Modern Methods in Heterogeneous Catalysis

Lectures at Fritz-Haber-Institut

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Microkinetic Modeling

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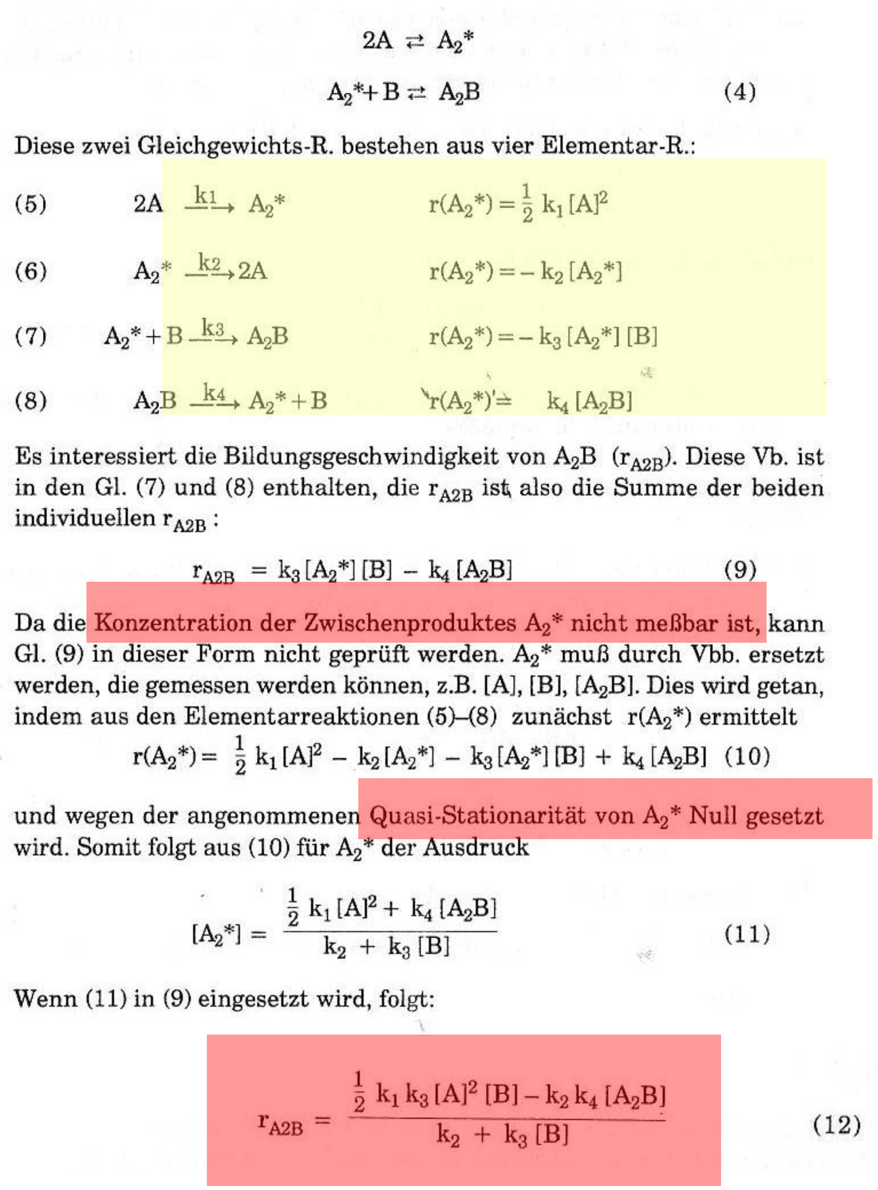


$$2A \rightleftarrows A_2^*$$

$$A_2^* + B \rightleftarrows A_2B \qquad (4)$$

Diese zwei Gleichgewichts-R. bestehen aus vier Elementar-R.:

(5) $2A \xrightarrow{k1} A_2^*$ $\qquad r(A_2^*) = \frac{1}{2}\, k_1\, [A]^2$

(6) $A_2^* \xrightarrow{k2} 2A$ $\qquad r(A_2^*) = -\, k_2\, [A_2^*]$

(7) $A_2^* + B \xrightarrow{k3} A_2B$ $\qquad r(A_2^*) = -\, k_3\, [A_2^*]\, [B]$

(8) $A_2B \xrightarrow{k4} A_2^* + B$ $\qquad r(A_2^*) = \quad k_4\, [A_2B]$

Es interessiert die Bildungsgeschwindigkeit von A_2B (r_{A2B}). Diese Vb. ist in den Gl. (7) und (8) enthalten, die r_{A2B} ist also die Summe der beiden individuellen r_{A2B} :

$$r_{A2B} = k_3\, [A_2^*]\, [B] - k_4\, [A_2B] \qquad (9)$$

Da die Konzentration der Zwischenproduktes A_2^* nicht meßbar ist, kann Gl. (9) in dieser Form nicht geprüft werden. A_2^* muß durch Vbb. ersetzt werden, die gemessen werden können, z.B. [A], [B], $[A_2B]$. Dies wird getan, indem aus den Elementarreaktionen (5)–(8) zunächst $r(A_2^*)$ ermittelt

$$r(A_2^*) = \frac{1}{2}\, k_1\, [A]^2 - k_2\, [A_2^*] - k_3\, [A_2^*]\, [B] + k_4\, [A_2B] \quad (10)$$

und wegen der angenommenen Quasi-Stationarität von A_2^* Null gesetzt wird. Somit folgt aus (10) für A_2^* der Ausdruck

$$[A_2^*] = \frac{\frac{1}{2}\, k_1\, [A]^2 + k_4\, [A_2B]}{k_2 + k_3\, [B]} \qquad (11)$$

Wenn (11) in (9) eingesetzt wird, folgt:

$$r_{A2B} = \frac{\frac{1}{2}\, k_1\, k_3\, [A]^2\, [B] - k_2\, k_4\, [A_2B]}{k_2 + k_3\, [B]} \qquad (12)$$

Microkinetic analysis is a different approach !

Outline

- Why kinetic analysis ?
- What are main aspects of kinetic studies ?
- What are key problems in kinetic studies ?
- What is microkinetic analysis ?
- Which parameters ?
- Which theory is behind the parameters ?
- Which experiments ?
- How to build a microkinetic model ?
- How to describe methane partial oxidation ?

Why Kinetic Studies ?

- Industrial catalysis
  - Major aspect: effective catalytic processes

  ⤷ Need for *efficient approaches* to enhance development

- Development and optimization of catalytic processes
  - Chemical intuition and experience
  - Supplement with *quantitative analysis*

Aspects of kinetics studies

1. Kinetics studies for design purposes
2. Kinetics studies of mechanistic details
3. Kinetics as consequence of a reaction mechanism

1. Kinetics studies for design purposes

- Results of experimental studies are summarized in the form of an *empirical kinetic expression*
  - Design of chemical reactors
  - Quality control in catalyst production
  - Comparison of different brands of catalysts
  - Studies of deactivation
  - Studies of poisoning of catalysts

2. Kinetics studies of mechanistic details

- Experimental kinetic study used to determine details in the mechanism
  - Problem:

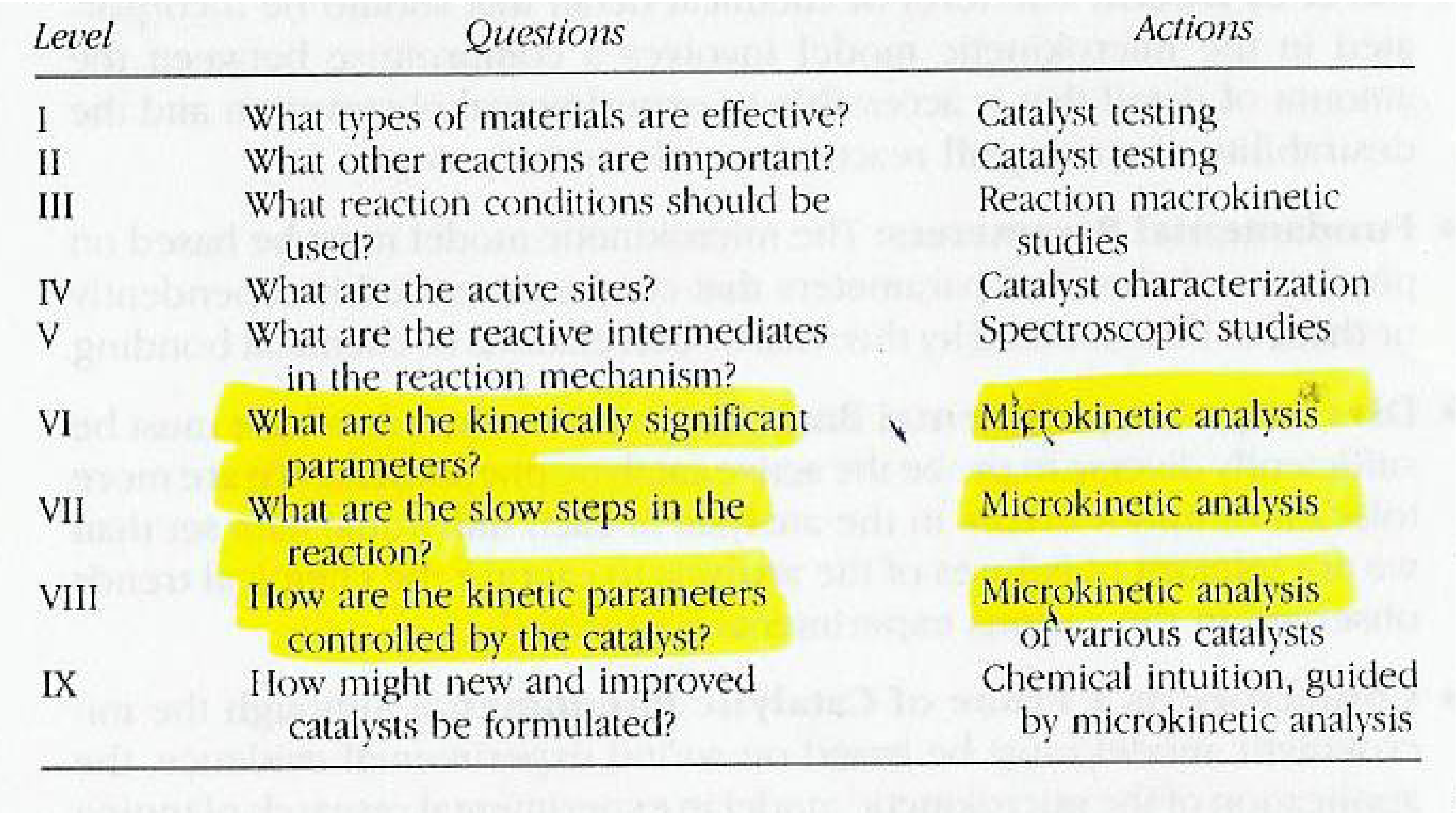
    Different models may fit data equally well

- Mechanistic considerations as guidance for kinetic studies

3. Kinetics studies as a consequence of a reaction mechanism

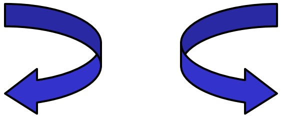
- Deduction of kinetics from a proposed reaction mechanism
- Historically macroscopic descriptions of the reaction kinetics were used
- Today, detailed scientific information available
  - Guidance for catalytic reaction synthesis at various levels of detail
  - Hierarchical studies

Levels of Catalytic Reaction Synthesis



Level	*Questions*	*Actions*
I	What types of materials are effective?	Catalyst testing
II	What other reactions are important?	Catalyst testing
III	What reaction conditions should be used?	Reaction macrokinetic studies
IV	What are the active sites?	Catalyst characterization
V	What are the reactive intermediates in the reaction mechanism?	Spectroscopic studies
VI	What are the kinetically significant parameters?	Microkinetic analysis
VII	What are the slow steps in the reaction?	Microkinetic analysis
VIII	How are the kinetic parameters controlled by the catalyst?	Microkinetic analysis of various catalysts
IX	How might new and improved catalysts be formulated?	Chemical intuition, guided by microkinetic analysis

Study of reaction mechanisms



Experiments on
well-defined systems

- Spectroscopic studies on single crystal surfaces
- Structure and reactivity of well-defined catalyst models

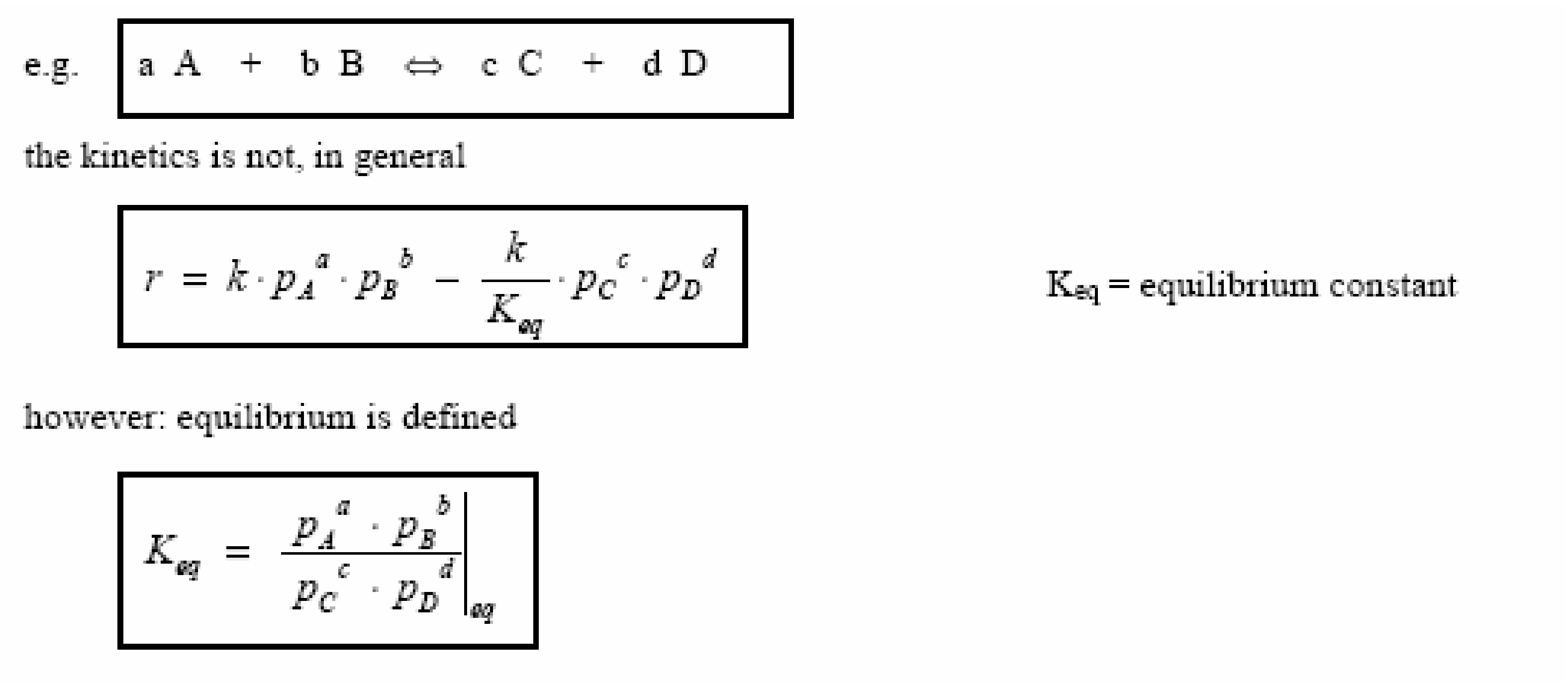
Detailed calculations
for individual molecules
and intermediates

- Electron structure calculations including calculations for transition states
- Monte Carlo (Kinetic MC)

Key Problems of Kinetic Studies

Key problems for kinetic studies

- Deduction of kinetics from net recation is not possible



e.g. $\boxed{a\ A \ + \ b\ B \ \Leftrightarrow \ c\ C \ + \ d\ D}$

the kinetics is not, in general

$$\boxed{r = k \cdot p_A^{\ a} \cdot p_B^{\ b} - \frac{k}{K_{eq}} \cdot p_C^{\ c} \cdot p_D^{\ d}}$$

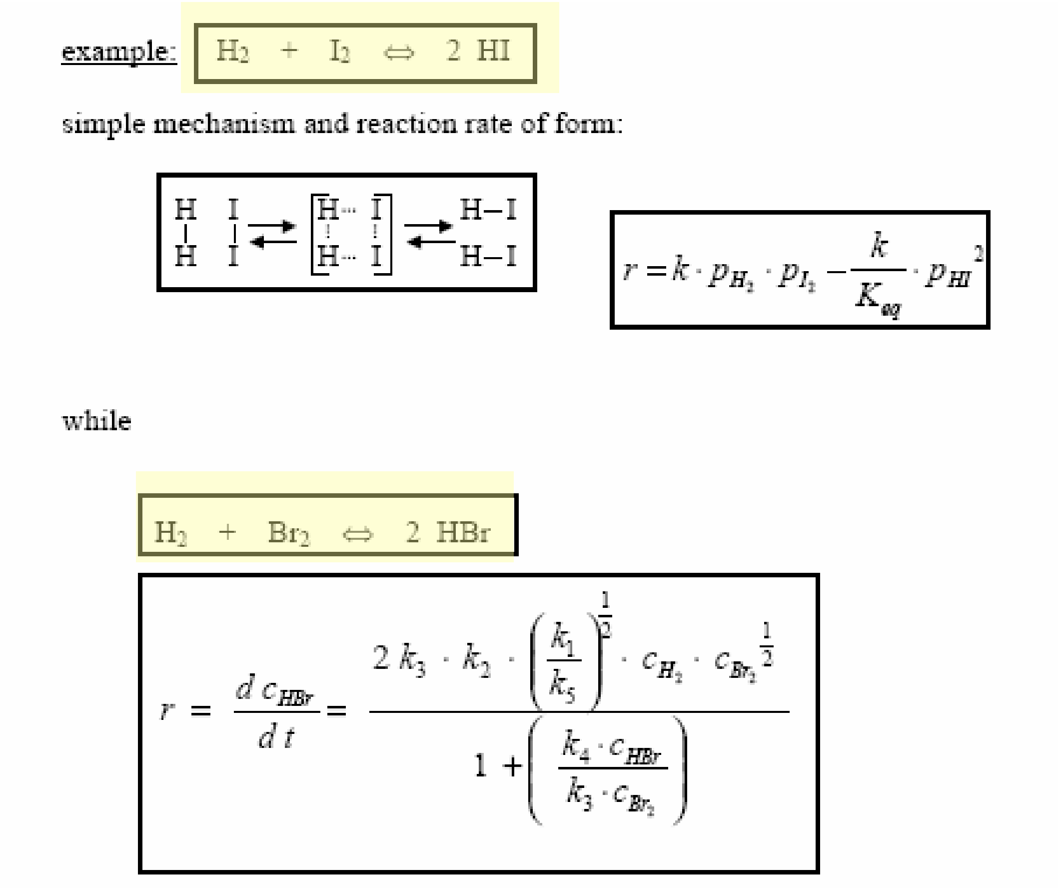
K_{eq} = equilibrium constant

however: equilibrium is defined

$$\boxed{K_{eq} = \left.\frac{p_A^{\ a} \cdot p_B^{\ b}}{p_C^{\ c} \cdot p_D^{\ d}}\right|_{eq}}$$

Key problems for kinetic studies

- Analogy may misleading



example: $H_2 + I_2 \Leftrightarrow 2\ HI$

simple mechanism and reaction rate of form:

$$r = k \cdot p_{H_2} \cdot p_{I_2} - \frac{k}{K_{eq}} \cdot p_{HI}^{2}$$

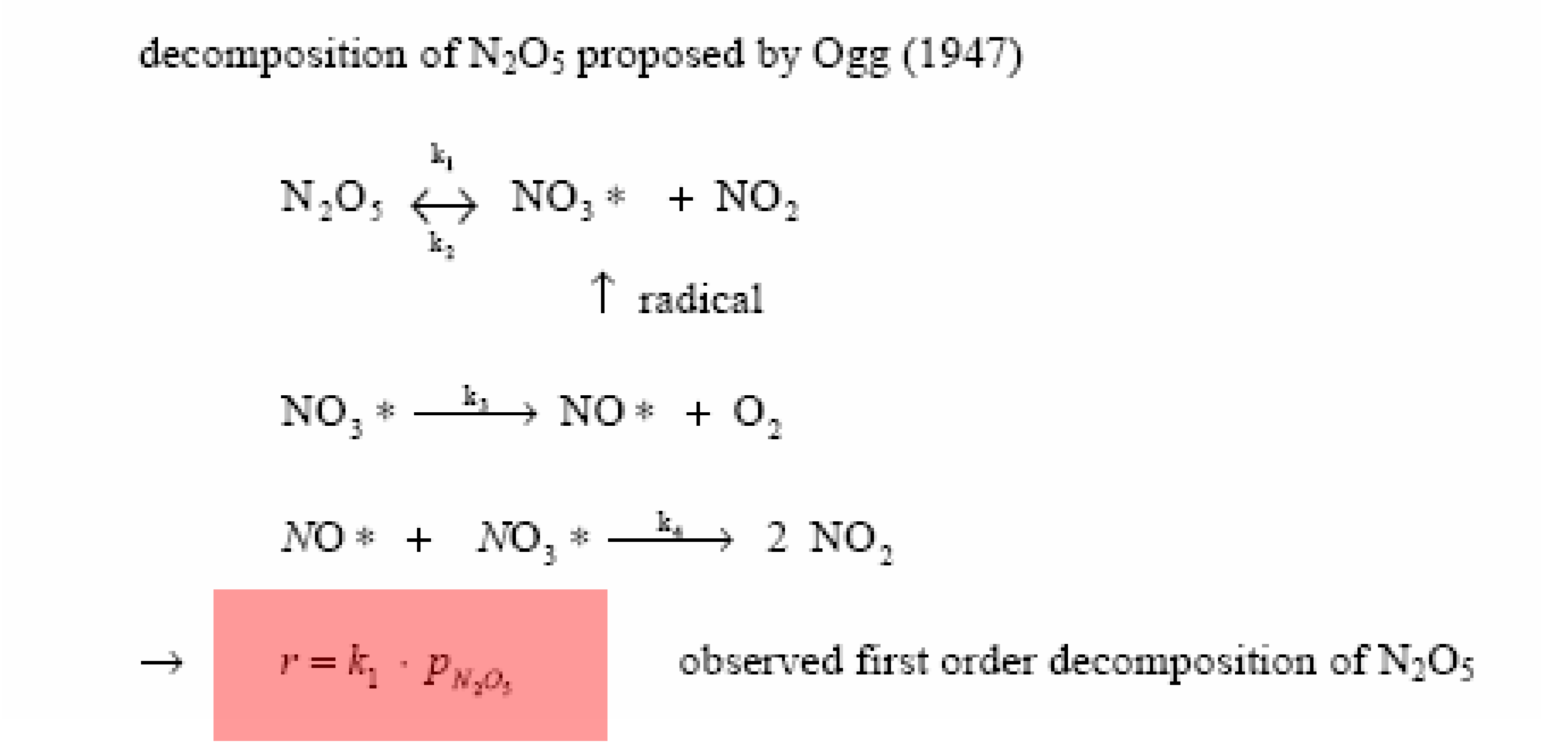
while

$H_2 + Br_2 \Leftrightarrow 2\ HBr$

$$r = \frac{d\,c_{HBr}}{d\,t} = \frac{2\,k_3 \cdot k_2 \cdot \left(\frac{k_1}{k_5}\right)^{\frac{1}{2}} \cdot c_{H_2} \cdot c_{Br_2}^{\frac{1}{2}}}{1 + \left(\frac{k_4 \cdot c_{HBr}}{k_3 \cdot c_{Br_2}}\right)}$$

Key problems for kinetic studies

- Simple kinetics ≠ simple mechanism



decomposition of N_2O_5 proposed by Ogg (1947)

$$N_2O_5 \underset{k_2}{\overset{k_1}{\longleftrightarrow}} NO_3* \; + NO_2$$

↑ radical

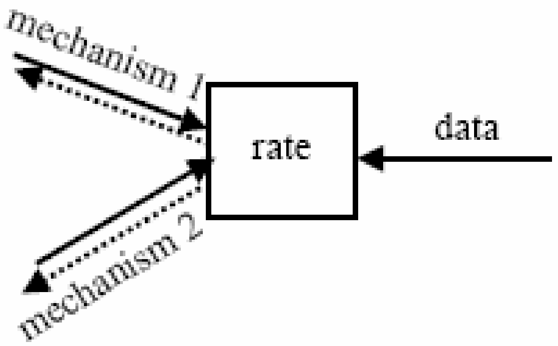
$$NO_3* \xrightarrow{k_3} NO* \; + O_2$$

$$NO* \; + \; NO_3* \xrightarrow{k_4} 2\ NO_2$$

→ $r = k_1 \cdot p_{N_2O_5}$ observed first order decomposition of N_2O_5

Key problems for kinetic studies

- Different reaction mechanisms may predict the same overall reaction rate; unable to distinguish between the two mechanisms



Microkinetic Analysis

Microkinetics

- *Reaction kinetic analysis* that attempt to incorporate into the kinetic model the *basic surface chemistry* involved in the catalytic reaction

- The kinetic model is based on a description of the catalytic process in terms of information and /or assumptions about the *active sites* and the *nature of elementary steps* that comprise the reaction scheme.

Microkinetics

- Convenient tool for the *consolidation* of fundamental information about a catalytic process and for *extrapolation* of this information to other conditions or catalysts involving related reactants, intermediates and products.

- Use of kinetic model for description of
  - Reaction kinetic data
  - Spectroscopic observations
  - Microcalorimetry and TPD

Microkinetic Analysis

- Combination of available experimental data, theoretical principles and appropriate correlations relevant to the catalytic process in a *quantitative* fashion
- Starting point is the formulation of the *elementary* chemical reaction *steps* that capture the *essential surface chemistry*
- Working tool that must be *adapted continually* to new results from experiments

MA – what is different ?

- *No initial assumptions !*
  - Which steps of the mechanism are kinetically significant ?
  - Which surface species are most abundant ?
- Estimations of the *rates* of elementary reactions and surface *coverages* are a *consequence of the analysis* not a basis !
- *Beyond* the fit of *steady-state* reaction kinetic data

What delivers MA ?

- Expected to describe experimental data from
  - Steady-state reaction kinetic data **+**
  - Data from related experimental studies
    - TPD
    - Isotope-tracer studies
    - Spectroscopic studies
- Feature: usage of *physical* and *chemical parameters* that can be measured independently or estimated by theory

Reaction Mechanism

- Net reaction $A_2 + 2\,B \rightleftharpoons 2\ AB$

  consists of a number of steps

  $$A_2 + B \rightleftharpoons A_2B$$

  $$A_2B + B \rightleftharpoons 2\ AB$$

- Concept of *elementary steps*: further subdivision and introduction of hypothetical intermediates

  $$A_2 + B \rightleftharpoons A_2B$$

  $$A_2B + B \rightleftharpoons A_2B_2$$

  $$A_2B_2 \rightleftharpoons 2\ AB$$

Elementary Reactions

- A step in a reaction mechanism is *elementary* if it is the *most detailed*, sensible description of the step.
- A step which consists of a *sequence* of two or more *elementary steps* is a *composite step*.
- What makes a step in a reaction mechanism elementary ?
  - depends on available information

The *key feature* of a mechanistic kinetic model is that it is *reasonable*, *consistent with known data* and *amenable to analysis.*

Parameters and Theory

Parameters for MA

- Sticking coefficients
- Surface bond energies
- Preexponential factors for surface reactions
- Activation energies for surface reactions
- Surface bonding geometries
- Active site densities and ensemble sizes

Theory behind the parameters

- Collision and transition-state theory
- Activation-energy-bond-strength correlations
  - Evans-Polanyi-correlation
- Molecular orbital correlations
  - Bond-order-conservation
  - Electronegativity scales
  - Drago-Wayland correlations
  - Proton affinity and ionization potential correlations

Concepts

- A *fundamental principle* in microkinetic analysis is the use of kinetic parameters in the rate expressions that have *physical meaning* and, as much as possible, that can be *estimated theoretically* or *experimentally*.

- *Framework* for quantitative *interpretation*, *generalization*, and *extrapolation* of experimental data and theoretical concepts for catalytic processes

Collision Theory (CT)

- Rate for a gas-phase bimolecular reaction

$$\boxed{r_{AB} = P_s \, \pi \, \sigma_{AB}^2 \sqrt{\frac{8 \, k_b \, T}{\pi \, \mu_{AB}}} \exp\left(-\frac{E_a}{k_b \, T} \right) n_A \, n_B}$$

σ_{AB}	*...collision factor*
$\sqrt{\frac{8 k_b T}{\pi \mu_{AB}}}$	*...average relative velocity from Maxwell – Boltzmann velocity distribution*
μ_{AB}	*...reduced mass*
P_s	*...steric factor*
E_a	*...activation energy*

Collision Theory

- Bimolecular rate constant

$$\boxed{k_{AB} = P_s \, \pi \, \sigma_{AB}^2 \sqrt{\frac{8 \, k_b \, T}{\pi \, \mu_{AB}}} \exp\left(- \frac{E_a}{k_b \, T} \right)}$$

- Preexponential factor

$$\boxed{A_{AB} = P_s \, \pi \, \sigma_{AB}^2 \sqrt{\frac{8 \, k_b \, T}{\pi \, \mu_{AB}}}}$$

- Example: with $P_s \approx 1$ and estimate of σ_{AB}

→ upper limit for preexponential factor

CT- Bimolecular surface reaction

- Modification to represent bimolecular reactions between mobile species on surfaces

$$\boxed{r_{AB} = 2\,P_s\,\sigma_{AB}\sqrt{\frac{\pi\,k_b\,T}{2\,\mu_{AB}}}\exp\left(-\frac{E_a}{k_b\,T}\right)\rho_A\,\rho_B}$$

$\sqrt{\dfrac{\pi\,k_b\,T}{2\,\mu_{AB}}}$ ...*two dimensional average relative velocity*

$\sigma_{A,B}$ ...*surface concentrations*

CT- Adsorption processes

- Use for definition of rate constants for adsorption processes in terms of the number of gas-phase molecules colliding with a unit surface area *F*$_i$

$$\boxed{r_A = F_i\,\sigma(T)\,f(\theta) = \frac{P_i\,\sigma(T)\,f(\theta)}{\sqrt{2\pi\,m_A\,k_B\,T}}}$$

  - Example: with σ (sticking coefficient) $\approx$ 1

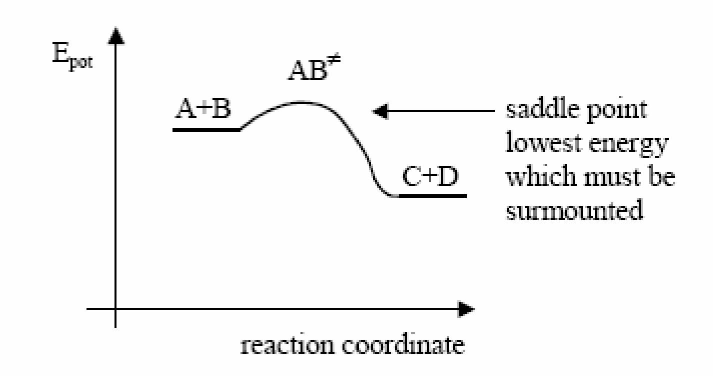
  $\rightarrow$ upper limit for preexponential factor and rate constant for adsorption

Transition-State Theory (TS)

- Incorporation of details of molecular structure
- Critical assumption: equilibrium between reactants and activated complex and products
- Bimolecular gas-phase reaction

$$A + B \rightleftharpoons AB^{\#} \rightleftharpoons C + D$$

- Potential energy diagram as multidimensional surface
- Definition of a reaction coordinate



Transition-State Theory

- Ideal gas equilibrium constant for the activated complex AB$^{\#}$

$$\boxed{K^{\#} = \frac{n_{AB^{\#}}}{n_A\, n_B}}$$

- Rate of chemical reaction

$$\boxed{r_{AB} = \frac{k_b\, T}{h} K^{\#}\, n_A\, n_B}$$

n_i ...concentrations

$\frac{k_b\, T}{h}$ ...frequency factor

h ...Planck´s constant

TS Theory

- *Macroscopic formulation* of TS isobtained by writing $K^{\#}$ in terms of standard entropy, $\Delta S^{0\#}$, and enthalpy, $\Delta H^{0\#}$, changes

$$\boxed{r_{AB} = \frac{k_b T}{h} \exp\left(\frac{\Delta S^{0\#}}{k_b}\right) \exp\left(-\frac{\Delta H^{0\#}}{k_b T}\right) n_A n_B}$$

- *Microscopic formulation* of TS is obtained by writing $K^{\#}$ in terms of molecular partition functions Q_i

$$\boxed{r_{AB} = \frac{k_b T}{h} \frac{Q_{AB^{\#}}}{Q_A Q_B} \exp\left(-\frac{\Delta E^{0\#}}{k_b T}\right) n_A n_B}$$

TS Theory

- Molecular *partition function* for a gas-phase species is a product of contributions from *translational*, rotational and *vibrational* degrees of freedom

$$\boxed{Q_i = q_{i,trans}\, q_{i,rot}\, q_{i,vib}}$$

$$\boxed{q_{i,trans} = \frac{(2\pi m_i k_b T)^{3/2}}{h^3}}$$

$$\boxed{q_{i,rot} = \frac{8\pi^2 I_i k_b T}{\sigma_r h^2} \qquad (linear\ \ molecule)}$$

$$\boxed{q_{i,vib} = \prod_j \frac{1}{1 - \exp\left(-\dfrac{h\upsilon_{ij}}{k_b T}\right)}}$$

I_i ... *moment of inertia*

σ_r ... *rotaional symmetry number*

υ_{ij} ... *frequencies of normal modes of vibration*

TS Theory

$$\boxed{r_{AB} = \frac{k_b T}{h} \frac{Q_{AB^\#}}{Q_A Q_B} \exp\left(-\frac{\Delta E^{0\#}}{k_b T}\right) n_A n_B}$$

- Order-of-magnitude estimates

$k_B T/h = 10^{13}\ \mathrm{s}^{-1}$

$q_{i,trans} = 5*10^8\ \mathrm{cm}^{-1}$ (per degree of translational freedom)

$q_{i,rot} = 10$ (per degree of rotational freedom)

$q_{i,vib} = 1$ (per degree of vibrational freedom)

TS – Adsorption processes

1) $A_{(g)} \rightleftharpoons A^{\#} \longrightarrow A^{*}$

- Rate of reaction for an activated complex of complete surface mobility

$$\boxed{r_A = \frac{k_b T}{h} \frac{Q_{A^{\#}}}{Q_{Ag}} \exp\left(-\frac{\Delta E^{0\#}}{k_b T}\right) n_A}$$

TS – Adsorption processes

2) $A_{(g)} + * \rightleftharpoons A^{\#} \longrightarrow A^{*}$

- Rate of reaction for an immobile activated complex

$$\boxed{r_A = \frac{k_b\,T}{h}\,\frac{Q_{A^{\#}}}{Q_{A_g}}\exp\left(-\frac{\Delta E^{0\#}}{k_b\,T}\right) n_A\,\theta^{*}}$$

$$Q_{A^{\#}} = \rho^{sat}\ q_{A^{\#}_r}\,q_{A^{\#}_v}$$

TS – Desorption processes

$$A^{*} \rightleftharpoons A^{\#} \longrightarrow A_{(g)}$$

- Rate of desorption

$$r_d = \frac{k_b T}{h}\frac{Q_{A^{\#}}}{Q_{A^{*}}}\exp\left(-\frac{\Delta E^{0\#}}{k_b T}\right)\rho_A$$

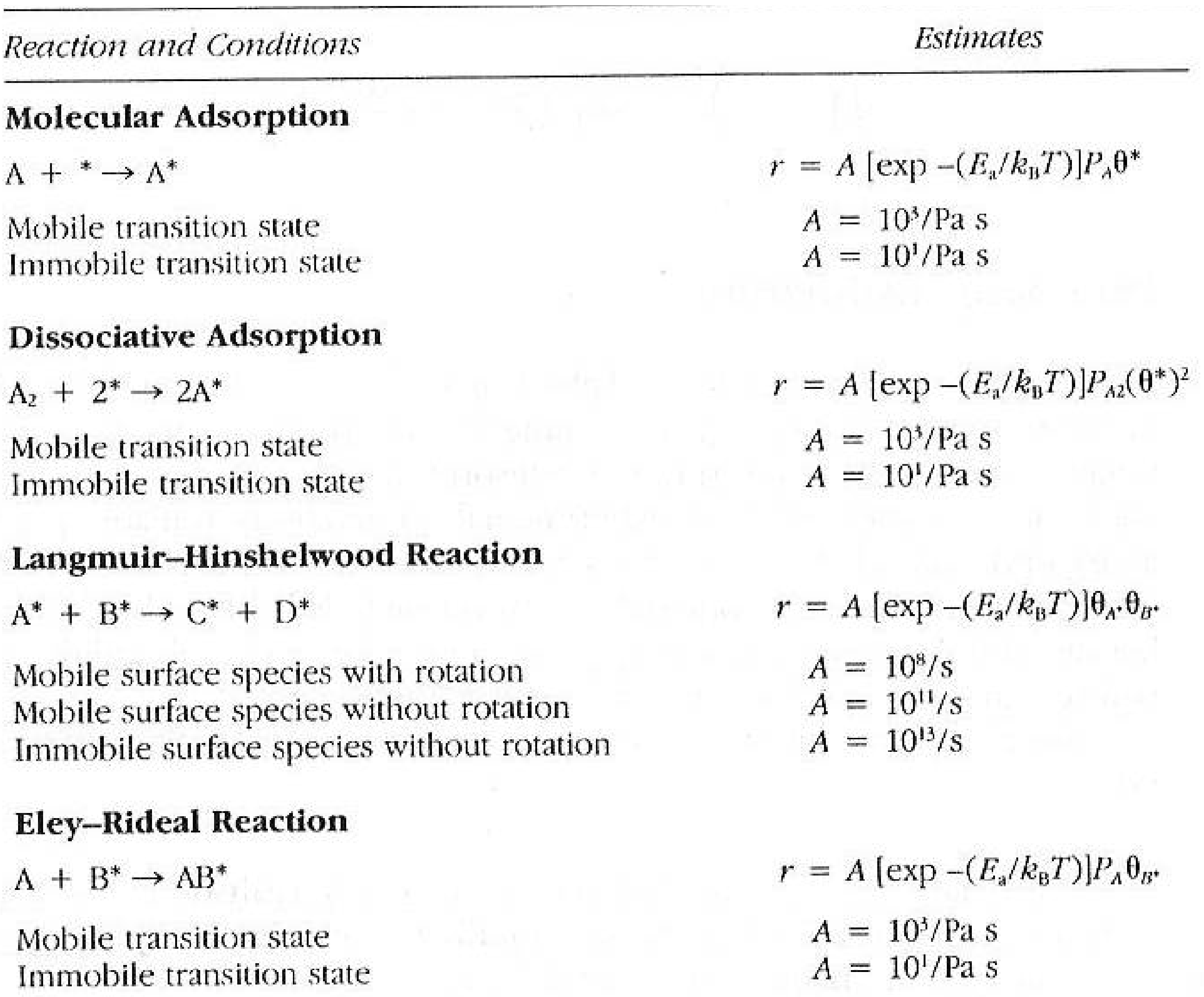
$$\boxed{r_d = \frac{k_b T}{h}\exp\left(-\frac{\Delta E^{0\#}}{k_b T}\right)\rho_A}$$

ρ_A *...concentration of species A on the surface*

$$\boxed{\frac{Q_{A^{\#}}}{Q_{A^{*}}} \approx 1}$$

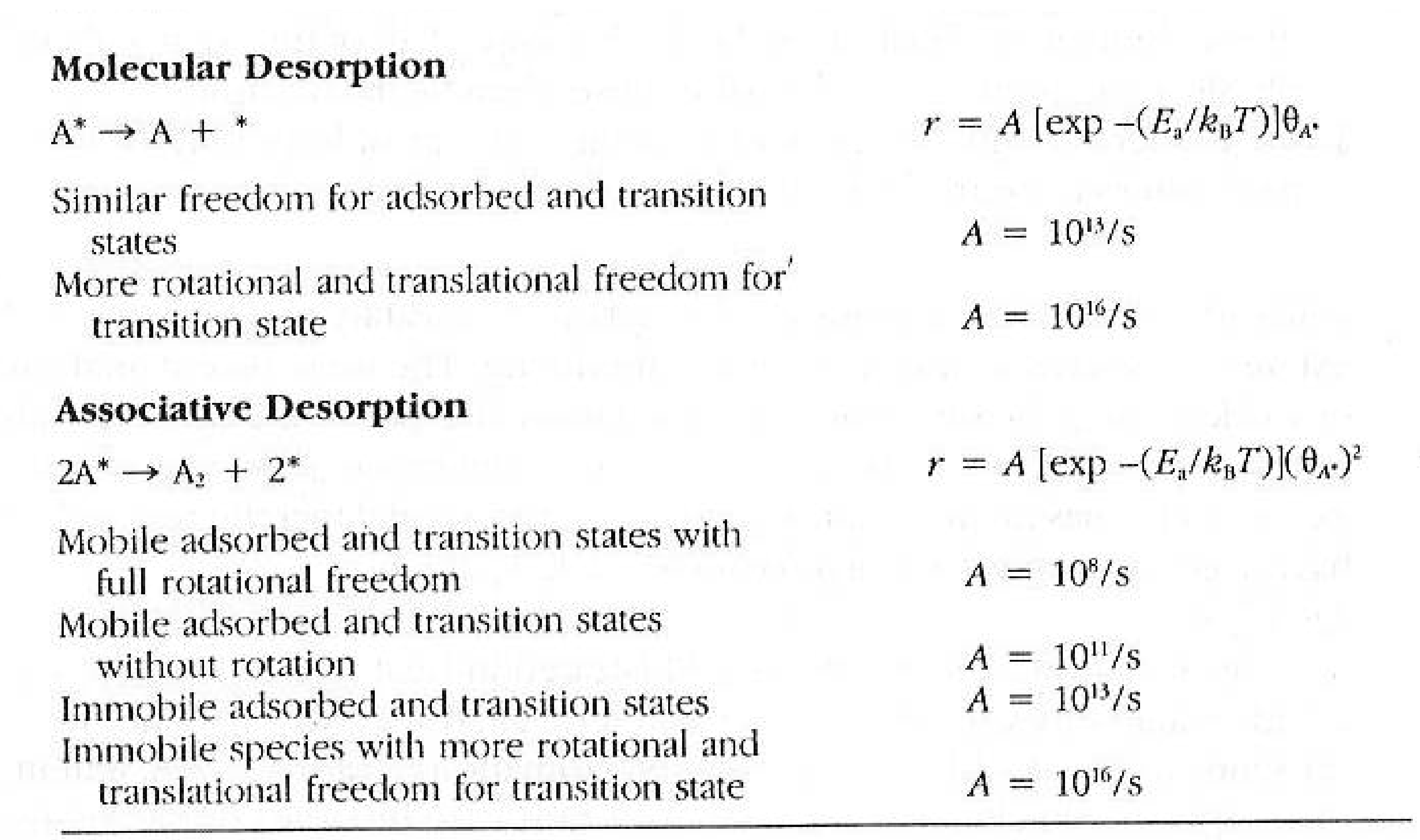
$$\boxed{\frac{k_b T}{h} \approx 10^{13} / s}$$

TS – Preexponential Factors Estimates



Reaction and Conditions	*Estimates*
Molecular Adsorption	
$A + * \rightarrow A^*$	$r = A\,[\exp -(E_a/k_BT)]P_A\theta^*$
Mobile transition state	$A = 10^3/\mathrm{Pa\ s}$
Immobile transition state	$A = 10^1/\mathrm{Pa\ s}$
Dissociative Adsorption	
$A_2 + 2^* \rightarrow 2A^*$	$r = A\,[\exp -(E_a/k_BT)]P_{A2}(\theta^*)^2$
Mobile transition state	$A = 10^3/\mathrm{Pa\ s}$
Immobile transition state	$A = 10^1/\mathrm{Pa\ s}$
Langmuir–Hinshelwood Reaction	
$A^* + B^* \rightarrow C^* + D^*$	$r = A\,[\exp -(E_a/k_BT)]\theta_{A^*}\theta_{B^*}$
Mobile surface species with rotation	$A = 10^8/\mathrm{s}$
Mobile surface species without rotation	$A = 10^{11}/\mathrm{s}$
Immobile surface species without rotation	$A = 10^{13}/\mathrm{s}$
Eley–Rideal Reaction	
$A + B^* \rightarrow AB^*$	$r = A\,[\exp -(E_a/k_BT)]P_A\theta_{B^*}$
Mobile transition state	$A = 10^3/\mathrm{Pa\ s}$
Immobile transition state	$A = 10^1/\mathrm{Pa\ s}$

TS – Preexponential Factors Estimates



Molecular Desorption	
$A^* \rightarrow A + *$	$r = A\,[\exp -(E_a/k_BT)]\theta_{A^*}$
Similar freedom for adsorbed and transition states	$A = 10^{13}/s$
More rotational and translational freedom for transition state	$A = 10^{16}/s$
Associative Desorption	
$2A^* \rightarrow A_2 + 2^*$	$r = A\,[\exp -(E_a/k_BT)](\theta_{A^*})^2$
Mobile adsorbed and transition states with full rotational freedom	$A = 10^{8}/s$
Mobile adsorbed and transition states without rotation	$A = 10^{11}/s$
Immobile adsorbed and transition states	$A = 10^{13}/s$
Immobile species with more rotational and translational freedom for transition state	$A = 10^{16}/s$

Estimates for Activation Energies

- Rate constant = f (A ; E_A)
- E_A estimation difficult

1) Empirical correlations for E_A from heats of reaction
   - Bond-order conservation (BOC) by Shustorovich

$$A_2 \rightleftharpoons A^* + A^*$$

$$\boxed{E_A = D_{A_2} - \frac{3}{2} E_{A_{nMetal}}}$$

E_A ... act. energy for diss. adsorption

D_{A_2} ... strength of $A-A$ bond

$E_{A_{nMetal}}$ ... adsorption strength of A^* on site with n metal atoms

Estimates for Activation Energies

2) Conversion of elementary steps into families of reactions

- especially for large mechanisms where limited experimental data are available
- example: reaction of a paraffin over a metal surface including hydrogenation and dehydrogenation steps

Evans-Polanyi correlation

$$\boxed{\begin{aligned} E_{Ai} &= E_0 + \alpha\, \Delta H_i \qquad & exoth. \\ E_{Ai} &= E_0 - (1-\alpha)\, \Delta H_i \qquad & endoth. \end{aligned}}$$

E_0, α ... *Evans – Polanyi constants for the family*

ΔH_i ... *heat of formation*

i ... *elementary step*

Consistency of the Model

1) Stoichiometric consistency

reactants → → products :

reactants, intermediates have to be formed and consumed to form products

2) Thermodynamic consistency

If two or more different sequences lead from reactants to products, these sequences must describe the same gas-phase thermodynamics.

Thermodynamic consistency

$$\boxed{\begin{aligned} E_{i,rev} &= E_{i,for} - \Delta H_i^{\,0} \\ A_{i,rev} &= A_{i,for} \exp\left(\frac{\Delta G_i^{\,0} - \Delta H_i^{\,0}}{RT}\right) \end{aligned}}$$

E_i ... *forward, reverse activation energies*

A_i ... *forward, reverse preexp. factors*

$\Delta G_i^{\,0}$ ...*standard Gibbs free – energy changes of reaction*

$\Delta H_i^{\,0}$ ...*standard enthalpy changes of reaction i*

$$\boxed{\sum_i \sigma_i\,(E_{i,for}) - \sum_i \sigma_i\,(E_{i,rev}) = \Delta H_{net}^{\,0}}$$

$$\boxed{\prod_i \left(\frac{A_{i,rev}}{A_{i,for}}\right)^{\sigma_i} = \exp\left(\frac{\Delta G_{net}^{\,0} - \Delta H_{net}^{\,0}}{RT}\right)}$$

σ_i ...*stoichiometric number of elementary step*

Informative Experiments

Experimental Techniques

How can information from these techniques be used in microkinetic analysis ?

- Physical techniques → bulk structure, surface area, pore structure
- Spectroscopic studies → probe of composition and morphology of the surface
- Kinetic & therm. studies → probe catalytic properties of the surface; quantification of kinetic parameters

Techniques that probe catalyst properties:

- X ray diffraction
- X-ray absorption spectroscopy
- extended X-ray absorption fine structure
- transmission and scanning electron microscopies
- magnetic susceptibility
- Mössbauer spectroscopy
- solid-state nuclear magnetic resonance spectroscopy
- electron paramagnetic resonance spectroscopy
- X-ray photoelectron spectroscopy
- ultraviolet photoelectron spectroscopy
- Auger electron spectroscopy
- scanning tunneling and atomic force microscopies
- low-energy electron diffraction
- infrared and Raman spectroscopies
- electron energy loss spectroscopy
- physical adsorption measurements

Techniques that probe adsorbed species:

- X-ray photoelectron spectroscopy
- ultraviolet photoelectron spectroscopy
- electron energy loss spectroscopy
- magnetic susceptibility
- low-energy electron diffraction
- infrared and Raman spectroscopies
- nuclear magnetic resonance spectroscopy
- electron paramagnetic resonance spectroscopy

Techniques that probe kinetic and thermodynamic properties:

- temperature programmed desorption
- isotope tracing
- microcalorimetry
- chemisorption measurements
- reaction kinetic measurements

X-ray Diffraction

- Crystal structure determines the coordination of the various catalyst components and bond distances between elements → surface structure and nature of active sites

- Measurement of average particle sizes with help of Scherrer equation → structure-sensitive behaviour

- Analysis of peak shapes can be used to probe the size of crystallites → particel size distribution

Photoelectron Spectroscopy - XPS

- Quantitative analysis of surface composition

  ! Surface and bulk composition may be different

- Information about surface oxidation state

- Use of treatment chamber – quantification of surface coverage by a particular species

- UPS: probe of valence levels of the catalyst surface

Infrared Spectroscopy

- Probe for vibrational properties of the catalyst surface groups

- Example: O-H stretching vibration
  - Intensity of O-H band in the IR spectrum provides a measure of the surface hydroxyl concentration depending on the catalyst treatment
  - Position of O-H band gives information about the nature of the hydroxyl group

Building a Microkinetic Model

Building a Microkinetic Model

- Build a set of elementary reactions which reflect all experimental and theoretical information
- Calculate for each reaction the thermodynamics

  (for all gaseous species and all adsorbed species)

$$\boxed{K_{i,eq} = \frac{k_{i,for}}{k_{i,rev}} = \exp\left(\frac{\Delta S_i^0}{k_B}\right)\exp\left(-\frac{\Delta H_i^0}{k_B T}\right)}$$

- Choose material balance of an appropriate reactor and characterize in and out flows

Reactor Models

- General types of ideal reactors
  - Batch reactor
  - Continuous-flow stirred tank reactor (CSTR)
  - Plug flow reactor (PFR)

- Typical characteristics of reactors
  - Batch: reactor volume V_R and holding time t
  - Flow: reactor volume V_R and space time τ

Reactor Models in MA

- For catalytic reactions the space time may be replaced by τ_P, defined as *number of catalytic sites* in the reactor, S_R, divided by the molecular flow rate of feed to the reactor, F
- Material balance for species *i* in a general flow reactor is given by

$$\boxed{F_i^0 + R_i = F_i + \left\{ \frac{dN_i}{dt} \right\}}$$

F_i^0 ...flow in reactor

F_i ...flow out of reactor

R_i ...rate of production of species i

N_i ...number of species i in reactor

Reactor Models in MA

- Batch reactor

$$\boxed{\frac{dN_i}{dt} = V_R\, r_i = S_R\, \Omega_i}$$

with Ω_I as turnover frequency (number of reaction events per active site per second)

- CSTR

$$\boxed{F_i - F_i^0 = V_R\, r_i = S_R\, \Omega_i}$$

- PFR

$$\boxed{F_i - F_i^0 = \int r_i\, dV_R = \int \Omega_i\, dS_R}$$

Example

Methane Oxidation by Mo/V-Oxides

M.D. Amiridis,J.E. Rekoske, J.A. Dumesic, D.F. Rudd, N.D. Spencer, C.J. Peireira. *AIChE J*. 37 (1991) 87.

Development of a microkinetic model of the partial oxidation of methane over MoO_3-SiO_2 and V_2O_5- SiO_2 catalysts

Problem: limited data available
Start : seek of experimental data and theoretical concepts from related or analogous catalytic systems

…continued

Aim is to reproduce the kinetic data for methane partial oxidation

$CH_4 \longrightarrow CH_3OH, HCHO, CO, CO_2, H_2O$

which includes also independent kinetic data for these subsequent partial oxidations

$CH_3OH \longrightarrow HCHO, CO, CO_2,$ H2O

$HCHO \longrightarrow CO, CO_2,$ H2O

$CO \longrightarrow CO_2$

Macrokinetic analysis of the problem

- Kinetic investigations showed quantitative differences in the performances of MoO_3-SiO_2 and V_2O_5-SiO_2 catalysts
  - Selectivity to CO_2 at low CH_4 conversion was zero for the V-catalyst; for the Mo-catalyst it was between 10-20 %
  - CO_2 is a direct product of methane oxidation over Mo-catalyst and a secondary over V-catalyst
  - Need of two pathways to CO_2 to describe both catalysts

Macrokinetic analysis of the problem

- Addition of sodium leads to decrease in conversion level and drop in the selectivity to HCHO for both catalysts
  - Effect to be analyzed by semiempirical MO calculations

  d-band characteristics:
    - empty, to reduce CO_2 formation
    - located at sufficient low energy to accept electrons during methane activation to form methoxy and hydroxyl surface species
    - tetrahedral coordination for high conversion

Development of the model

Oxidation of CO

- Kinetic investigations on V-catalyst
- @ 733 K reaction is first order in CO and zero order in oxygen
- Activation energy in ΔT: 673-773 K is 25.2 kcal/mol

$$2M + O_2 \rightleftharpoons 2MO$$

$$CO + MO \rightleftharpoons MOCO$$

$$MOCO \rightleftharpoons CO_2 + M$$

Development of the model

Oxidation of HCHO

Kinetic investigations on Mo-catalyst @ 600-925 K

- CO is principal product with small amounts of CO_2 at higher T
- Kinetic investigations on V-catalyst @ 500-900 K
- CO production passes through a maximum near 800 K and CO_2 production increases monotonically with T
- IR data

$$H_2CO + M \rightleftharpoons MOCH_2$$

$$H_2CO + MO \rightleftharpoons MOCH_2O$$

$$MOCH_2OM + 2MO \rightleftharpoons CO_2 + 2MOH + 2M$$

$$MOCH_2O + MO \rightleftharpoons CO + 2MOH$$

$$2MOH \rightleftharpoons H_2O + MO + M$$

Development of the model

Oxidation of CH_3OH

- Catalytic activity of Mo-catalyst starts at 500 K with complete conversion at 700 K
- Methoxy species (IR, EPR)

$$\mathrm{CH_3OH + M + MO \rightleftharpoons MOCH_3 + MOH}$$

$$\mathrm{MOCH_3 + 2MO \rightleftharpoons MOCH_2OM + MOH}$$

$$\mathrm{MOCH_3 + MO \rightleftharpoons MOCH_2 + MOH}$$

Development of the model

Oxidation of CH_4

$$CH_4 + 2MO \rightleftharpoons MOCH_3 + MOH$$

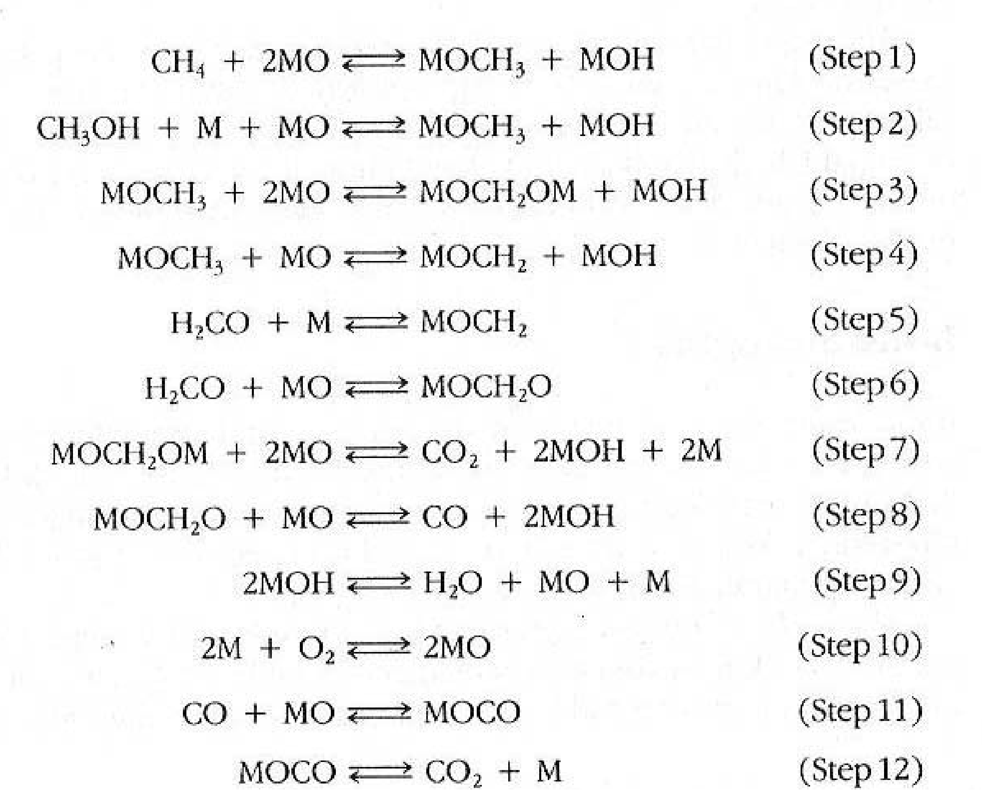
Two possible ways of methane adsorption on the surface

1) initial formation of a precursor state on the surface and consecutive dissociation into methoxy- and hydroxyl groups

2) activation of surface Oxygen to O^- and consecutive dissociative adsorption of methane

Development of the model

Mechanism as combination of all steps



$$\mathrm{CH_4 + 2MO \rightleftharpoons MOCH_3 + MOH} \qquad \text{(Step 1)}$$

$$\mathrm{CH_3OH + M + MO \rightleftharpoons MOCH_3 + MOH} \qquad \text{(Step 2)}$$

$$\mathrm{MOCH_3 + 2MO \rightleftharpoons MOCH_2OM + MOH} \qquad \text{(Step 3)}$$

$$\mathrm{MOCH_3 + MO \rightleftharpoons MOCH_2 + MOH} \qquad \text{(Step 4)}$$

$$\mathrm{H_2CO + M \rightleftharpoons MOCH_2} \qquad \text{(Step 5)}$$

$$\mathrm{H_2CO + MO \rightleftharpoons MOCH_2O} \qquad \text{(Step 6)}$$

$$\mathrm{MOCH_2OM + 2MO \rightleftharpoons CO_2 + 2MOH + 2M} \qquad \text{(Step 7)}$$

$$\mathrm{MOCH_2O + MO \rightleftharpoons CO + 2MOH} \qquad \text{(Step 8)}$$

$$\mathrm{2MOH \rightleftharpoons H_2O + MO + M} \qquad \text{(Step 9)}$$

$$\mathrm{2M + O_2 \rightleftharpoons 2MO} \qquad \text{(Step 10)}$$

$$\mathrm{CO + MO \rightleftharpoons MOCO} \qquad \text{(Step 11)}$$

$$\mathrm{MOCO \rightleftharpoons CO_2 + M} \qquad \text{(Step 12)}$$

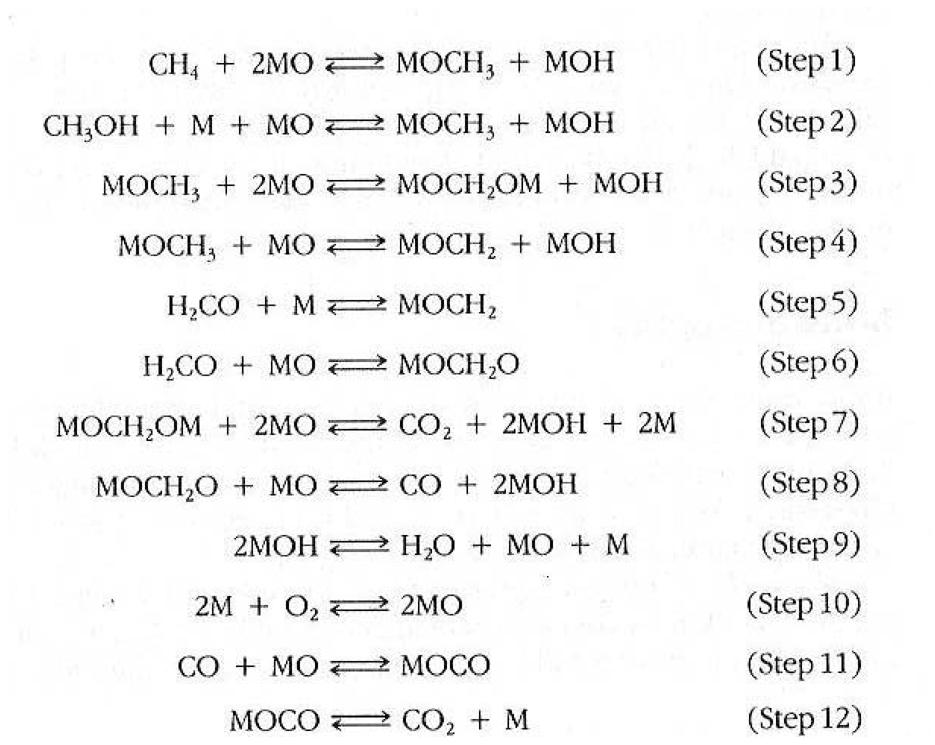
Development of the model

- Combined consideration of the oxidations of carbon monoxide, formaldehyde, methanol, and methane

- Agreement with available literature

- No assumptions about the existence of rate-determining steps or most abundant surface intermediates

- All steps reversible; two pathways for CO_2 formation



$CH_4 + 2MO \rightleftharpoons MOCH_3 + MOH$ (Step 1)

$CH_3OH + M + MO \rightleftharpoons MOCH_3 + MOH$ (Step 2)

$MOCH_3 + 2MO \rightleftharpoons MOCH_2OM + MOH$ (Step 3)

$MOCH_3 + MO \rightleftharpoons MOCH_2 + MOH$ (Step 4)

$H_2CO + M \rightleftharpoons MOCH_2$ (Step 5)

$H_2CO + MO \rightleftharpoons MOCH_2O$ (Step 6)

$MOCH_2OM + 2MO \rightleftharpoons CO_2 + 2MOH + 2M$ (Step 7)

$MOCH_2O + MO \rightleftharpoons CO + 2MOH$ (Step 8)

$2MOH \rightleftharpoons H_2O + MO + M$ (Step 9)

$2M + O_2 \rightleftharpoons 2MO$ (Step 10)

$CO + MO \rightleftharpoons MOCO$ (Step 11)

$MOCO \rightleftharpoons CO_2 + M$ (Step 12)

$$\boxed{K_{i,eq} = \frac{k_{i,for}}{k_{i,rev}} = \exp\left(\frac{\Delta S_i^0}{k_B}\right)\exp\left(-\frac{\Delta H_i^0}{k_B T}\right)}$$

Calibration of the model

Estimation of preexp. factors

Estimation of ΔH for each elementary step + additional use of Evans-Polanyi correl.

Estimation of bond strength (constrained to physically reasonable limits)

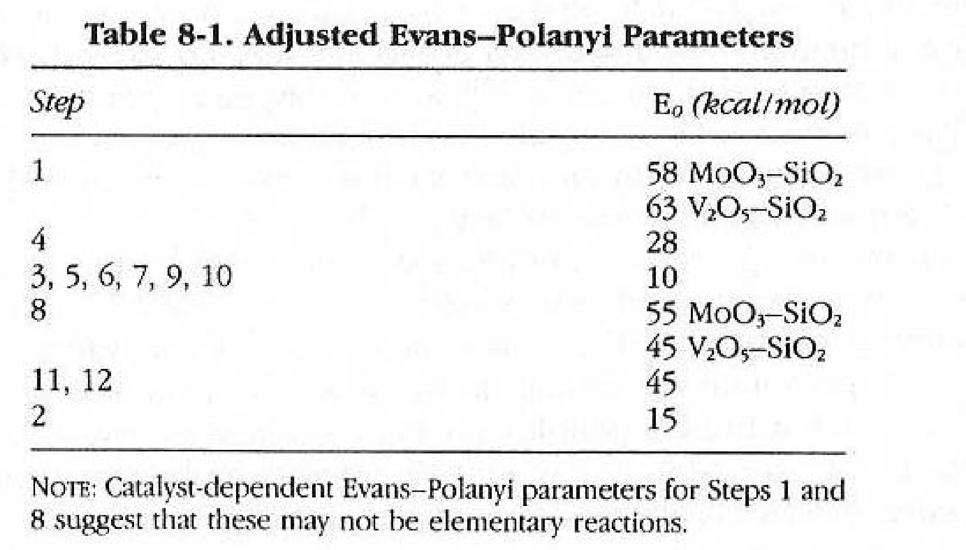


Table 8-1. Adjusted Evans–Polanyi Parameters

Step	E_0 *(kcal/mol)*
1	58 MoO_3–SiO_2 63 V_2O_5–SiO_2
4	28
3, 5, 6, 7, 9, 10	10
8	55 MoO_3–SiO_2 45 V_2O_5–SiO_2
11, 12	45
2	15

NOTE: Catalyst-dependent Evans–Polanyi parameters for Steps 1 and 8 suggest that these may not be elementary reactions.

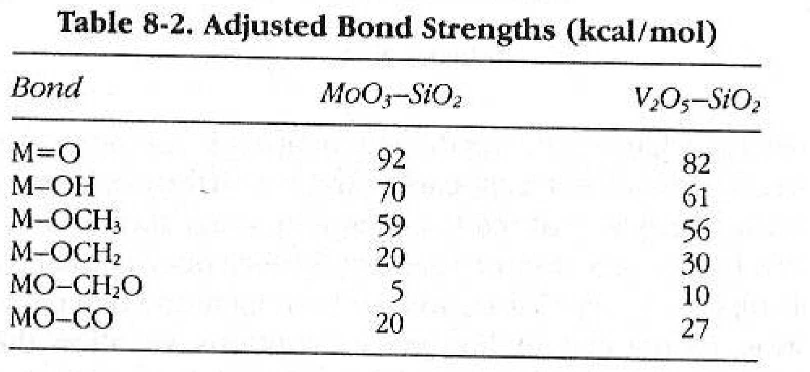


Table 8-2. Adjusted Bond Strengths (kcal/mol)

Bond	*MoO_3–SiO_2*	*V_2O_5–SiO_2*
M=O	92	82
M–OH	70	61
$M–OCH_3$	59	56
$M–OCH_2$	20	30
$MO–CH_2O$	5	10
MO–CO	20	27

Comparison of Experiment and Model

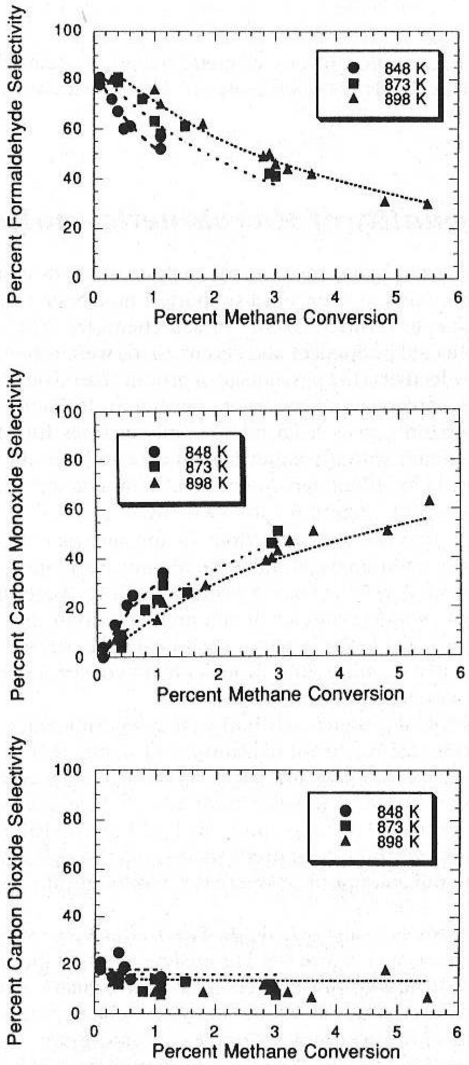


Figure 8-1. Calculated and experimental HCHO, CO, and CO_2 selectivities versus CH_4 conversion over MoO_3–SiO_2. Symbols correspond to experimental data, and lines to model predictions.

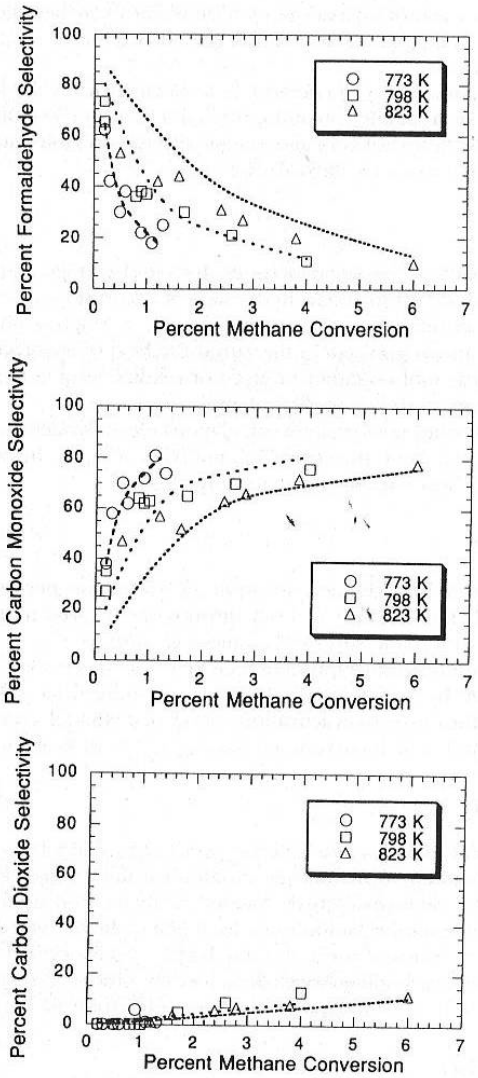


Figure 8-2. Calculated and experimental HCHO, CO, and CO_2 selectivities versus CH_4 conversion over V_2O_5–SiO_2. Symbols correspond to experimental data, and lines to model predictions.

Comparison of Experiment and Model

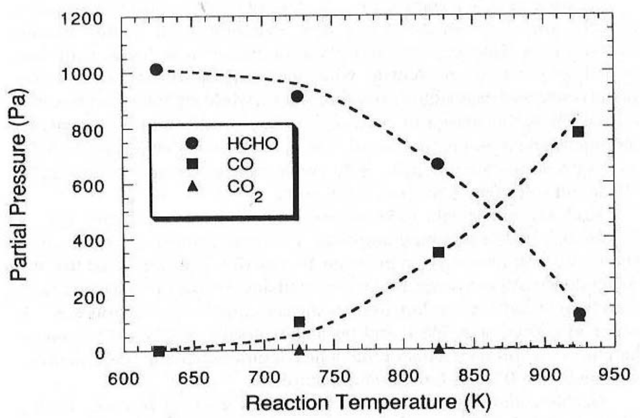


Figure 8-3. Calculated and experimental product distribution from HCHO oxidation over MoO_3–SiO_2. Symbols correspond to experimental data, and lines to model predictions.

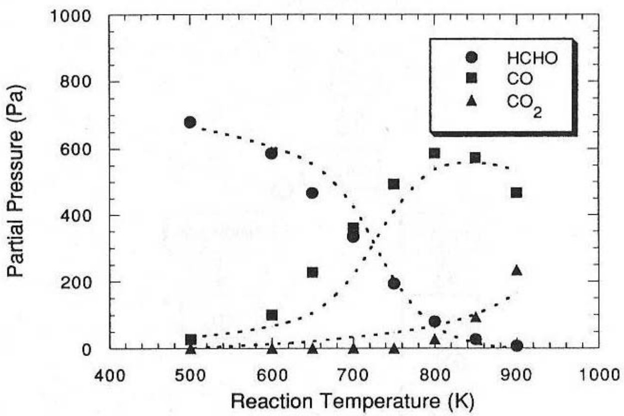


Figure 8-5. Calculated and experimental product distribution from HCHO oxidation over V_2O_5–SiO_2. Symbols correspond to experimental data, and lines to model predictions.

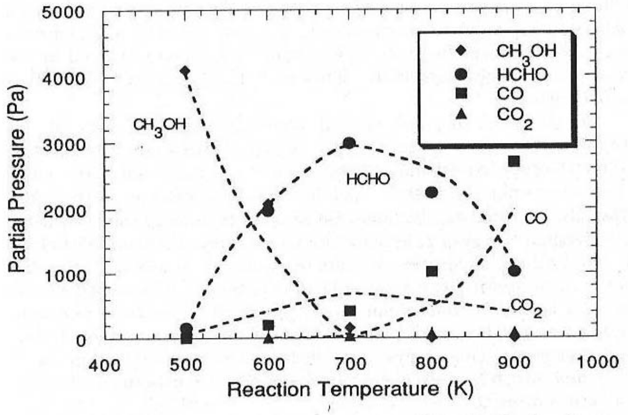
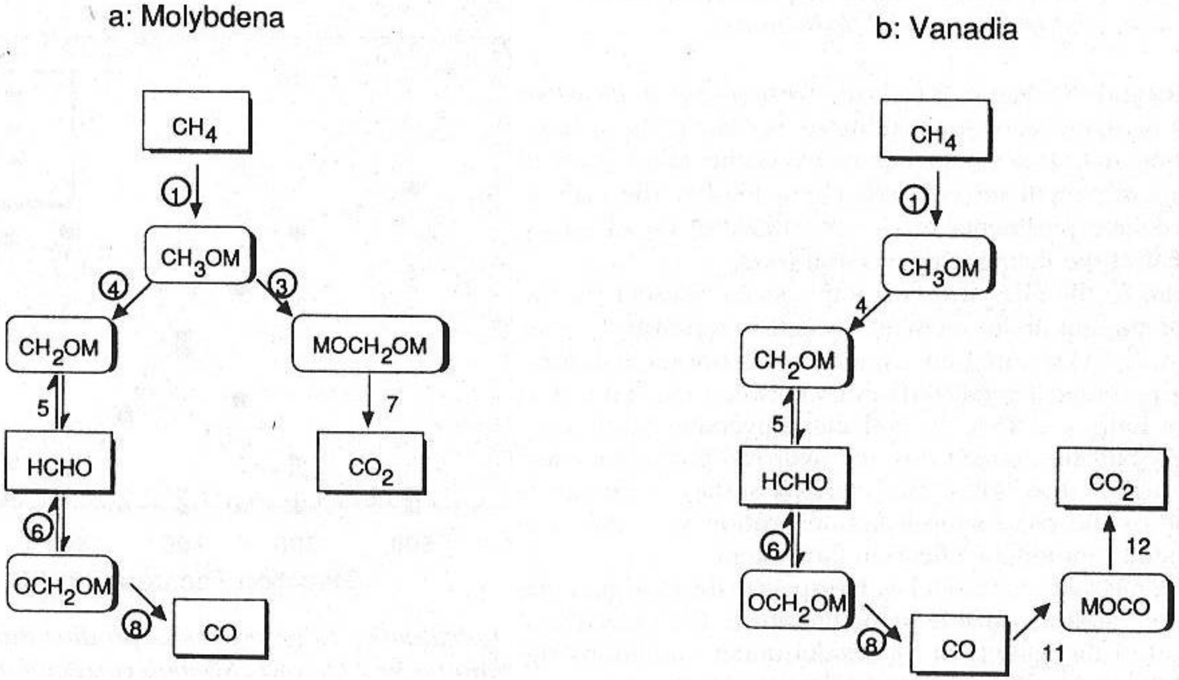


Figure 8-4. Calculated and experimental product distribution from CH_3OH oxidation over MoO_3–SiO_2. Symbols correspond to experimental data, and lines to model predictions.

Agreement of model and experimental data for different temperatures and different experimental conditions

Active Steps during CH_4 partial oxidation



Molecular Orbital Studies

Coordination number affects the electronic structure of transition metal oxides

Major effect of cation coordination is the energy of the d bands

The number of d-orbitals with high energy number increases with coordination

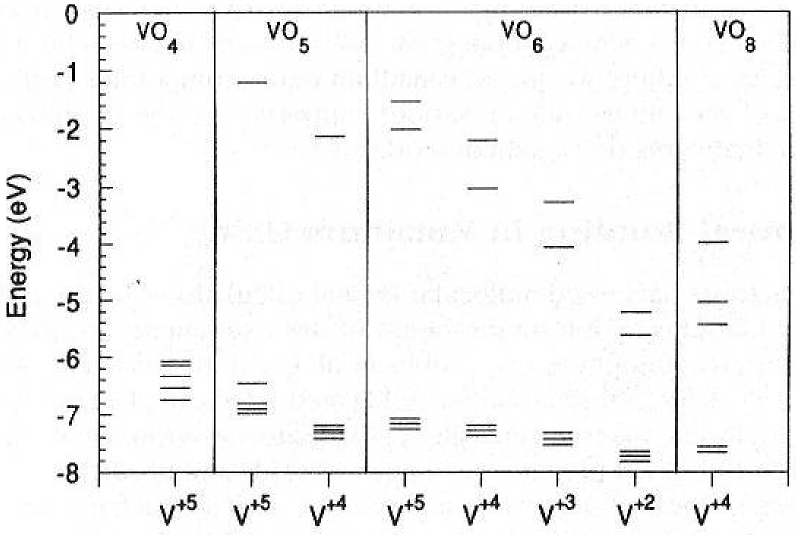


Figure 8-7. Effect of coordination number on the d-orbital energies in vanadium oxides.

Analysis of Adsorption

$$CH_4 + 2MO \rightleftharpoons MOCH_3 + MOH$$

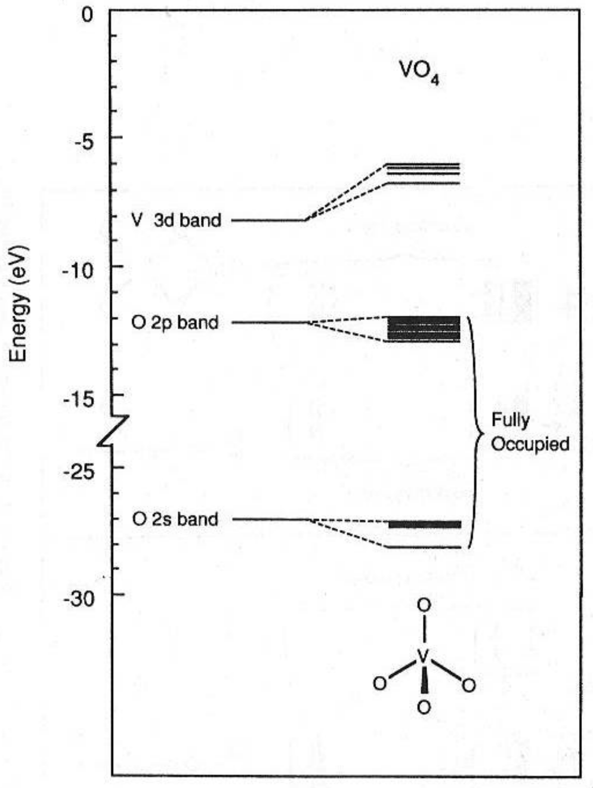


Figure 8-8. Electronic correlation diagram for VO_4^{3-}.

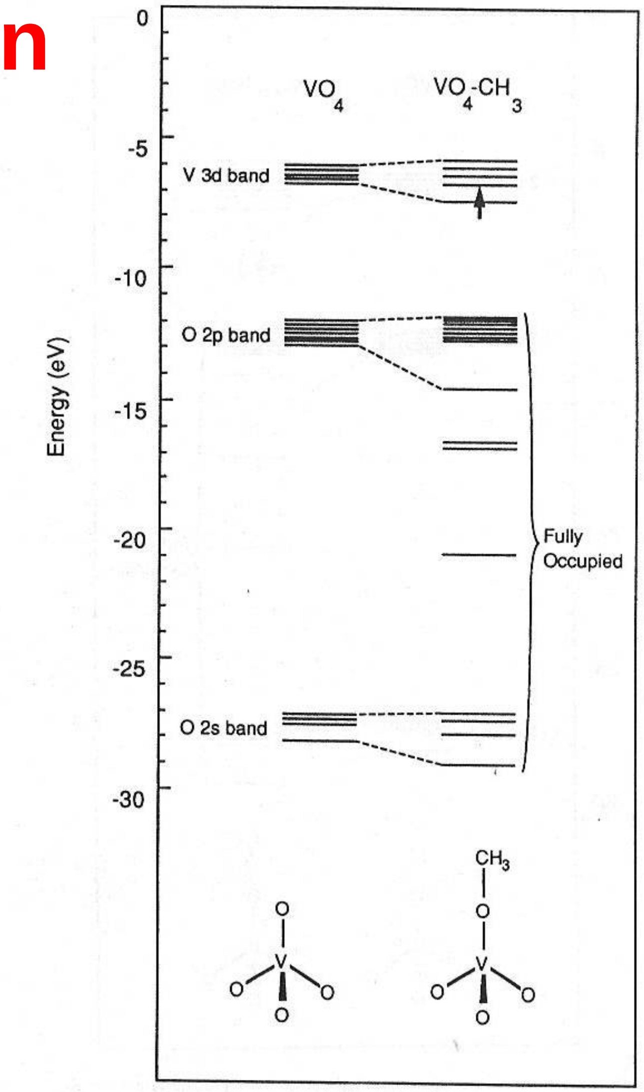


Figure 8-9. Electronic correlation diagram for CH_3 *adsorption*
VO_4^{3-}.

Microkinetic Analysis

Combination of available *experimental* data, *theoretical* principles and appropriate correlations relevant to the catalytic process in a *quantitative* fashion

Literature

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