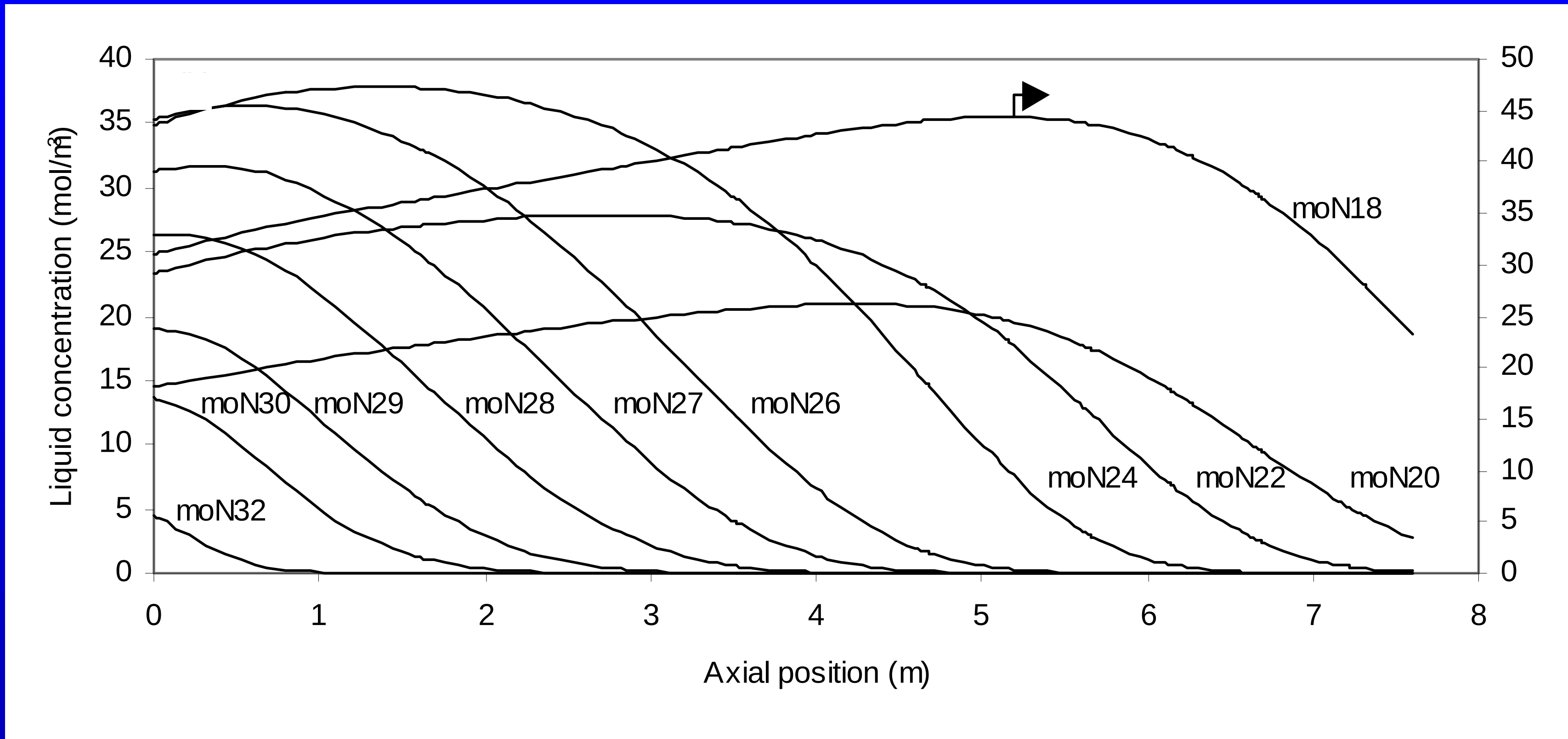
LPG	C_3-C_4	<315 K
Naphtha	C_5-C_9	315-425 K
Middle distillates	C_{10}-C_{18}	425-620 K
Residue	C_{18}^{+}	>620 K

Hydrocracking: product streams



G.G.Martens and G.B. Marin (AIChEJ,2001)

Hydrocracking: product streams



Martens and Marin (2001)

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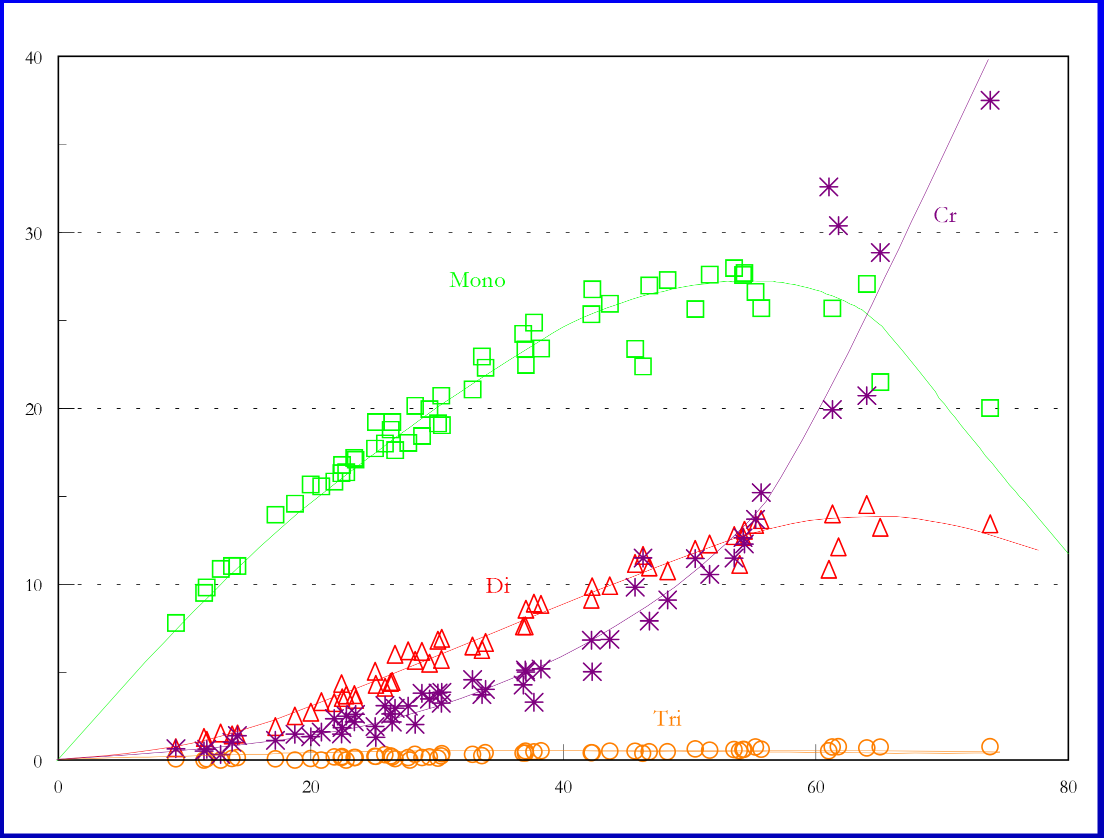
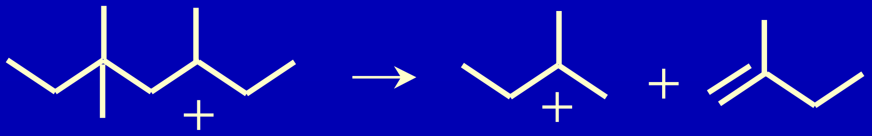
n-alkane hydrocracking

Product Yield (%)

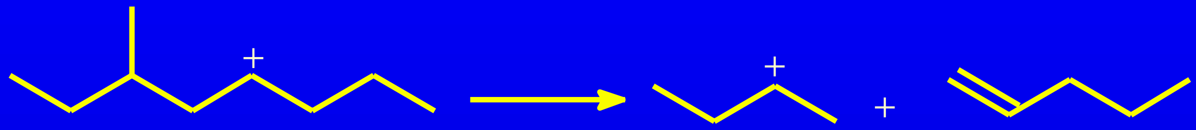


Conversion (%)

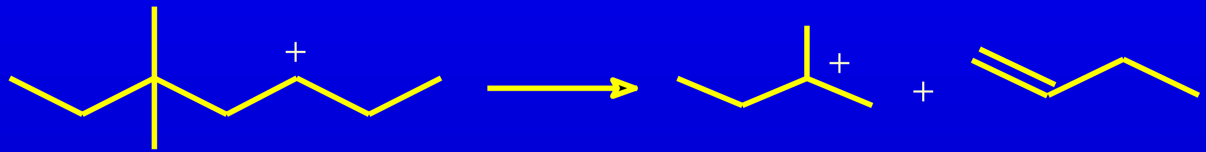


Elementary reaction family: cracking

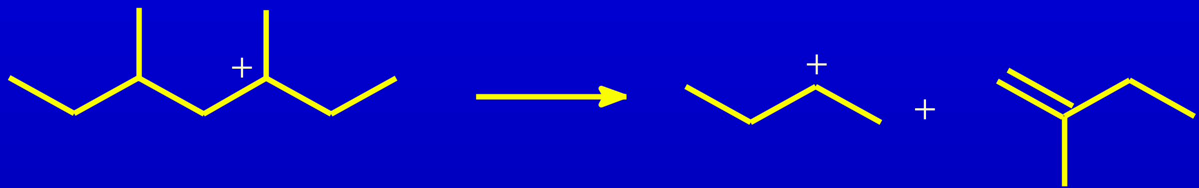
- Cr(s;s)



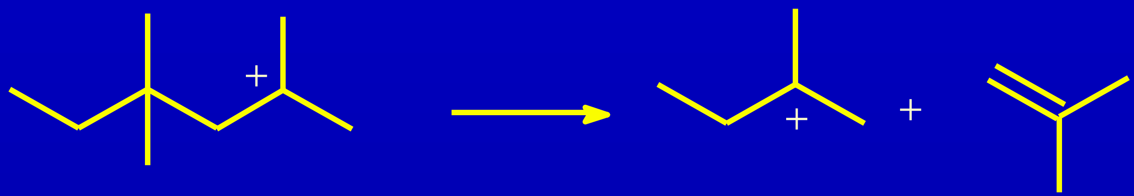
- Cr(s;t)



- Cr(t;s)

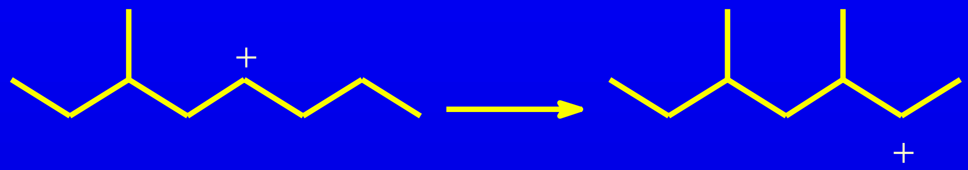


- Cr(t;t)

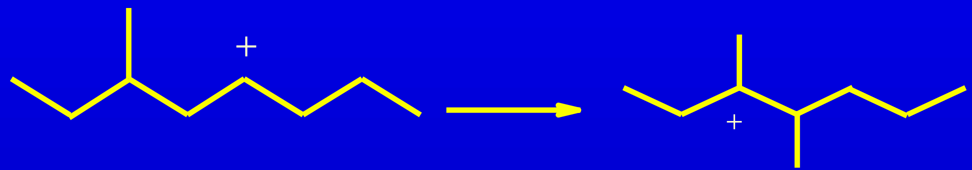


Elementary reaction family: branching isomerisation

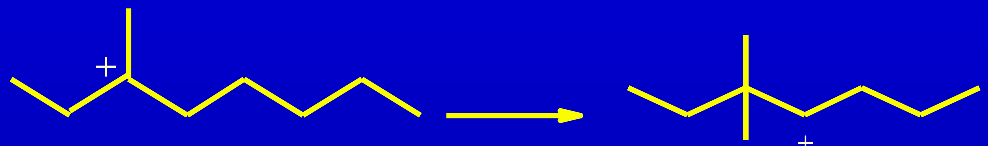
- PCP(s;s)



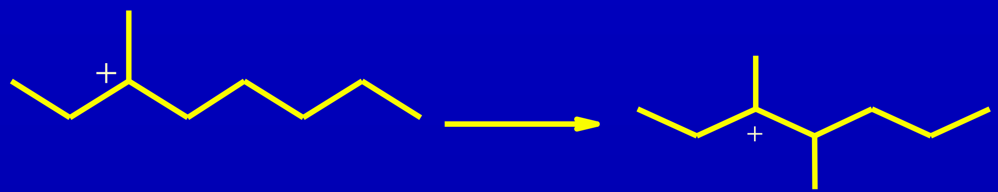
- PCP(s;t)



- PCP(t;s)



- PCP(t;t)



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Number of adjustable parameters

	Froment (95)	van Santen (97)
Feed	octane	n-hexane
Catalyst	Pt/US-Y	Pt/MOR&Pt/ZSM-5 [a]
Number of :		
molecules	97	23
intermediates	57	23 + (15 + 24) [b]
steps	811	420 [c]
parameters	16	1

a with similar acidity

b including intermediates in (de)hydrogenation

c including (de)hydrogenation and transfer

Hydrocracking: rate equations revisited

parameters to be estimated : $k^{comp} = k\,K_{prot}$

calculated via thermodynamic data

$$r = \frac{C_{sat}\,C_t\;k\,K_{prot}\,K_{deh}\,K_L\;p_P\;p_{H_2}^{-1}}{1 + K_L p_P}$$

determined by NH_3-TPD

determined by physisorption experiments

Entropy and Enthalpy terms

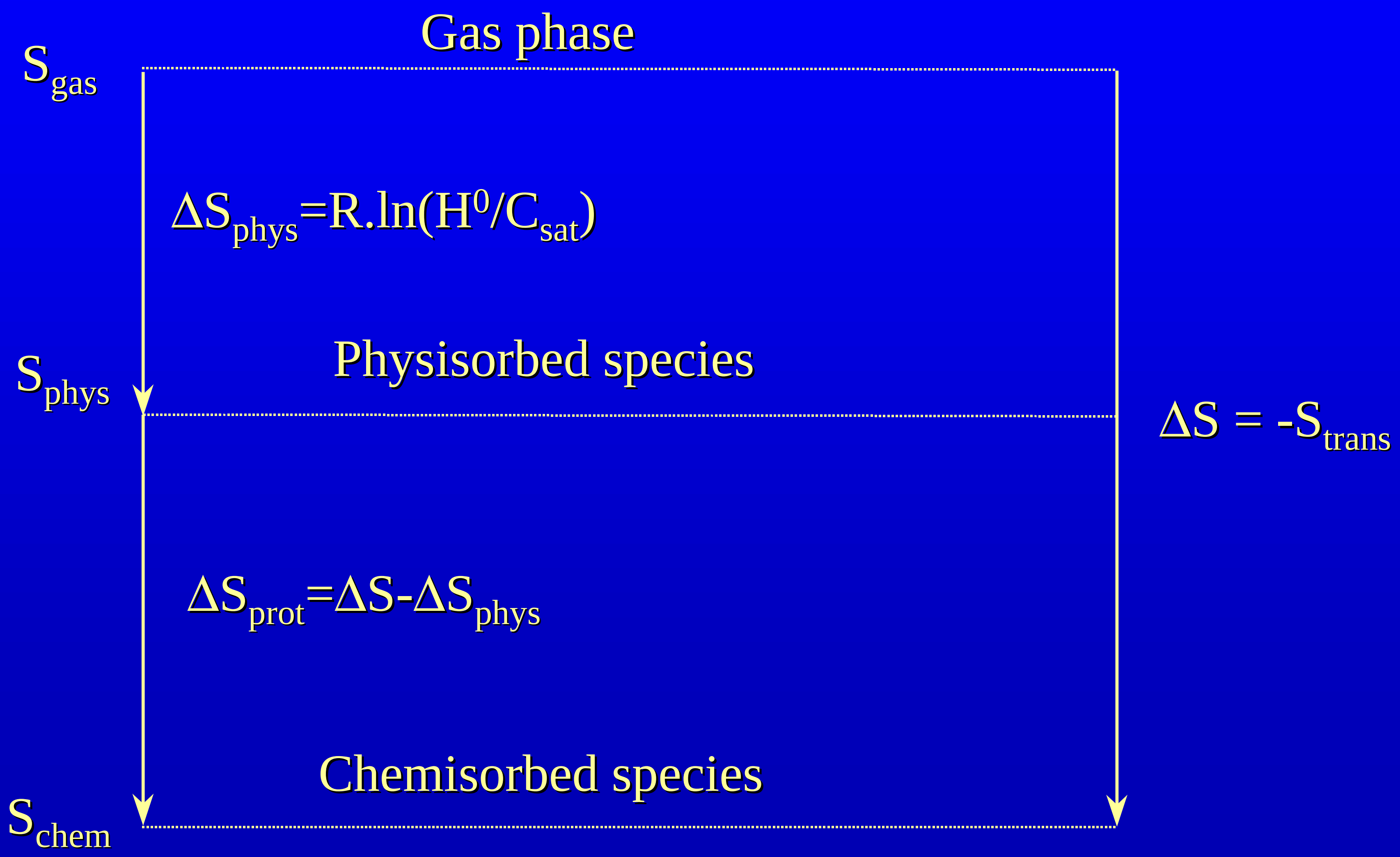
$$K_{prot(m1)} = e^{\frac{\Delta S_{prot(m1)}}{R}} e^{-\frac{\Delta H_{prot(m1)}}{RT}}$$

$$k^{SE}_{reac(m1;m2)} = \frac{k_B T}{h} e^{\frac{\Delta S^{\neq}_{reac(m1;m2)}}{R}} e^{-\frac{\Delta H^{\neq}_{reac(m1;m2)}}{RT}}$$

$$\Downarrow$$

$$k^{comp} = \frac{\sigma_{m1}}{\sigma_{\neq}} \frac{k_B T}{h} e^{\frac{\Delta S_{prot(m1)} + \Delta S^{\neq}_{reac(m1,m2)}}{R}} e^{-\frac{\Delta H_{prot(m1)} + \Delta H^{\neq}_{reac(m1;m2)}}{RT}}$$

Standard protonation entropy



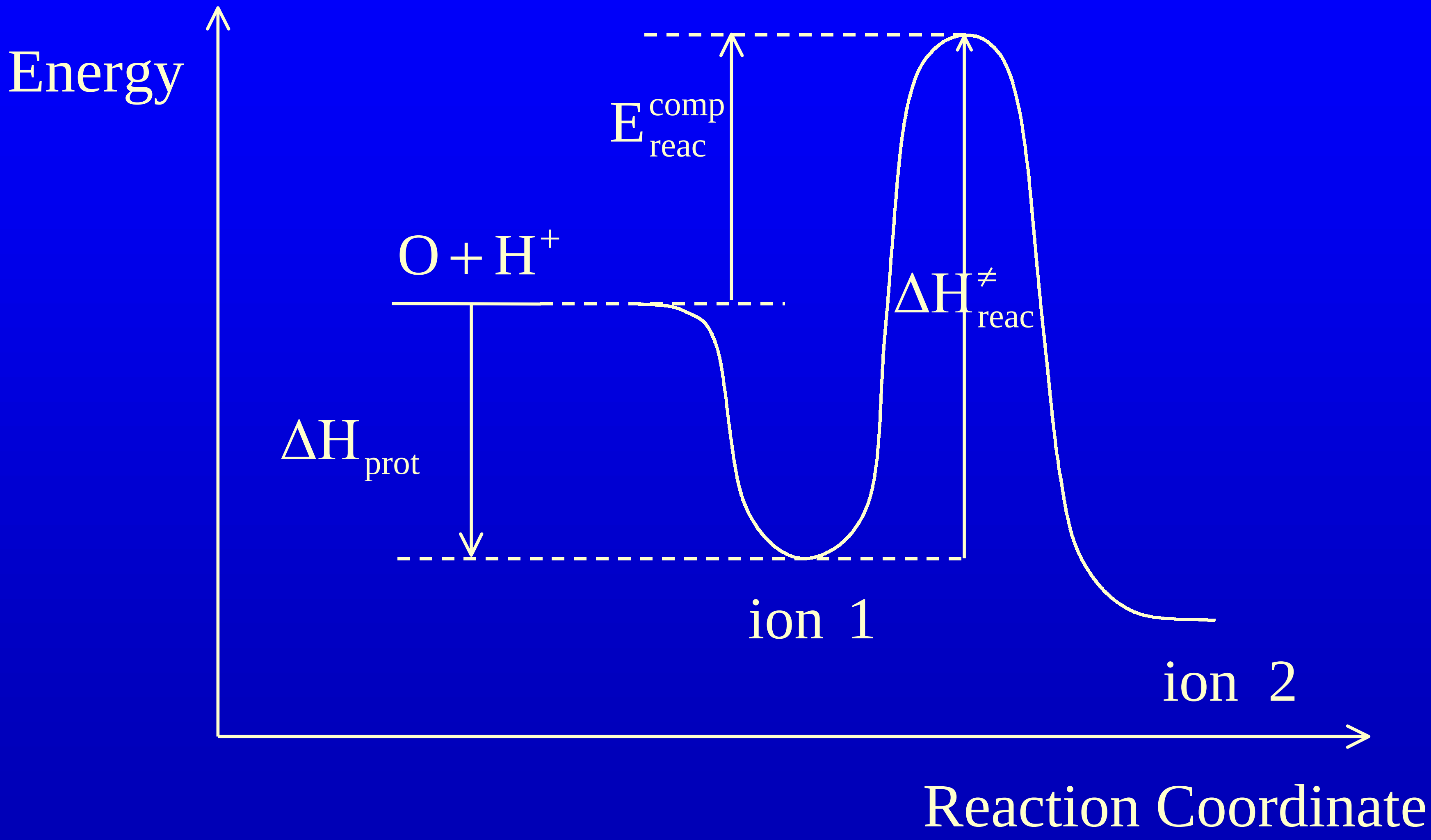
Standard activation entropy

Branching isomerisation : $\Delta S^{\neq} = 0$

Cracking : $\Delta S^{\neq} = \dfrac{S_{trans}}{3}$

$$= \frac{1}{3}\left(R\,ln\left(\frac{V_m}{N_A}\left(\frac{2\pi(M_w / N_A)k_B T}{h^2} \right)^{3/2} \right) + \frac{5}{2}R \right)$$

Composite activation energy



$$E_{reac}^{comp} = \Delta H_{prot} + \Delta H_{reac}^{\neq}$$

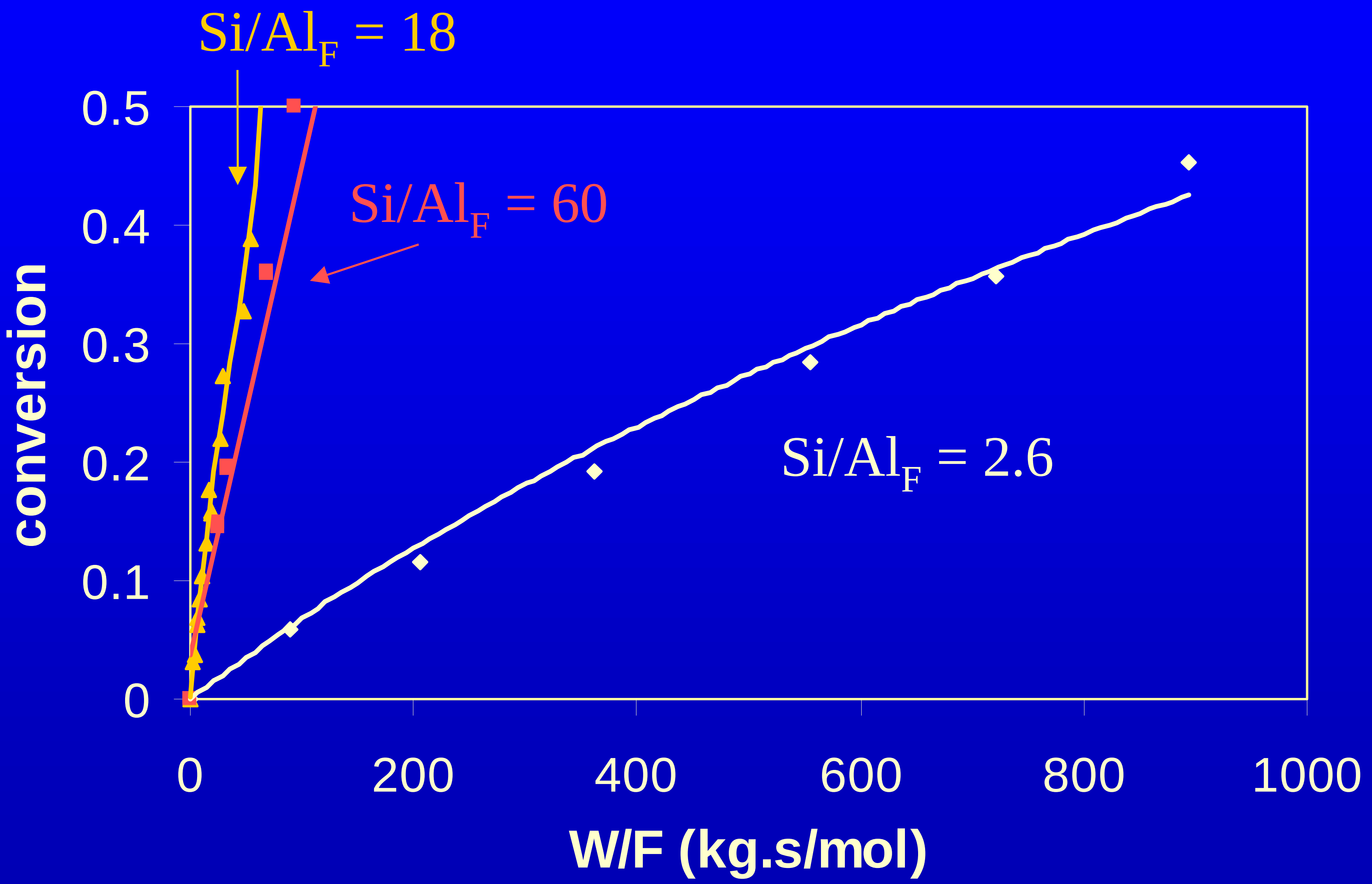
Composite activation energy

Composite activation energy (kJ mol^{-1})	*n-C_8*	*n-C_{10}*	*n-C_{12}*	
PCP(s,s)	45.7±0.2	43.8±0.1	44.8±0.2	43.7±0.1
PCP(s,t)=PCP(t,s)	47.5±32.8	26.3±3.8	38.5±7.8	36.5±5.3
PCP(t,t)	31.4±1.6	31.8±2.3	29.9±2.5	31.8±2.5
Cr(s,s)	70.0±1.0	69.7±0.8	69.7±0.6	69.5±1.0
Cr(s,t)	60.9±9.1	55.5±1.3	56.0±1.0	57.0±2.8
Cr(t,s)	50.9±0.9	54.7±1.5	53.4±1.2	55.1±2.9
Cr(t,t)	32.1±2.2	29.7±0.8	32.1±0.7	29.5±0.8

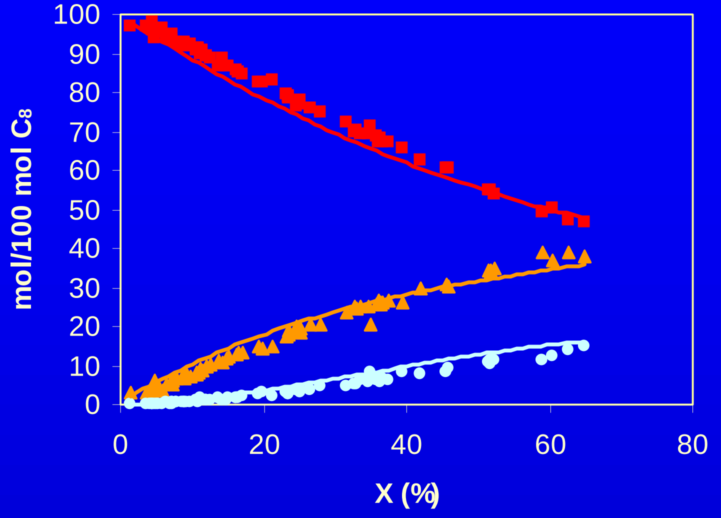
$$E^{comp} = \Delta H_{prot} + \Delta H^{\neq}_{reac}$$

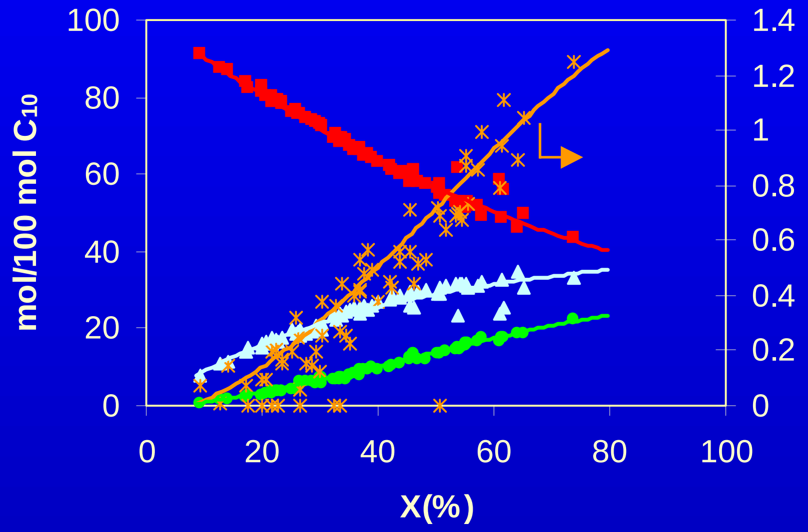
Martens et al. (2000)

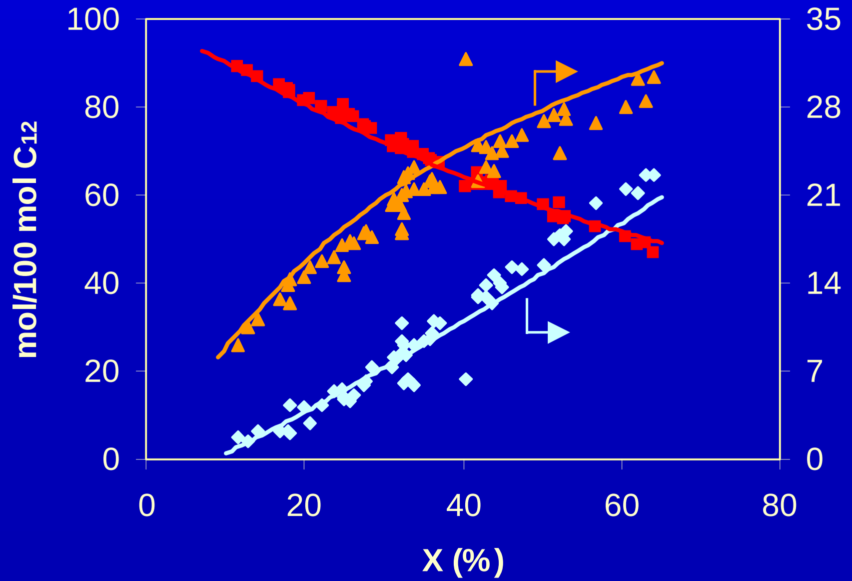
Activity: conversion versus space-time



Product distribution : isomers

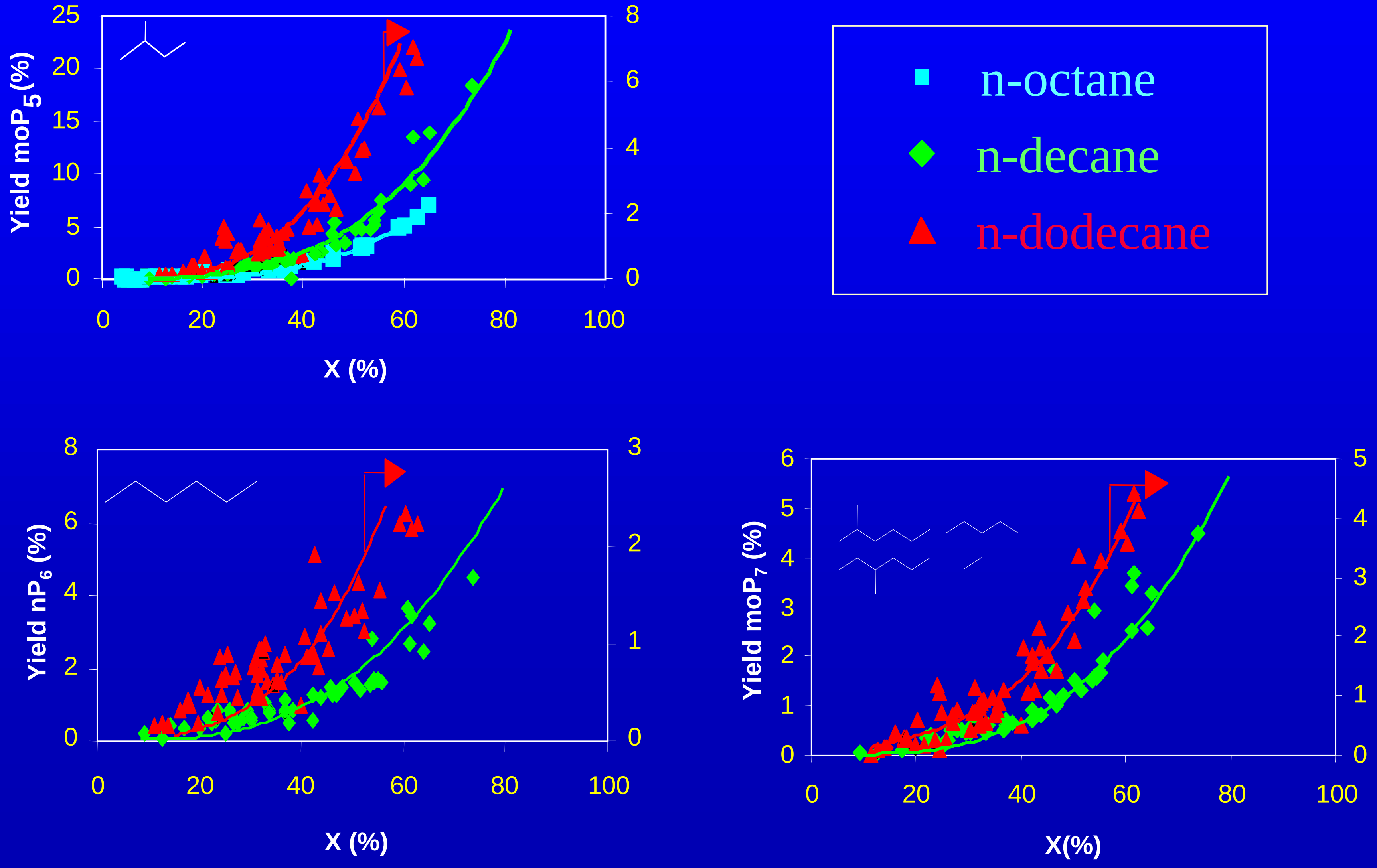






Martens et al. (2000)

Product distribution : cracking products



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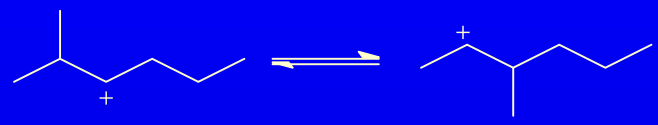
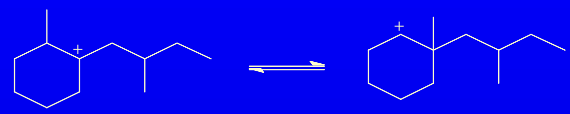
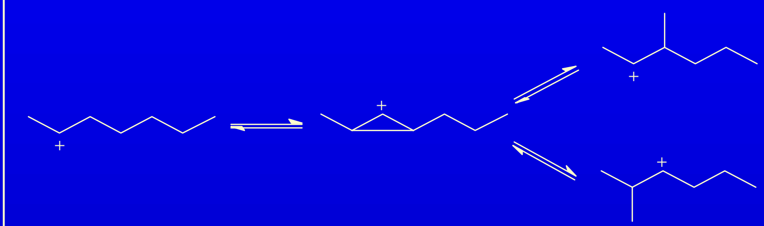
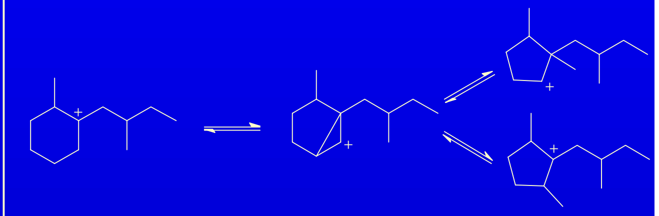
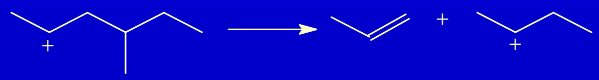
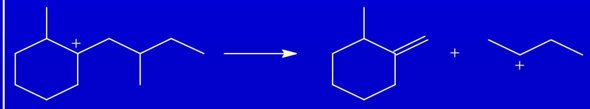
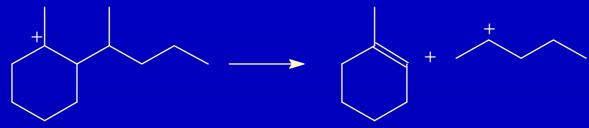
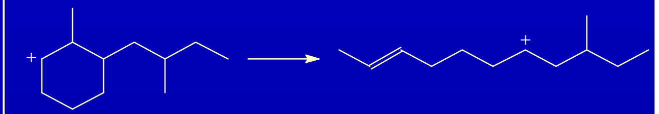
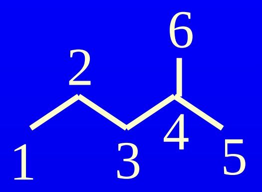
Acid catalysed reaction families

	Alkanes	Cycloalkanes
Alkyl shift		
PCP branching		
Acyclic cracking		
Exocyclic cracking		
Ring opening		

Matrix representation



$$\begin{bmatrix} 1 & 2 & 3 & 4 & 4 \\ 2 & 3 & 4 & 5 & 6 \end{bmatrix}$$

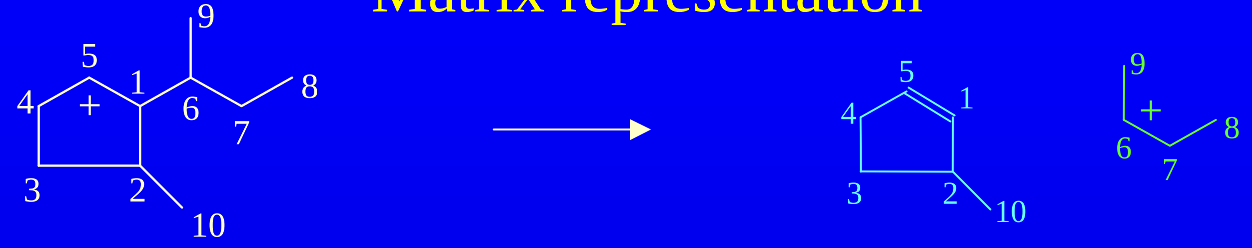
graph

$$\underline{\underline{M}} = \begin{array}{c} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{array} \begin{array}{c} \begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 & 6 \end{array} \\ \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix} \end{array}$$

boolean matrix

vectors: double bond, conjugated double bond, ring, aromatic

Matrix representation



	1	2	3	4	5	6	7	8	9	10
1	0	1	0	0	1	1	0	0	0	0
2	1	0	1	0	0	0	0	0	0	1
3	0	1	0	1	0	0	0	0	0	0
4	0	0	1	0	1	0	0	0	0	0
5	1	0	0	1	0	0	0	0	0	0
6	1	0	0	0	0	0	1	0	1	0
7	0	0	0	0	0	1	0	1	0	0
8	0	0	0	0	0	0	1	0	0	0
9	0	0	0	0	0	1	0	0	0	0
10	0	1	0	0	0	0	0	0	0	0

→

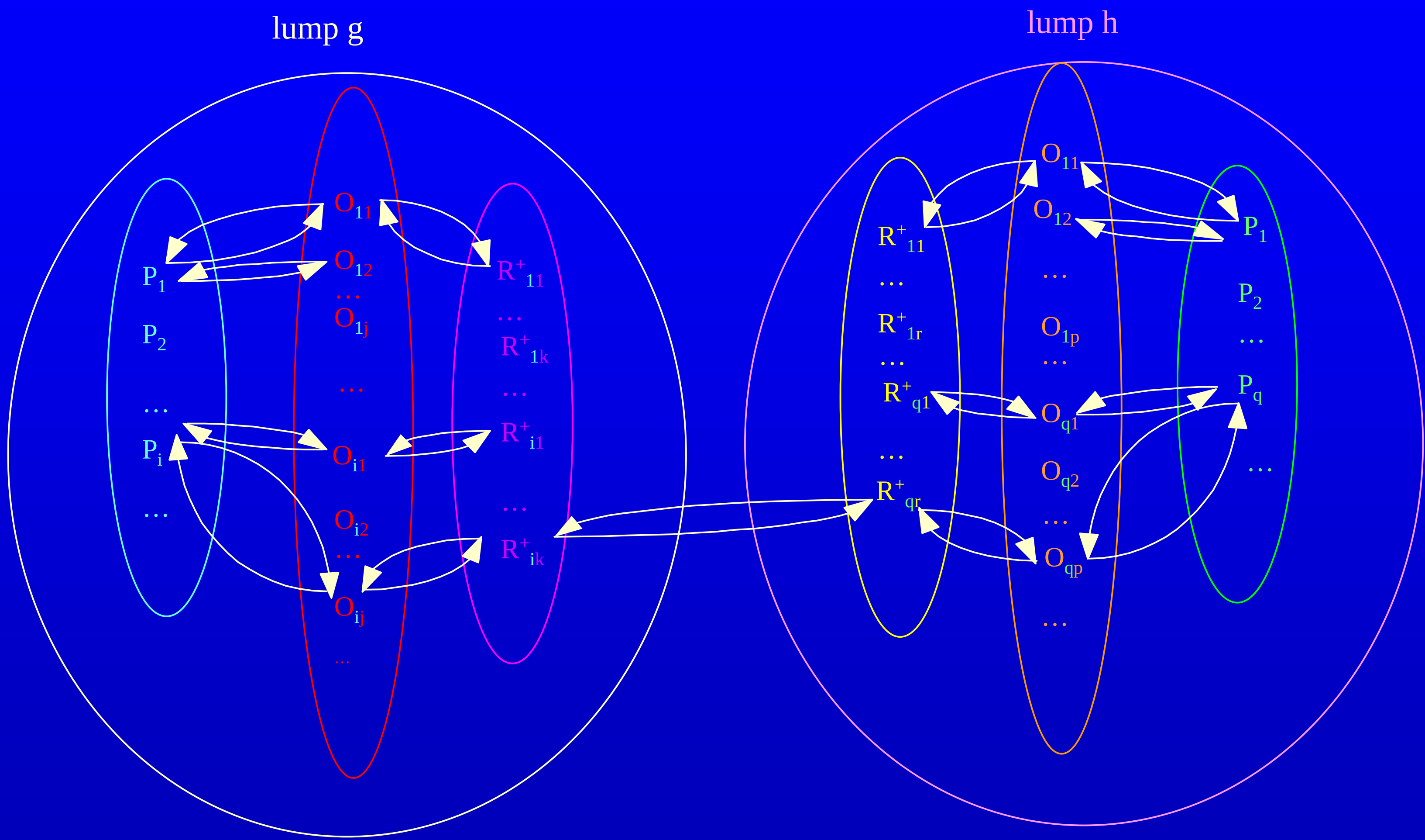
	1	2	3	4	5	6	7	8	9	10
1	0	1	0	0	1	0	0	0	0	0
2	1	0	1	0	0	0	0	0	0	1
3	0	1	0	1	0	0	0	0	0	0
4	0	0	1	0	1	0	0	0	0	0
5	1	0	0	1	0	0	0	0	0	0
6	0	0	0	0	0	0	1	0	1	0
7	0	0	0	0	0	1	0	1	0	0
8	0	0	0	0	0	0	1	0	0	0
9	0	0	0	0	0	1	0	0	0	0
10	0	1	0	0	0	0	0	0	0	0

e.g. n-C_{19} : 1981 alkanes , 25065 alkenes, 20437 carbenium ions

⇓

25065 (de)hydrogenations, 42600 (de)protonations, 12470 alkyl shifts, 15970 PCP branching and 6429 β–scissions

Relumping concept



$$r_{isom}(g;h) = \sum_{i} \sum_{k} \sum_{q} \sum_{r} n_{e,ikqr}\, k_{isom}(m_{ik}, m_{qr})\, C_{R^{+}_{ik}}(m_{ik})$$

Relumping: lumping coefficients

$$r_{isom}(g;h) = \sum_i \sum_k \sum_q \sum_r n_{e,ikqr}\, k_{isom}(m_{ik}, m_{qr})\, C_{R^+_{ik}(m_{ik})}$$

+

$$C_{R^+_{ik}} = \frac{\sigma_{O_{ij}}}{\sigma_{R^+_{ik}}} \tilde{K}_{pr}(m_{ik}) \tilde{K}_{isom}(O_{ij}, O_r) K_{DH,ij} C_t C_{sat,i} \frac{K_{L,j}\, p_{P_i}}{(1+\sum_j K_{L,j}\, p_{P_j})\, p_{H_2}} \qquad p_{P_i} = y_{i,g} P_g$$

$$\Downarrow$$

$$r_{isom}(g;h) = \sum_{m_1=s,t} \sum_{m_2=s,t} \frac{(LC)_{isom(s,s)}(g;h) \tilde{K}_{pr}(m_1) k_{isom}(m_1;m_2) H_{L,g} C_t p_g}{(1+\sum_f K_{L,f}\, p_f)\, p_{H_2}}$$

$$(LC)_{isom(m_1,m_2)}(g;h) = \sum_{i\in g} \sum_{k\in g} \sum_{q\in h} \sum_{r\in h} \frac{n_{e,ikqr}\, \sigma_{O_{ij}}}{\sigma_{R^+_{ik}}} \tilde{K}_{isom}(O_{ij}, O_r) K_{DH,ij}\, y_{i,g}$$

Calculation of relumping coefficients

Definition: $$(LC)_{isom(m_1,m_2)}(g;h)=\sum_{i\in g}\sum_{k\in g}\sum_{q\in h}\sum_{r\in h}\frac{n_{e,ikqr}\,\sigma_{O_{ij}}}{\sigma_{R_{ik}^{+}}}\tilde{K}_{isom}(O_{ij},O_r)K_{DH,ij}\,y_{i,g}$$

Equilibrium within lump ⇒

$$y_{i,g}=\frac{K_{isom}(P_r\Leftrightarrow P_i)}{\sum_{j\in g}K_{isom}(P_r\Leftrightarrow P_i)}=\frac{\frac{\sigma_{P_r}}{\sigma_{P_i}}e^{-\frac{\Delta\tilde{G}_f^0(P_i)-\Delta\tilde{G}_f^0(P_r)}{RT}}}{\sum_{j\in g}\frac{\sigma_{P_r}}{\sigma_{P_j}}e^{-\frac{\Delta\tilde{G}_f^0(P_r)-\Delta\tilde{G}_f^0(P_j)}{RT}}}=\frac{\frac{1}{\sigma_{P_i}}e^{-\frac{\Delta\tilde{G}_f^0(P_i)}{RT}}}{\sum_{j\in g}\frac{1}{\sigma_{P_j}}e^{-\frac{\Delta\tilde{G}_f^0(P_j)}{RT}}}$$

$$(LC)_{isom(m_1,m_2)}(g;h)=\sum_{i\in g}\sum_{k\in g}\sum_{q\in h}\sum_{r\in h}\frac{n_{e,ikqr}}{\sigma_{R_{ik}^{+}}\sigma_{H_2}}\frac{e^{-\frac{\Delta\tilde{G}_f^0(O_r)+\Delta\tilde{G}_f^0(H_2)}{RT}}}{\sum_{j\in g}\frac{e^{-\frac{\Delta\tilde{G}_f^0(P_j)}{RT}}}{\sigma_{P_j}}}=\frac{N_{isom(m_1,m_2)}K^{*}_{ref,g}(n;T)}{K^{*}_{g}(n;T)}$$

$$N_{isom(m_1,m_2)}=\sum_{i\in g}\sum_{k\in g}\sum_{q\in h}\sum_{r\in h}\frac{n_{e,ikqr}}{\sigma_{R_{ik}}\sigma_{H_2}}\qquad K^{*}_{ref,g}(n;T)=e^{-\frac{\Delta\tilde{G}_f^0(O_r)+\Delta\tilde{G}_f^0(H_2)}{RT}}\qquad K^{*}_{g}(n;T)=\sum_{i\in g}\frac{e^{-\frac{\Delta\tilde{G}_f^0(P_i)}{RT}}}{\sigma_{P_i}}$$

Calculation of $K^*_{ref,g}$

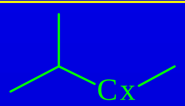
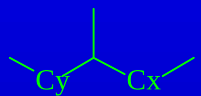
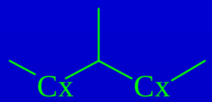
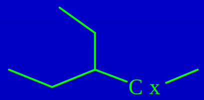
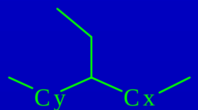
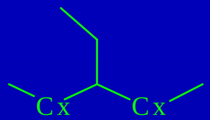
$K^*_{ref,g}$ dependent upon choice of O_r and carbon number $\Rightarrow$ 1 $K^*_{ref,g}$ for each type of HC i.e. alkanes, mono- ,di-, tri- and tetraring cycloalkanes

$$K^*_{ref,g} = e^{\frac{\Delta H_f^0(H_2) - T\tilde{S}^0(H_2)}{RT}} e^{\frac{\Delta H_f^0(O_r) - T\tilde{S}^0(O_r)}{RT}}$$

Calculation of K^*_g

Benson group contribution method for thermodynamic quantities

⇒ Structural classes ⇒ $$K^*_g(n;T) = \sum_i^{nclasses} \frac{\#_i}{\sigma_i} e^{-\frac{n_{p,i}\Delta\tilde{G}^0_{f,p}}{RT}} e^{-\frac{n_{s,i}\Delta\tilde{G}^0_{f,s}}{RT}} e^{-\frac{n_{t,i}\Delta\tilde{G}^0_{f,t}}{RT}} e^{-\frac{n_{q,i}\Delta\tilde{G}^0_{f,q}}{RT}} e^{-\frac{n_{gch,i}\Delta H^0_{f,gch}}{RT}}$$

Alkane class	$n_{p,i}$	$n_{s,i}$	$n_{t,i}$	$n_{q,i}$	σ_i	$n_{gch,i}$	*number of alkanes*
	3	n-4	1	0	27	1	1
	3	n-4	1	0	27/2	2	(n-6)/2 n even (n-5)/2 n odd
	3	n-4	1	0	27	2	1 n even 0 n odd
	3	n-4	1	0	27	3	1
	3	n-4	1	0	27/2	3	(n-8)/2 n even (n-9)/2 n odd
	3	n-4	1	0	27	3	0 n even 1 n odd

Calculation of $N_{\beta(m1,m2)}(g;h)$

Reaction : $diP_n \rightarrow moP_{n-4} + nP_4$

1) Structural classes of reactant ions

according to symmetry number and $n_{e,ikqr}$

2) Determination of number

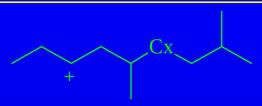
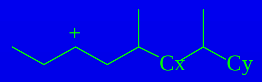
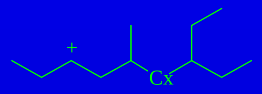
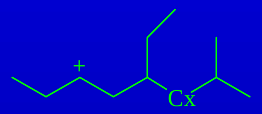
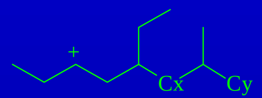
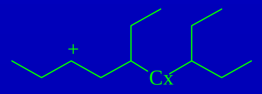
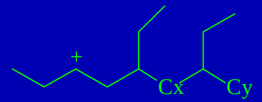
of ions in each class

⇓

$$\sum_{j=1}^{nclasses} \frac{n_{e,ikqr}\,\#_j}{\sigma_{R^+_{ik}}\,\sigma_{H_2}} \quad \text{with } \sigma_{H_2} = 2$$

⇓

$$N_{\beta(s,s)}(diP_n; moP_{n-4}, nP_4) = \frac{8(n-10)}{81}$$

carbenium ion class R^+_{ik}	*global symmetry number*	*number of ions, $\#_i$*	$n_{e,ikqr}$
	81/2	1	1
	81/4	n-9	1
	81/2	1	1
	81/4	n-11	1
	81/2	1	1
	81/4	n-10	1
	81/2	1	1
	81/4	n-12	1

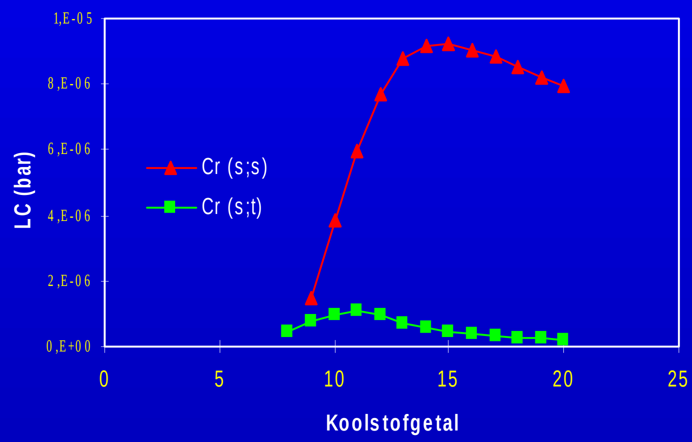
Calculation of Lumping Coefficients

via combination of K^*_g , $K^*_{ref,g}$ and $N_{\beta(m1,m2)}(g;h)$

Reaction $diP_n \rightarrow moP_{n-4} + nP_4$

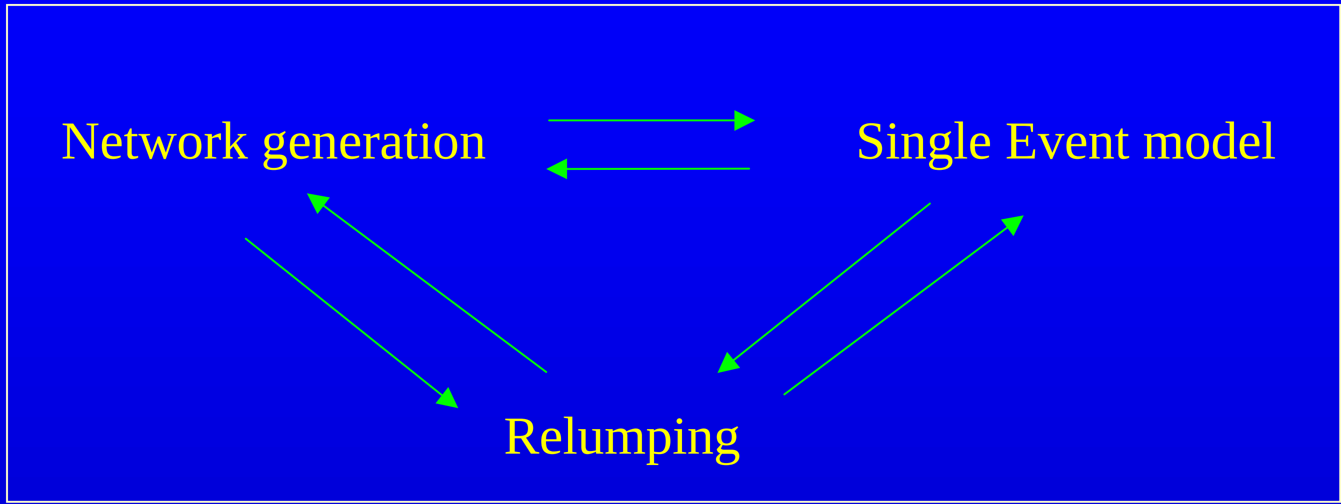
$$(LC)_{\beta(s,s)}(diP_n;moP_{n-4},nP_4)=\frac{8(n-10)}{81}\frac{K^*_{ref,Par}}{K^*_{di}} \quad n\geq13$$

LC voor β-scissie van diR_n in moR_{n-4} en nO_4

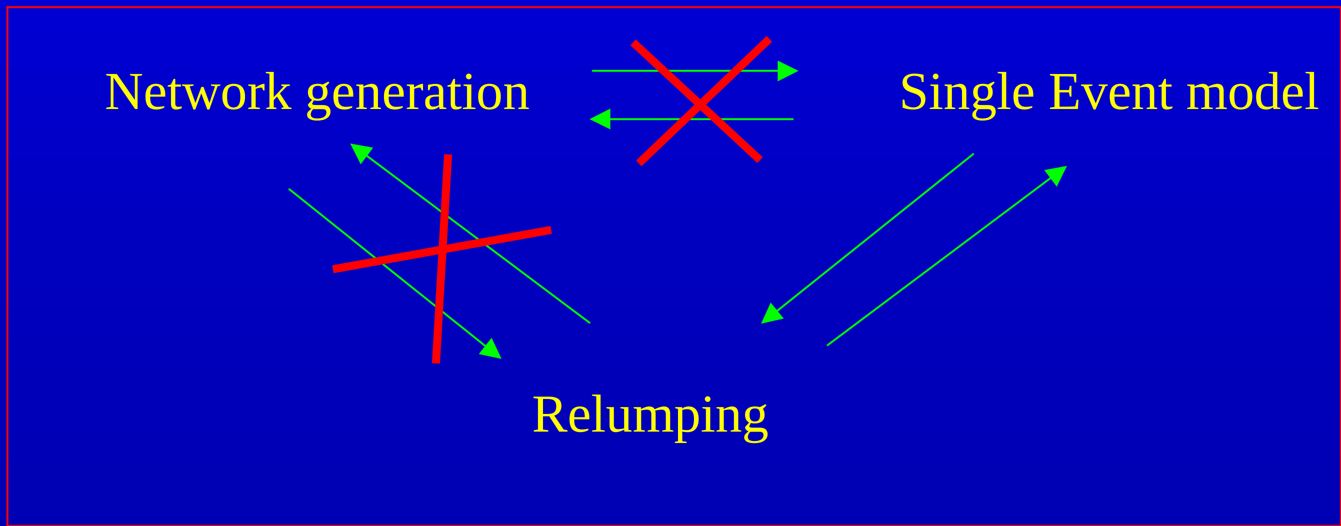


Detailed Model without Network Generation

Old



New



Summary Relumped Rate Equations

- **Reaction Rate Equation :** $r_{isom}(g;h) = \dfrac{k^{L}_{isom}(g;h) H_{L,g}\, p_g C_t}{(1+\sum_f K_{L,f}\, p_f)\, p_{H_2}}$

- **Rate coefficient :**

$$k^{L}_{isom}(g;h) = (LC)_{isom(s,s)}(g;h) k^{comp}_{isom}(s,s) + (LC)_{isom(s,t)}(g;h) k^{comp}_{isom}(s,t)$$

$$+ (LC)_{isom(t,s)}(g;h) k^{comp}_{isom}(t,s) + (LC)_{iosm(t,t)}(g;h) k^{comp}_{isom}(t,t)$$

- **Composite rate coefficient :**

$$k^{comp}_{isom}(m_1, m_2) = \tilde{K}_{\Pr}(m_1) k_{isom}(m_1, m_2) = A^{0,com}_{isom(m_1,m_2)} e^{-\frac{E^{comp}_{isom(m_1,m_2)}}{RT}}$$

- **Lumping coefficient :** $(LC)_{isom(m_1,m_2)}(g;h) = \dfrac{N_{isom(m_1,m_2)} K^{*}_{ref,g}(n;T)}{K^{*}_{g}(n;T)}$

- Introduction / Scope
- Case: Hydrocracking
- Families of elementary reactions
- Adjustable parameters
- Network
- Conclusions

Conclusions

- intrinsic kinetics / elementary reactions
- lab reactor ⇔ industrial reactor
- fundamental kinetic parameters
  - limited number
  - independent expts (e.g. physisorption)
  - transition state theory
  - catalyst properties
  - network generation
- scale-up to industrial reactor straight forward

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