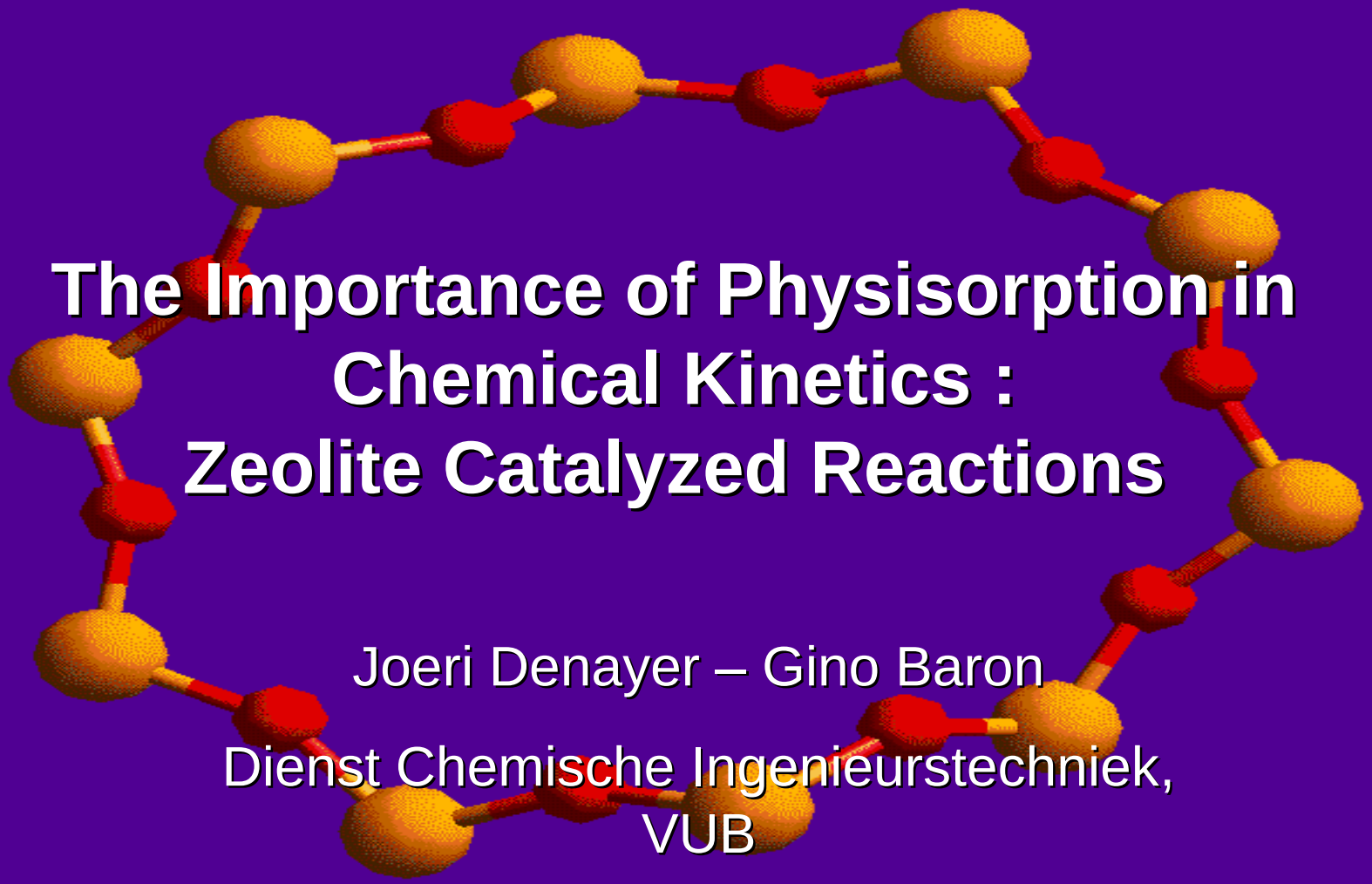
The Importance of Physisorption in Chemical Kinetics : Zeolite Catalyzed Reactions



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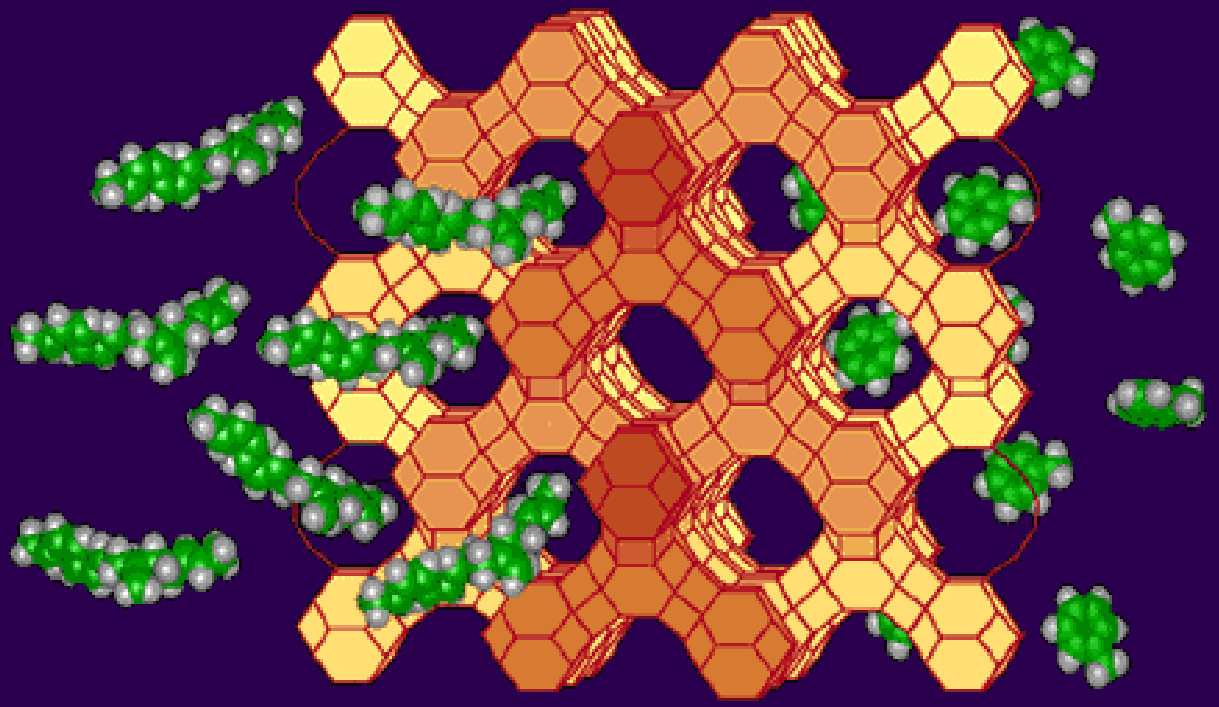
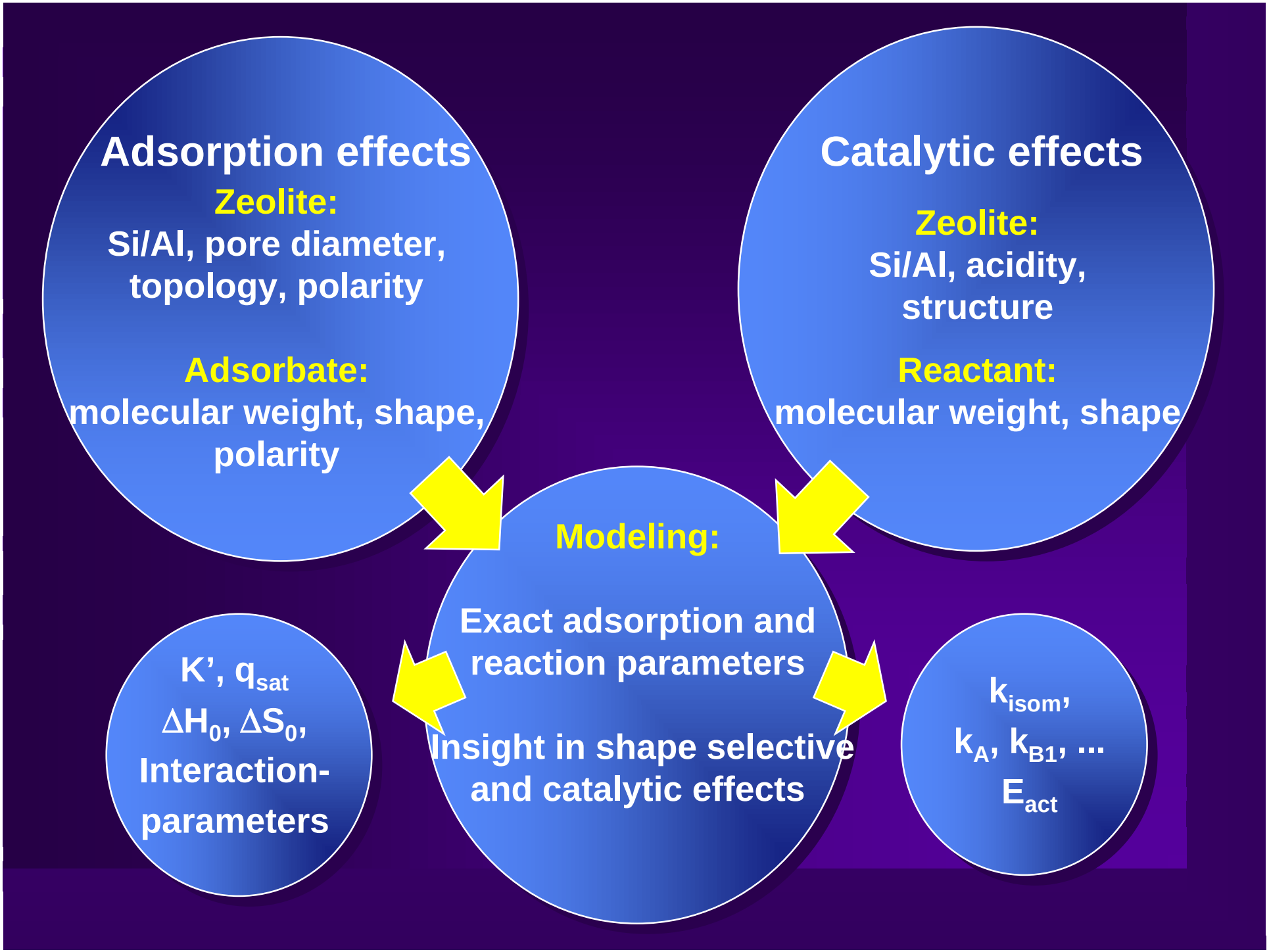
VUB

Zeolite Catalysis: Diffusion, Adsorption, Reaction



Interference of several adsorption and reaction phenomena


Adsorption effects
Zeolite:
Si/Al, pore diameter, topology, polarity
Adsorbate:
molecular weight, shape, polarity
Catalytic effects
Zeolite:
Si/Al, acidity, structure
Reactant:
molecular weight, shape
Modeling:
Exact adsorption and reaction parameters
Insight in shape selective and catalytic effects
K', q_{sat}
ΔH_0, ΔS_0,
Interaction-parameters
k_{isom},
k_A, k_{B1}, ...
E_{act}

Overview

- ✓ Adsorption
  - Low zeolite coverage
  - Intermediate coverage
  - Complete coverage
- ✓ Reaction
  - Hydrocracking of alkanes on Y zeolites
    - Vapor phase
    - Liquid phase

Adsorption

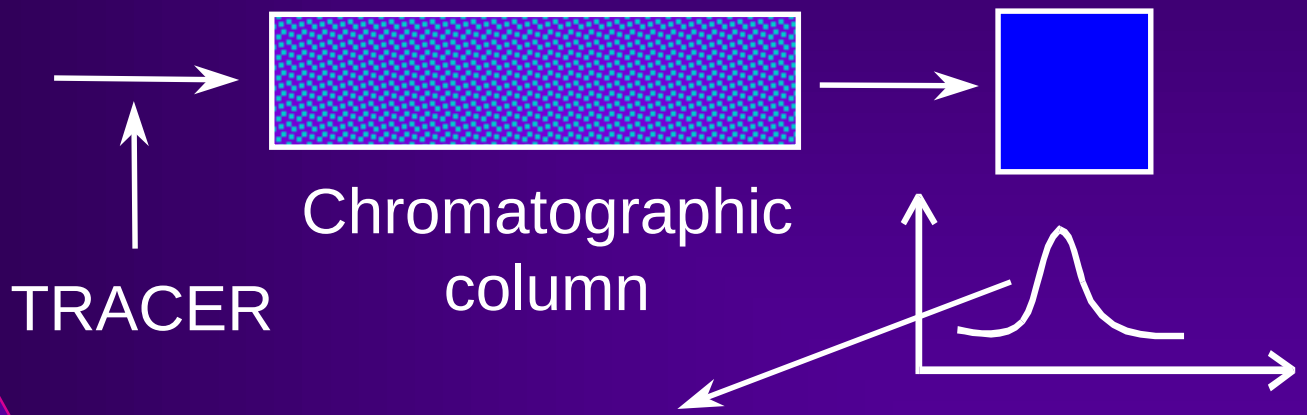
- Chromatographic techniques
- C5 - C12 linear and branched alkanes, alkenes, ...
- 20 - 400 °C
- Gas, vapor and liquid phase
- Series of zeolites

⇒ rational relationships between system parameters and adsorption properties ???

Gas and liquid chromatography

MOBILE PHASE
- inert gas
- inert gas + component
- mixture
- liquid

DETECTOR: TCD, MS, Refractometer



TRACER

Chromatographic column

K', q_{sat} ΔH_0, ΔS_0, Interaction-parameters

$$\mu_i = \frac{L}{v_f}\left[\varepsilon + \varepsilon(1-x)\frac{\partial q_1}{\partial p_i}\right]$$

Methods of moments: adsorption constants

$$v_f\, p \frac{\partial x_i}{\partial z} + \left(\varepsilon_{ext} + \varepsilon_{macr}\right) p \frac{\partial x_i}{\partial t} + \left(1 - \varepsilon_{ext} - \varepsilon_{macr}\right)\left(\frac{\partial q_i}{\partial t}\right) = 0 \qquad i = 1\ldots 3 \qquad \varphi_i = \frac{K'_i\, px_i}{1 + L_1 px_1 + L_2 px_2}$$

- **component 1 in inert carrier**

$$\mu = \frac{L}{v_f}\left[\left(\varepsilon_{ext} + \varepsilon_{macr}\right) + \left(1 - \varepsilon_{ext} - \varepsilon_{macr}\right)\left(K'_1\, \rho_{crys} RT\right)\right]$$

- **component 2 in adsorbing carrier 2**

$$\mu_2 = \frac{L}{v_f}\left[\left(\varepsilon_{ext} + \varepsilon_{macr}\right) + \left(1 - \varepsilon_{ext} - \varepsilon_{macr}\right)\left(\frac{K'_2\, \rho_{crys} RT}{\left(1 + L_2 px_2\right)^2}\right)\right]$$

- **component 1 in adsorbing carrier 2**

$$\mu_1 = \frac{L}{v_f}\left[\left(\varepsilon_{ext} + \varepsilon_{macr}\right) + \left(1 - \varepsilon_{ext} - \varepsilon_{macr}\right)\left(\frac{K'_1\, \rho_{crys} RT}{1 + L_2 px_2}\right)\right]$$

Mass transfer

Method of moments

$$\frac{\sigma^2}{2\mu^2} = \frac{L}{v_f}\frac{\left(1-\varepsilon_{ext}-\varepsilon_{macr}\right)\left(RT\rho_c K_i'\right)}{\mu^2}\left(\frac{r_c^2}{15D_{micr}} + \frac{R_p^2\left(1+\left(RT\rho_c K_i'\right)\left(\frac{1-\varepsilon_p}{\varepsilon_p}\right)\right)}{15D_{macr}}\right) + \frac{D_{ax}\varepsilon_{ext}}{v_f L}$$

Fitting of breakthrough curves or pulse responses

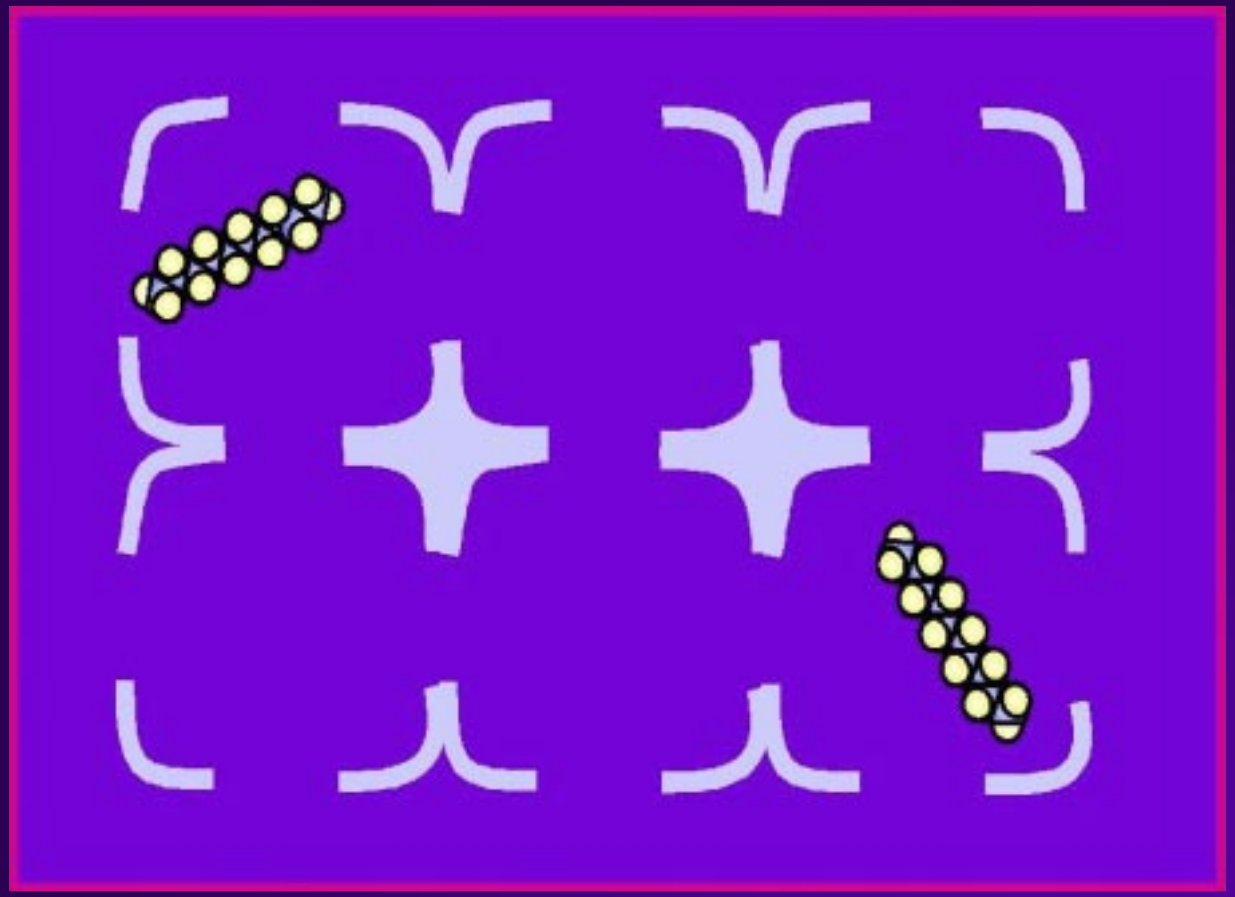
$$-D_{ax}p\frac{\partial^2 x_i}{\partial z^2} v_f p\frac{\partial x_i}{\partial z} + \left(\varepsilon_{ext}+\varepsilon_{macr}\right)p\frac{\partial x_i}{\partial t} + \left(1-\varepsilon_{ext}-\varepsilon_{macr}\right)\left(\frac{\partial q_i}{\partial t}\right) = 0$$

$$\frac{\partial q}{\partial t} = \frac{1}{R^2}\frac{\partial}{\partial R}\left(D_c R^2 \frac{\partial q}{\partial R}\right) \qquad \bar{q} = \frac{3}{R_c^3}\int_0^R qR^2 dR$$

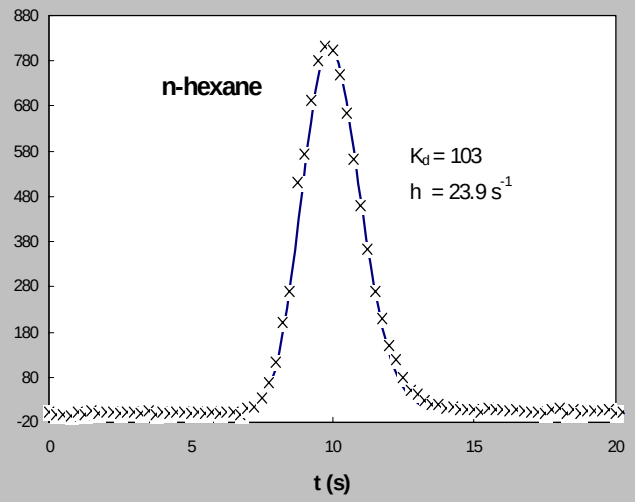
Chromatography: merits

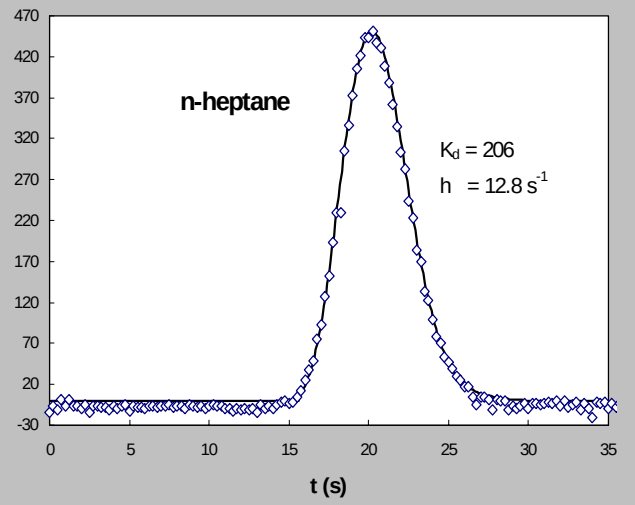
- Rapid measurement
- Broad range of components
- Broad range of operating conditions
- Simultaneous determination adsorption & diffusion

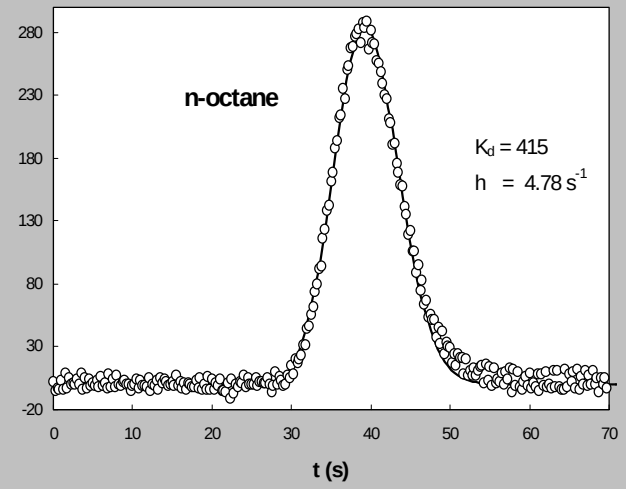
Adsorption at low coverage

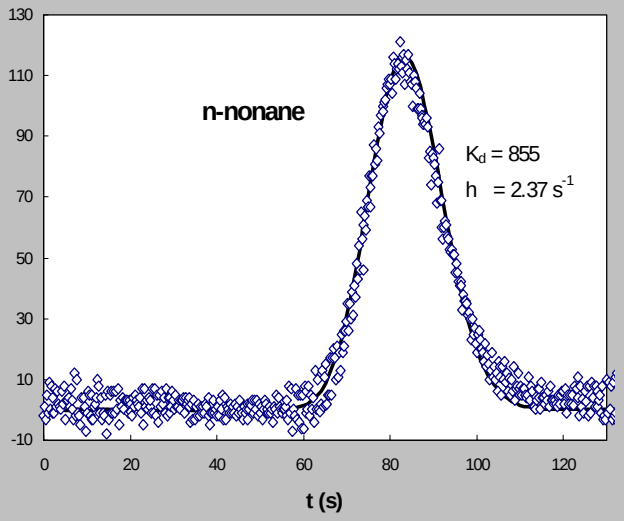


No interactions between adsorbed molecules


n-hexane
K_d = 103
h = 23.9 s^{-1}
t (s)


n-heptane
K_d = 206
h = 12.8 s^{-1}
t (s)


n-octane
K_d = 415
h = 4.78 s^{-1}
t (s)


n-nonane
K_d = 855
h = 2.37 s^{-1}
t (s)

Gas phase diffusion

Macropore diffusion model:

$$D_{macr} \cong \frac{D_{mol} \cdot \varepsilon}{\tau}$$

pellet porosity = 0.3

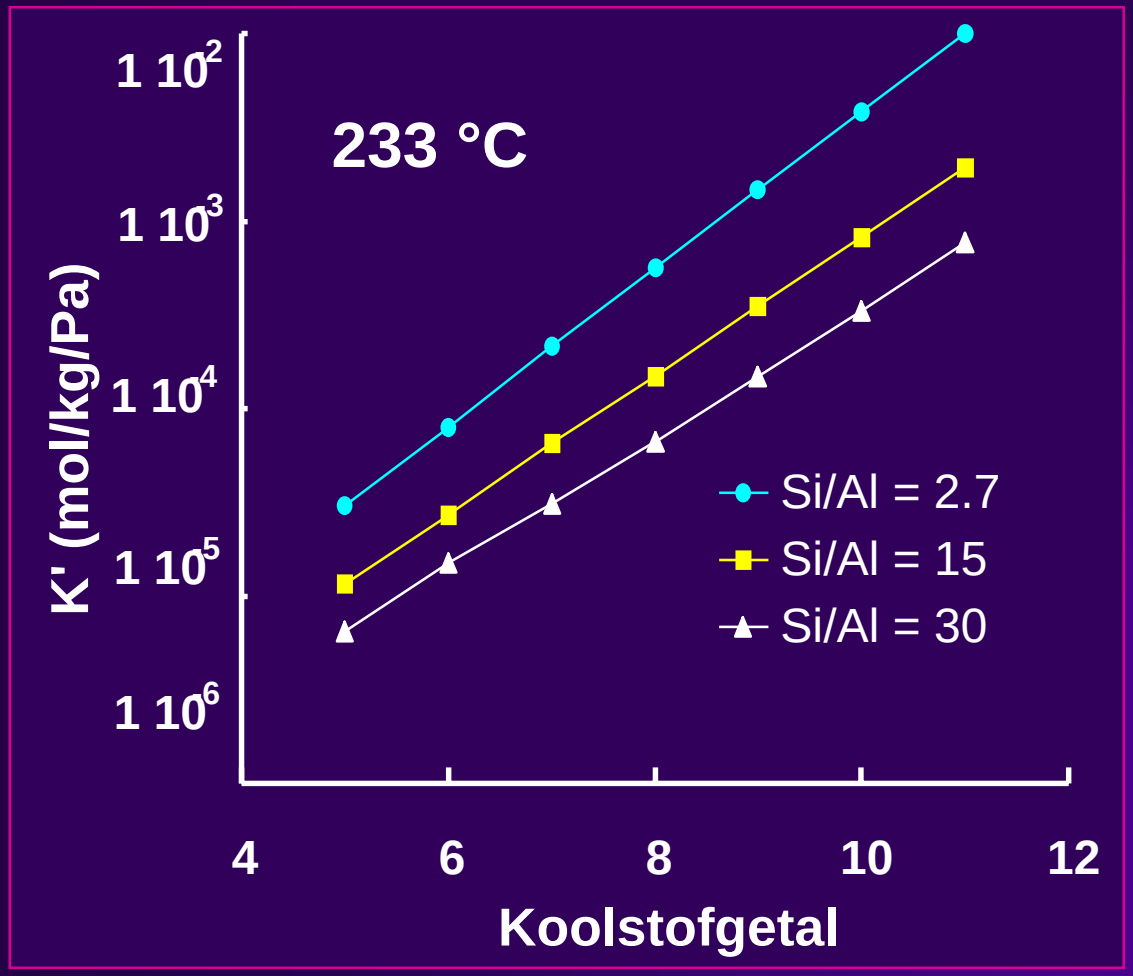
tortuosity factor = 3

$\Rightarrow D_{macr} = D_{mol}/10$

sorbate	D_{mol} (m^2/s)	D_{macr} (m^2/s)
n-hexane	$5.1\ 10^{-5}$	$3.8\ 10^{-6}$
n-heptane	$4.7\ 10^{-5}$	$4.8\ 10^{-6}$
n-octane	$4.4\ 10^{-5}$	$4.8\ 10^{-6}$
n-nonane	$4.1\ 10^{-5}$	$6.4\ 10^{-6}$
n-decane	$3.8\ 10^{-5}$	$2.4\ 10^{-6}$
n-undecane	$3.6\ 10^{-5}$	$4.8\ 10^{-6}$
n-dodecane	$3.4\ 10^{-5}$	$6.2\ 10^{-6}$

⇨ **Mass transfer is dominated by macropore diffusion**

Influence Si/Al - Y zeolites

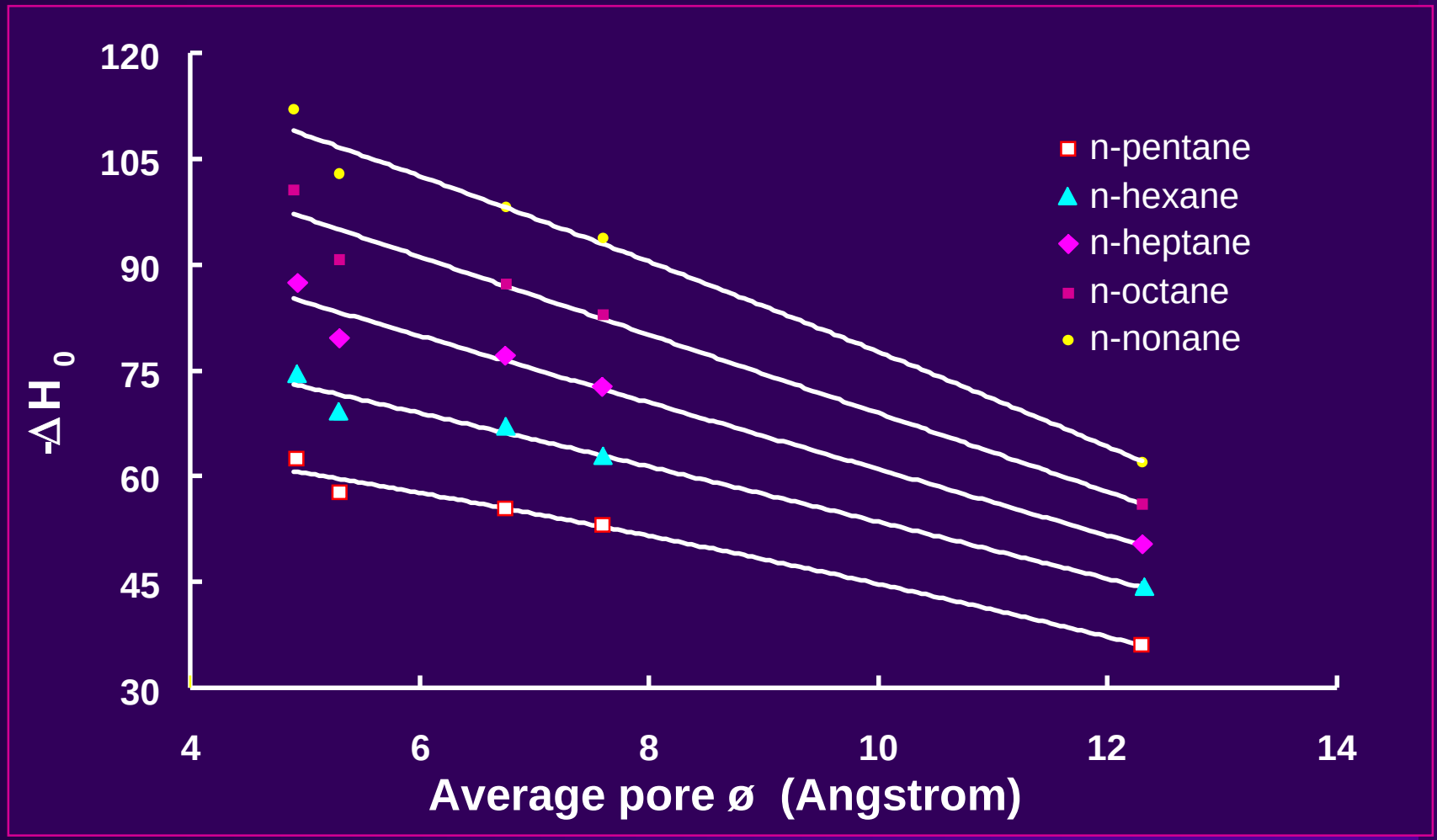


$K' = A.\exp(B.CN)$

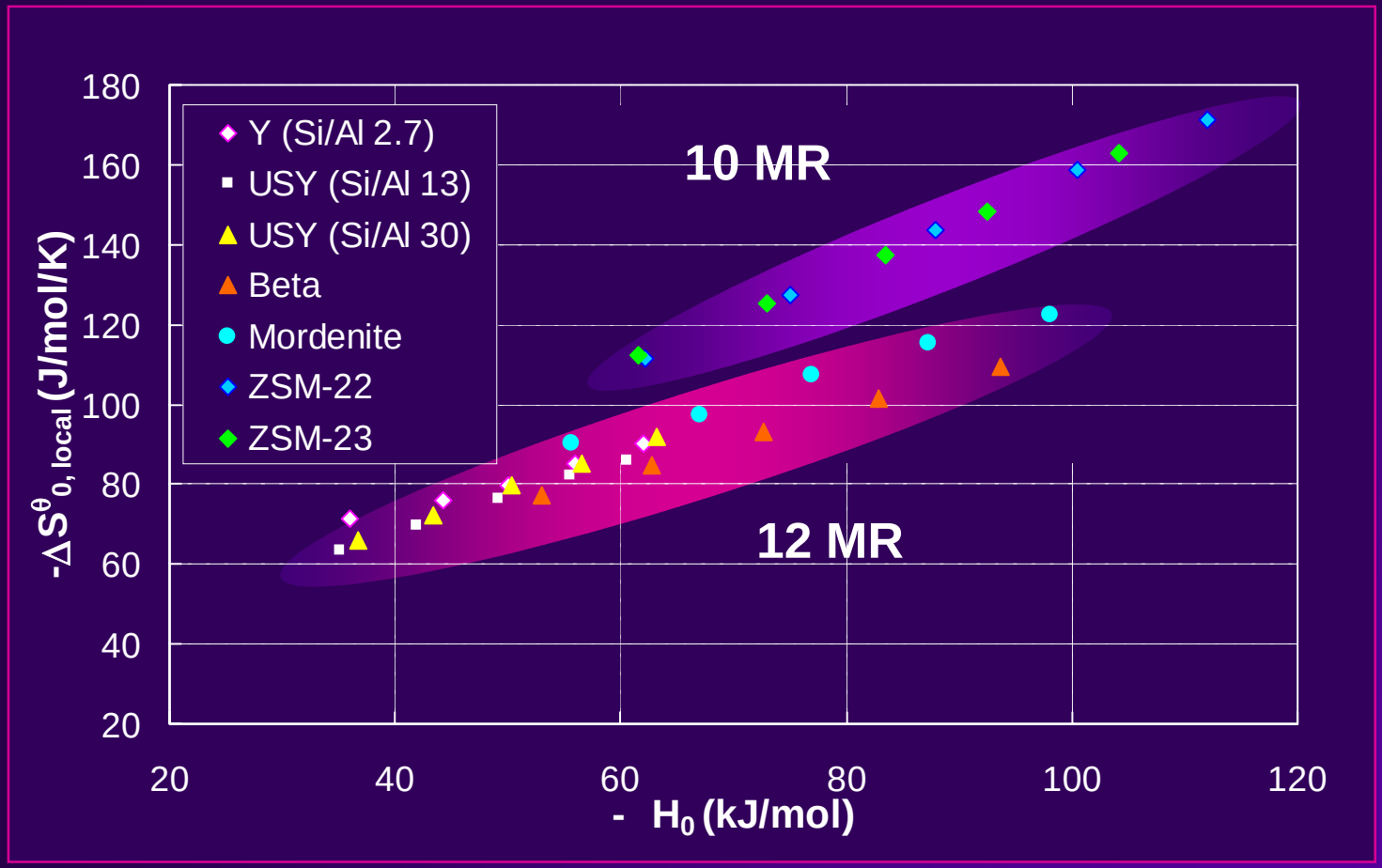
Si/Al	A	B
2.7	$2.41\ 10^{-7}$	0.97
15	$1.64\ 10^{-7}$	0.85
30	$1.25\ 10^{-7}$	0.79

⇨ Exponential factor B decreases with Al content

Influence pore diameter



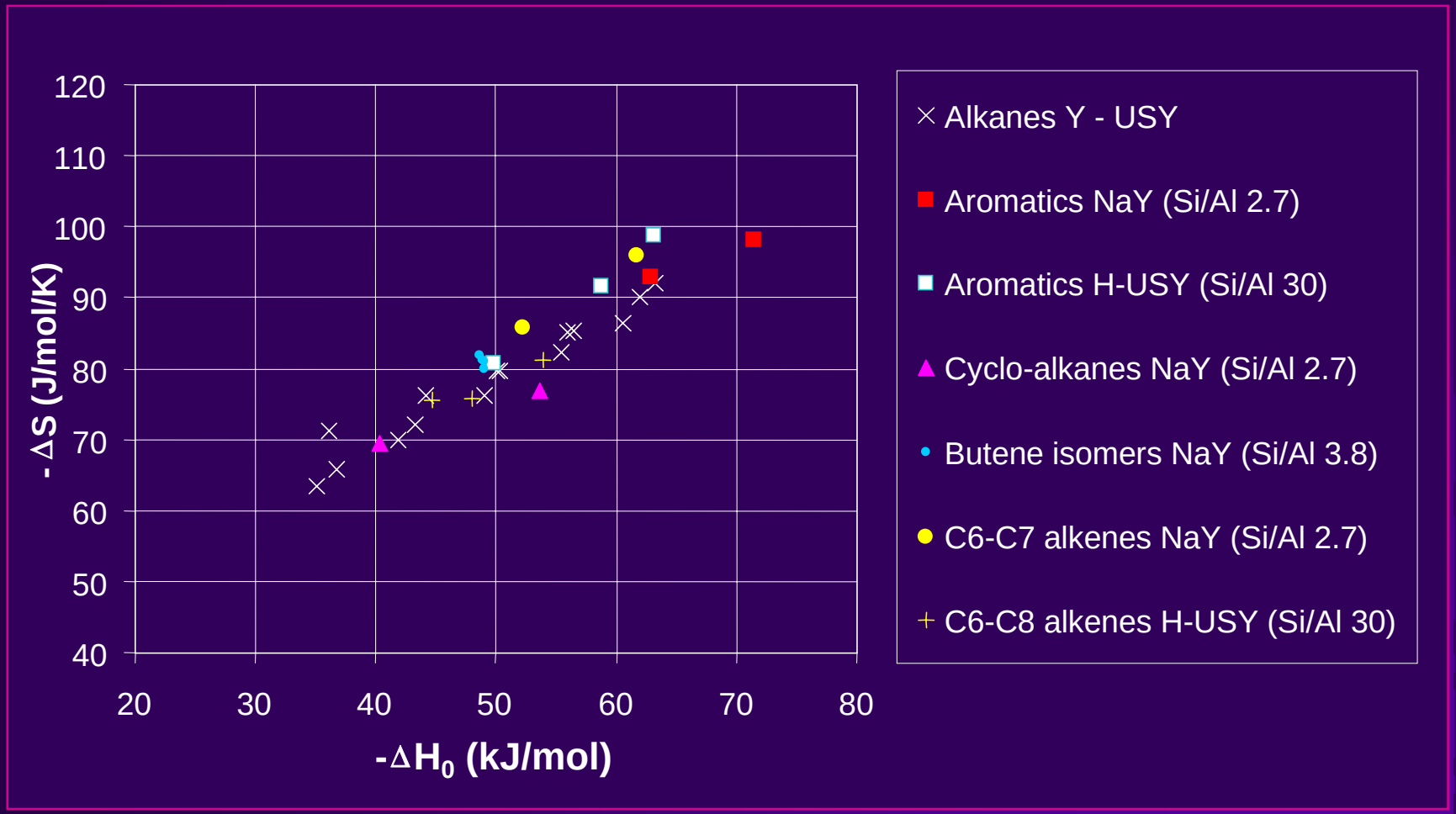
Compensation – effect : influence pore size



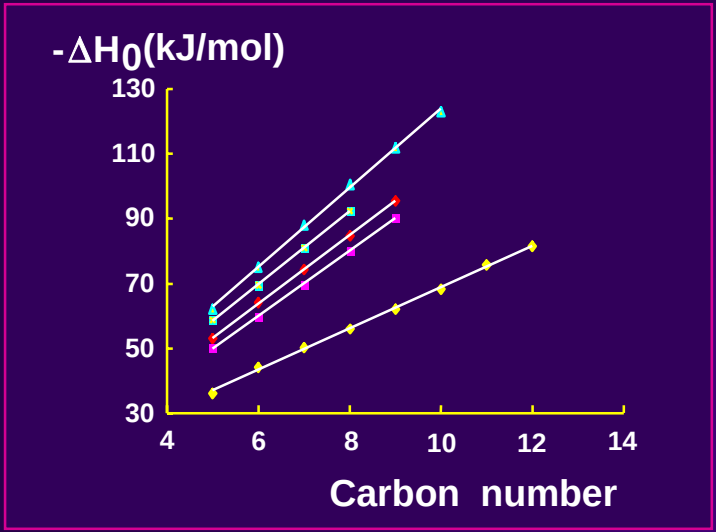
⇨ Compensation betweenn adsorption entropy and enthalpy

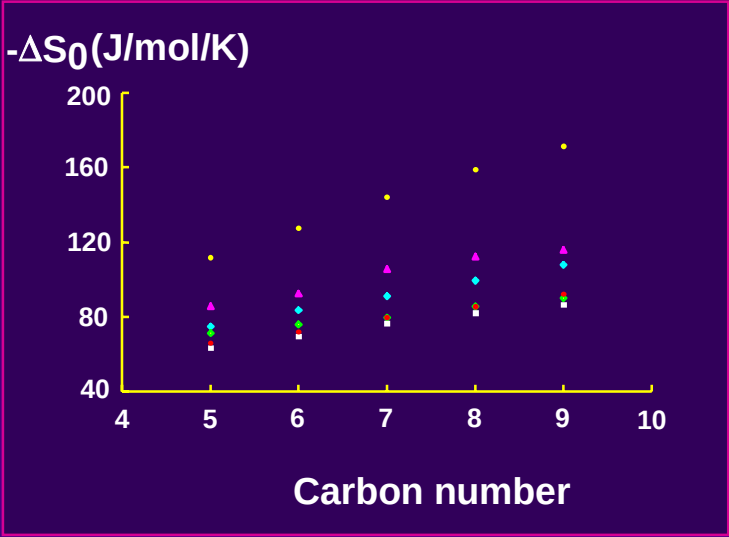
⇨ All 12 MR and 10 MR zeolites same characteristic curve

Compensation – effect : influence molecule type



General correlation for the Henry constants



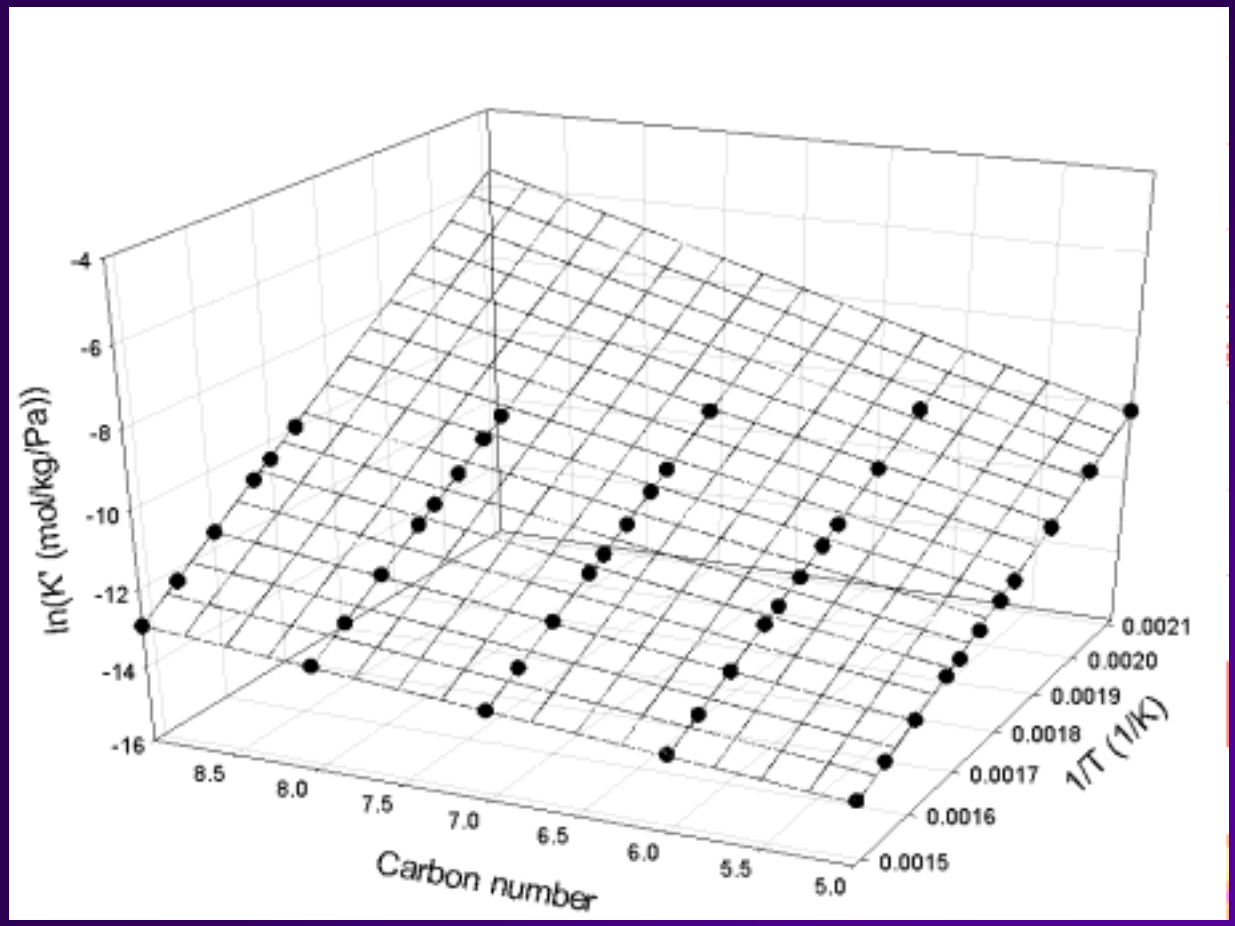


$$-\Delta H_0 = \alpha\, CN + \beta$$

$$-\Delta S^{\theta}_{0,\mathrm{local}} = \gamma\, \mathrm{CN} + \delta$$

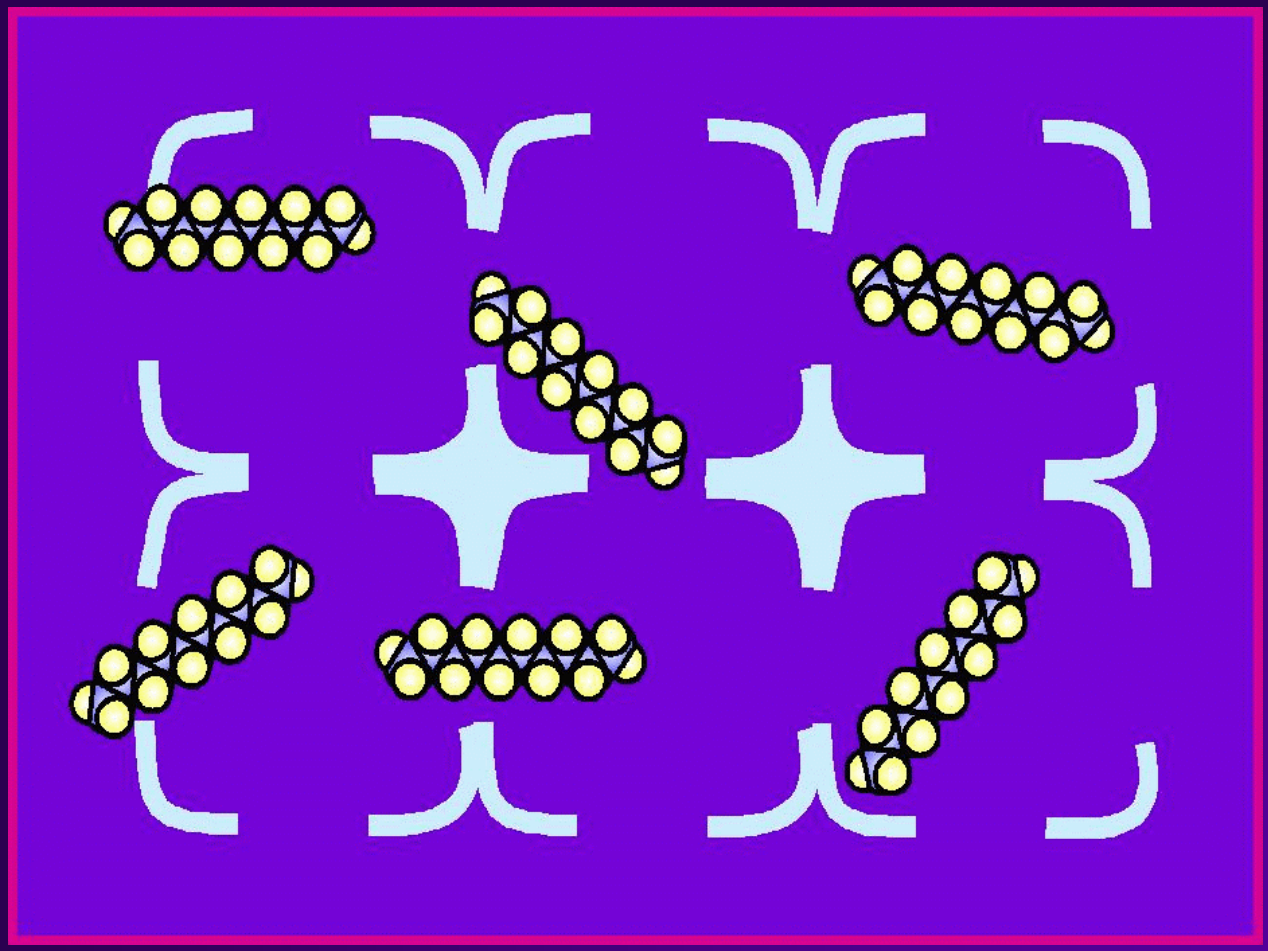
$$\ln K' = \left(\frac{\alpha}{RT} - \frac{\gamma}{R}\right)\mathrm{CN} + \left[\ln\left(\frac{n_T}{2p^{\theta}}\right) + \frac{\beta}{RT} - \frac{\delta}{R}\right]$$

3D fitting of experimental data



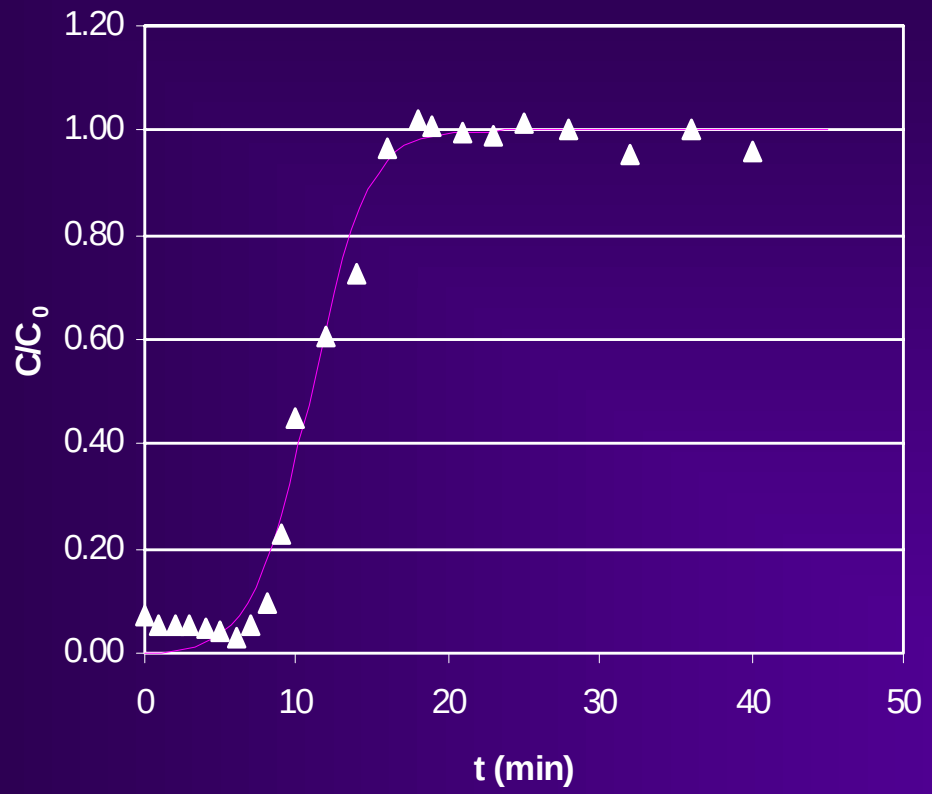
α = 11.0 kJ/mol	β = 1.3 kJ/mol
γ = 13.3 J/mol/K	δ = 14.8 J/mol/K

Adsorption at intermediate coverage



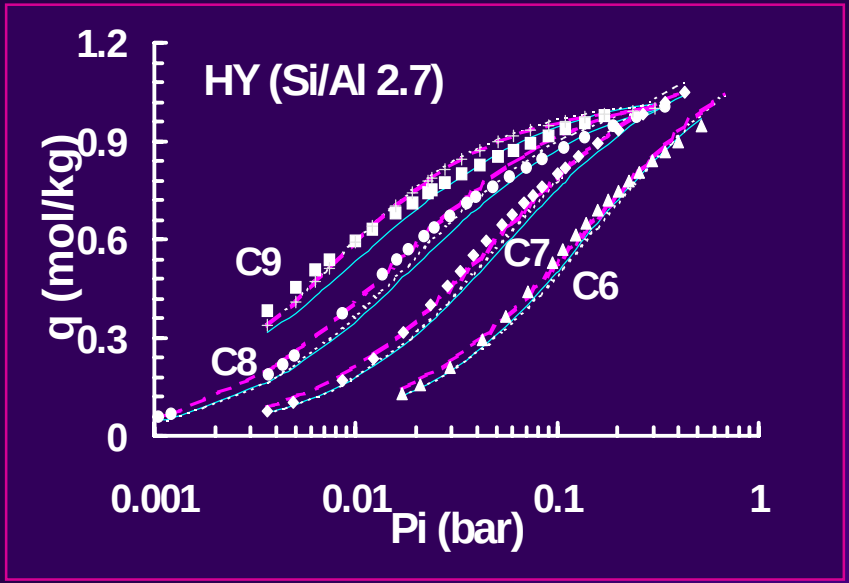
interaction between adsorbed molecules ?

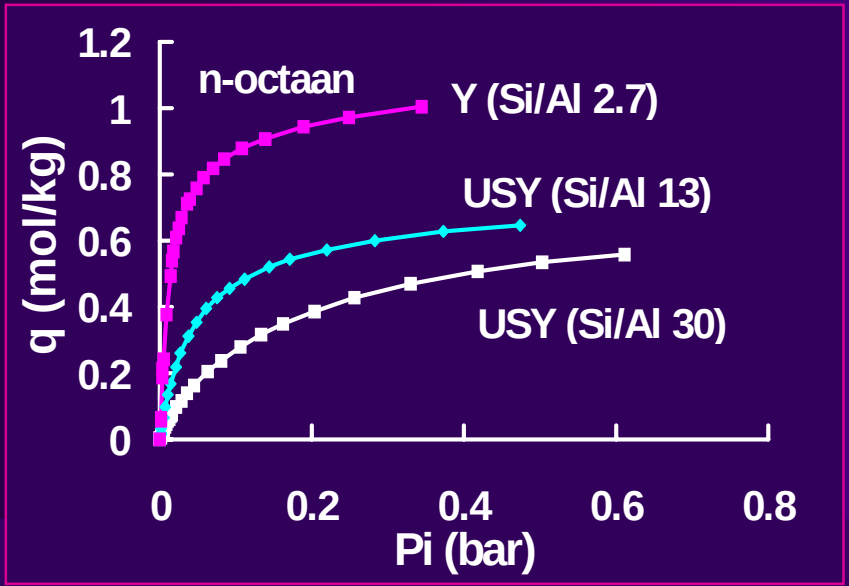
Breakthrough curves



$$-D_{ax}\rho\frac{\partial^2 x_i}{\partial z^2}v_f\rho\frac{\partial x_i}{\partial z}+\left(\varepsilon_{ext}+\varepsilon_{macr}\right)\rho\frac{\partial x_i}{\partial t}+\left(1-\varepsilon_{ext}-\varepsilon_{macr}\right)\left(\frac{\partial q_i}{\partial t}\right)=0 \qquad \frac{\partial \bar{q}}{\partial t}=k\left(q^*-q\right)=hK(c-c^*)$$

Isotherm fitting





- **Langmuir:**

$$q(p,T) = \frac{Kp}{1+Lp}$$

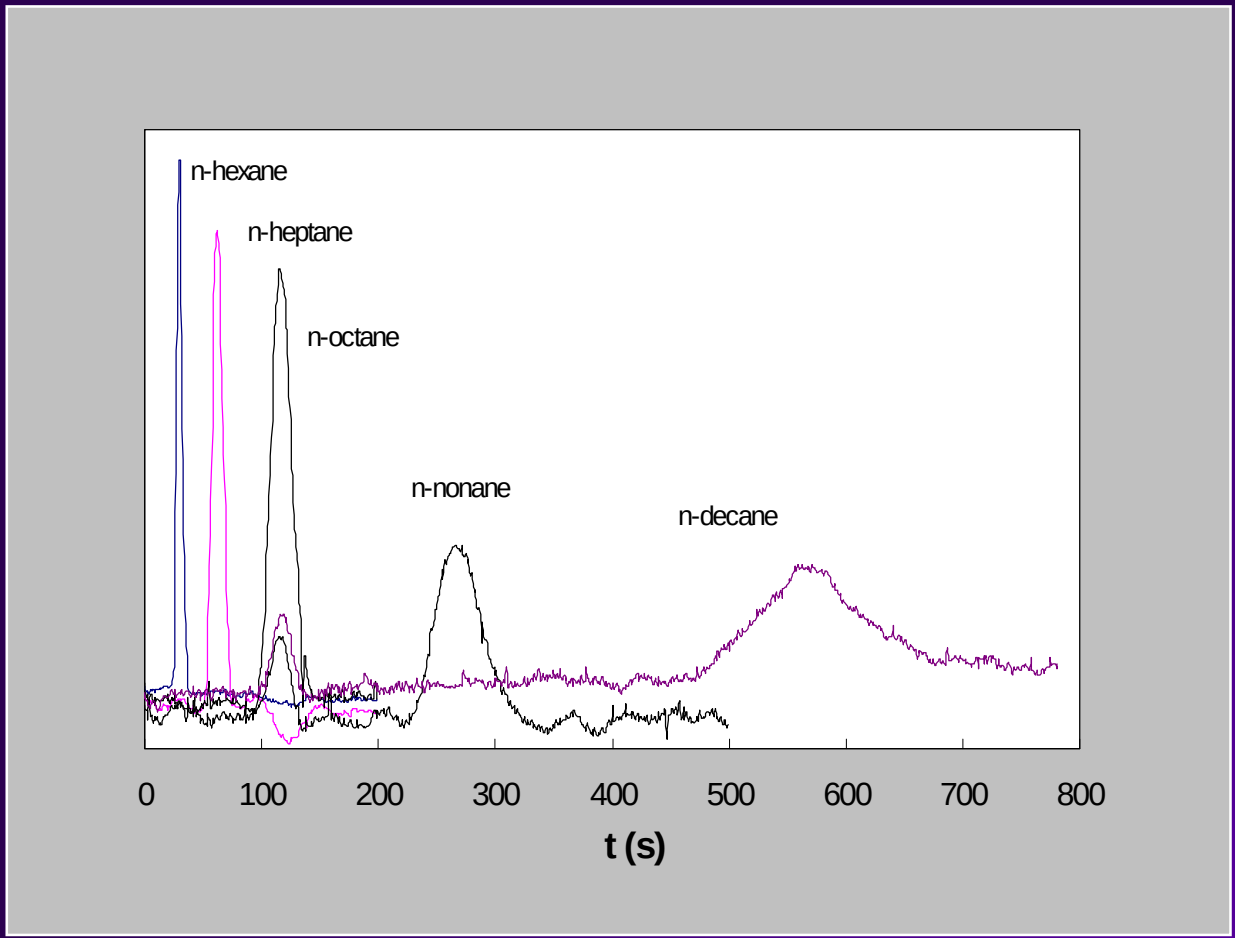
- **Langmuir-Freundlich:**

$$q(p,T) = \frac{Kp^B}{1+Lp^B}$$

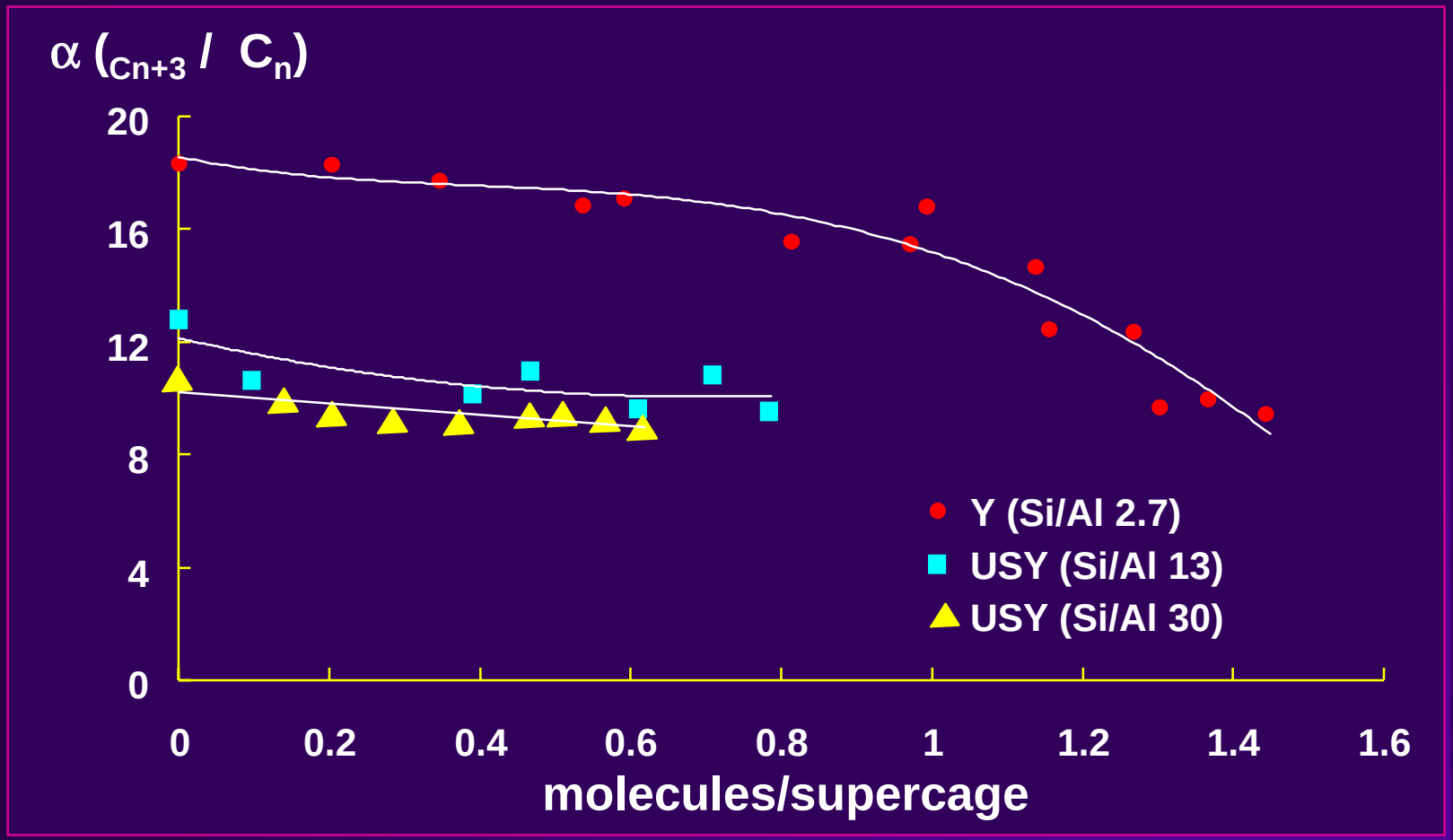
- **Langmuir + Interaction:**

$$q(p,T) = \frac{Kpe^{w\frac{q}{q_S}}}{1+Lpe^{w\frac{q}{q_S}}}$$

Perturbation chromatography

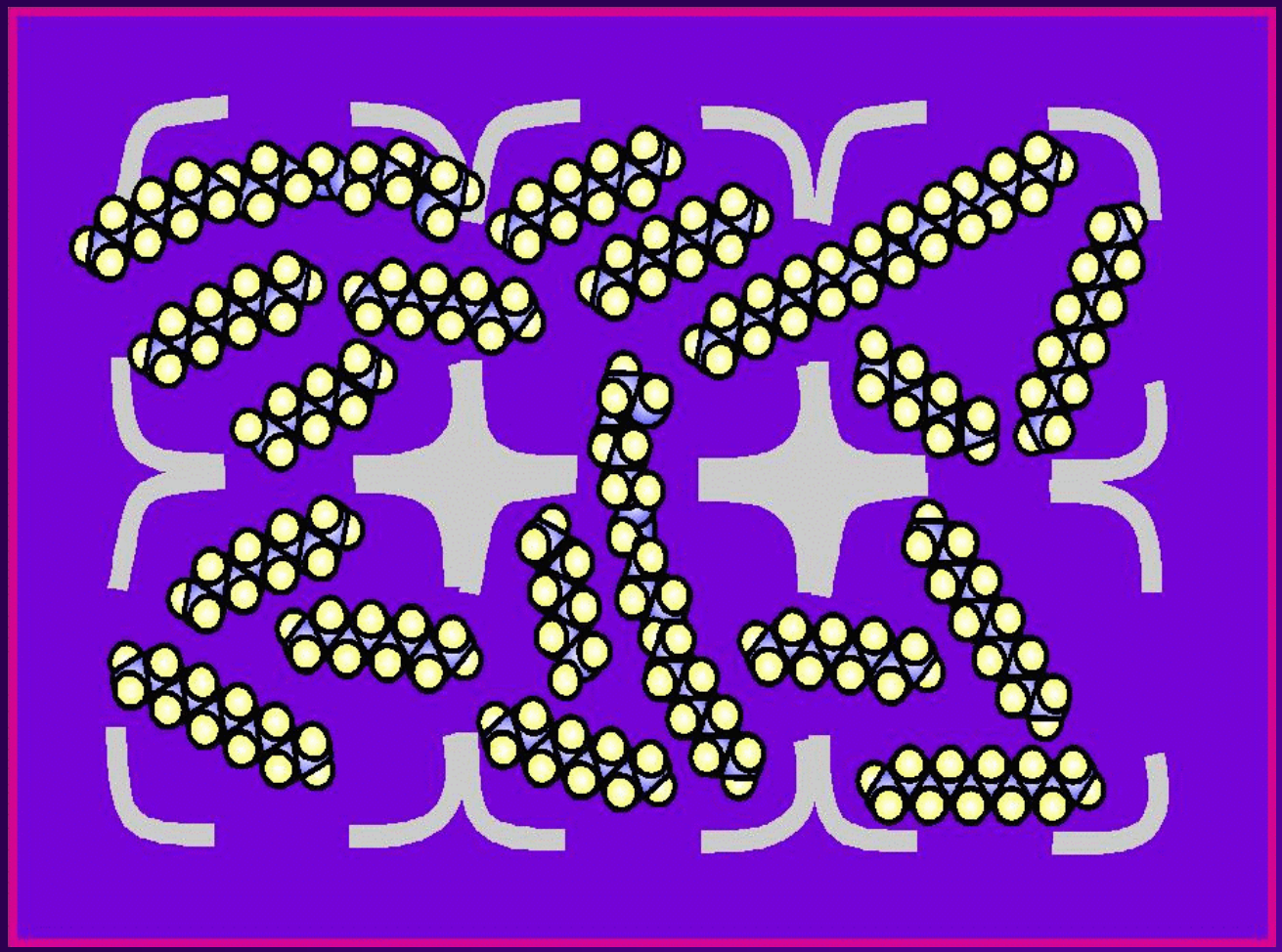


Influence zeolite loading on competition

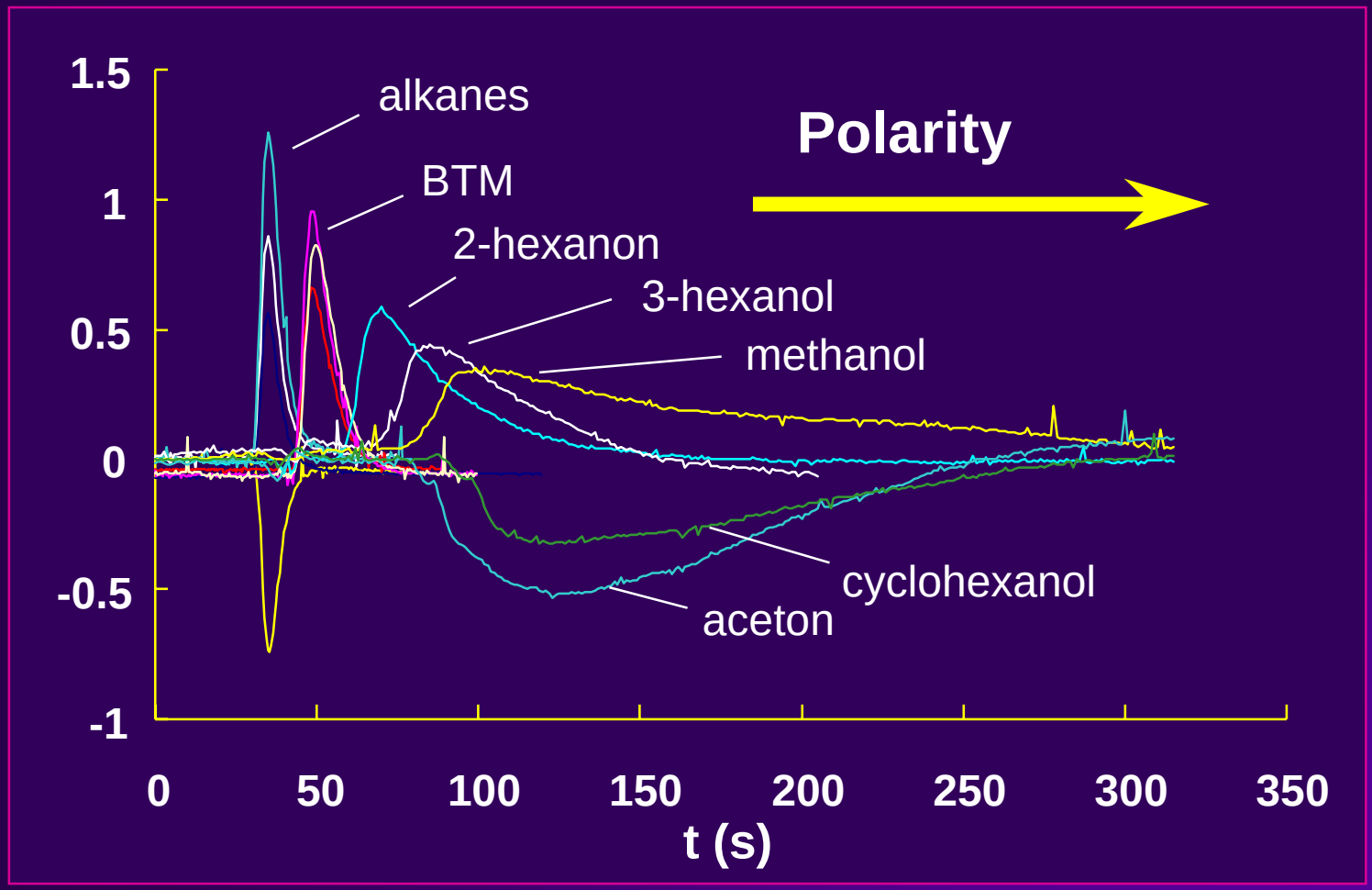


⇒ More than 1 molecule supercage: separation factor decreases strongly

Adsorption at complete pore filling

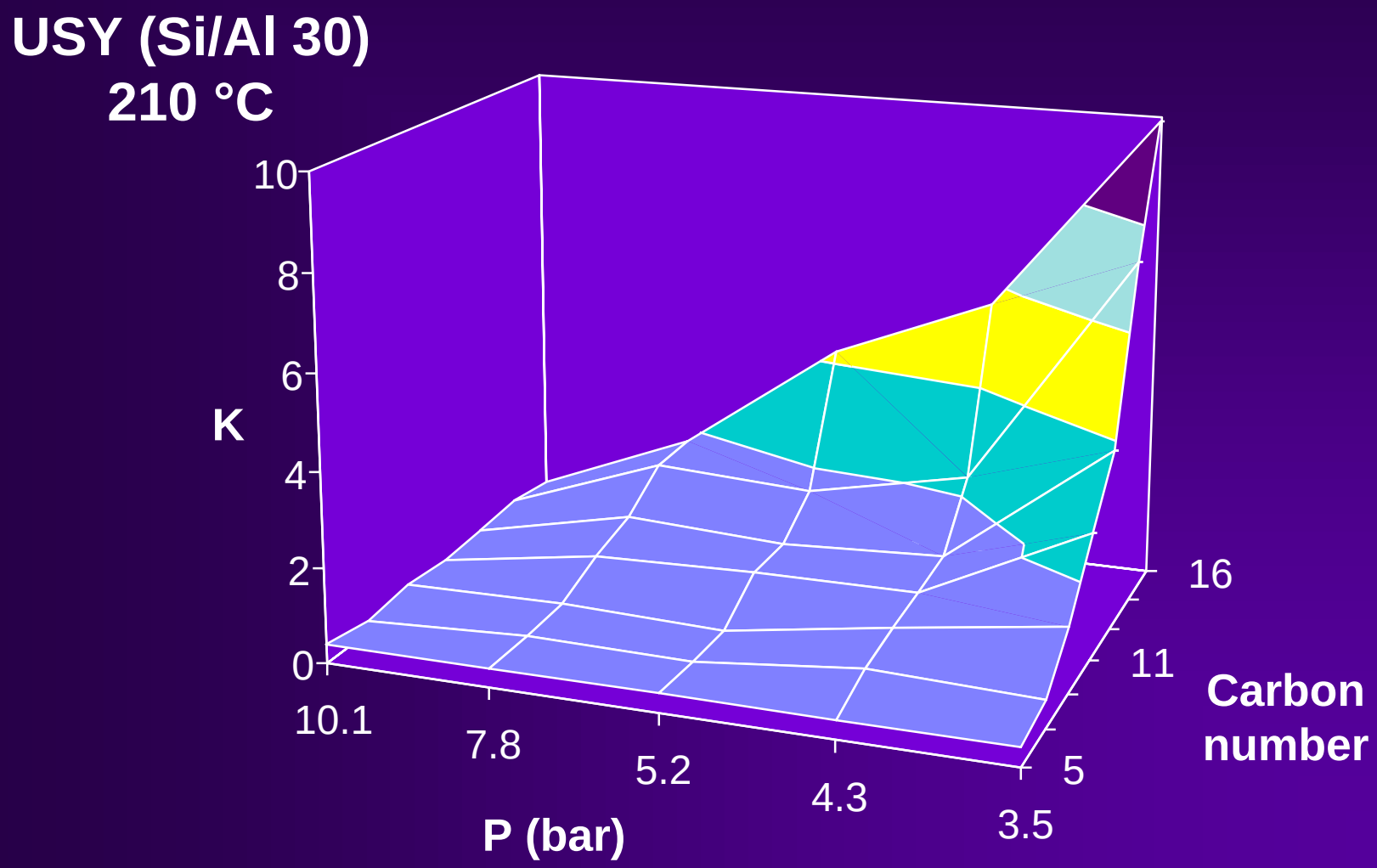


Zeolite Y (Si/Al 30), mobile phase octane



⇨ **no pronounced difference between short and long alkanes**

Influence fluidum density on competition



Liquid phase adsorption

Statistical isotherm

$$q_1 = \frac{\overline{N_1}}{M} = \frac{K'_1 p_1 + \sum_j \sum_i \frac{\left[(K'_1 p_1)^i (K'_2 p_2)^j (1 - i\beta_1 / v - j\beta_2 / v)^{i+j} \right]}{(i-1)!\, j!}}{1 + K'_1 p_1 + K'_2 p_2 + \sum_j \sum_i \frac{\left[(K'_1 p_1)^i (K'_2 p_2)^j (1 - i\beta_1 / v - j\beta_2 / v)^{i+j} \right]}{(i)!\, j!}}$$

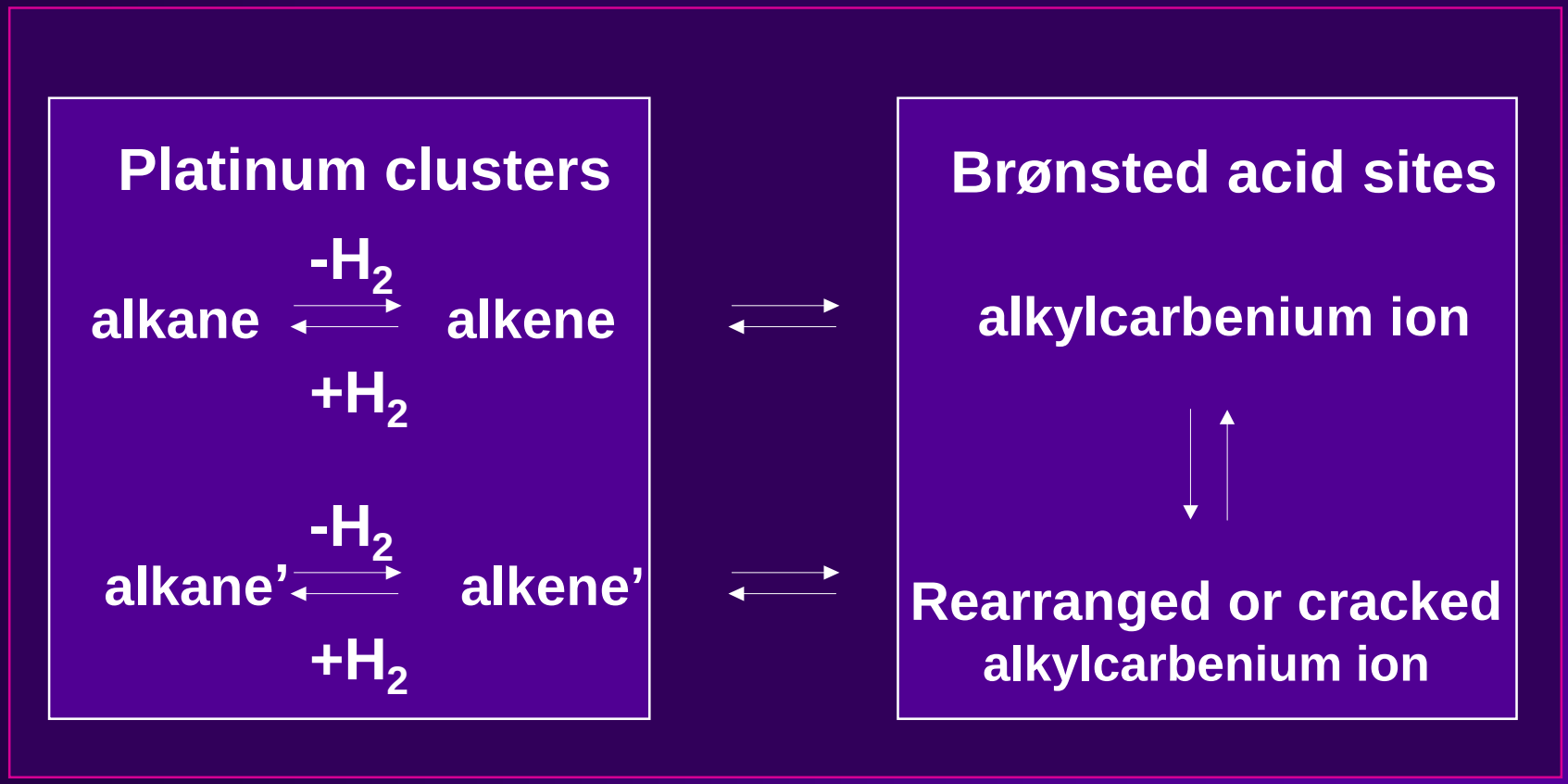
- Consider each supercage as independent system
- β_l : volume component i
- v: volume supercage

Partition coefficient model

$$q_i = K_i c_i$$

$$K_i = \overline{q}_s V_m$$

Catalysis



Decoupling adsorption and reaction properties

Rate equations

Adsorption

Vapor phase

$$q_i(p,T) = \frac{K'_i\, p_j e^{w_i \frac{q_T}{\bar{q}_s}}}{1 + \sum_j L_j p_j e^{w_j \frac{q_T}{\bar{q}_s}}}$$

$$-\Delta H_{0,i} = \alpha\, CN + \beta \qquad -\Delta S^{\theta}_{0,local} = \gamma\, CN + \delta$$

$$\ln(K_i') = \frac{-\Delta H_i}{RT_m} + \left[\frac{\Delta S^{\theta}_{0,local,i}}{R} + \ln\left(\frac{n_T}{2p^{\theta}} \right) \right]$$

Liquid phase

$$q_i = K_i c_i$$

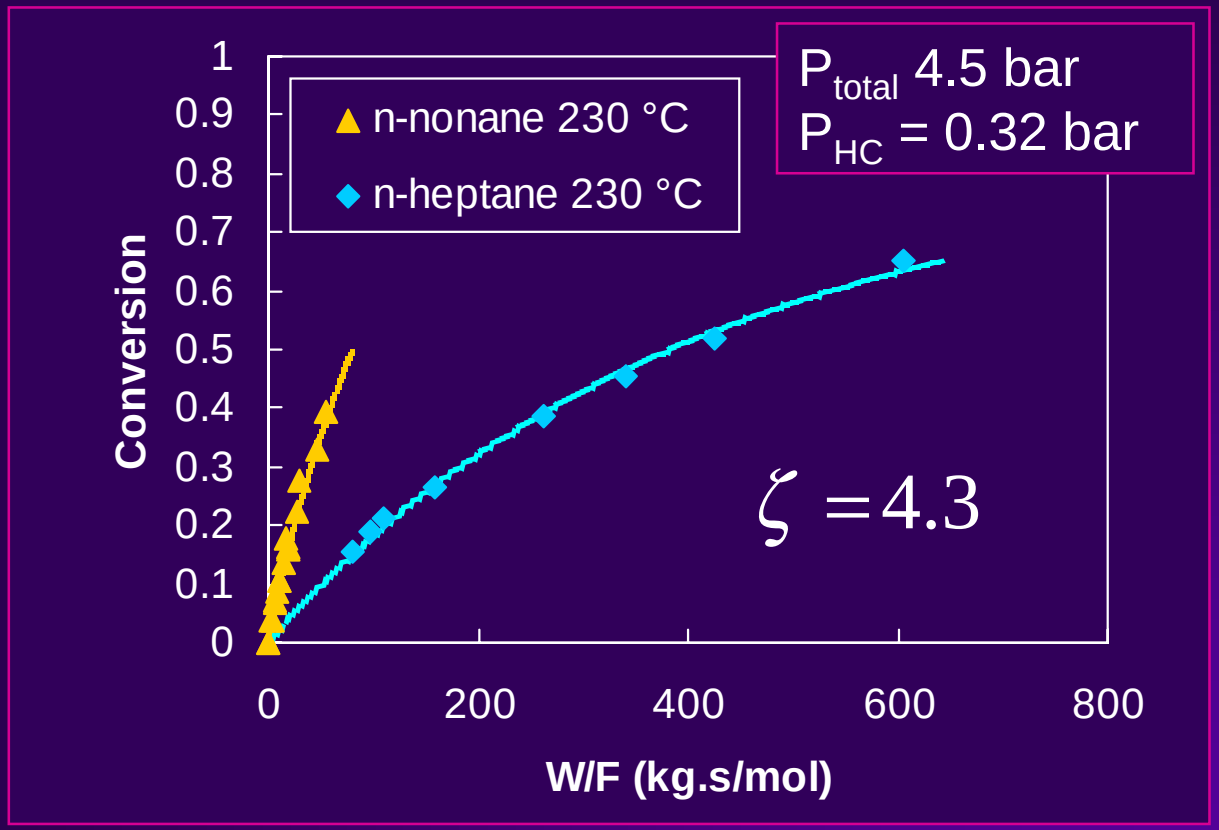
$$K_i = \bar{q}_s V_m$$

Kinetics

$$r_{nC4} = 2f_3 k_c q_{MB} + \left(f_{2,2} k_{B1} + \frac{1}{2} f_{2,4} k_{B_2} + 2f_{3,4} k_c \right) q_{DB} + f_{2,2,3} k_{B_1} q_{TB}$$

...

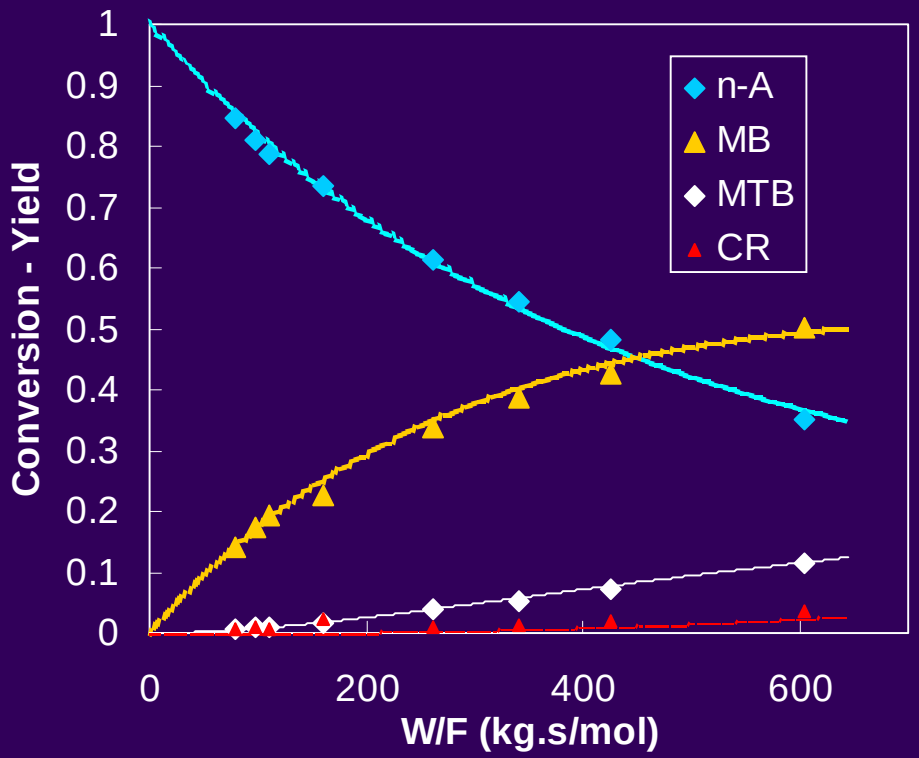
Competition effects in vapor phase



$$\zeta = \frac{r^{0}_{nC9}}{r^{0}_{nC7}}$$

Molecular competition factor

Lumped reaction model



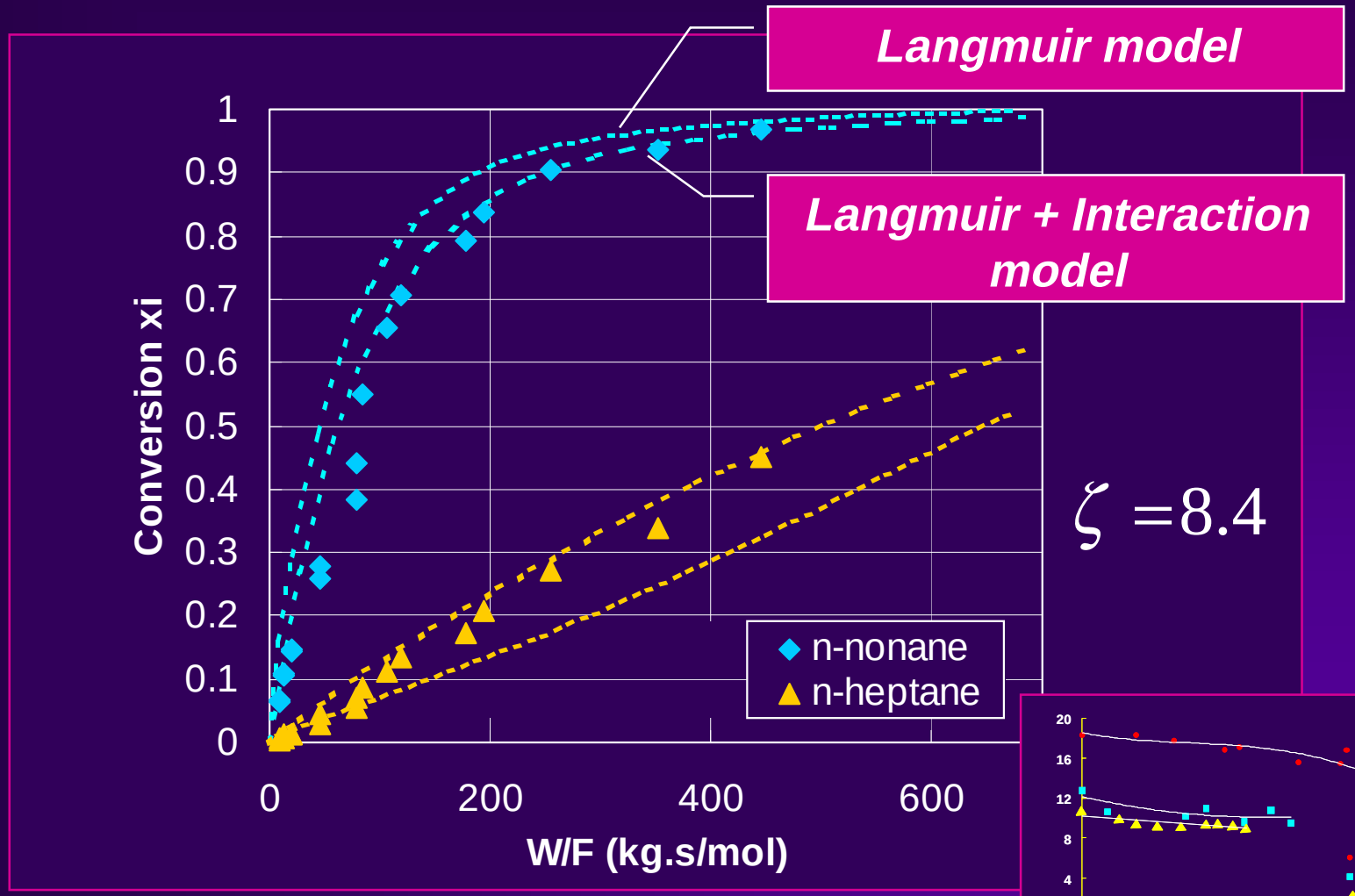
$$\text{n-alkane} \xrightarrow{k_{MB}} \underset{\leftarrow}{} \text{MB} \xrightarrow{k_{MTB}} \underset{\leftarrow}{} \text{MTB} \xrightarrow{k_{CR}} \text{CR}$$ *

*** Froment, G.F., Catalysis Today, 1987, 1, 455**

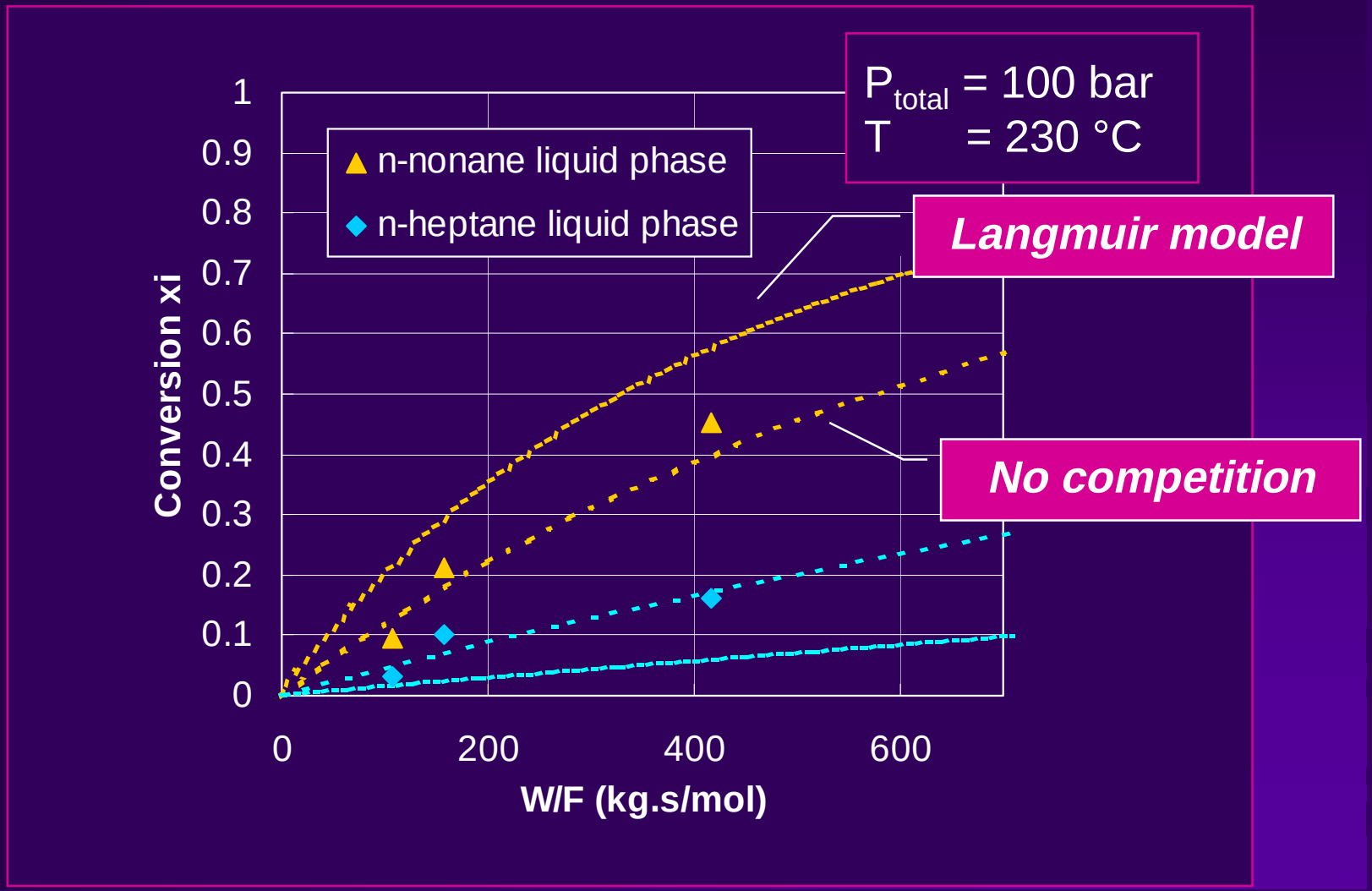
Adsorption & kinetic parameters

	K’ (mol/kg/bar)	L (1/bar)	q_s (mol/kg)	$k_{intr} * K_{DH}$ (1/bar/s)
nC7	6.91	9.8	0.7	0.023
nC9	37.4	60.0	0.62	0.063
Ratio	5.4			2.74

Competition in vapor phase

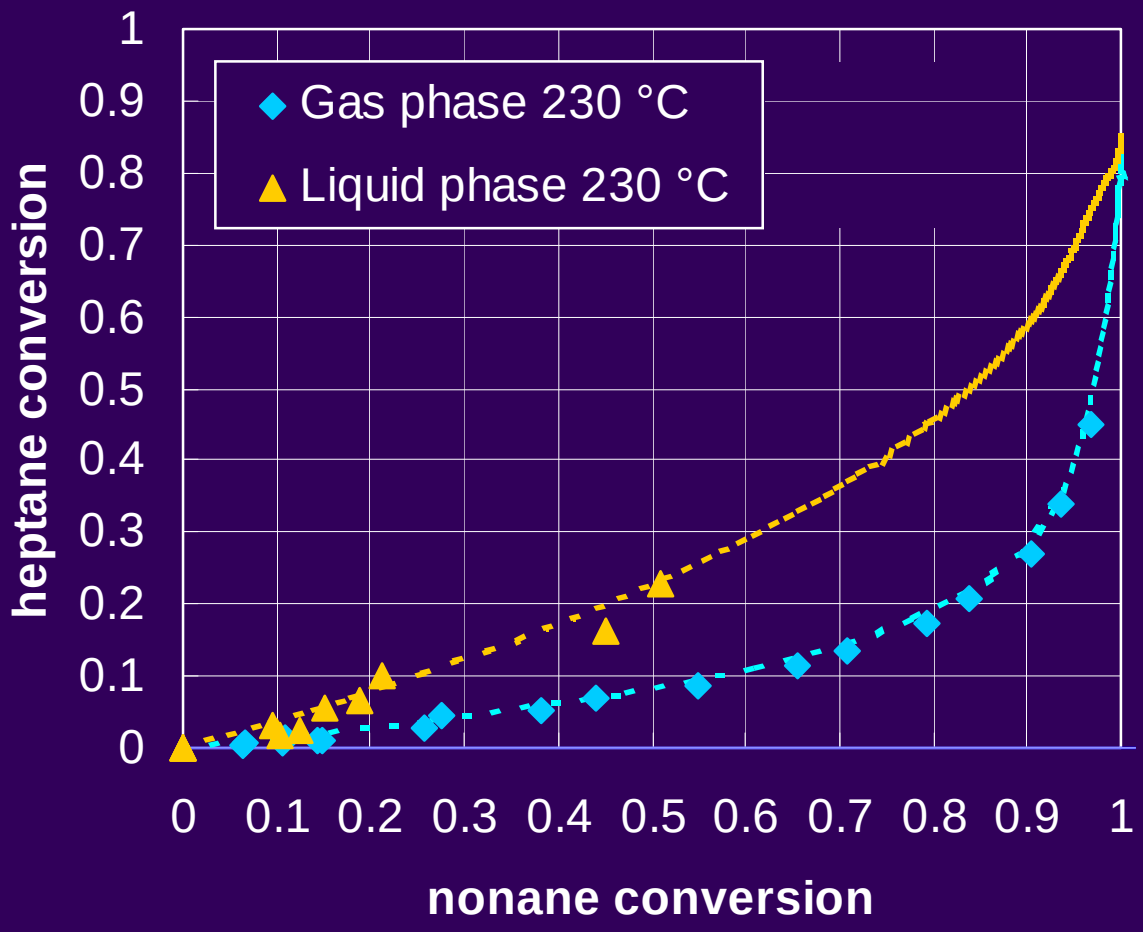


Competition in liquid phase



Denayer *et al*, *J.Catal*, In press

Vapor versus Liquid



Pure components

$$\zeta = 4.3$$

Vapor, binary

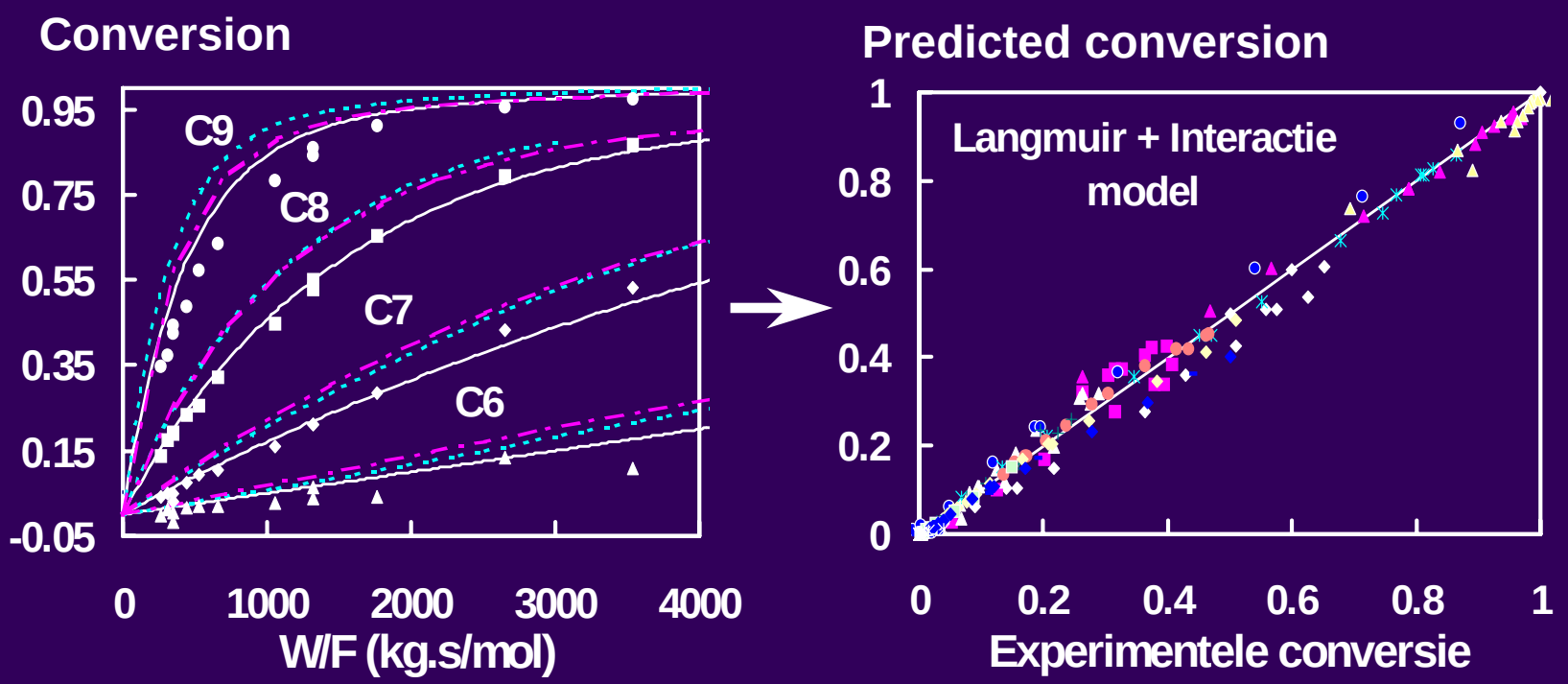
$$\zeta = 8.4$$

Liquid, binary

$$\zeta = 2.7$$

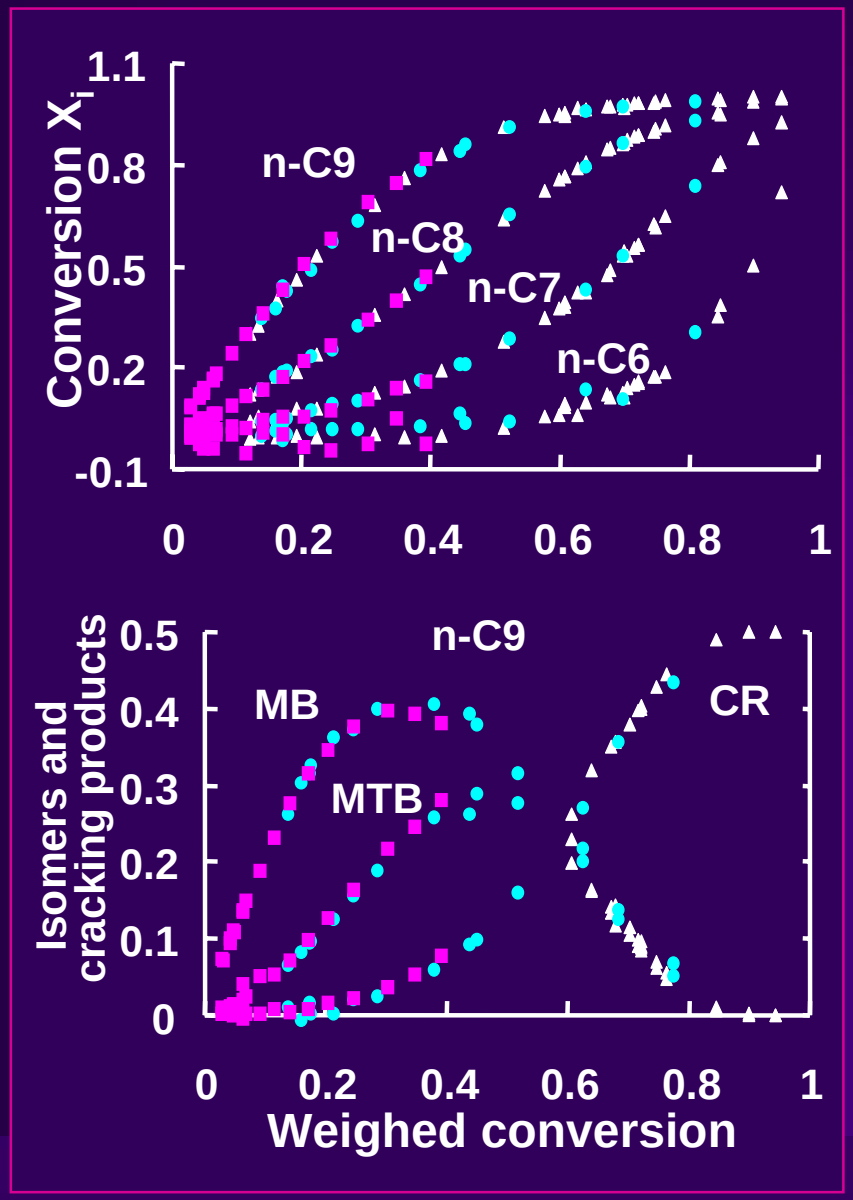
= Ratio of kinetic constants

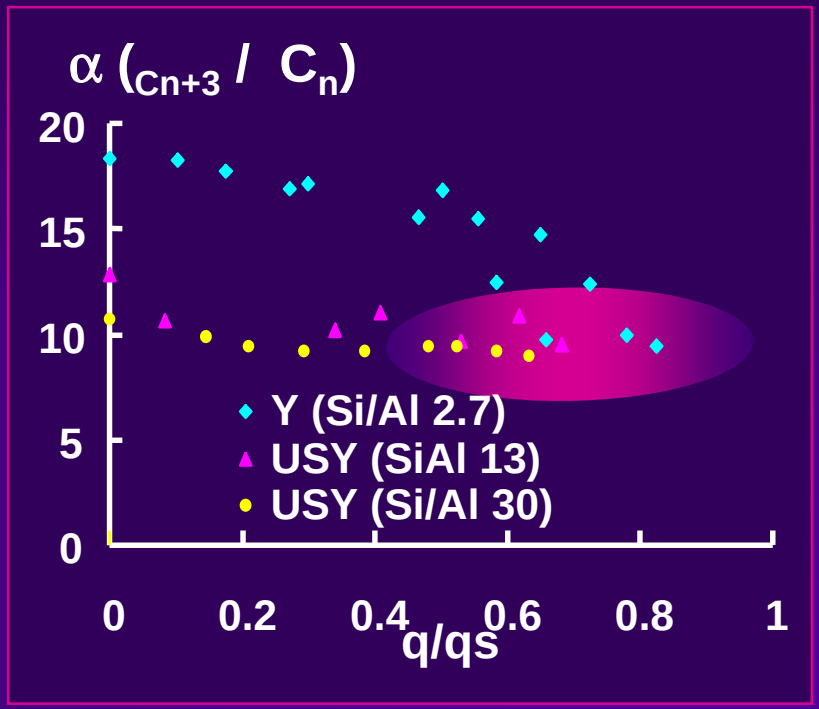
Conversion of mixtures



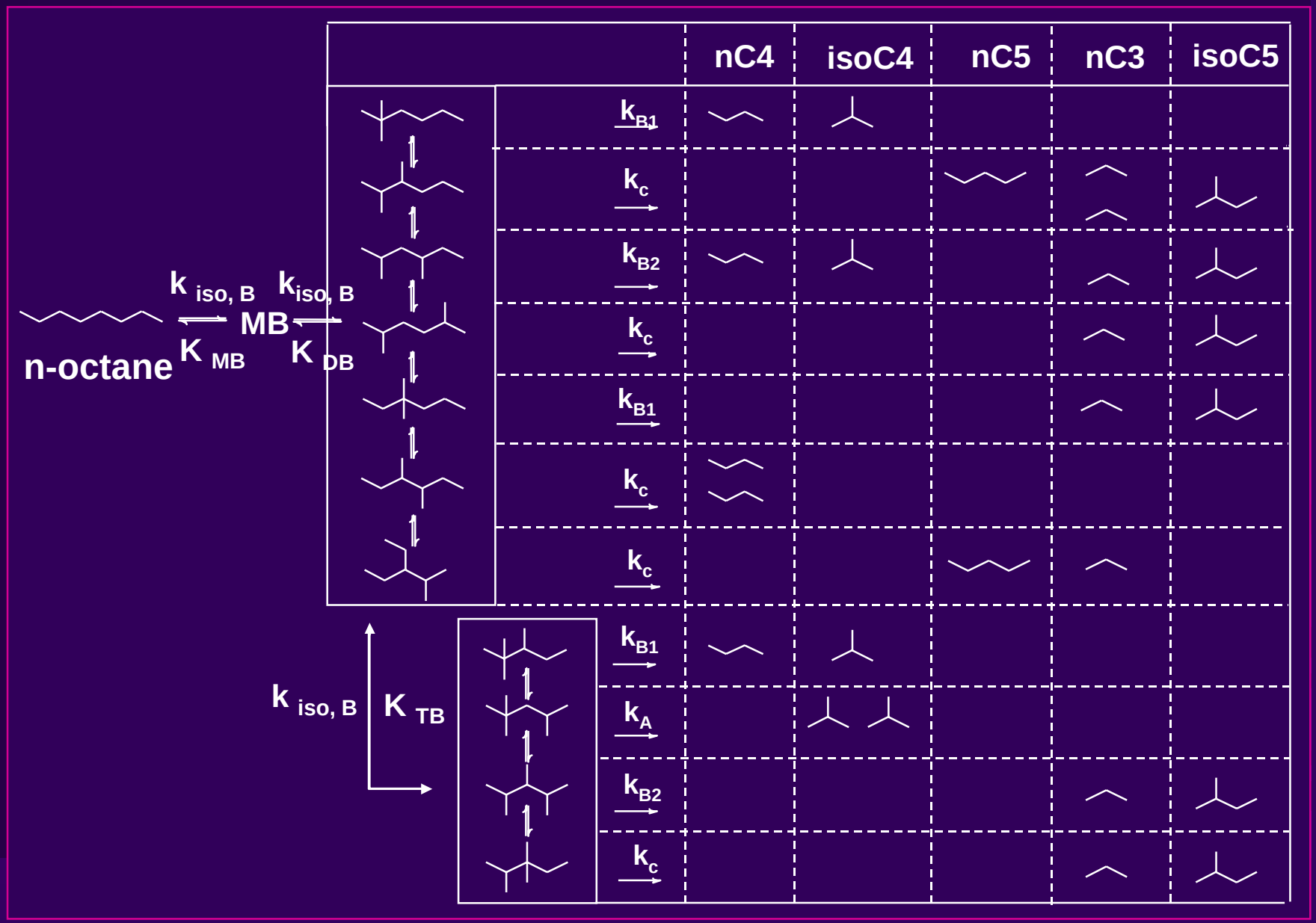
Conversion of mixture very well predicted using single component kinetic parameters and multicomponent adsorption equilibria

Conversion of mixtures

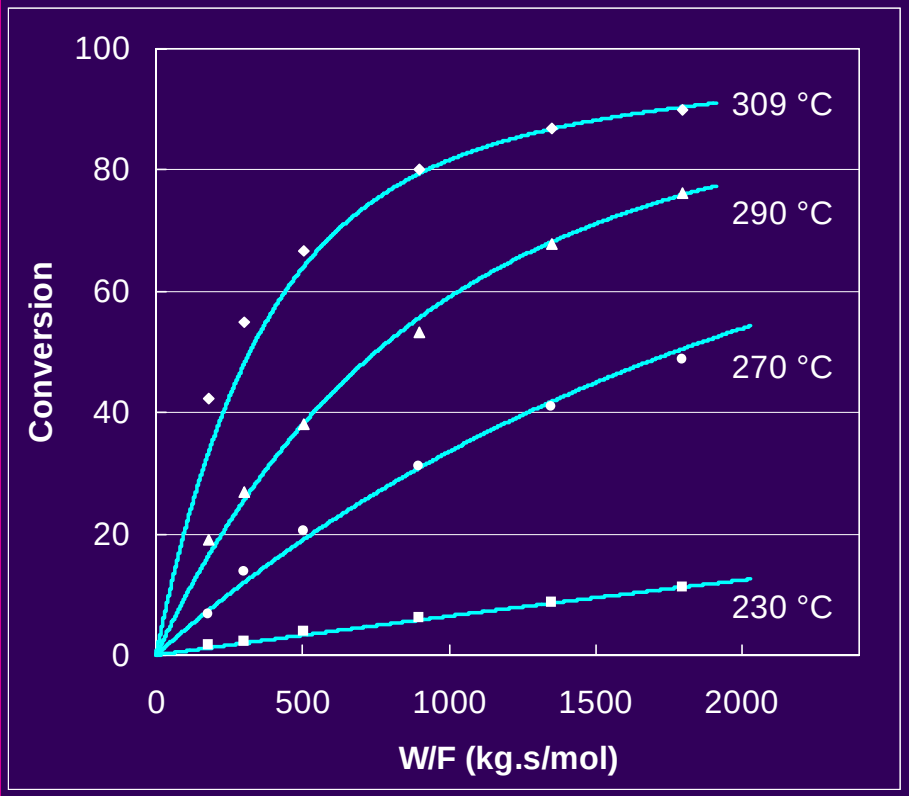


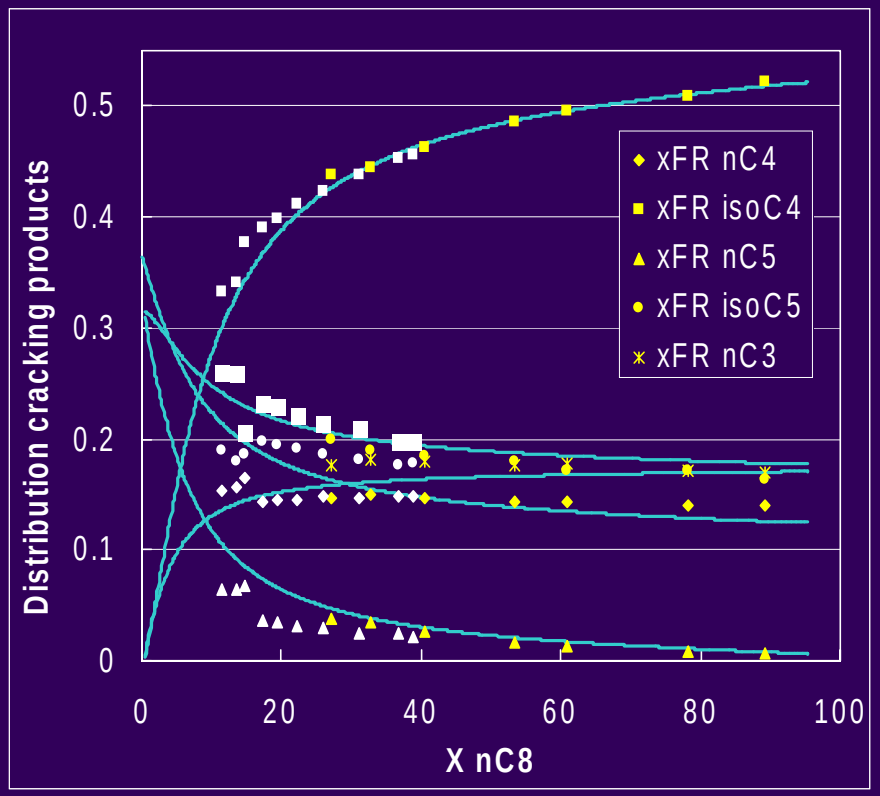


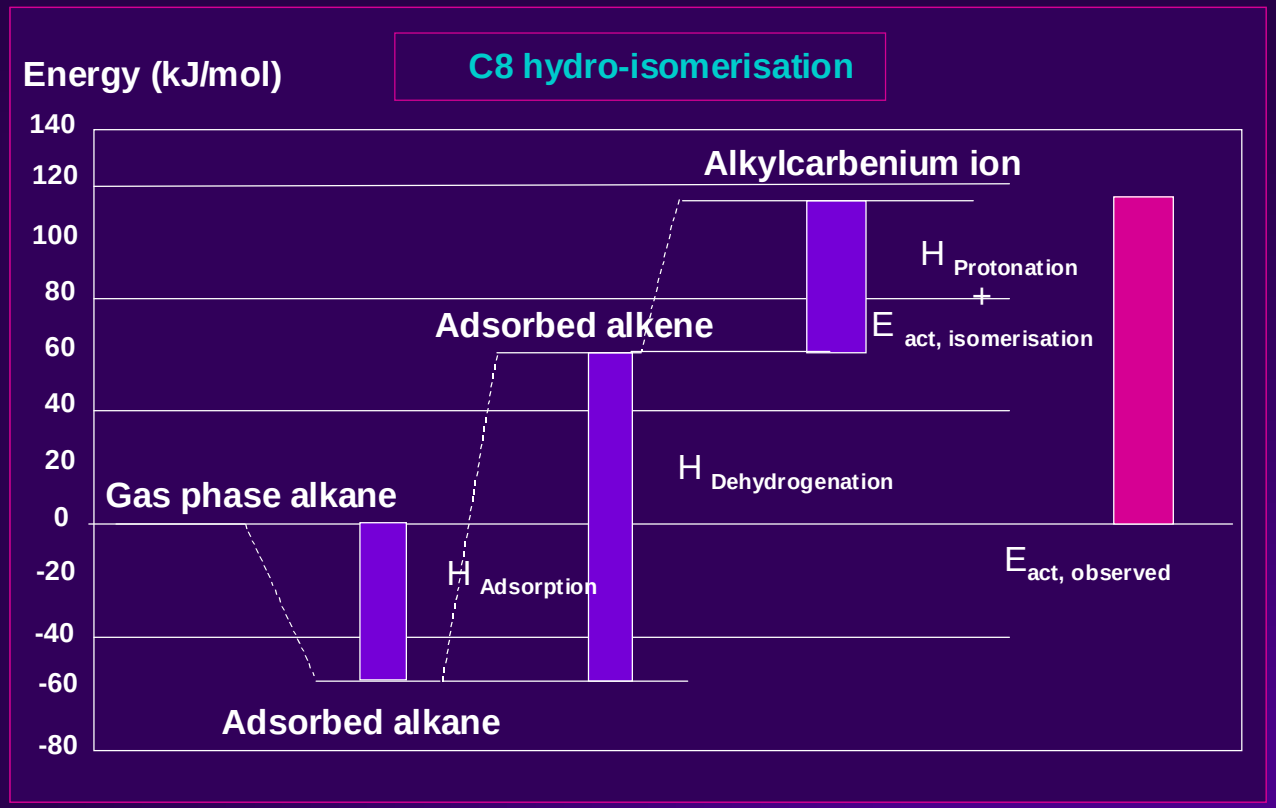
Reaction scheme



n-octane conversion



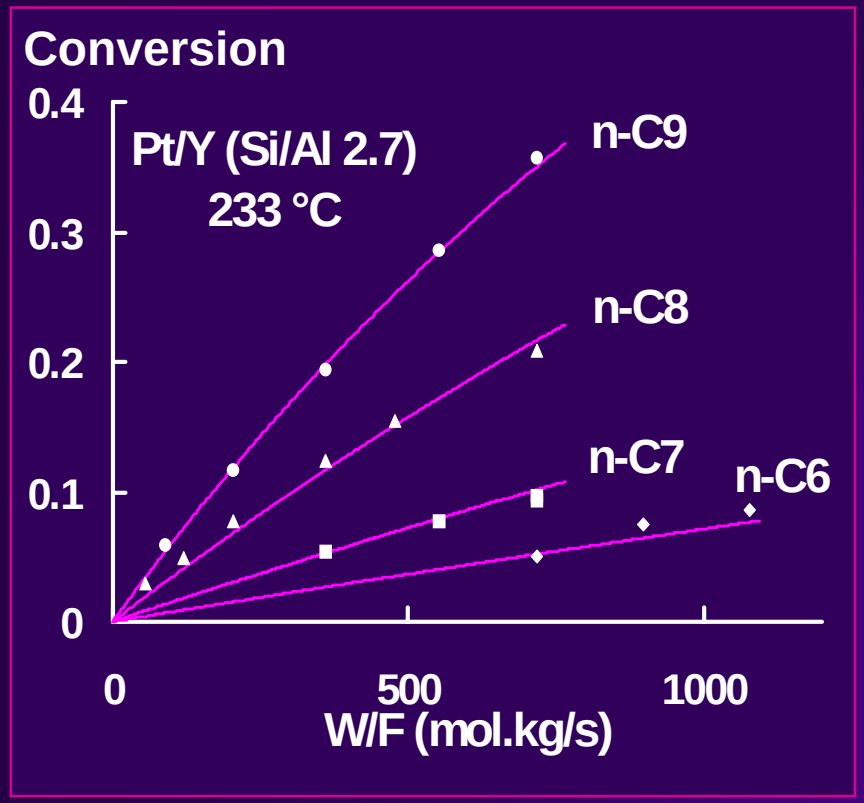


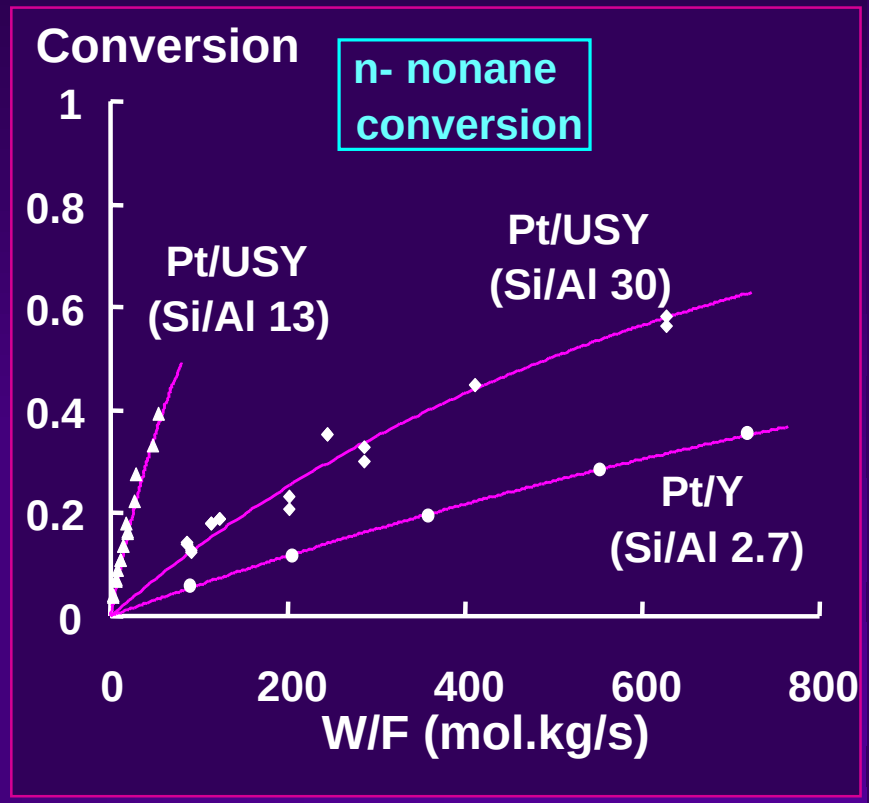


	$k_{270\,°C}$ (1/s)		$E_{act,\,global}$ (kJ/mol)		$\Delta\,\Delta H_{Prot}$ (kJ/mol)
	Pt/CBV720	Pt/CBV760	Pt/CBV720	Pt/CBV760	
MB	$3.89\ 10^{-1}$	$5.50\ 10^{-2}$	33.9	38.3	4.4
DB	$2.20\ 10^{-1}$	$3.24\ 10^{-2}$	32.3	38.0	5.7
TB	$5.19\ 10^{-2}$	$7.35\ 10^{-3}$	29.6	35.5	5.8
A	$6.50\ 10^{1}$	$9.21\ 10^{0}$	27.5	30.9	3.4
B1	$1.50\ 10^{-1}$	$2.15\ 10^{-2}$	59.2	62.4	3.2
B2	$3.51\ 10^{-1}$	$5.10\ 10^{-2}$	52.2	56.8	4.6
C	$2.10\ 10^{-3}$	$2.83\ 10^{-4}$	71.9	75.7	3.8

Martens, G.G., Marin, G.B., Martens, J.A., Jacobs, P.A., Baron, G.V. 2000., J. Cat., 195, 253-267.

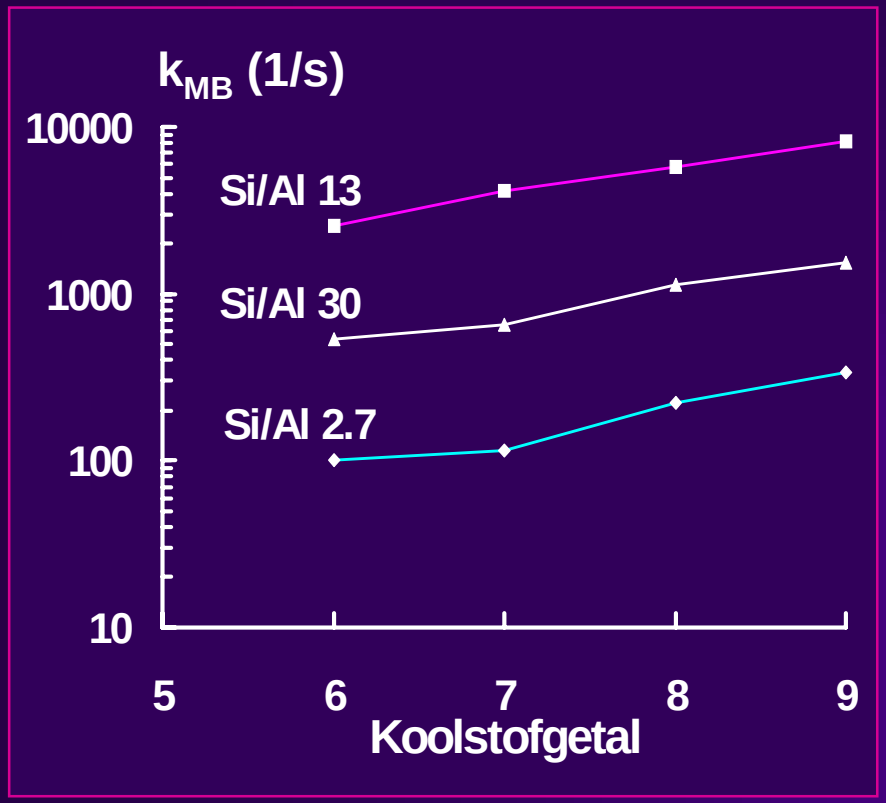
Influence chain length and Si/Al

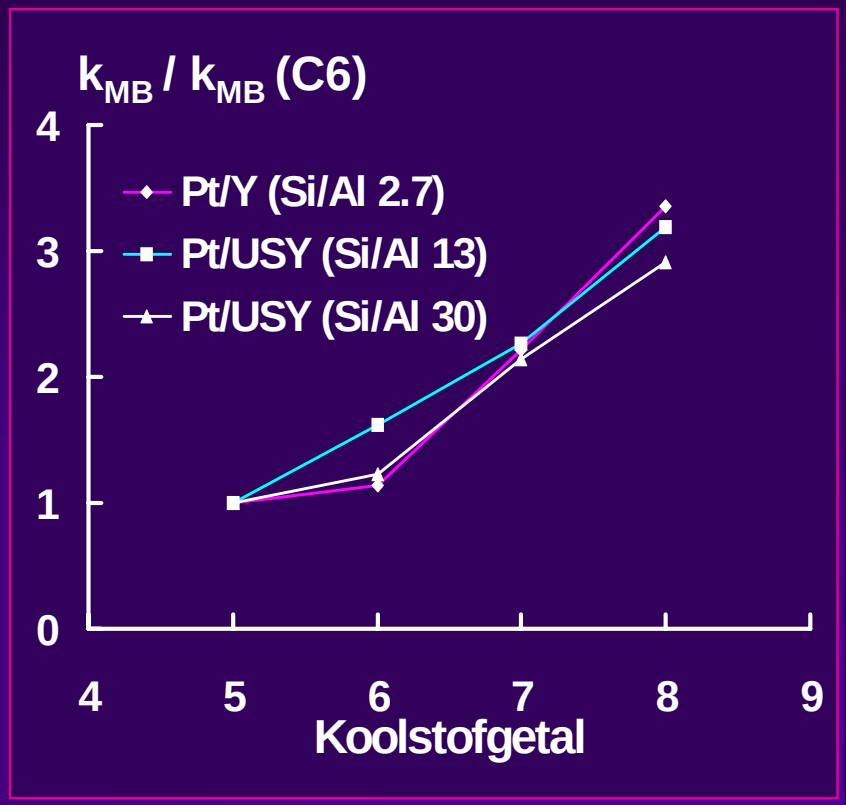




- Reactivity ~ Chain length
- Strong influence of Si/Al on observed activity

Kinetic parameters





$\Rightarrow$ Relative reaction rates independent of Si/Al and acidity

Conclusions

- ✓ Several experimental and theoretical techniques to determine adsorption parameters in catalytic conditions
- ✓ Integrated adsorption - reaction study:

  Deeper insight in relation :

  zeolite - reactivity - selectivity - adsorption - shape selective properties

- ✓ Development and screening new materials, better process control, straightforward modeling

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