Liquid phase kinetics based on gas phase experimental data

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Sonning Common (UK), February 6 2006

- Introduction / Scope
- Physisorption
- Families of elementary reactions
- Kinetic parameters
- Acidity
- From vapour to liquid
- Conclusions

Scale-up

intrinsic kinetic
laboratory data

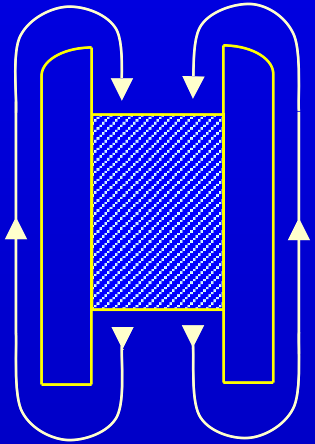
intrinsic chemical kinetics
based on elementary steps

conservation laws, including
transport phenomena

industrial reactor
design & optimization

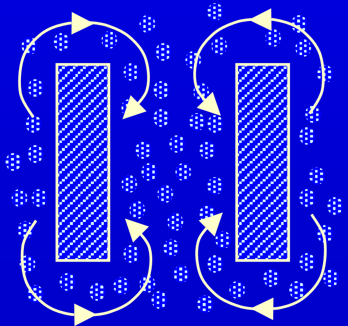
Reactors: laboratory versus industrial

BERTY



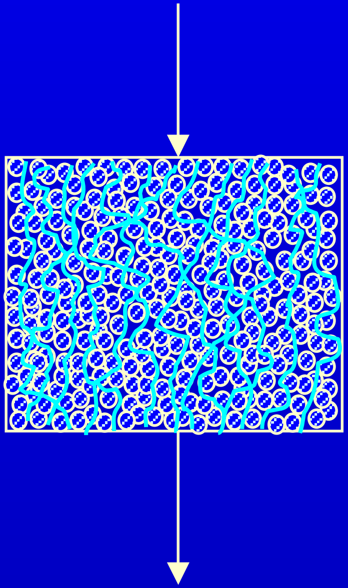
1 dm^3

ROBINSON-MAHONEY



1 dm^3

TRICKLE FLOW



100 m^3

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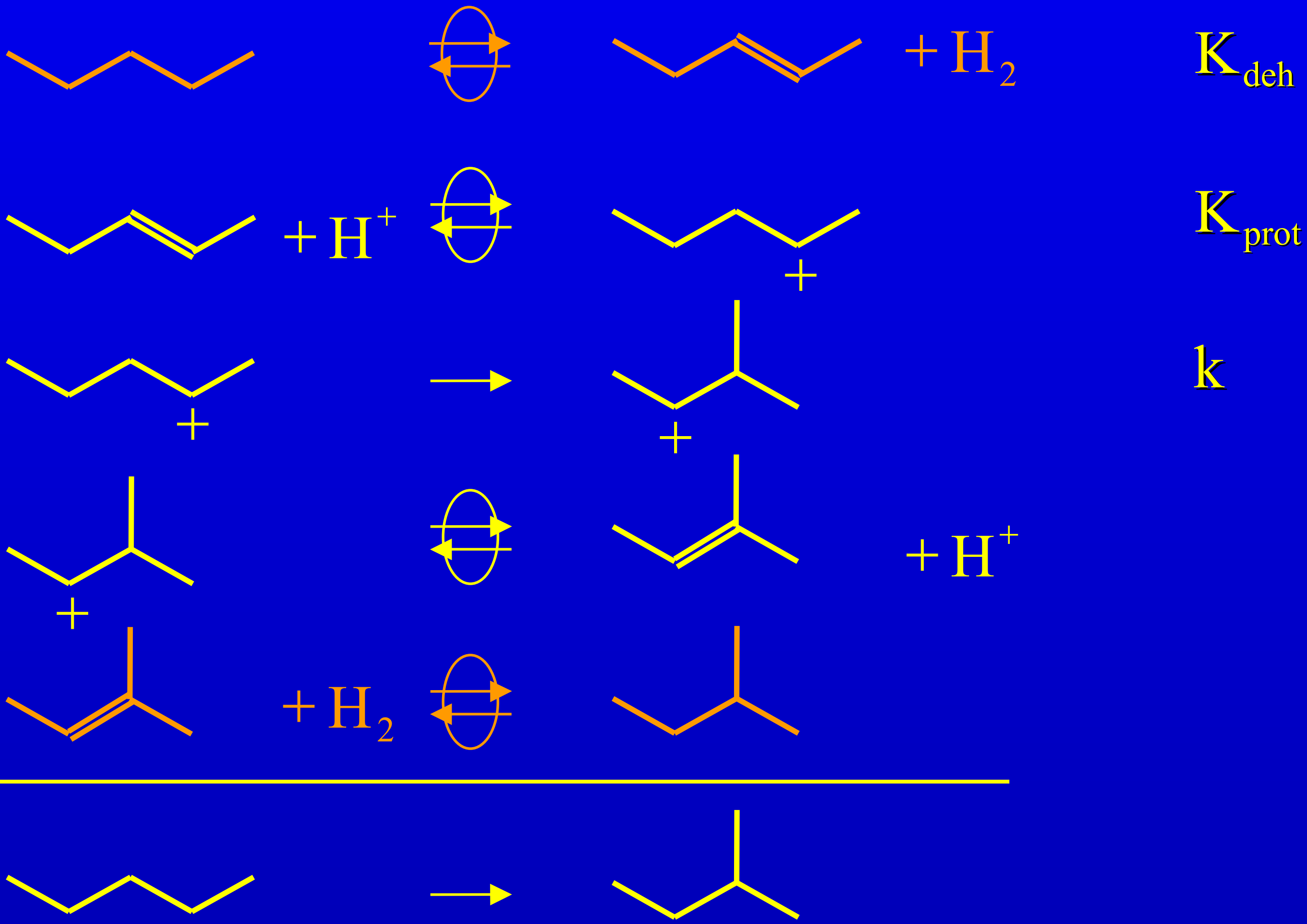
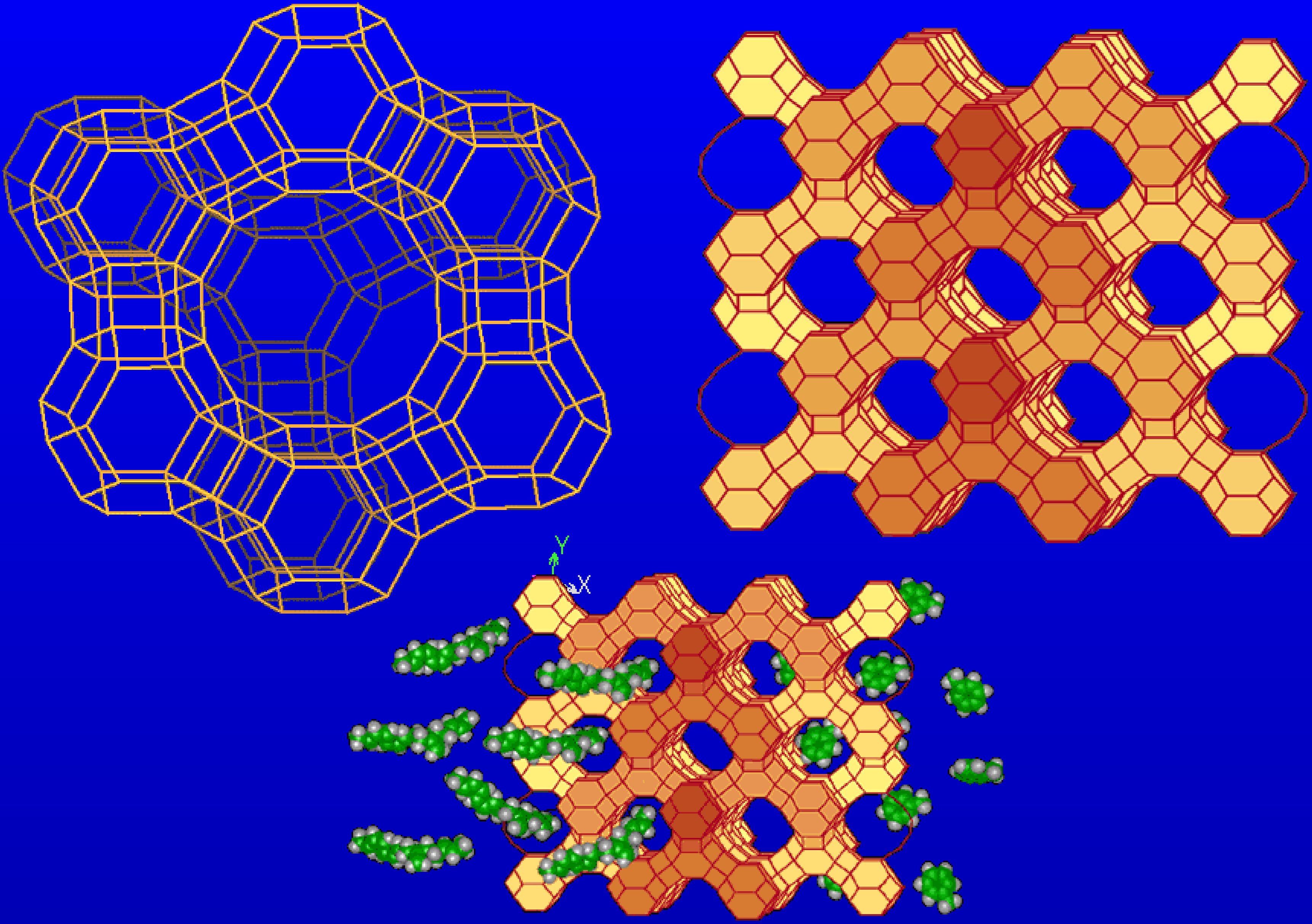
Hydroisomerization



Hydrocracking: catalyst

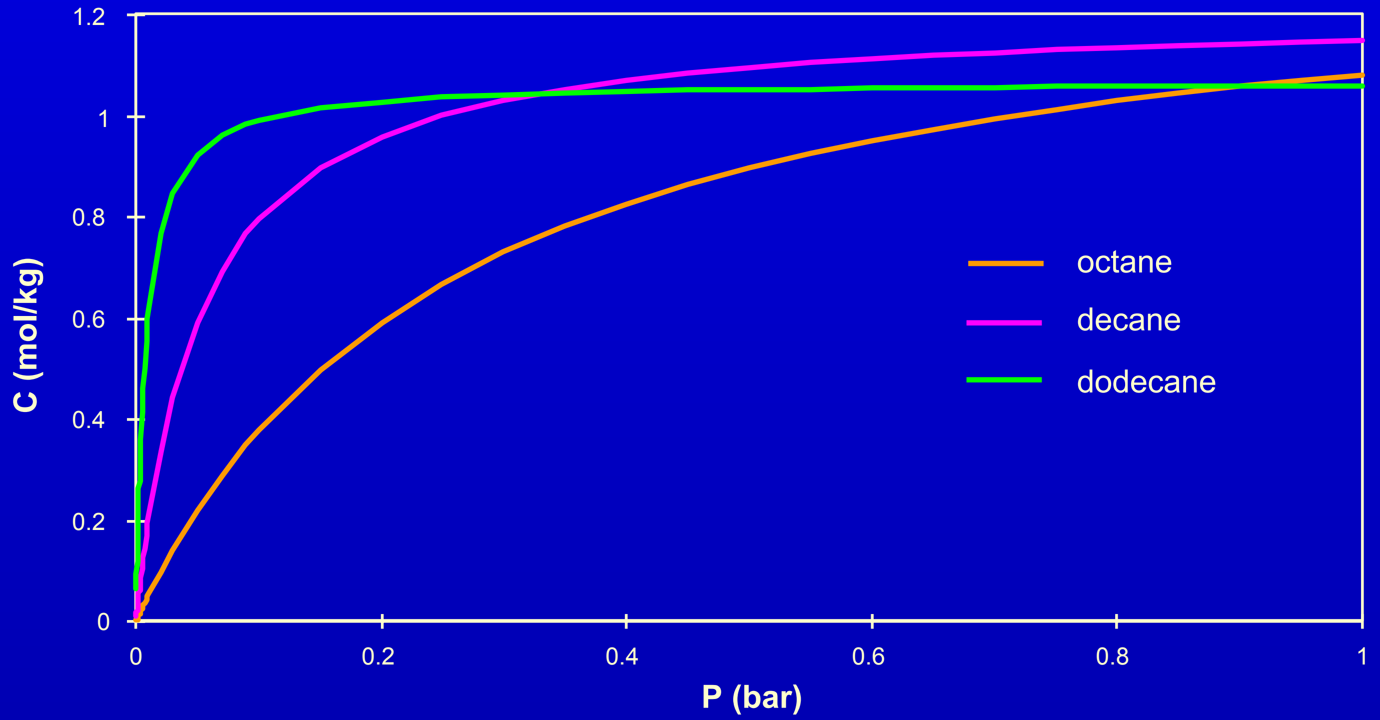


Langmuir isotherm for physisorption from ***ideal vapour phase***

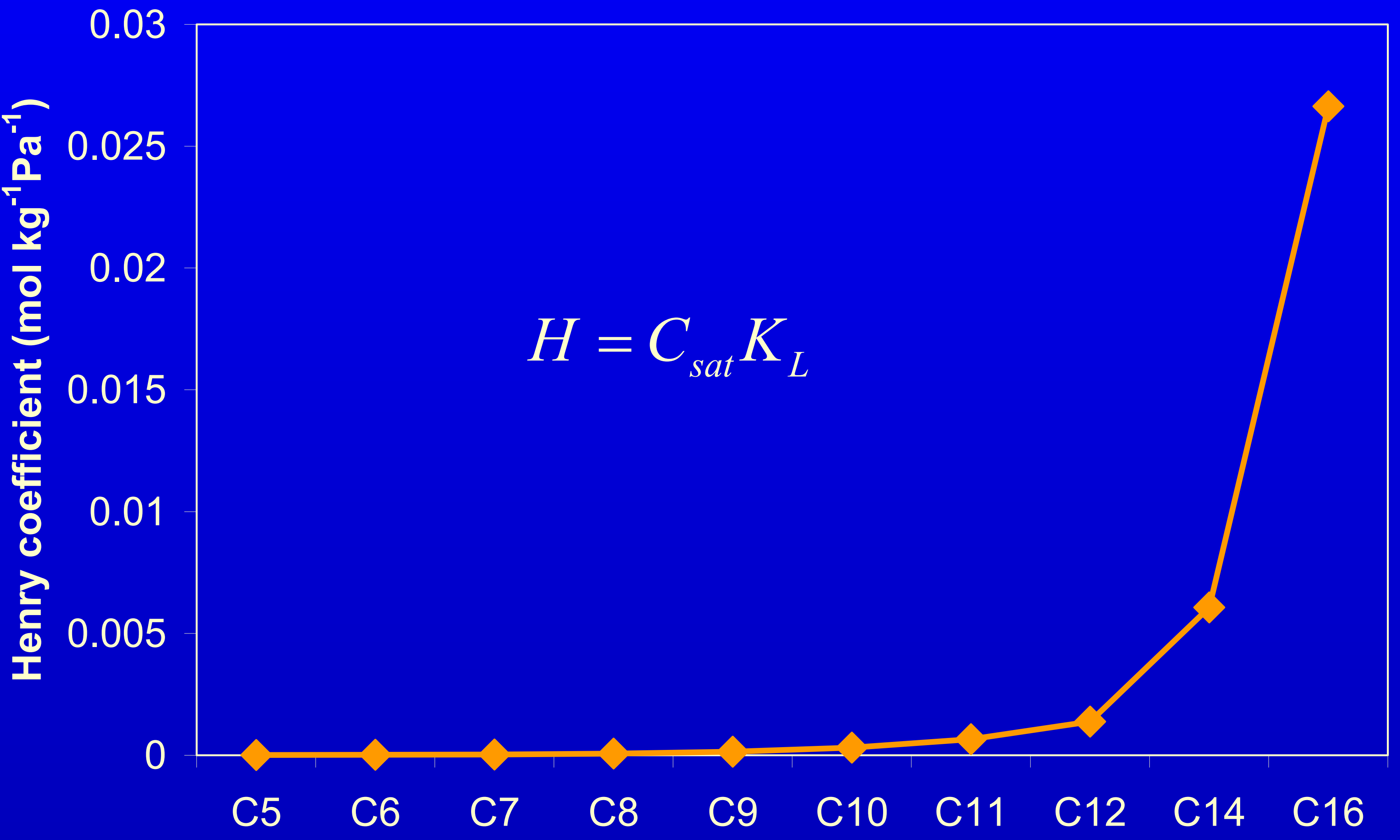
Langmuir isotherm: $C_{phys,i} = \frac{C_{sat,i} K_{L,i} p_i}{1 + K_{L,i} p_i}$

with $K_{L,i}$ from: $K_{L,i} = \frac{H_i^0 \exp\left(-\Delta H_{phys,i} / R T\right)}{C_{sat,i}}$

and H^0_i and $\Delta H_{phys,i}$ from Baron et al. (1998)



Henry coefficient on USY zeolite



$$H = C_{sat} K_L$$

Temperature: 506K

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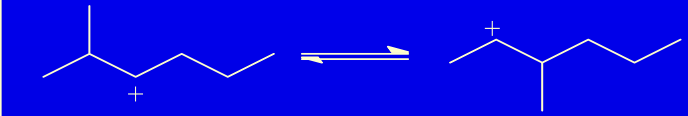
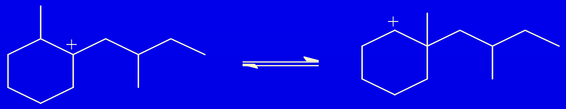
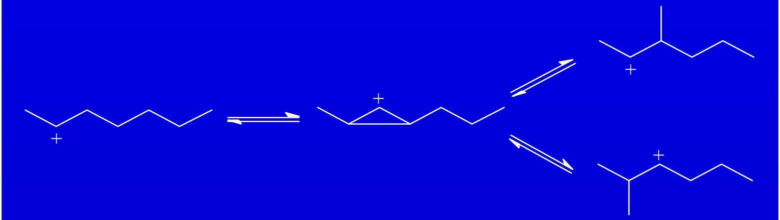
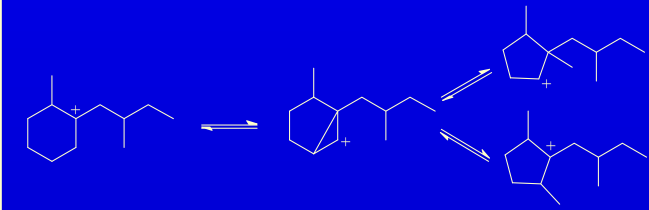
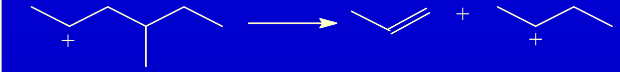
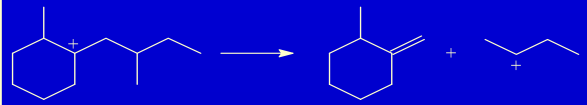
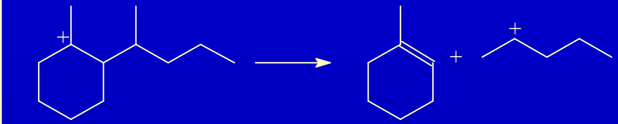
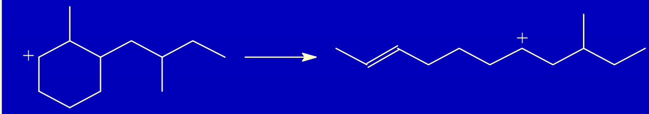
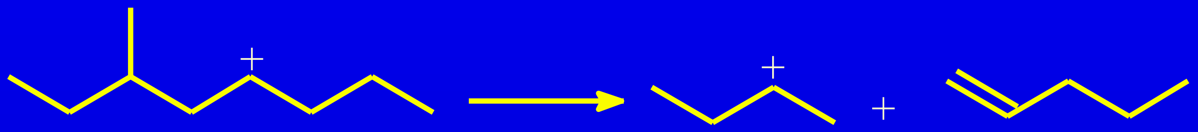
Acid catalysed reaction families

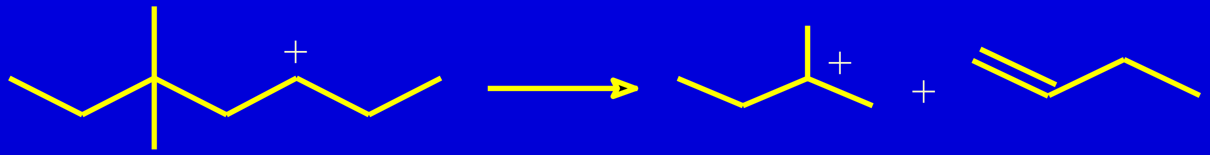
	Alkanes	Cycloalkanes
Alkyl shift		
PCP branching		
Acyclic cracking		
Exocyclic cracking		
Ring opening		

Elementary reaction family: cracking

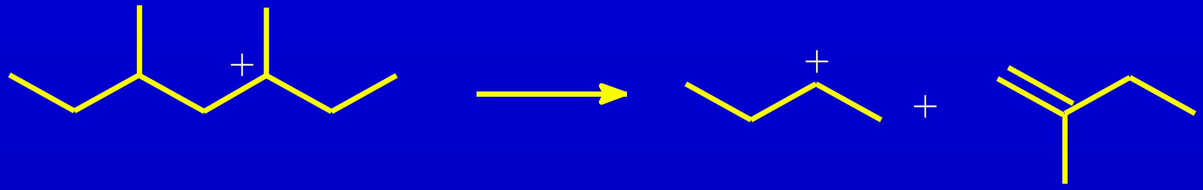
- Cr(s;s)



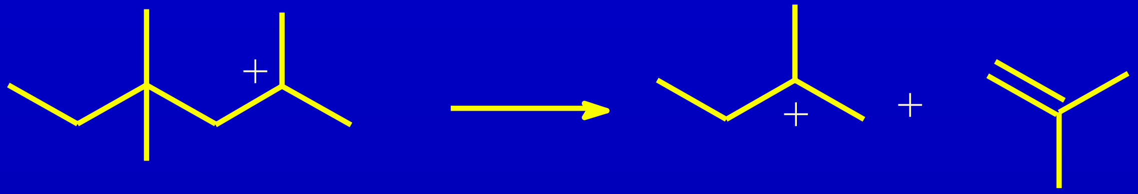
- Cr(s;t)



- Cr(t;s)



- Cr(t;t)



Hydrocracking: rate equations

$$\left.\begin{array}{l}\text{alkylshift}\\ \text{PCP-branching}\\ \beta\text{-scission}\end{array}\right\}\ \text{RDS} \qquad r = k\, C_{R^+}$$

(de-)protonation

$$C_{R^+} = \frac{C_t K_{prot} C_O}{1 + K_{prot} C_O} \cong C_t K_{prot} C_O$$

(de-)hydrogenation

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

physisorption

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

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

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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

Hydrocracking: rate equations accounting for finite carbenium ion concentrations

parameters to be estimated : k, K_{prot}

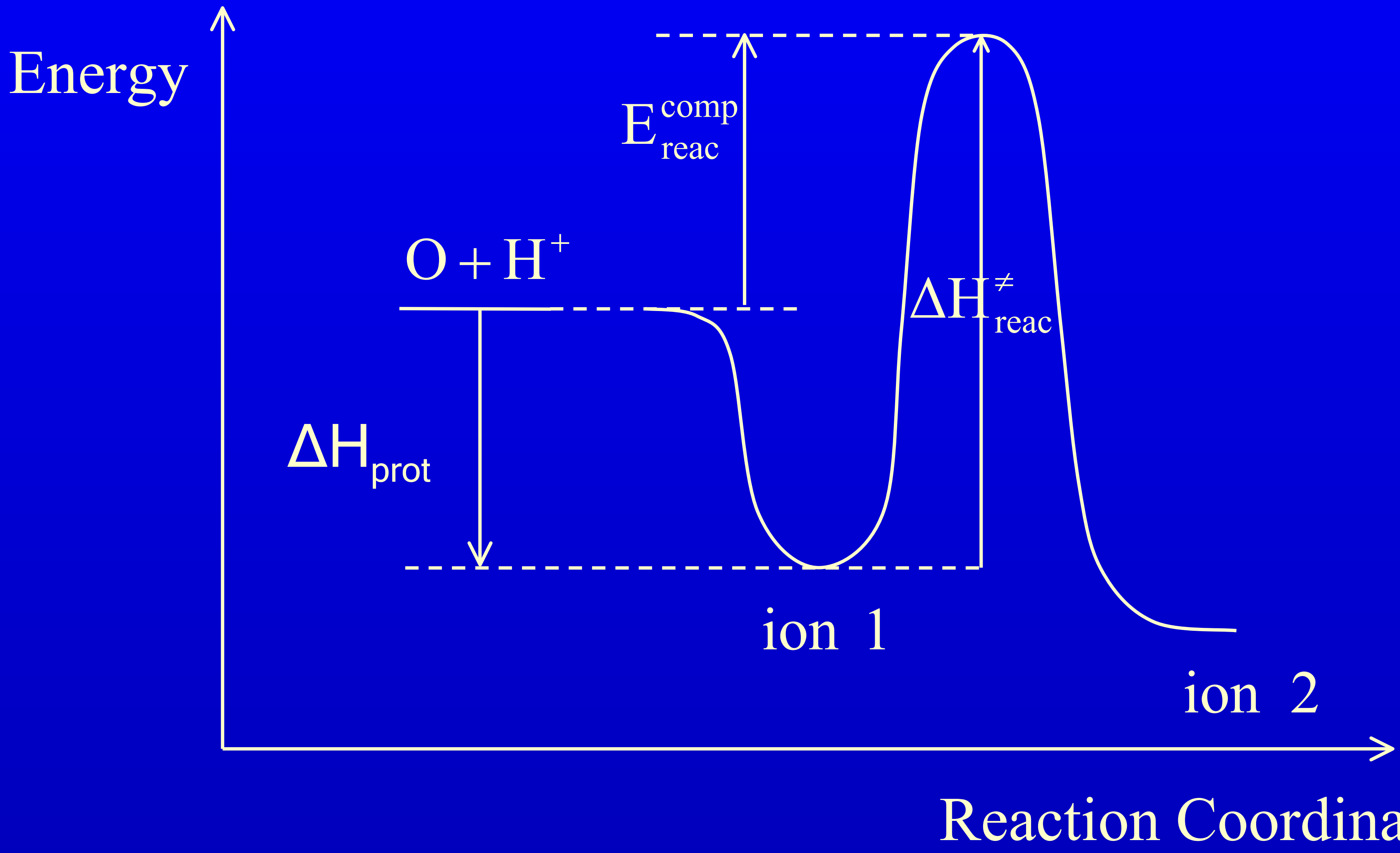
calculated via thermodynamic data

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

determined by NH_3-TPD

determined by physisorption experiments

protonation enthalpy and activation energy



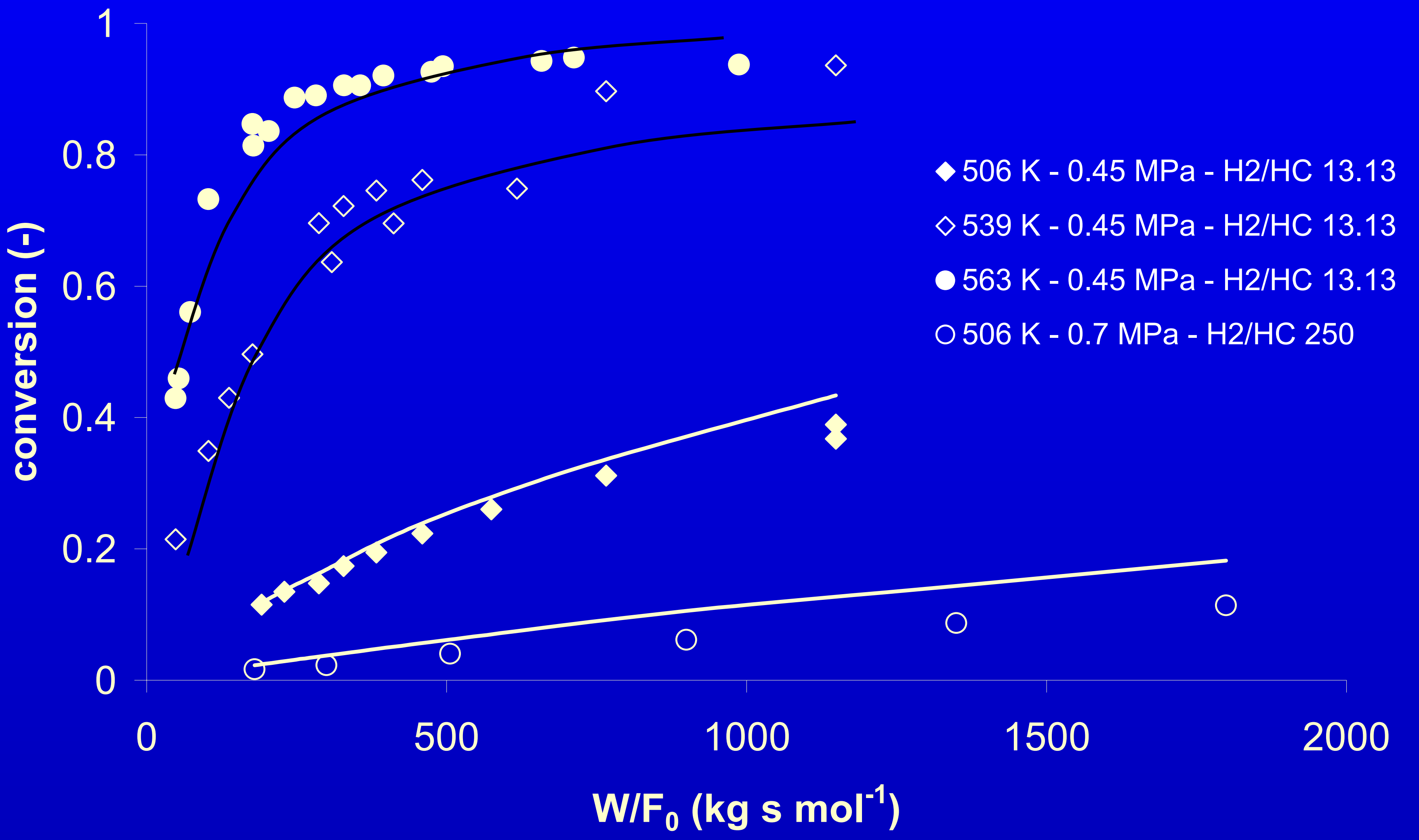
parameter values

activation energy

	Alkylshift	PCP-branching	β-scission	protonation enthalpy
	(kJ mol^{-1})			
(s;s)	77.5 (±0.2)	108.7 (±0.7)	142.7 (±1.0)	-64.9 (±0.5)
(s;t)	74.4 (±0.1)	98.6 (±1.9)	127.9 (±4.9)	
(t;s)			148.6 (±1.0)	-95.6 (±1.2)
(t;t)	104.5 (±1.2)	127.9 (±3.3)	125.1 (±3.8)	

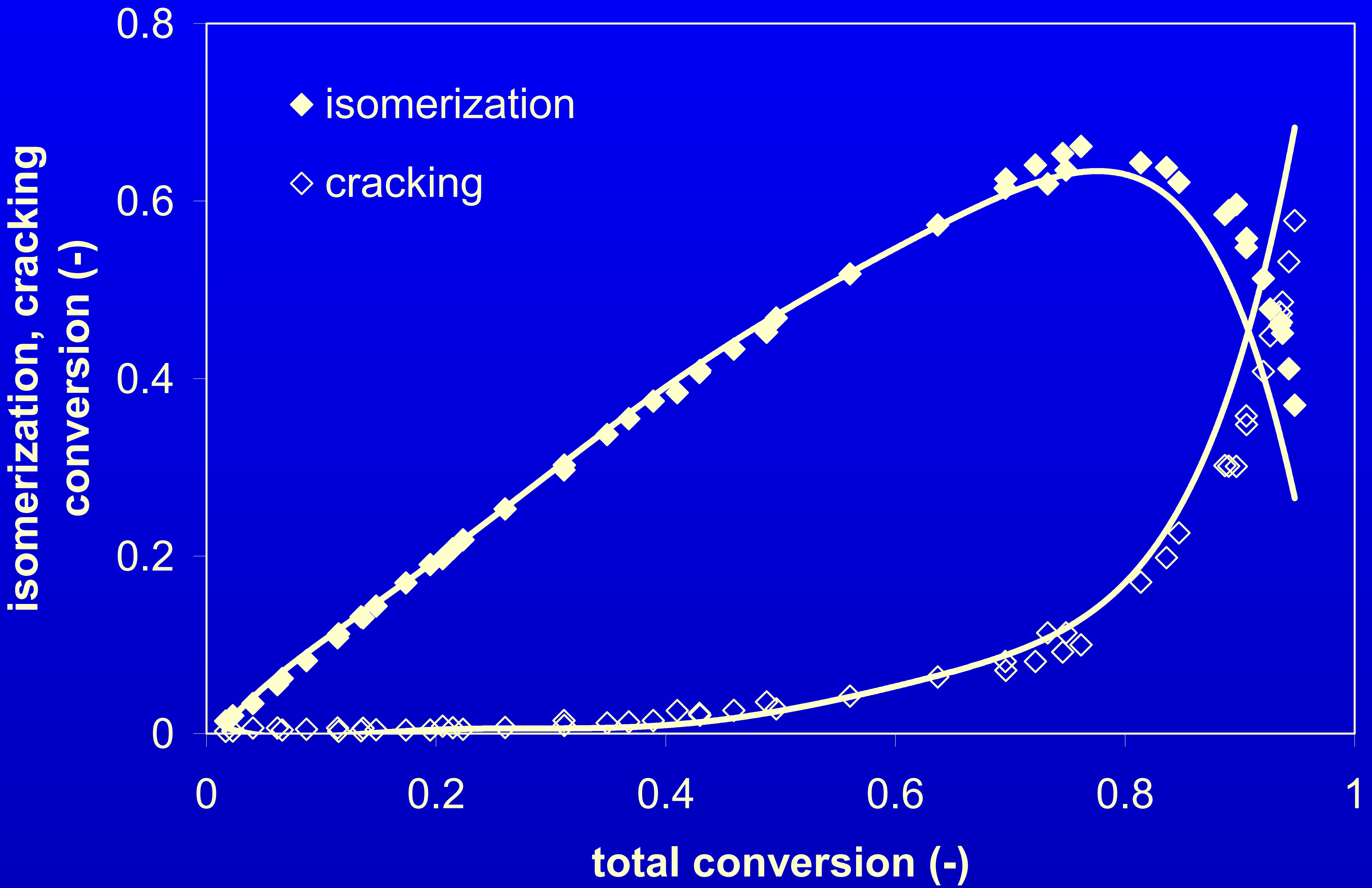
J.W. Thybaut et al. ,Catal. Lett. (2004)

Model adequacy: activity



J.W. Thybaut et al. ,Catal. Lett. (2004)

Model adequacy: selectivity



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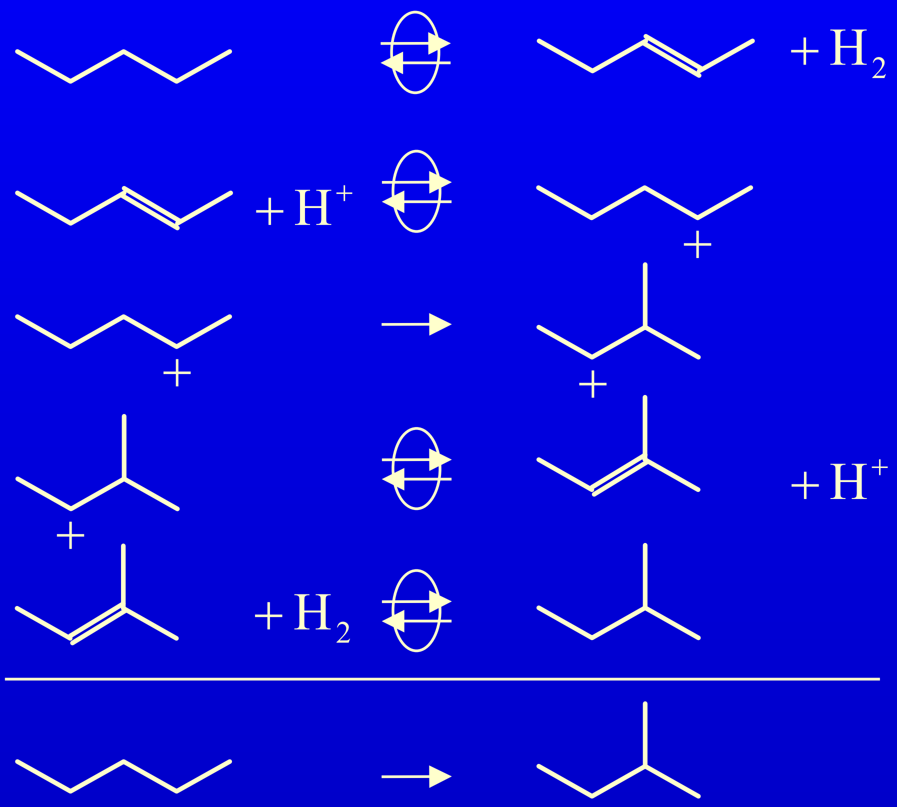
Catalyst acidity



strength

ΔH_{prot}

number

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

Catalyst acidity: Si/Al ratio

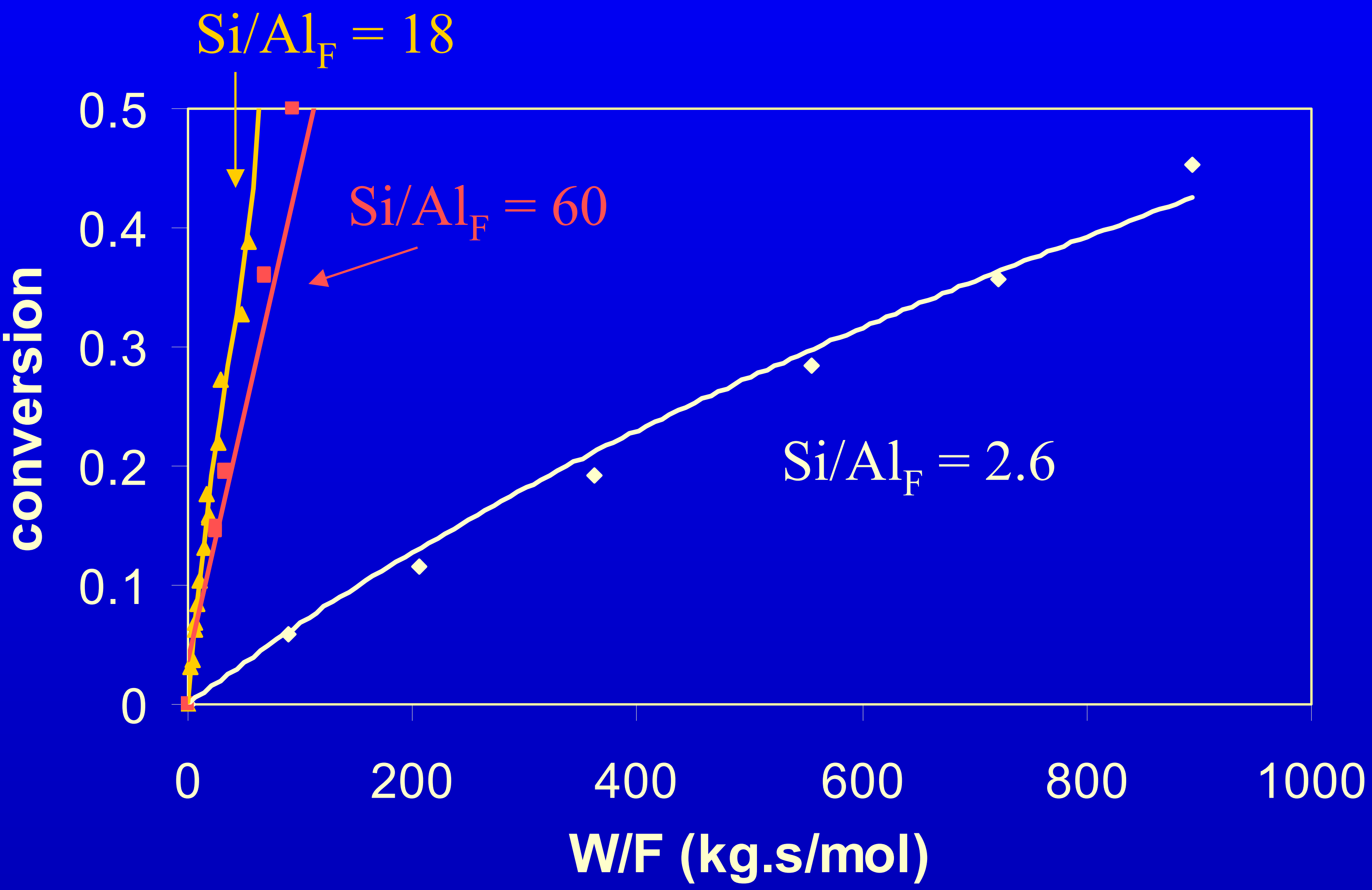
- physisorption
- ΔC_t
- $\Delta\left(\Delta H_{prot}\right)$

  ↳ 1 adjustable parameter accounting for conversion changes

Catalyst acidity: Si/Al ratio

	company	Si/Al-ratio	C_t (mol/kg$_{cat}$)
H-Y	Zeocat	2.6	4.6 10^{-6}
CBV-720	PQ	18	0.60 10^{-6}
CBV-760	PQ	60	0.22 10^{-6}

Catalyst acidity: activity



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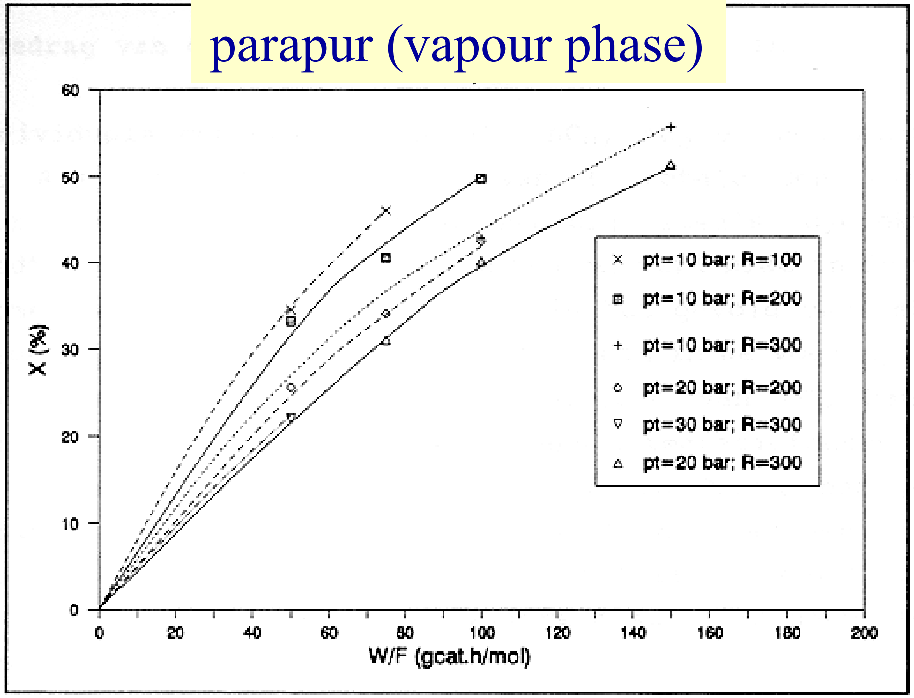
vapour phase versus liquid phase hydroconversion rates

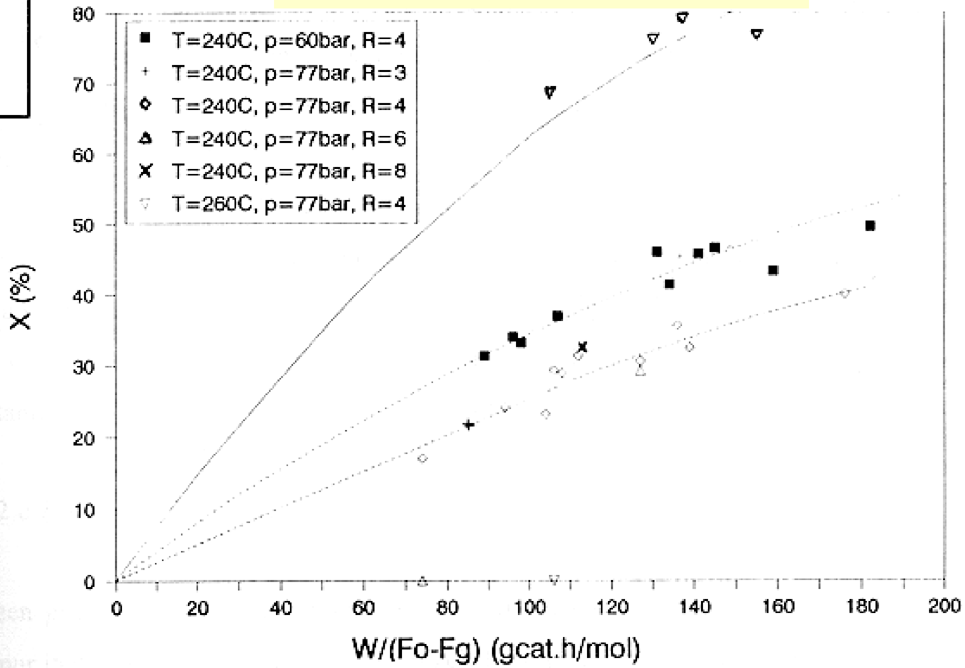
parapur (vapour phase)



rates overlap

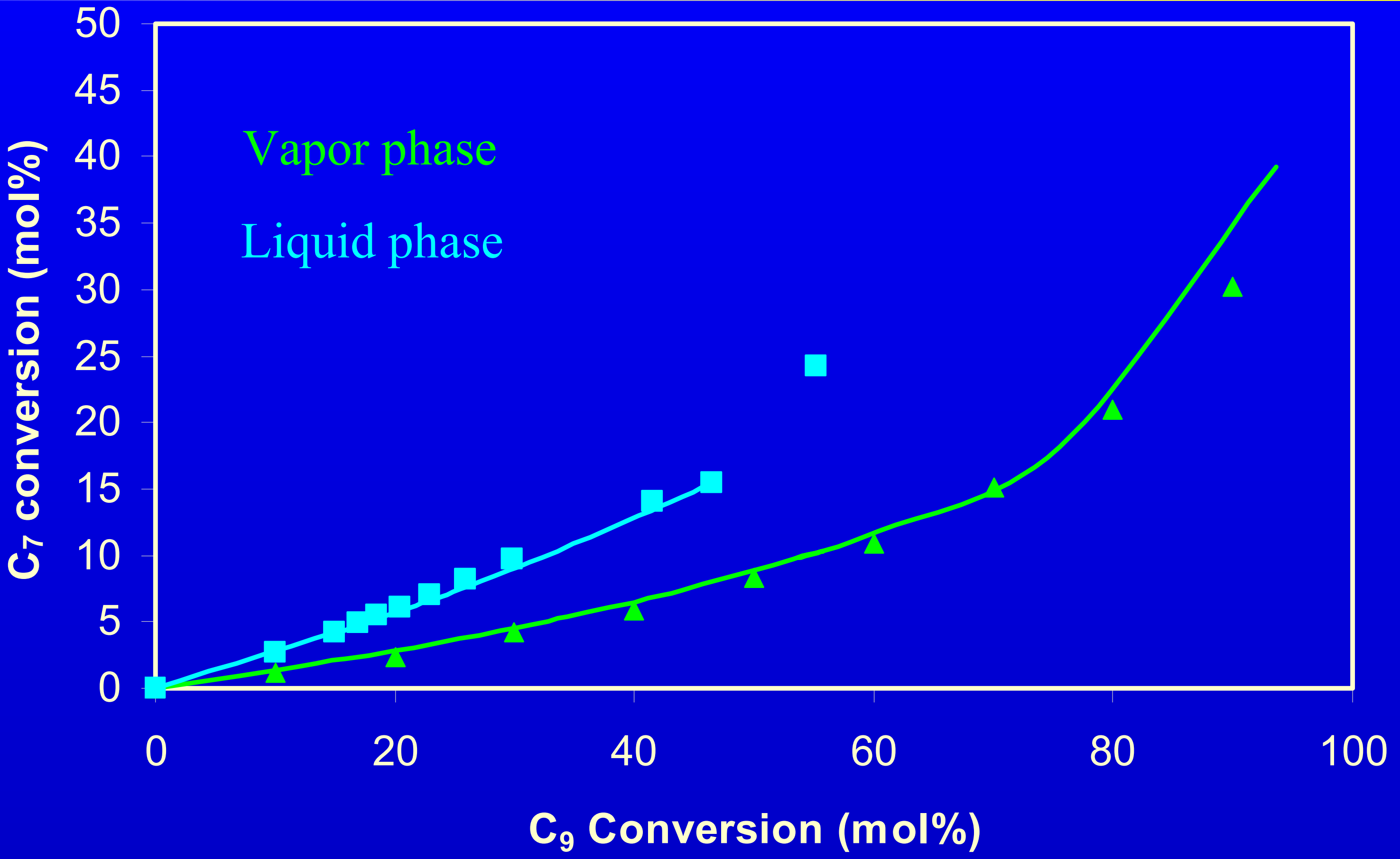
difficult comparison because of differences in operating conditions

parapur (liquid phase)



liquid phase: enhanced competition in binary mixtures

503 K



$\frac{r^{o}_{nC_7}}{r^{o}_{nC_9}}$	Experimental
Vapor phase	0.12
Liquid phase	0.37

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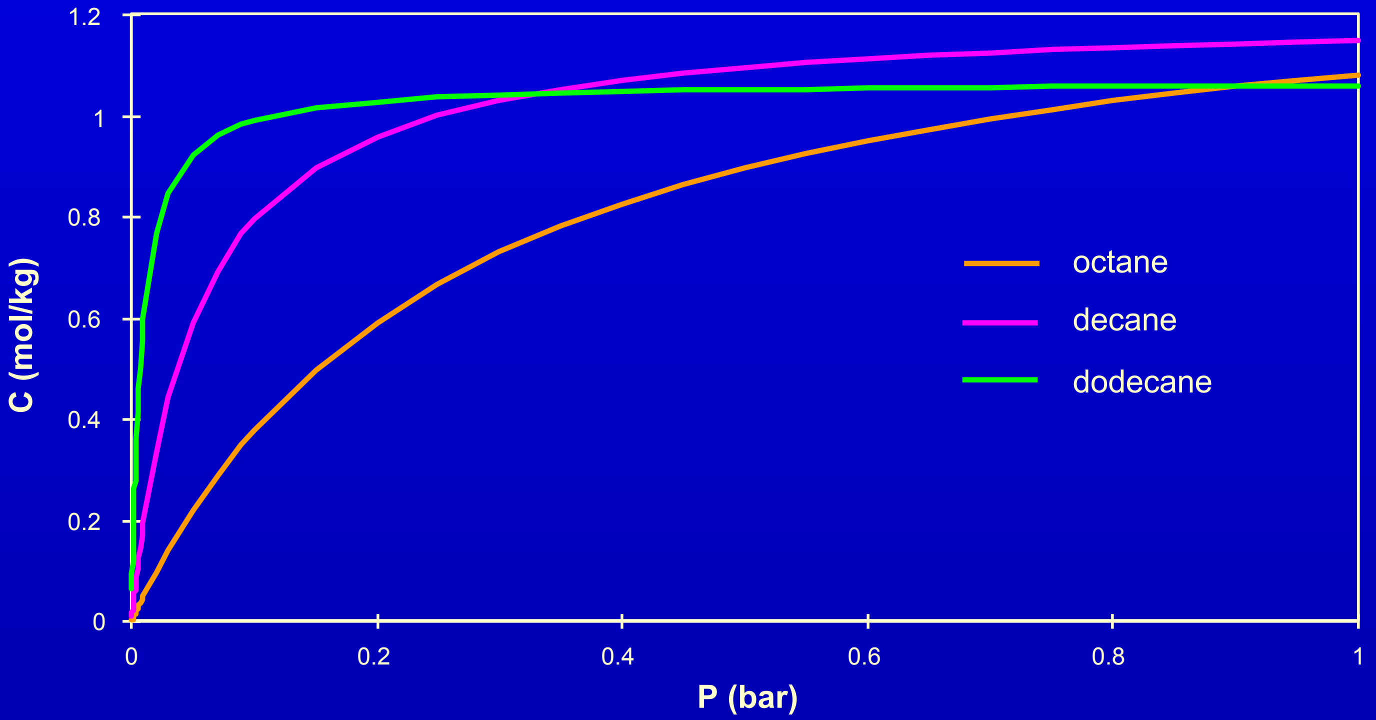
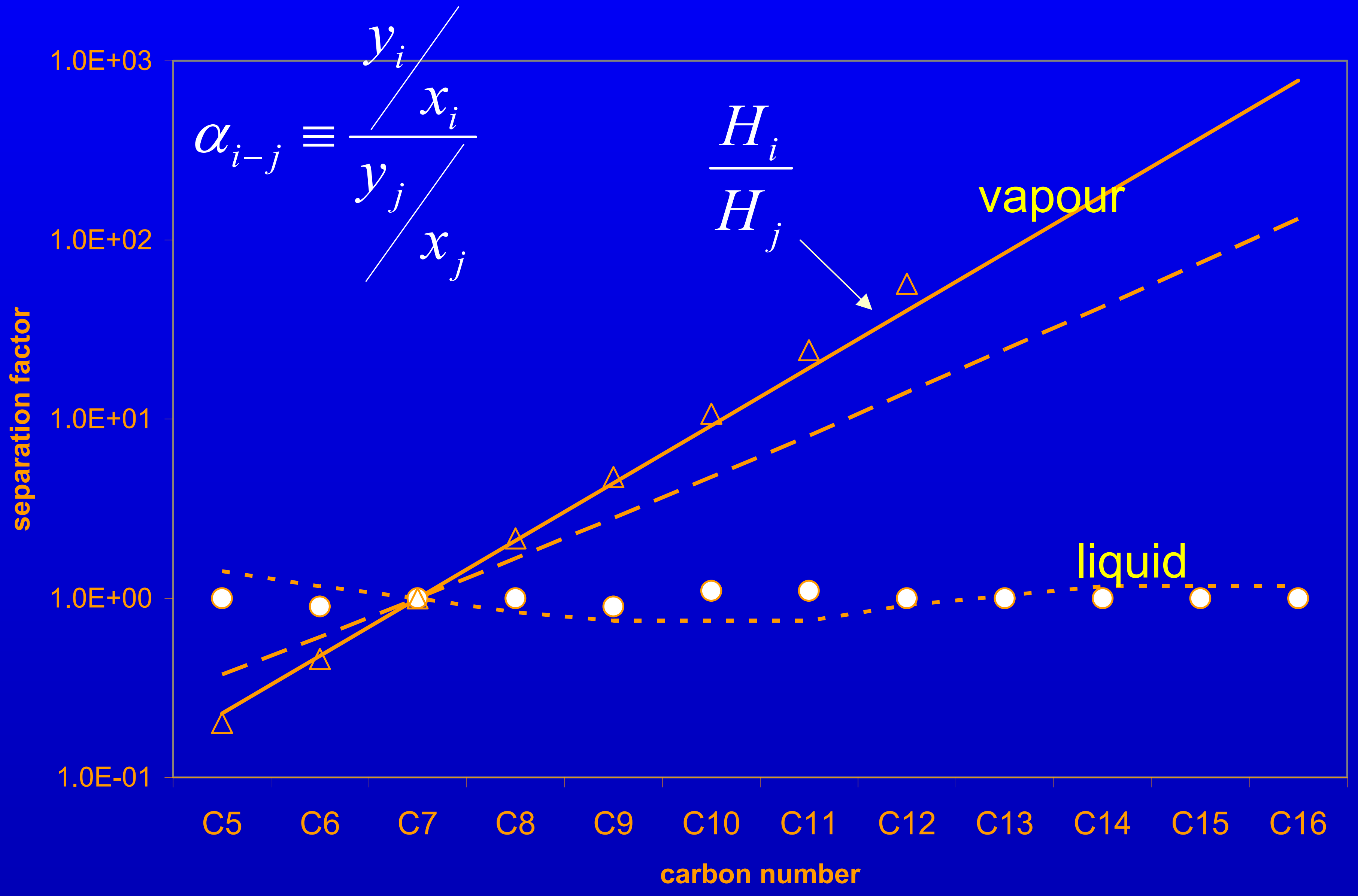
and H^0_i and $\Delta H_{phys,i}$ from Baron et al. (1998)



From vapour to liquid: separation factors α for binary mixtures



$$\alpha_{i-j} \equiv \frac{y_i / x_i}{y_j / x_j}$$

$$\frac{H_i}{H_j}$$

Langmuir isotherm for physisorption accounting for non ideality 1: fugacity

Langmuir isotherm: $$C_i = \frac{C_{sat} K^*_{L,i} f_i}{1 + K^*_{L,i} f_i}$$

with now f_i and $K^*_{L,i}$ rather than p_i and $K_{L,i}$

fugacity $$f_i = \boxed{\phi_i\, p_i} = \phi_i\, y_i\, p_t = \boxed{\phi_i\, C_i\, V_m\, p_t}$$

bulk aggregation state: liquid

bulk aggregation state: vapour

non ideality: fugacity coefficients (ideal gas state as reference state)

Cubic equation of state:

$$Z^3 - \left(1 + B^* - uB^*\right)Z^2 + \left(A^* + wB^{*2} - uB^* - uB^{*2}\right)Z^2$$
$$- A^*B^* - wB^{*2} - wB^{*3} = 0$$

fugacity coefficients calculated from:

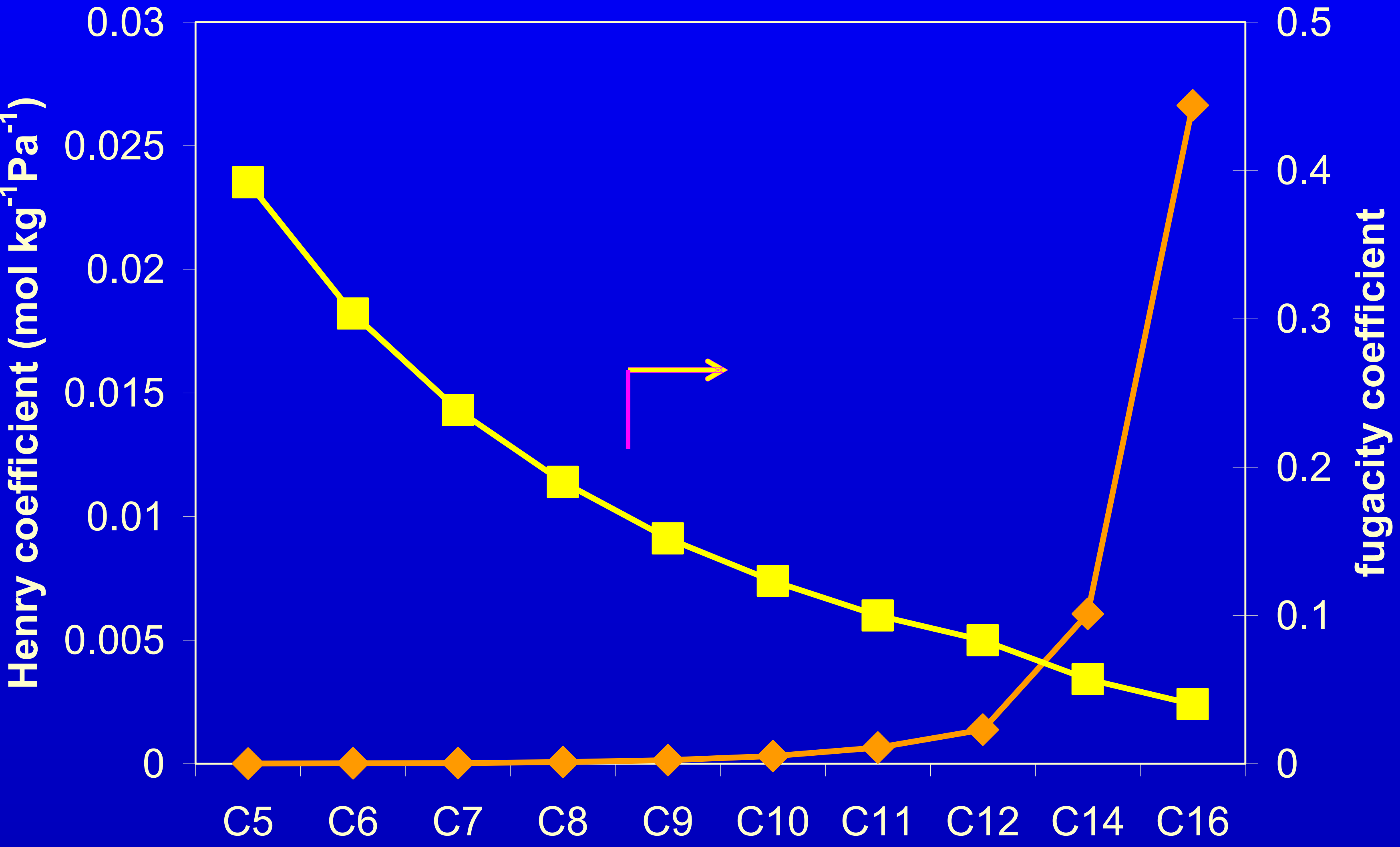
$$\ln\left(\phi_i\right) = \frac{b_i}{b}(Z-1) - \ln(Z - B^*)$$
$$+ \frac{A^*}{B^*\sqrt{\left(u^2 - 4w\right)}}\left(\frac{b_i}{b} - \delta_i\right)\ln\left(\frac{2Z + B^*\left(u + \sqrt{u^2 - 4w}\right)}{2Z + B^*\left(u - \sqrt{u^2 - 4w}\right)}\right)$$

Peng-Robinson: u=2, w=-1

other coefficients:

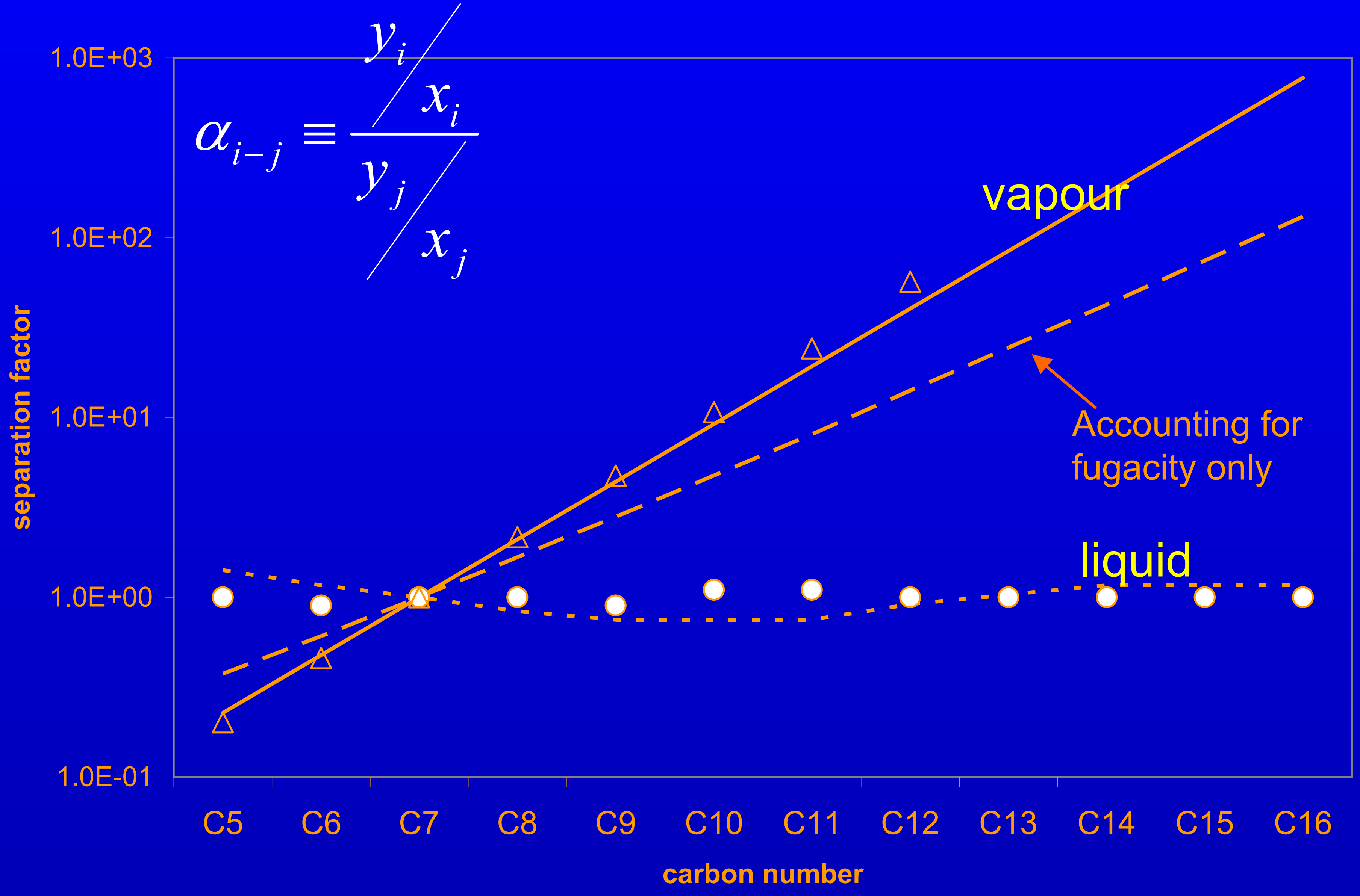
“Properties of gases and liquids”

fugacity coefficient



Temperature: 506K and Pressure: 8MPa

From vapour to liquid: separation factors α for binary mixtures

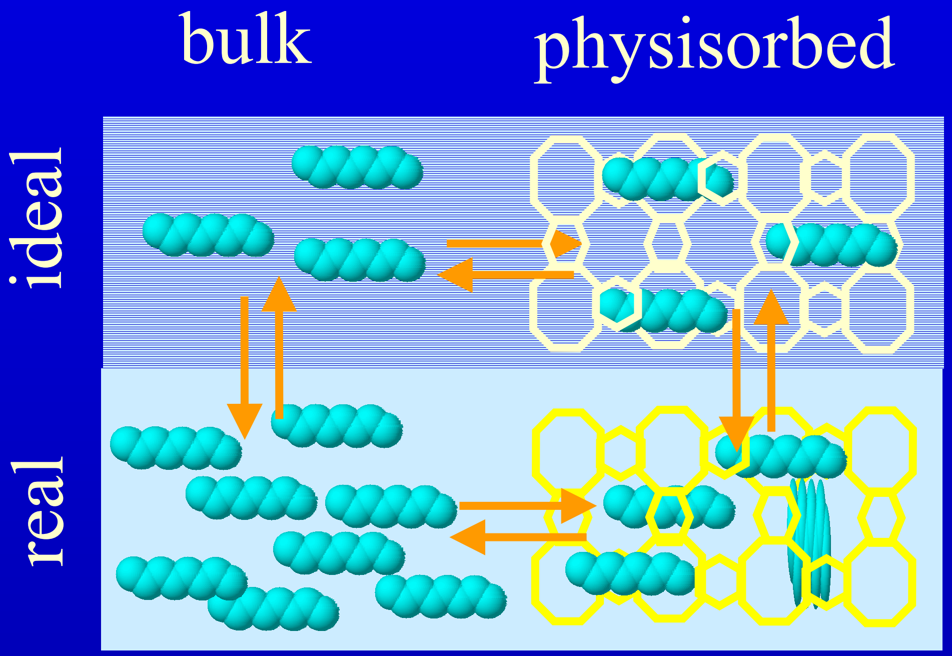


$$\alpha_{i-j} \equiv \frac{y_i / x_i}{y_j / x_j}$$

Langmuir isotherm for physisorption accounting for non ideality
2: “Langmuir” coefficient $K^*_{L,i}$

Born-Haber cycle

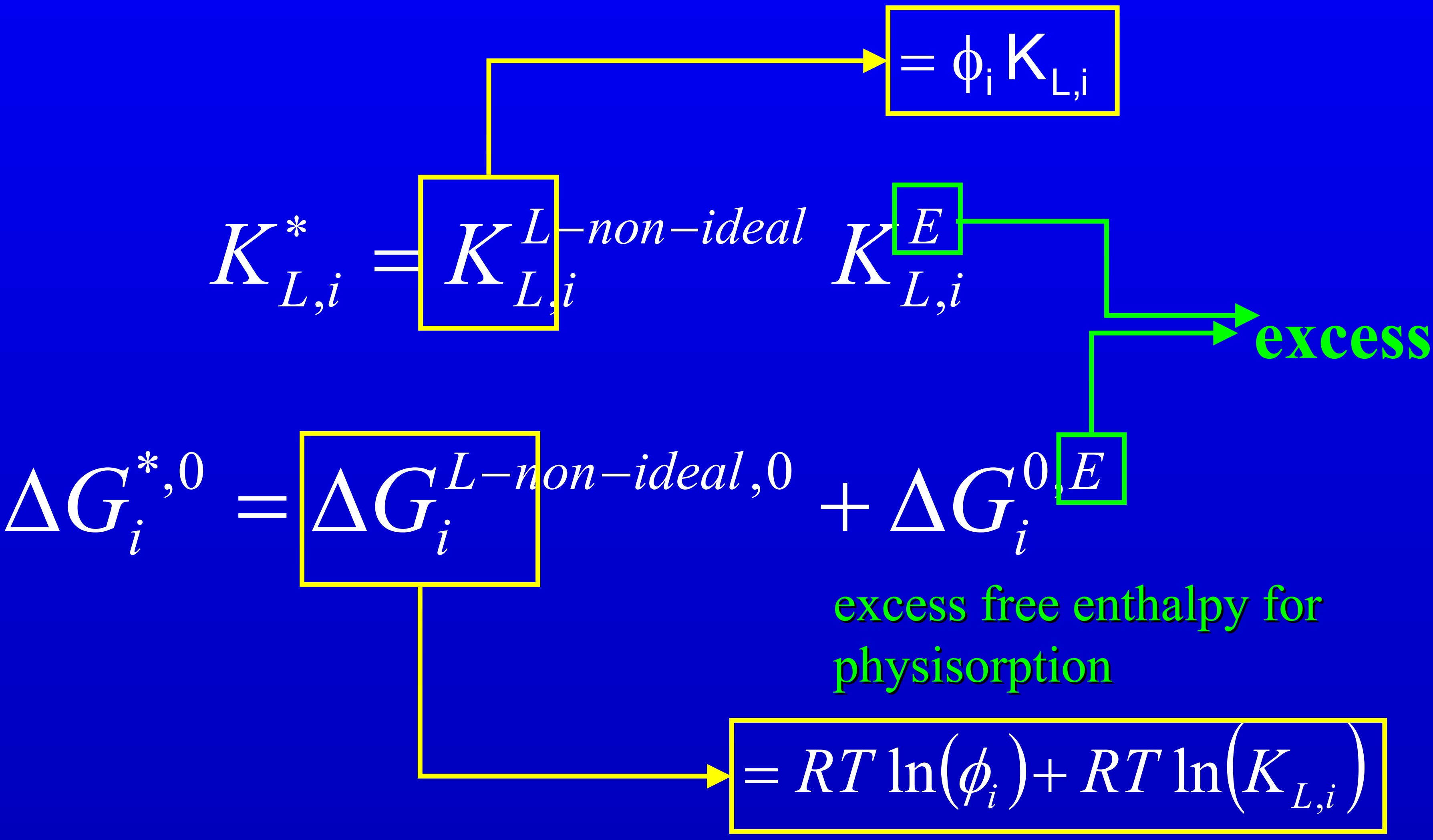
$$\begin{tikzcd}
P_i^{id} \arrow[r, shift left, "K_{L,i}"] \arrow[d, shift left] & P_{phys,i}^{id} \arrow[l, shift left] \arrow[d, shift left] \\
P_i \arrow[u, shift left, "\phi_i"] \arrow[r, shift left, "K^*_{L,i}"] & P_{phys,i} \arrow[l, shift left] \arrow[u, shift left, "K^E_{L,i}"']
\end{tikzcd}$$



physisorbed state depends on the non-ideality of the bulk state

→ $K^E_{L,i} \neq 1$

Langmuir isotherm for physisorption accounting for non ideality 2: “Langmuir” coefficient $K^*_{L,i}$



$$\boxed{= \phi_i K_{L,i}}$$

$$K^*_{L,i} = \boxed{K_{L,i}^{L-non-ideal}} K_{L,i}^{\boxed{E}}$$

excess

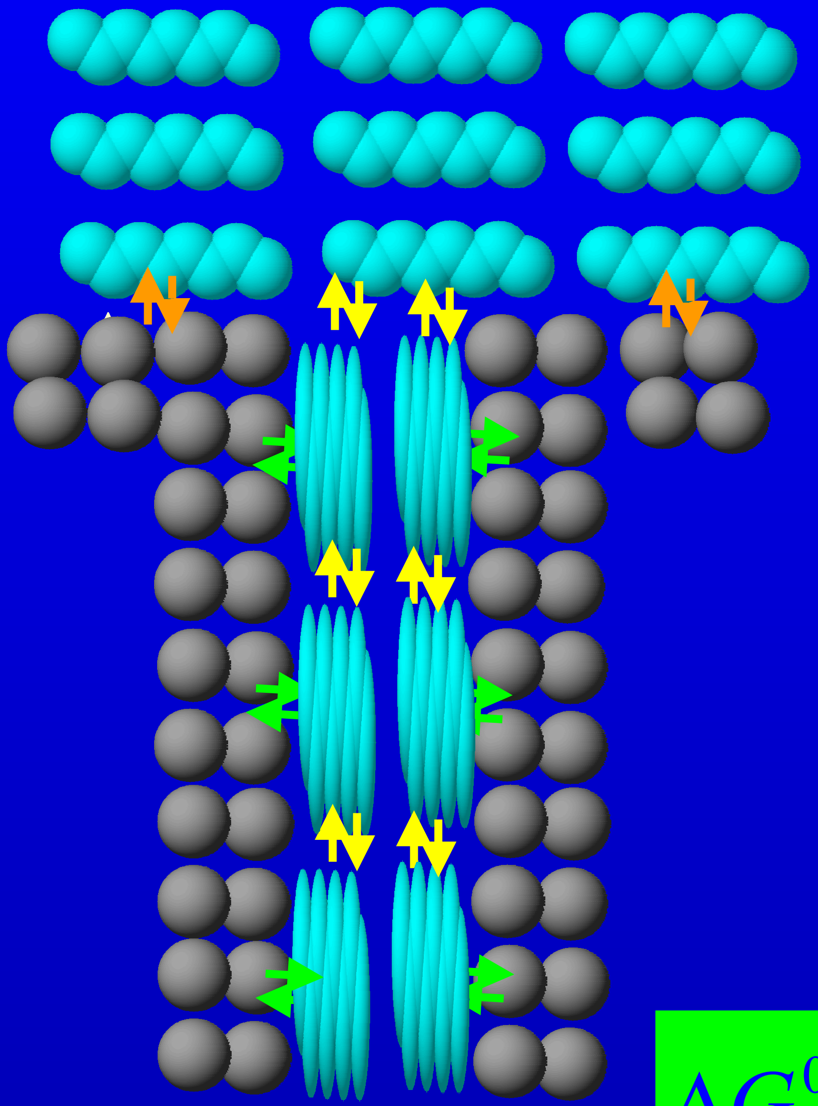
$$\Delta G_i^{*,0} = \boxed{\Delta G_i^{L-non-ideal,0}} + \Delta G_i^{0,\boxed{E}}$$

excess free enthalpy for physisorption

$$\boxed{= RT\ln\left(\phi_i\right) + RT\ln\left(K_{L,i}\right)}$$

bulk non ideality

2: excess free enthalpy in non-ideal physisorption



bulk non ideality affects intersorbate distances:

- compression effect on sorbate: sorbate dependent, analogous to bulk non ideality

$$\Rightarrow \quad \Delta G_i^{0,E} \sim \ln \phi_i$$

- solvating effect on sorbent framework: sorbent dependent scaling of compression effect

$$\Delta G_i^{0,E} = c^E \ln \phi_i \qquad K_{L,i}^E = \phi_i^{-c^E/RT}$$

estimation of c^E from experimental data

liquid phase binary physisorption isotherms:

$$\boxed{y_i} = \frac{\alpha_{i-j} x_i}{(1 + \alpha_{i-j} x_i - \boxed{x_i})}$$

physisorbed

bulk

with:

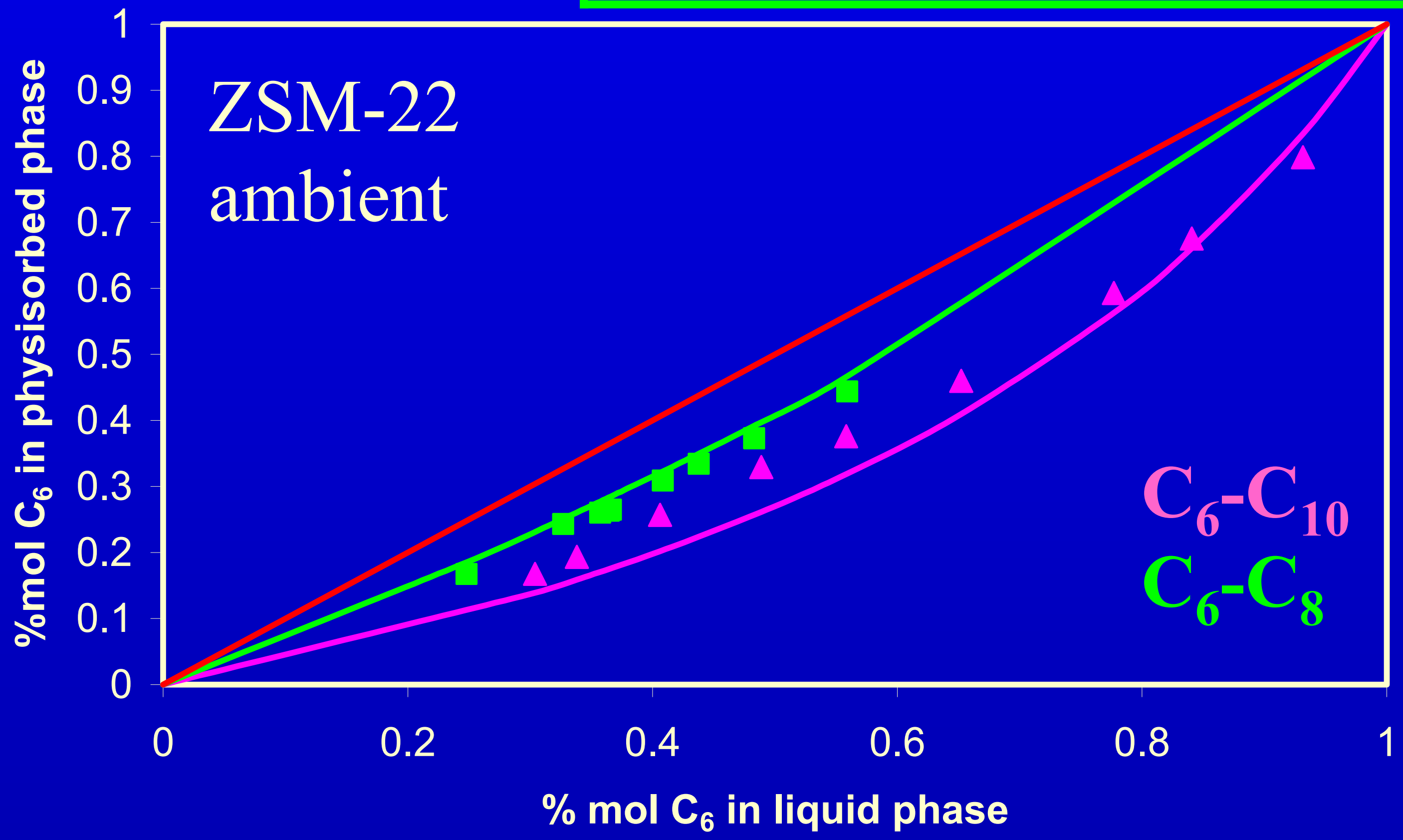
$$\boxed{\alpha_{i-j}} \equiv \frac{y_i / x_i}{y_j / x_j} = \frac{H_i \phi_i^{1-\frac{c^E}{RT}}}{H_j \phi_j^{1-\frac{c^E}{RT}}}$$

separation factor

2: excess physisorption coefficient $K^{E}_{L,i}$ in liquid phase

$$K^{E}_{L,i} = \phi_i^{\boxed{-c^{E}}/RT}$$

	kJ mol^{-1}
ZSM-22	-3.68±0.07
ZSM-5	-3.03±0.10
USY	-1.55±0.04



2: excess physisorption coefficient ^{E} in liquid phase

$$K_{L,i}^{E} = \phi_i^{\boxed{-c^{E}}/RT}$$

	kJ mol^{-1}
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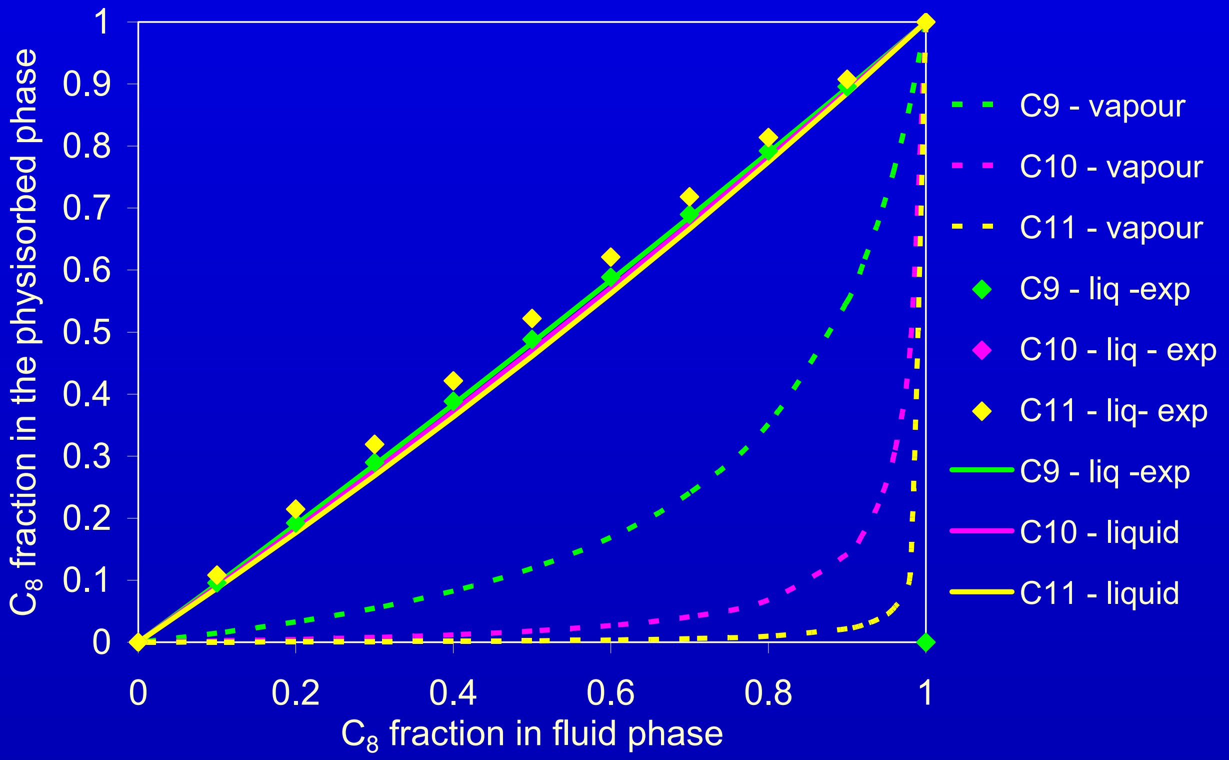
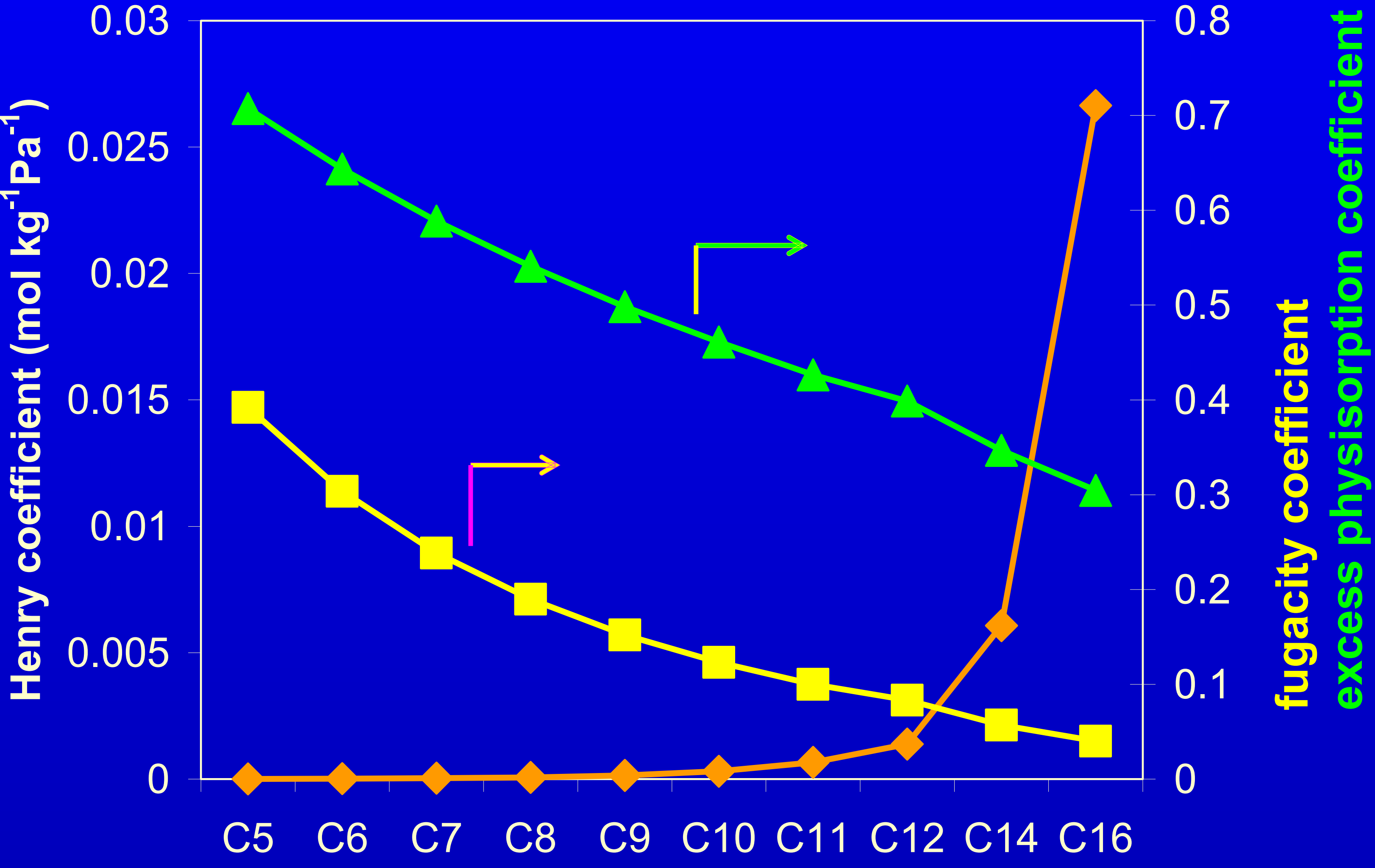
USY: binary mixtures with n-octane

ambient conditions



Excess physisorption coefficient $K_{L,i}^{E}$ in liquid phase on USY zeolite

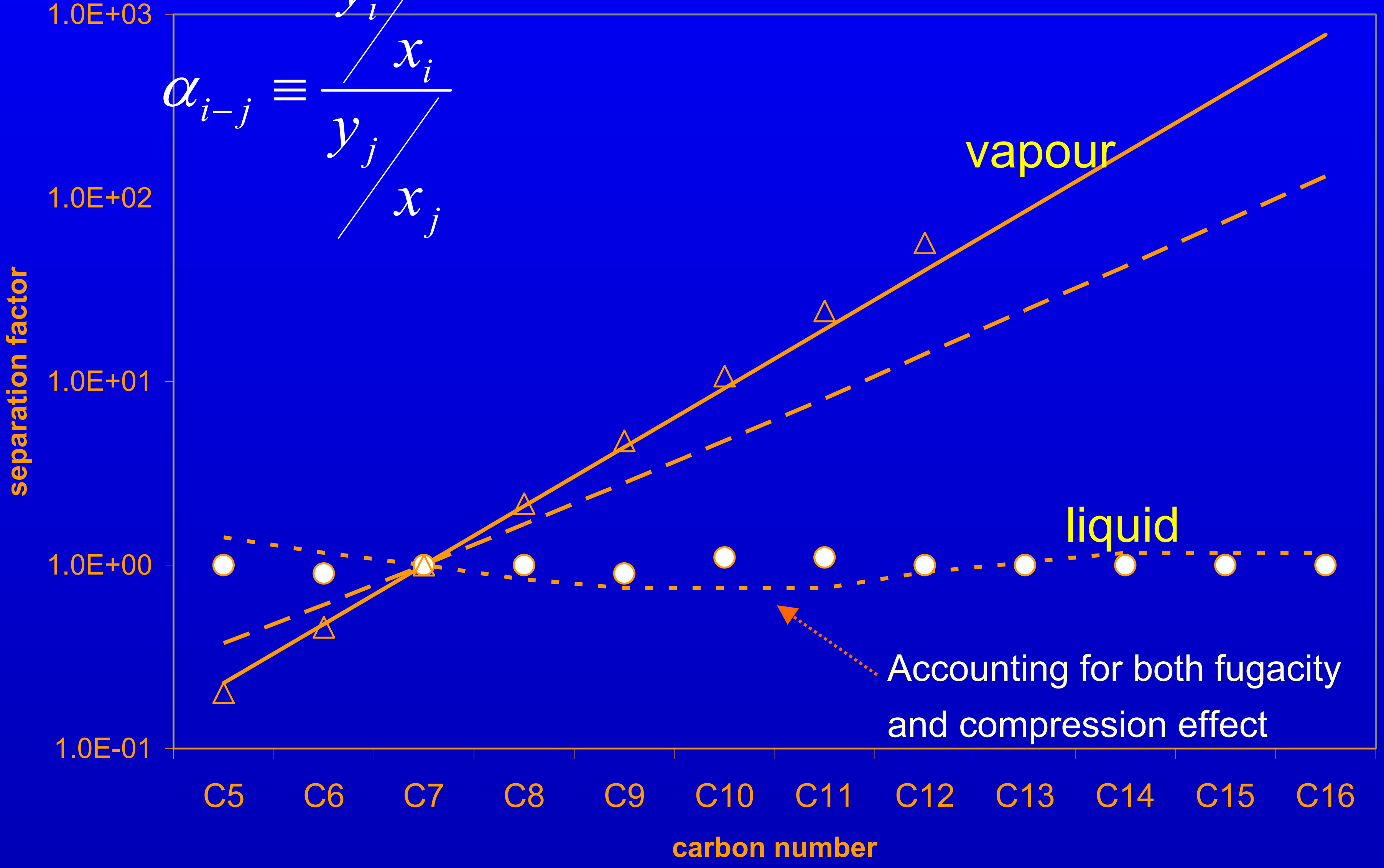


$$K_{L,i}^{E} = \phi_i^{-c^{E}/RT}$$

Temperature: 506K and Pressure: 8MPa

From vapour to liquid: separation factors α for binary mixtures

$$\alpha_{i-j} \equiv \frac{y_i / x_i}{y_j / x_j}$$



Accounting for both fugacity and compression effect

conclusions liquid phase physisorption

$$C_{phys,i} = \frac{C_{sat} K_{L,i} K_L^E \phi_i C_i V_m p_t}{1 + K_{L,i} K_L^E \phi_i C_i V_m p_t}$$

with $K_L^E = \phi_i^{-\frac{c^E}{RT}}$

liquid phase conditions are disfavouring physisorption:

- fugacity coefficients $\phi_i < 1$
- excess physisorption coefficient $K^E_L < 1$ for $c^E < 0$ (for $\phi_i < 1$): compression effect
- disfavouring more pronounced for larger alkanes (even selectivity reversal possible)

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Hydrocracking: rate equations

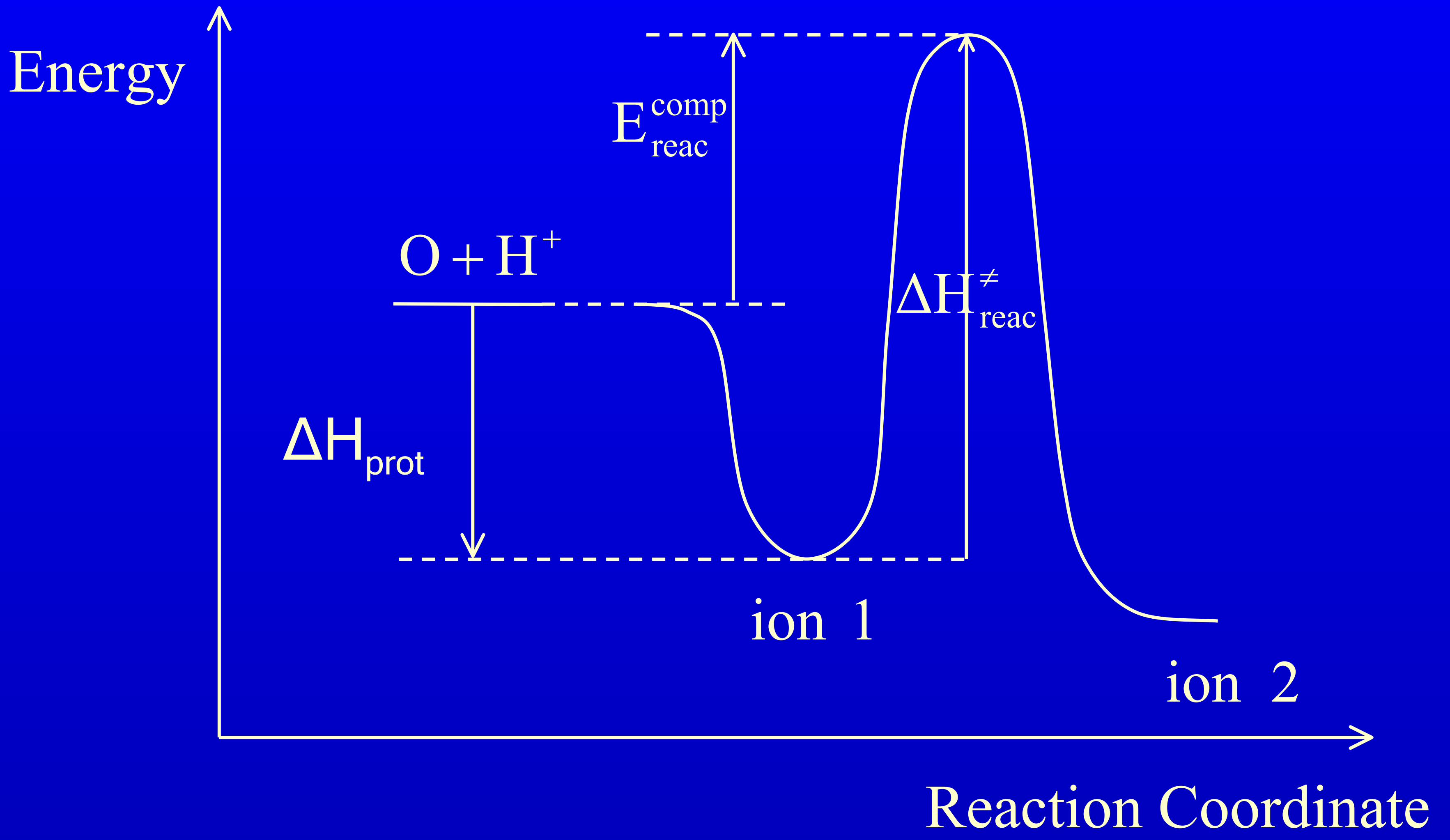
vapour phase

$$r = \frac{C_{sat} C_t k K_{prot} K_{deh} K_L \, p_P / p_{H_2}}{\left(1 + K_L p_P\right)\left(1 + \dfrac{C_{sat} K_{prot} K_{deh} K_L \, p_P / p_{H_2}}{1 + K_L p_P}\right)}$$

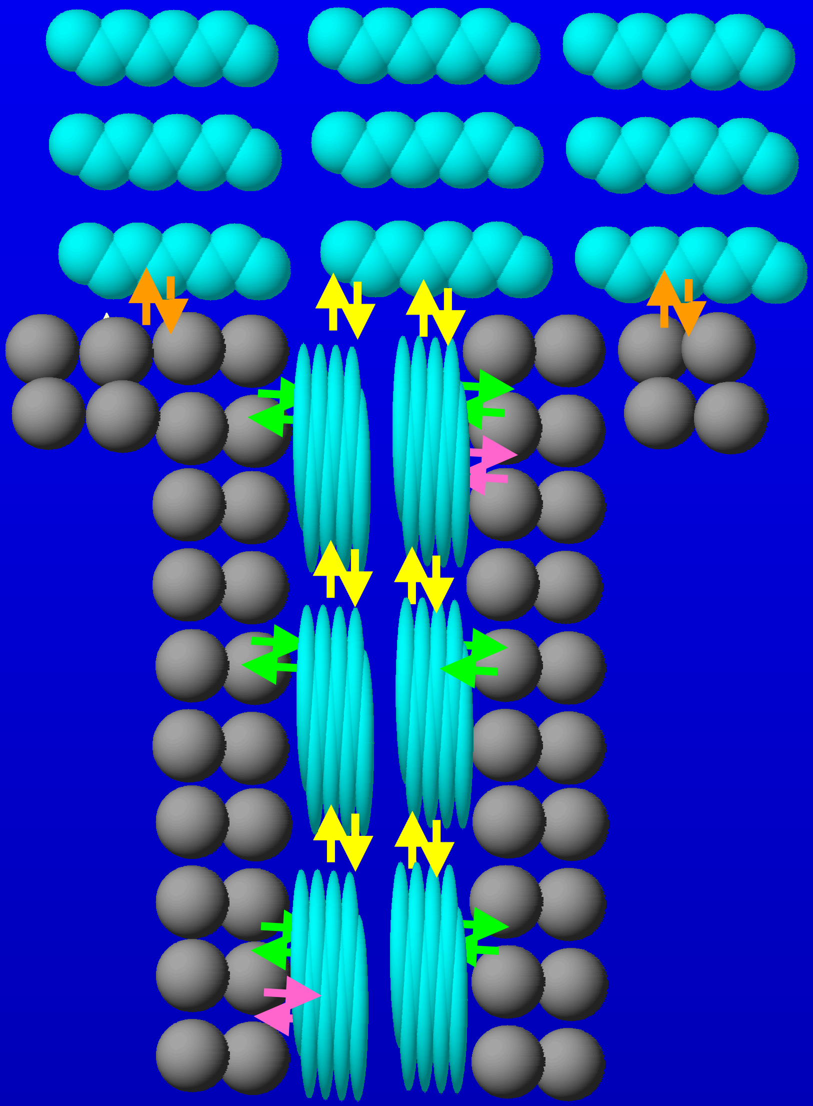
liquid phase

$$r = \frac{C_{sat} C_t k K^{*}_{prot} K_{deh} K_L K_L^E \dfrac{\phi_P C_P}{\phi_{H_2} C_{H_2}}}{\left(1 + K_L K_L^E \phi_P C_P V_m p_t\right)\left(1 + \dfrac{C_{sat} K^{*}_{prot} K_{deh} K_L K_L^E \dfrac{\phi_P C_P}{\phi_{H_2} C_{H_2}}}{1 + K_L K_L^E \phi_P C_P V_m p_t}\right)}$$

protonation enthalpy and activation energy



protonation coefficient accounting for non ideality $K^*_{prot,i}$



- solvating effect on sorbent framework:

  modified strength of the acid sites

$$\begin{tikzcd}
O^{id}_{phys;i} \arrow[r, shift left, "K_{prot,i}"] \arrow[d, shift left] & R_i^{+,id} \arrow[l, shift left] \arrow[d, shift left, "{K^E_{prot,i} = K^E_{L,i}\, K^E_{chem,i}}"] \\
O_{phys;i} \arrow[r, shift left, "K^*_{prot,i}"] \arrow[u, shift left, "{{K^E_{L,i}}^{-1}}"] & R_i^{+} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

Born-Haber cycle

protonation coefficient $K^*_{prot,i}$

$$K^*_{prot,i} = K_{prot,i}\boxed{K^E_{chem,i}}$$

excess due to chemical interactions

$$\Delta G^{*,0}_{prot,i} = \Delta G^0_{prot,i} + \boxed{\Delta G^{0,E}_{chem,i}}$$

excess standard protonation free enthalpy

estimation of liquid phase excess standard protonation enthalpy

modified strength of the acid sites:

- no effect on entropy
- only effect on standard protonation enthalpy

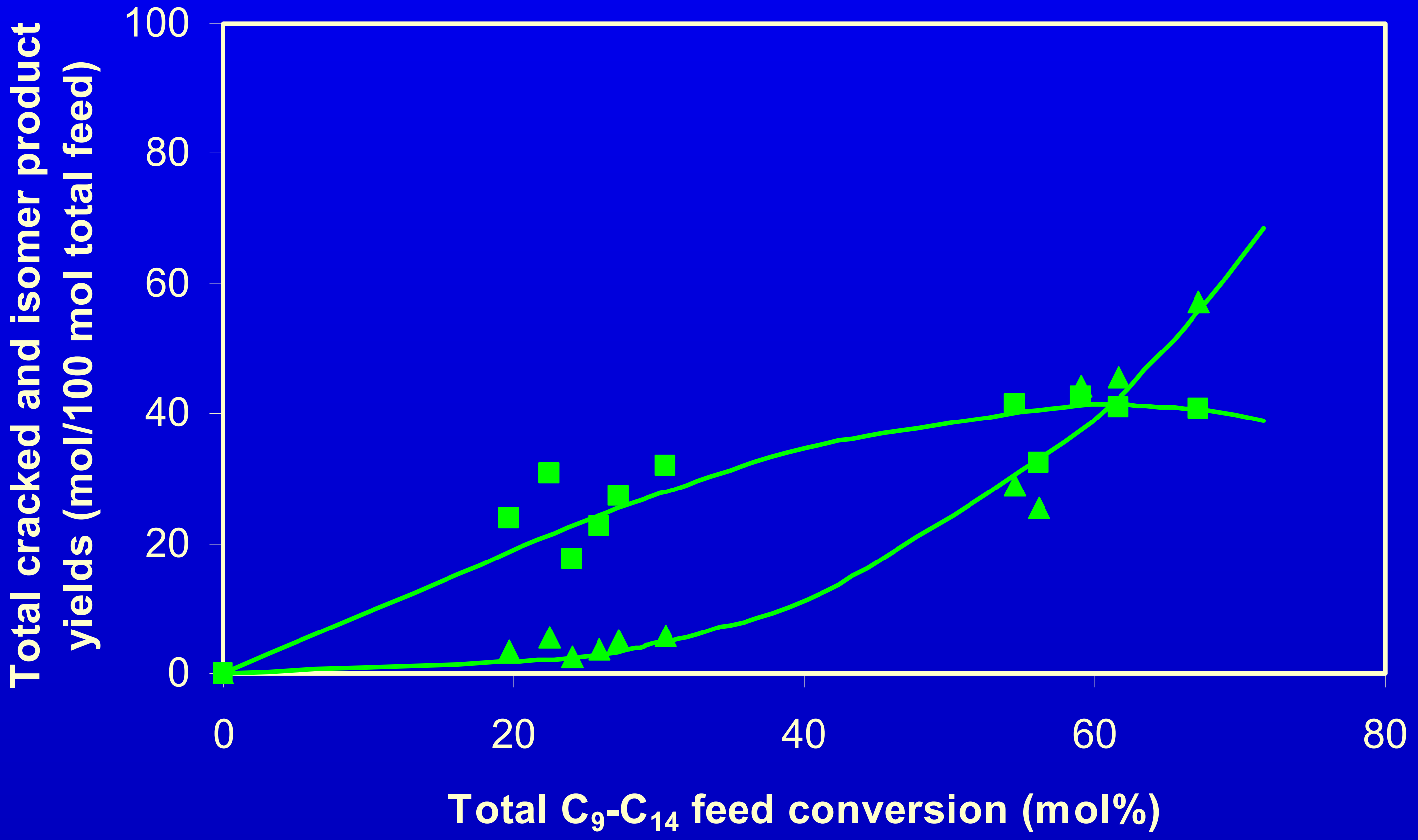
$$\Delta H_{prot}^{0,E} = -6.0 \pm 0.4\ \mathrm{kJmol^{-1}}$$

on USY zeolite

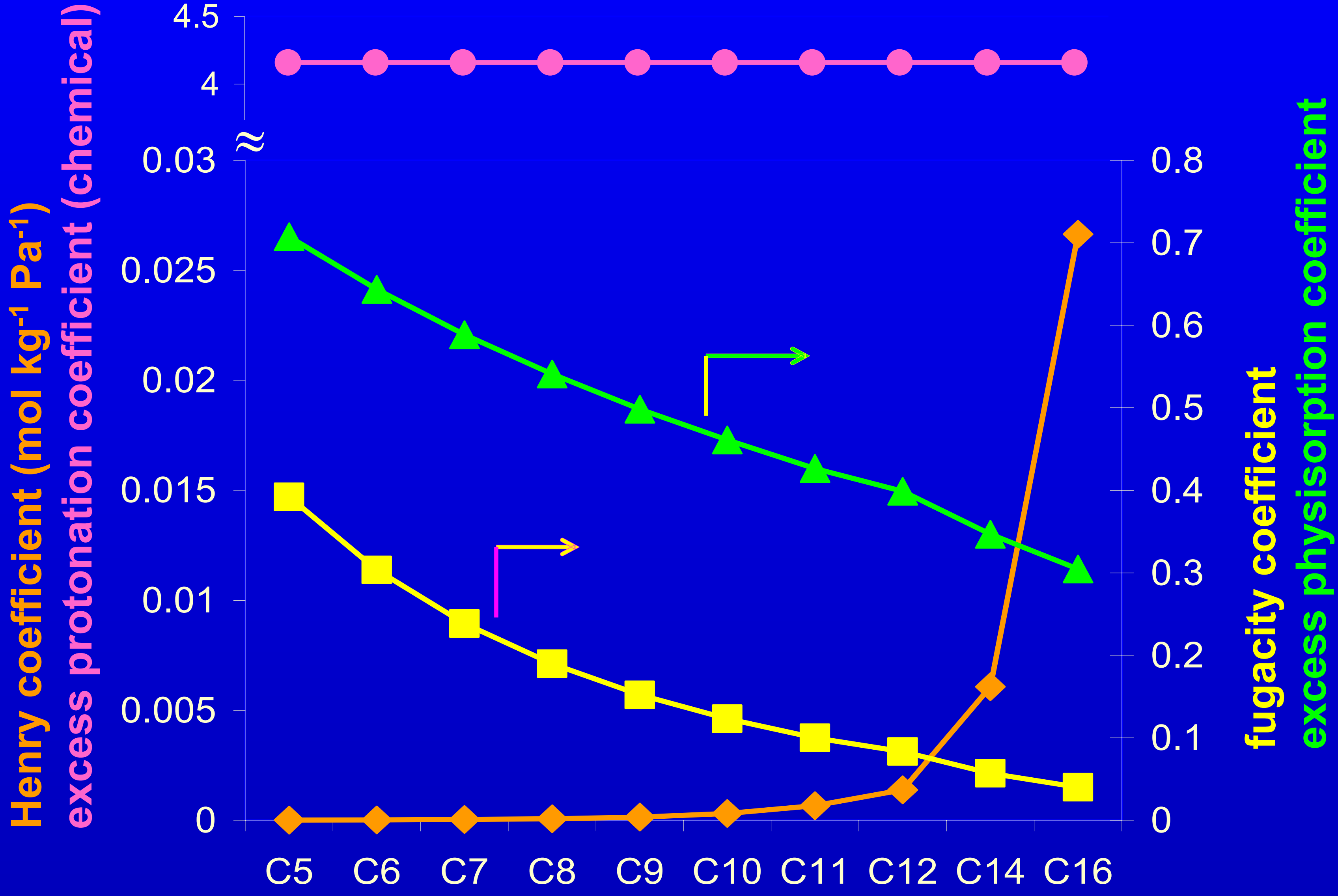
➔ increased stability of carbenium ions

liquid phase model adequacy for hydroconversion on USY

C9-C14 mixture hydroconversion



Excess protonation coefficient (chemical) $K^{E}_{chem,i}$



Temperature: 506K and Pressure: 8MPa

Vapour phase versus liquid phase hydroconversion rates: limit cases

- carbenium ion concentration can be neglected
- liquid phase: saturation
- vapour phase: Henry regime

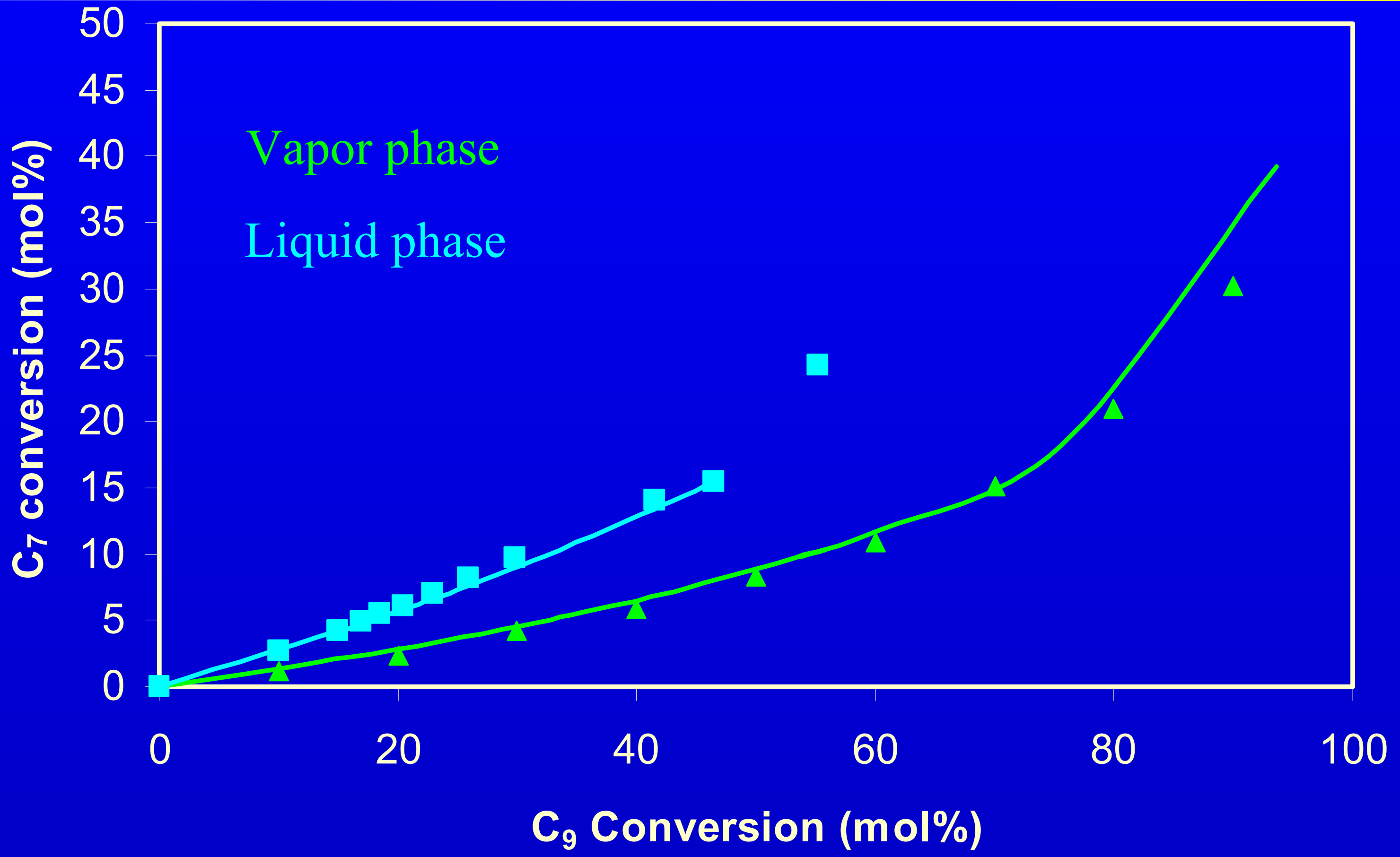
$$r_{liquid/vapour} = \frac{K^{E}_{chem}}{K_L p_P \phi_{H_2}}$$

- vapour phase: saturation

$$r_{liquid/vapour} = \frac{K^{E}_{chem}}{\phi_{H_2}}$$

liquid phase: enhanced competition in binary mixtures

503 K



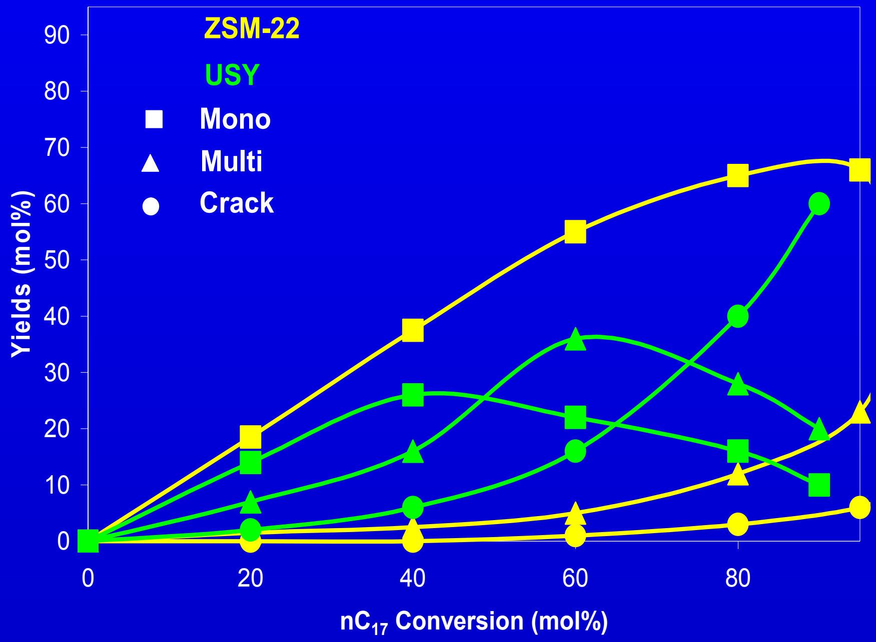
$\frac{r^{o}_{nC\ 7}}{r^{o}_{nC\ 9}}$	Experimental	Model
Vapor phase	0.12	0.10
Liquid phase	0.37	0.25

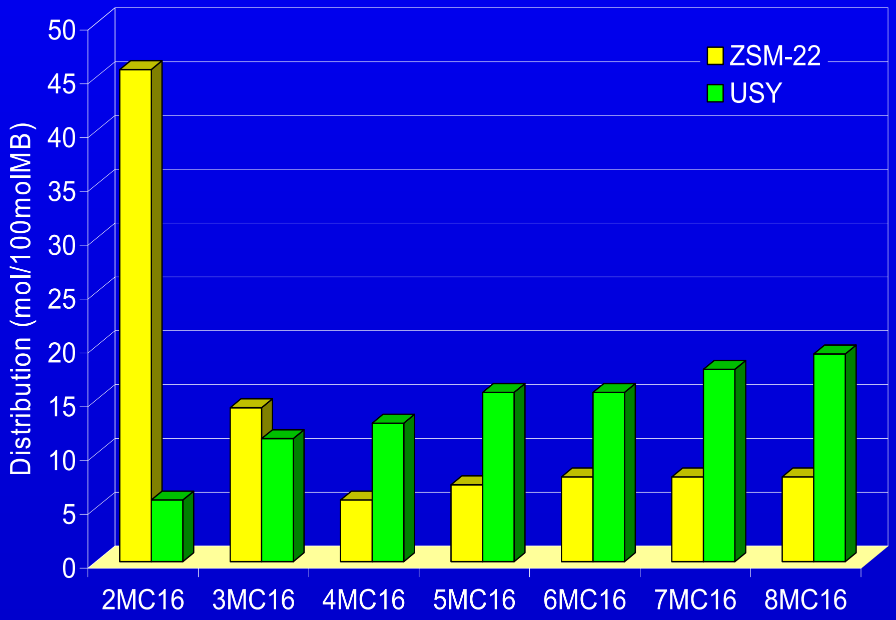
Ratio of reaction rates in mixtures: vapour versus liquid phase

$$r_{C_7/C_9}^{vapour} = \frac{k_{C_7}^{relump} H_{C_7} p_{C_7}}{k_{C_9}^{relump} H_{C_9} p_{C_9}}$$

$$r_{C_7/C_9}^{liquid} = \frac{k_{C_7}^{relump} H_{C_7} K_{L,C_7}^{E} \phi_{C_7} p_{C_7}}{k_{C_9}^{relump} H_{C_9} K_{L,C_9}^{E} \phi_{C_9} p_{C_9}} \overset{USY}{\approx} \frac{k_{C_7}^{relump} p_{C_7}}{k_{C_9}^{relump} p_{C_9}}$$

Shape selective hydroconversion: pore mouth and key lock catalysis





(Martens et al. Angew. Chem. Int. Ed. Engl. 34(22) 2528 1995)

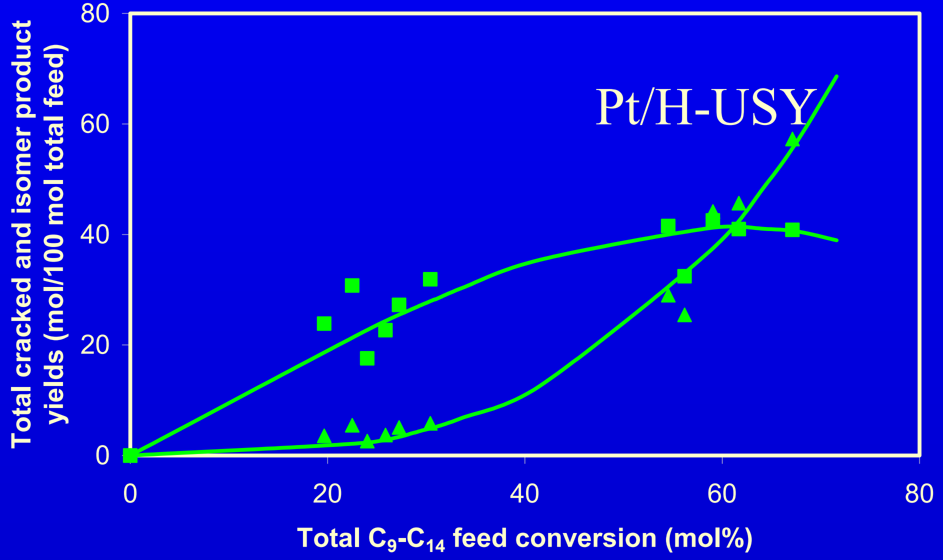
nC_{17} hydroconversion on Pt-H/USY & Pt-H/ZSM-22 at T=430-490K, P=1.5 bar, W/Fo=13000 kgsmol^{-1}

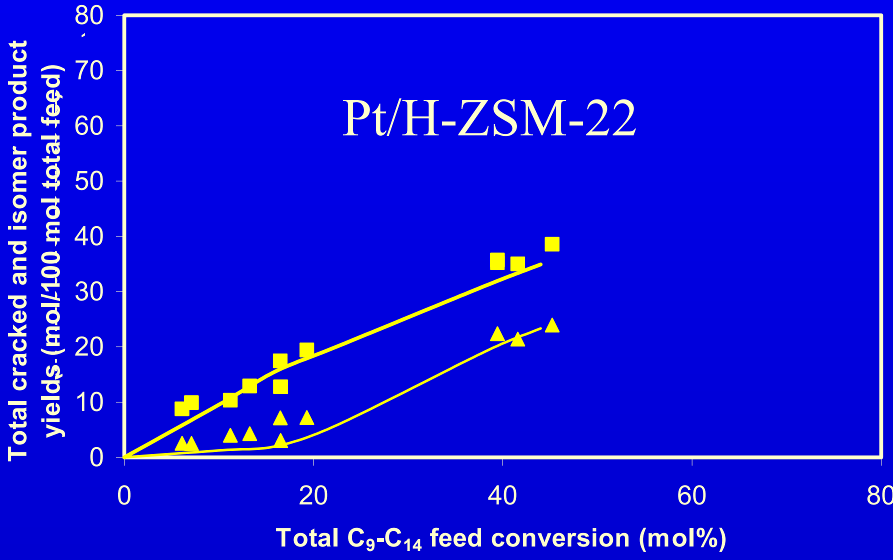
Vapour phase

liquid phase: shape selectivity of ZSM22 less pronounced

squares: isomerization
triangles: cracking

C9-C14 mixture hydroconversion

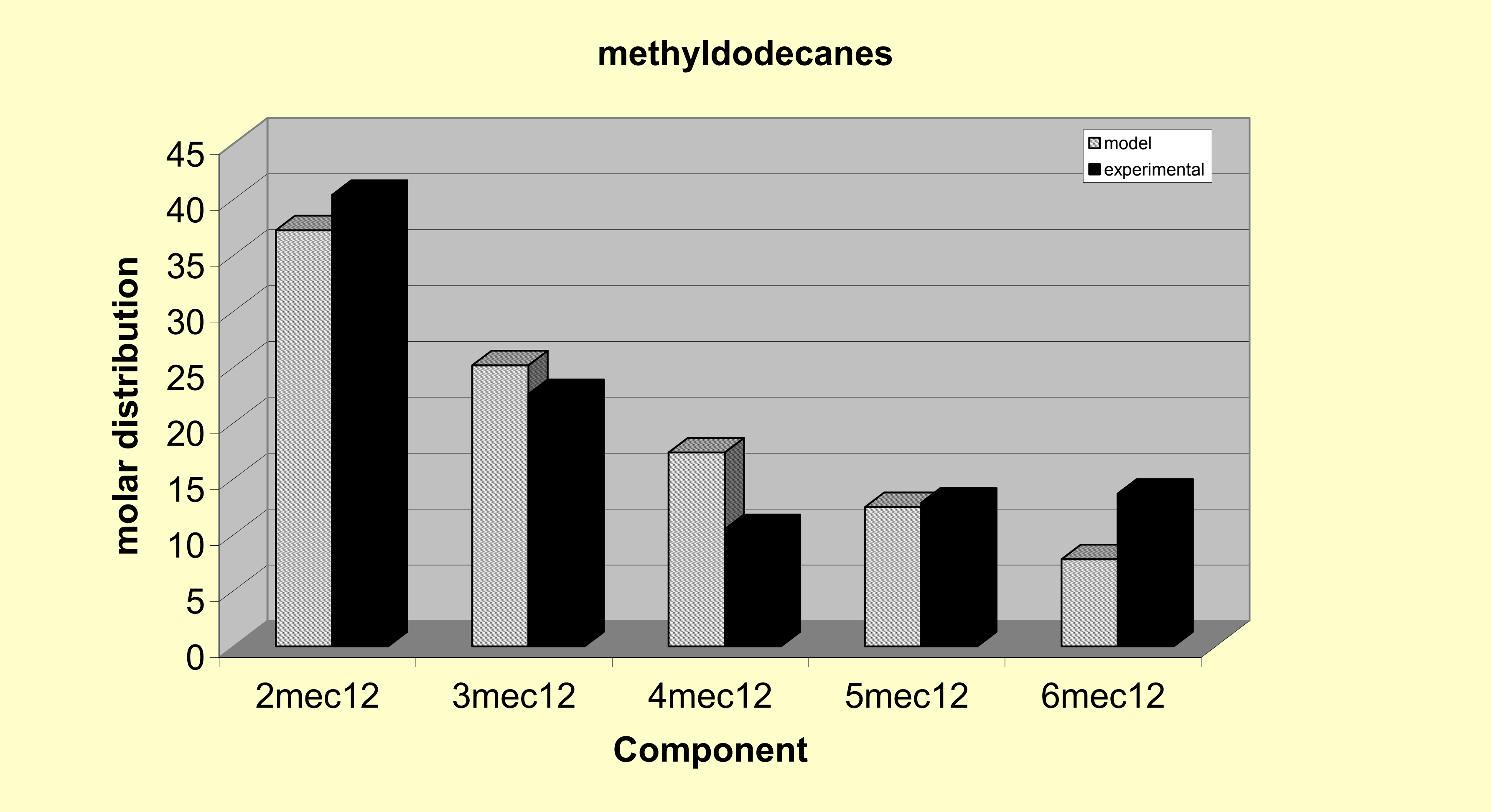




Enhanced competition between cracked products and feed molecules ➔
Enhanced secondary cracking in liquid phase, in particular for ZSM-22

Shape selectivity only for position Me branches

monobranched isomer distribution in liquid phase hydroconversion on ZSM-22



- Introduction / Scope
- Physisorption
- Families of elementary reactions
- Kinetic parameters
- Acidity
- From vapour to liquid
- Conclusions

Conclusions

- intrinsic kinetics / elementary reaction families
- kinetic parameters
  - limited number
  - independent expts (e.g. physisorption)
  - catalyst properties
- extrapolation from vapour to liquid
  - fugacity
  - single excess parameter c^E for physisorption
  - excess stabilisation of carbenium ions

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