A quantitative analysis of transient kinetic experiments: the oxidation of CO by O2/NO on Pt

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A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by $O_2$/NO on Pt

Jan Huinink
A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by O₂/NO on Pt

Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof. dr. J.H. van Lint, voor een commissie aangewezen door het College van Dekanen in het openbaar te verdedigen op woensdag 24 mei 1995 om 16.00 uur

Door

Jan Pieter Huinink

geboren te Amstelveen
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Summary

Transient response experiments provide an alternative approach for studying reaction kinetics. In comparison to steady-state experiments extra information is obtained due to the time-resolved observations, which allows in principle better discrimination between alternative kinetic models, as well as estimations of the reaction rate coefficients of the individual elementary steps. In this thesis emphasis was put on the development of a method for the quantitative determination of the reaction rate coefficients of the individual elementary steps from transient pulse experiments. This method was applied to the oxidation of carbon monoxide on polycrystalline platinum powder.

With the Temporal Analysis of Products (TAP) set-up, developed by Gleaves and co-workers, the kinetics of the elementary reaction steps can be studied on catalysts, similar to commercial ones, under relevant reaction conditions. Since January 1992 the "Laboratorium voor Chemische Technologie" at the Eindhoven University of Technology has a TAP apparatus at its disposal. In a typical TAP pulse experiment reactants are pulsed over the catalyst and the transient output response of reactants and products is followed with a mass spectrometer. The millisecond time resolution of TAP allows determination of fast elementary reaction steps. The coverage of surface species can be adjusted by the small pulse size.

The pulse moves through the catalyst bed as the result of a pressure gradient across the reactor. For the description of the gas transport, experiments with inert gases were performed to determine the influence of temperature, pulse size, molecular weight of the used gases, and interpellet and intrapellet void dimensions on the gas transport. By using an appropriate constitutive model for the gas transport, the effect of the inlet gas pulse size on the relative contribution to the flux of each mode of gas transport, namely Knudsen diffusion, molecular diffusion and viscous flow, was quantified. The interpretation of the kinetic experiments could be simplified to a large extent by performing the experiments in the Knudsen regime.
Contrary to stationary experiments, the elimination of diffusion limitations inside porous pellets is not straightforward under transient conditions. First a situation where chemical reactions are absent was analysed. The fixed bed consisted of porous pellets with a pellet size up to 0.25 mm and pores of diameters as low as 8 nm. A model was derived, taking into account Knudsen diffusion and accumulation in the interpellet void space and in the pores of the pellets. The Knudsen diffusion through the pores of the pellets occurred on a much smaller time scale than diffusion through the catalyst bed, meaning that at any time the concentration in the pores could be considered equal to the concentration at the external surface of the pellets. Therefore, intrapellet diffusion could be accounted for simply by adding to the interpellet void space the accumulation term corresponding to the intrapellet porosity. In zeolites diffusion in the pellet pores cannot be considered instantaneous and has to be taken fully into account.

Next, the occurrence of both reaction and transport was considered. The minimum and maximum values of the reaction rate coefficients that can be measured with the TAP microreactor were determined for a pseudo first order reaction. The upper limit follows from the requirement that the response signal has to be larger than the noise level. The lower limit is imposed by the requirement that the response signal has to be distinguishable from the signal in case of diffusion only. Pseudo first order reaction rate coefficients with values in a window between $1 \text{s}^{-1}$ and $1 \times 10^4 \text{s}^{-1}$ can be determined experimentally.

A model was derived, which describes the gas transport, adsorption, desorption and reaction processes occurring within the TAP microreactor after injecting a pulse. With the model the outlet molar flow rate of all gas phase reactants and products could be calculated as a function of time.

The carbon monoxide oxidation experiments were carried out in the temperature range of 323 to 365 K at pressures in the range of 0.1 to 1 mbar. On the time scale of an experiment migration of adsorbed carbon monoxide could be neglected. The results could only be explained by postulating the existence of islands of carbon monoxide and oxygen on the surface. Starting from a surface with a known coverage of oxygen or carbon monoxide, it was possible to investigate separate parts of the reaction pathway. A model taking into account a carbon monoxide physisorption equilibrium, followed by chemisorption of carbon monoxide on vacant surface sites next to carbon monoxide or oxygen islands and instantaneous reaction between chemisorbed carbon monoxide and oxygen at the periphery of the oxygen islands, described the experiments quantitatively. At temperatures from 323 to 365 K the rate coefficients for this model were determined as a function of the surface coverage. The carbon monoxide physisorption equilibrium coefficient was nearly independent of coverage and temperature. The probability that a carbon monoxide molecule chemisorbs on a vacant surface
site next to a carbon monoxide or an oxygen island was dependent on the degree of coverage and independent of temperature.

At temperatures above 150 K oxygen adsorbed dissociatively on platinum. Desorption of oxygen adatoms was negligible up to 490 K. The molecular adsorption of dioxygen was in equilibrium, the dissociation of molecular adsorbed oxygen being the rate-determining step. The dissociation of molecular adsorbed oxygen was slightly activated with an activation energy of 8.6 kJ mol⁻¹.

The simultaneous oxidation of carbon monoxide and reduction of nitric oxide over platinum was also investigated. At low temperatures, i.e. between 400 and 450 K, oxidation of carbon monoxide mainly took place via the bimolecular surface reaction between adsorbed carbon monoxide and nitric oxide leading to carbon dioxide and nitrogen adatoms. Nitric oxide did not dissociate at these temperatures. Dinitrogen was mainly formed by the dissociation of adsorbed nitrous oxide. The latter originating from the surface reaction between nitrogen adatoms and molecularly adsorbed nitric oxide. At high temperatures, i.e. between 500 and 700 K, carbon dioxide was formed through the reaction between adsorbed carbon monoxide and oxygen adatoms, the latter originating from nitric oxide dissociation. Nitrous oxide formation was absent and dinitrogen was formed by recombination of nitrogen adatoms, produced by nitric oxide dissociation.

Isotopic oxygen labelling experiments were performed at 479 K in order to investigate the interaction of carbon dioxide with the catalyst. Carbon dioxide adsorbed sufficiently on the platinum surface to exchange oxygen atoms with oxygen adatoms on the surface. The oxygen exchange was rather fast compared to carbon dioxide desorption.
A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by O\textsubscript{2}/NO on Pt
SAMENVATTING

Transiënte responseexperimenten vormen een alternatieve methode voor de bestudering van de reactiekinetiek. In vergelijking met stationaire experimenten wordt extra informatie verkregen uit de tijdsafhankelijke waarnemingen, waardoor in principe zowel een beter onderscheid gemaakt kan worden tussen de mogelijke kinetische modellen, als schattingen van de reactiesnelheidsoëfficiënten van de individuele elementaire stappen gemaakt kunnen worden. In dit proefschrift werd de nadruk gelegd op de ontwikkeling van een methode voor de kwantitatieve bepaling van de reactiesnelheidsoëfficiënten van de individuele elementaire stappen uit transiënte pulsexperimenten. Deze methode werd toegepast op de oxidatie van koolmonoxide over polykristallijn platina poeder.

Met de "Temporal Analysis of Products" (TAP) opstelling, ontwikkeld door Gleaves en medewerkers, kan de kinetiek van de elementaire reactiestappen worden bestudeerd op katalysatoren, die lijken op commerciële katalysatoren, onder relevante reactiecondities. Sinds januari 1992 beschikt het Laboratorium voor Chemische Technologie van de Technische Universiteit Eindhoven over een TAP-apparaat. In een typisch TAP-pulseexperiment worden de reactanten over de katalysator gepulst en wordt de transiënte uitlaatrespons van de reactanten en produkten gevolgd met een massaspectrometer. De milliseconden tijdsresolutie van TAP maakt detectie van snelle elementaire reactiestappen mogelijk. De bedekkingsgraad van oppervlakspecies kan worden ingesteld door de kleine pulsgrootte.

De puls beweegt door het katalysatorbed onder invloed van een drukverschil door de reactor. Voor het beschrijven van het gastransport werden experimenten met inerte gassen uitgevoerd om de invloed van de temperatuur, de pulsgrootte, het molecuulgewicht van de gebruikte gassen en de grootte van de lege ruimtes tussen de korrels en de inwendige poriën van de korrels op het stoftransport te bepalen. Door een geschikt samengesteld model voor het gastransport te gebruiken, kon het effect van de inlaatpulsgrootte op de relatieve bijdrage aan
de flux van iedere vorm van gastransport, te weten Knudsendiffusie, moleculaire diffusie en visceuze stroming, worden bepaald. De interpretatie van de kinetische experimenten kon in belangrijke mate vereenvoudigd worden door de experimenten uit te voeren onder Knudsencondities. In tegenstelling tot stationaire experimenten is het uitsluiten van diffusielimiteringen in de poreuze korrels niet rechtoe, rechtaan onder transiente condities. Allereerst werd de situatie geanalyseerd, waarin chemische reacties afwezig waren. Het vaste bed bestond uit poreuze korrels met een korreldiameter tot 0,25 mm en poriën met diameters vanaf 8 nm. Een model werd afgeleid, dat rekening houdt met Knudsendiffusie en accumulatie in de uitwendige ruimtes tussen de korrels en in de inwendige poriën van de korrels. De Knudsendiffusie in de poriën van de korrels vond op een veel kleinere tijdschaal plaats dan diffusie door het katalysatorbed, hetgeen betekent dat op ieder moment de concentratie in de poriën gelijk was aan de concentratie aan de buitenzijde van de korrels. Daarom kon met inwendige diffusie in de korrels rekening worden gehouden door de porositeit van de lege ruimtes tussen de korrels simpelweg te verhogen met de accumulatieterm, die correspondeert met de porositeit van de inwendige poriën. In zeolieten is de diffusie in de poriën van de korrels niet instantaan en dient volledig meegenomen te worden.

Vervolgens werd de situatie beschouwd waarin naast stoftransport ook reactie plaatsvindt. De minimaal en maximaal waarden voor reactiesnelheidscoëfficiënten die gemeten konden worden met de TAP-microreactor werden bepaald voor een pseudo eerste orde reactie. De bovenlimiet wordt bepaald doordat het responssignaal groter dient te zijn dan het ruïnsniveau. De onderlimiet wordt opgelegd doordat het responsignaal onderscheidbaar dient te zijn van het signaal indien alleen diffusie plaatsvindt. Waarden voor pseudo eerste orde reactiesnelheidscoëfficiënten kunnen verkregen worden in het venster van $10^{-4}$ tot $10^4$ s$^{-1}$.

Een model werd afgeleid, dat de transport-, adsorptie-, desorptie- en reactieprocessen beschrijft die plaatsvinden in de TAP-microreactor na het geven van een puls. Met het model konden de uitaat molaire debieten van alle gasfase reactanten en produkten berekend worden als functie van de tijd.

De koolmonoxide-oxidatie-experimenten werden uitgevoerd in het temperatuurgebied van 323 tot 365 K bij drukken van 0,1 tot 1 mbar. Op de tijdschaal van een experiment kon de migratie van geadsorbeerde koolmonoxide verwaarloosd worden. De resultaten konden alleen verklaard worden door de aanwezigheid van koolmonoxide- en zuurstofeilanden op het oppervlak te postuleren. Het was mogelijk afzonderlijke delen van het reactiepad te onderzoeken, uitgaande van een oppervlak met een bekende zuurstof- en koolmonoxidebedekkingsgraad. Een model dat koolmonoxidefysisorptie-evenwicht beschouwt, gevolgd door chemisorptie van koolmonoxide op vrije oppervlakplaatsen naast koolmonoxide- en zuurstofeilanden en instantane reactie tussen gecombineerde koolmonoxide en zuurstof op de rand van de zuurstofeilanden, beschrijft de experimenten kwantitatief. Bij temperaturen
van 323 tot 365 K werden de snelheidscoëfficiënten van dit model bepaald als functie van de oppervlak-bedekkingsgraad. De koolmonoxidefysisorptie-evenwichtscoëfficiënt was nagenoeg onafhankelijk van de bedekkingsgraad en temperatuur. De kans dat een koolmonoxide-molecuul chemisorbeert op een vrije plaats naast een koolmonoxide- of zuurstofeiland is afhankelijk van de bedekkingsgraad en onafhankelijk van de temperatuur.

Bij temperaturen boven 150 K adsorbeerde zuurstof dissociatief op platina. Desorptie van geadsorbeerde zuurstofatomen was verwaarloosbaar tot 490 K. De moleculaire adsorptie van dizuurstof was in evenwicht en de dissociatie van moleculair geadsorbeerde zuurstof was de snelheidsbepalende stap. De dissociatie van moleculair geadsorbeerde zuurstof was iets activer met een activeringsenergie van 8,6 kJ mol⁻¹.

De simultane oxidatie van koolmonoxide en reductie van stikstofmonoxide over platina werd bestudeerd. Bij lage temperaturen, d.w.z. tussen 400 en 450 K, vond de oxidatie van stikstofmonoxide hoofdzakelijk plaats via de bimoleculaire oppervlakreactie tussen geadsorbeerde koolmonoxide en stikstofmonoxide resulterend in de vorming van kooldioxide en geadsorbeerde stikstof. Stikstofmonoxide dissocieerde bij deze temperaturen niet. Distikstof werd hoofdzakelijk gevormd door dissociatie van geadsorbeerde distikstofmonoxide. Dit laatste werd gevormd door de oppervlakreactie tussen geadsorbeerde stikstofatomen en stikstofmonoxidemoleculen. Bij hoge temperaturen, d.w.z. tussen 500 en 700 K, werd kooldioxide gevormd door de reactie tussen geadsorbeerde koolmonoxide en zuurstof, het laatstgenoemde afkomstig van stikstofmonoxidedissociatie. Er werd geen distikstofmonoxide gevormd en distikstof werd gevormd door recombinatie van geadsorbeerde stikstofatomen, die afkomstig waren van stikstofmonoxidedissociatie.

Isotoop experimenten met gelabeled zuurstof werden uitgevoerd bij 479 K om de interactie van kooldioxide met de katalysator te onderzoeken. Kooldioxide adsorbeerde voldoende lang op het platina-oppervlak om zuurstofatomen uit te wisselen met geadsorbeerde zuurstofatomen op het oppervlak. De zuurstofuitwisseling was beduidend sneller dan de desorptie van kooldioxide.
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NOTATION

Roman symbols

\( a \)  
external catalyst surface area per unit catalyst volume  
\( m_c^2 m_c^{-3} \)

\( A \)  
cross section area of the reactor 
\( m_c^2 \)

\( A_0 \)  
pre-exponential factor  
reaction dependent

\( b \)  
maximum likelihood parameter estimate  
\( m_g^2 \)

\( b \)  
matrix of maximum likelihood parameter estimates 
\( \text{mol} m_g^{-3} \)

\( B_0 \)  
D'Arcy constant 
\( \text{mol} \)  
\( \text{mol} m_g^{-3} \)

\( C \)  
concentration  
\( \text{mol} m_g^{-3} \) or  
\( \text{mol} m_g^{-3} \)

\( \bar{C} \)  
Laplace transform of \( C \) with respect to dimensionless time or time  
\( \text{mol} m_g^{-3} \)

\( \bar{C}^* \)  
Laplace transform of \( C \) with respect to dimensionless time and position  
\( \text{mol} m_g^{-3} \)

\( \text{CO}^{*}_{\text{CO}} \)  
chemisorbed CO molecule not next to an O island  
\( m \)

\( \text{CO}^{*}_{0} \)  
chemisorbed CO molecule next to an O island  
\( m \)

\( d_i \)  
diameter of interstitial voids  
\( m \)

\( d_p \)  
pellet diameter  
\( m \)

\( D \)  
diffusion coefficient  
\( m_g^2 s^{-1} \)

\( D_{e} \)  
effective diffusion coefficient 
\( m_g^3 m_g^{-1} s^{-1} \) or \( m^2 s^{-1} \)

\( D_{D} \)  
Damköhler I number \( (= e_b k_1 l_2^2 D_e^{K+1}) \)  
\( J \text{ mol}^{-1} \)

\( E_a \)  
activation energy  
\( J \text{ mol}^{-1} \)

\( E_s \)  
surface migration activation energy 
\( J \text{ mol}^{-1} \)

\( F \)  
ratio of mean regression sum of squares to the residual sum of squares  
\( \text{mol} s^{-1} \)

\( F \)  
molar flow rate
<table>
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<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
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<tr>
<td>$\mathcal{F}$</td>
<td>Laplace transform of $F$ with respect to dimensionless time or time</td>
<td>mol s$^{-1}$ or mol</td>
</tr>
<tr>
<td>$\tilde{F}$</td>
<td>calculated molar flow rate</td>
<td>mol s$^{-1}$</td>
</tr>
<tr>
<td>FWHH</td>
<td>full width at half height</td>
<td>s</td>
</tr>
<tr>
<td>$g(s)$</td>
<td>function, defined by equation 3.68</td>
<td>s</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>enthalpy</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$I_e$</td>
<td>electric current</td>
<td>C s$^{-1}$</td>
</tr>
<tr>
<td>$k$</td>
<td>summation index</td>
<td>reaction dependent</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction rate coefficient</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$k_c$</td>
<td>chemisorption rate coefficient</td>
<td>$\text{m}_g^3 \text{m}_e^{-2}$</td>
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<tr>
<td>$K_p$</td>
<td>physisorption equilibrium coefficient</td>
<td>$\text{m}_g^3 \text{m}_e^{-1} \text{s}^{-1}$</td>
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<tr>
<td>$K_e$</td>
<td>effective viscous flow factor</td>
<td>$\text{m}$</td>
</tr>
<tr>
<td>$l$</td>
<td>length</td>
<td>$\text{m}$</td>
</tr>
<tr>
<td>$l_b$</td>
<td>bed length</td>
<td>$\text{m}$</td>
</tr>
<tr>
<td>$l_p$</td>
<td>length of intraparticle pores</td>
<td>$\text{m}$</td>
</tr>
<tr>
<td>$l_1$</td>
<td>bed length of first inert bed</td>
<td>$\text{m}$</td>
</tr>
<tr>
<td>$l_2$</td>
<td>bed length of catalytic bed</td>
<td>$\text{m}$</td>
</tr>
<tr>
<td>$l_3$</td>
<td>bed length of second inert bed</td>
<td>$\text{m}$</td>
</tr>
<tr>
<td>$L$</td>
<td>maximal molar concentration per square meter catalyst surface</td>
<td>mol m$^{-2}$</td>
</tr>
<tr>
<td>$m_i$</td>
<td>$i^{th}$ moment</td>
<td>mol s$^{-1}$</td>
</tr>
<tr>
<td>$M$</td>
<td>molecular mass</td>
<td>kg mol$^{-1}$</td>
</tr>
<tr>
<td>$n$</td>
<td>number</td>
<td></td>
</tr>
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<td>$n$</td>
<td>number of observations</td>
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<tr>
<td>$n$</td>
<td>summation index</td>
<td></td>
</tr>
<tr>
<td>$N$</td>
<td>molar flux with respect to fixed reactor coordinates</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$N_{A,p}$</td>
<td>molar flux of component A into pellets</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$\mathcal{N}_{A,p}$</td>
<td>Laplace transform of $N_{A,p}$ with respect to time</td>
<td>mol m$^{-2}$</td>
</tr>
<tr>
<td>$N_i$</td>
<td>set of stoichiometric numbers for global reaction $i$</td>
<td>mol</td>
</tr>
<tr>
<td>$N_p$</td>
<td>amount of a component in inlet pulse</td>
<td></td>
</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$p$</td>
<td>Laplace transform variable with respect to dimensionless position</td>
<td></td>
</tr>
<tr>
<td>$p$</td>
<td>number of parameters</td>
<td></td>
</tr>
<tr>
<td>$r$</td>
<td>reaction rate</td>
<td>mol m$^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>$r$</td>
<td>function, defined by equation 4.37</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$R_i$</td>
<td>production rate of component $i$ on the surface</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
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<td>gas constant</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>RT</td>
<td>molar thermal energy</td>
<td>J mol$^{-1}$</td>
</tr>
</tbody>
</table>
\( s \)  
Laplace transform variable with respect to dimensionless time or time  
- or \( s^{-1} \)

\( s(h) \)  
estimated standard errors

\( S(h) \)  
objective function

\( t \)  
time

\( t(n-p,1-\alpha/2) \)  
tabulated \( \alpha/2 \)-percentage point of the \( t \)-distribution with \( n-p \) degrees of freedom

\( \bar{t} \)  
mean residence time

\( T \)  
temperature

\( \nu \)  
number of responses

\( V \)  
volume

\( \overline{v} \)  
average molecular speed

\( V_{pot} \)  
potential energy

\( x \)  
mole fraction

\( x \)  
alxial coordinate in reactor

\( \Delta x \)  
distance between two mesh points

\( X \)  
conversion

\( y \)  
pellet coordinate

\( z \)  
dimensionless axial coordinate (\( = x \) \( l_b^{-1} \))

\( s|_{\text{co}} \)  
vacant surface site not next to an \( O \) island

\( s|_{\text{o}} \)  
vacant surface site next to an \( O \) island

**Greek symbols**

\( \alpha \)  
see \( t(n-p,1-\alpha/2) \)

\( \beta \)  
parameter

\( \beta \)  
matrix of parameters

\( \delta_x \)  
delta function with respect to axial coordinate = \( \delta(x=0) \)

\( \delta_z \)  
delta function with respect to dimensionless axial coordinate = \( \delta(z=0) \)

\( \varepsilon_b \)  
bed porosity

\( \varepsilon_p \)  
pellet porosity

\( \varepsilon_r \)  
total porosity of reactor

\( \theta \)  
fractional coverage on the catalyst surface

\( \theta_{co}|_{\text{co}} \)  
fraction of chemisorbed CO molecules not next to \( O \) islands

\( \theta_{co}|_{\text{o}} \)  
fraction of chemisorbed CO molecules next to \( O \) islands

\( \theta_{v|\text{co}} \)  
fraction of vacant surface sites not next to \( O \) islands

\( \theta_{v|\text{o}} \)  
fraction of vacant surface sites next to \( O \) islands
A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by O₂/NO on Pt

\[ \Theta \] characteristic time \hspace{1cm} \text{s}

\[ \lambda_{a}^{2} \] function, defined by equation 4.36 \hspace{1cm} \text{s}^{-1}

\[ \mu \] dynamic viscosity \hspace{1cm} \text{Pa s}

\[ \mu_{i} \] \( i \)th normalised moment \((= \frac{m_{i}}{m_{0}^{2}})\) \hspace{1cm} \text{s}^{-1}

\[ \nu \] atomic and structural diffusion volume increment \hspace{1cm} \text{mol}^{-1}

\[ \zeta \] dummy integration variable \hspace{1cm} \text{s}

\[ \sigma \] stoichiometric number

\[ \sigma^{*} \] element of the inverse of the error variance-covariance matrix

\[ \tau \] normalised time \((= \frac{D_{c,A}^{K} \cdot \varepsilon_{b} \cdot l_{b}}{l_{b}})\) \hspace{1cm} \text{mol}^{-2}

\[ \tau_{b} \] bed tortuosity \hspace{1cm} \text{mol}^{-2}

\[ \tau_{p} \] pellet tortuosity \hspace{1cm} \text{mol}^{-2}

**Superscripts**

b \hspace{1cm} backwards
d \hspace{1cm} diffusion
K \hspace{1cm} Knudsen
LH \hspace{1cm} Langmuir-Hinshelwood
m \hspace{1cm} molecular
s \hspace{1cm} surface
v \hspace{1cm} viscous
0 \hspace{1cm} initial or inlet condition

**Subscripts**

a \hspace{1cm} adsorption
ads \hspace{1cm} adsorption
A \hspace{1cm} with respect to A
b \hspace{1cm} bed; interstitial voids
c \hspace{1cm} catalyst
B \hspace{1cm} with respect to B
BET \hspace{1cm} specific surface area using the BET method
d \hspace{1cm} desorption
des \hspace{1cm} desorption
dif \hspace{1cm} diffusion
diss \hspace{1cm} dissociation
e \hspace{1cm} effective
**Notation**

- **i**: component i; interstitial
- **j**: component j
- **k**: bed number
- **LH**: Langmuir-Hinshelwood
- **m**: molecular; number of mesh points
- **merc.**: mercury porosimetry
- **p**: pellet; particle; intraparticle; physisorbed
- **QMS**: quadrupole mass spectrometer
- **r**: reaction
- **reac**: reaction
- **s**: surface
- **t**: total
- **l**: first order reaction
- **v**: vacant sites
A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by O₂/NO on Pt
The knowledge of the kinetics of chemical reactions, i.e. the way in which the rates of reactions depend upon process conditions, forms the basis for the design and optimisation of chemical reactors. Most industrial reactors are operated at steady-state. The time scale of changes in process conditions is large compared to the time scale of the reactions. The development of steady-state rate equations provides some insight into the reaction mechanism. In the steady-state approximation the accumulation of reactive intermediates is neglected, which is equivalent to the assumption that the rates of the consecutive individual steps making up the global reaction are equal to each other. Steady-state rate equations often correspond to more than one reaction mechanism. Moreover regression of steady-state kinetic data provides usually estimates of combinations of individual kinetic parameters, rather than estimates of the individual parameters themselves. Therefore steady-state studies are sufficient to describe the overall performance of a catalyst, but they generally do not provide an adequate picture of a complex reaction mechanism.

Transient response experiments form an alternative approach for studying reaction kinetics. Wagner and Hauffe (1938) were the first to apply the transient response technique. They studied the reaction between oxygen and adsorbed hydrogen on palladium by measuring the electrical conductivity response to the change of oxygen flow, but the results obtained were rather qualitative. Bennett (1967, 1982) proposed the use of the transient response method for a heterogeneous catalytic reaction and suggested that this method could be used to calculate the reaction rate coefficients of the individual steps. In recent years transient experiments have found wide application in heterogeneous catalytic research.

Transients or perturbations are introduced by changing one or more of the state variables such as feed concentration, molar flow rate, pressure or temperature. Examples of transient techniques are concentration modulated non steady-state reactor experiments, temperature
programmed experiments and molecular beam scattering experiments. The latter technique is only applied to single crystals. Transient techniques provide information on the kinetics of the elementary steps, because the steady-state approximation cannot be applied to the reactive intermediates and the rates of the consecutive individual steps in a reaction sequence are not equal any more to each other during the imposed transient. A measurement of the individual rates leads to the kinetic parameters of the individual steps. The transient or perturbation should be imposed on a time scale, which is small compared to the relaxation time of the sequence of elementary steps, i.e. the time interval that allows a sequence of elementary steps to reach the steady-state after an instantaneous perturbation.

Until recently, an experimental non steady-state reactor set-up had a time resolution around 1 s. Both the introduction of the perturbation and the sampling of the response signal were limiting the latter. The Temporal Analysis of Products (TAP) set-up, developed by Gleaves and co-workers (Gleaves et al. (1988)) operates in the millisecond time regime, i.e. more than two orders of magnitude better than the conventional transient experimental set-ups by paying special attention to both limiting factors. Since January 1992 the "Laboratorium voor Chemische Technologie" at the Eindhoven University of Technology has a TAP apparatus at its disposal. With the TAP set-up the kinetics can be studied on catalysts, similar to commercial ones, under relevant reaction conditions. In a typical TAP pulse experiment, reactants are pulsed over the catalyst and the transient output response of reactants and products is followed with a mass spectrometer. The millisecond time resolution of TAP allows determination of fast elementary reaction steps. The coverage of surface species can be adjusted by the small pulse size.

The aim of the present thesis was to develop a method for the quantitative determination of kinetic parameters of elementary reaction steps from transient pulse experiments. This method was applied to the oxidation of carbon monoxide by oxygen or nitric oxide on polycrystalline platinum. The reactions have been studied by means of transient kinetic experiments with the TAP set-up. In addition to the obvious environmental significance, there was also the potential to gain fundamental insight into heterogeneous catalysis.

The simultaneous oxidation of carbon monoxide and reduction of nitric oxide over noble metal catalysts is a widely used heterogeneous catalytic reaction for the removal of these pollutants from the exhaust gas of automobiles. Automotive exhaust catalysis has grown in importance since 1970, when the United States Congress approved a series of amendments to the Clean Air Act. The most controversial aspect of these amendments was the assessment of the emission standards for carbon monoxide, nitric oxide and hydrocarbons for automobiles (Vonkeman, 1990). Since 1981, automobile catalytic converters have been mandatory for all gasoline powered automobiles in the United States (Statman, 1991). Since then, the emission standards have become more and more rigid.
The automobile catalytic converter should remove three harmful pollutants simultaneously, and is therefore referred to as a three-way catalyst. Carbon monoxide in the exhaust gas has to be further oxidised to carbon dioxide, nitric oxide should be reduced to nitrogen and unburned hydrocarbons need to be oxidised to carbon dioxide and water. The first three-way catalyst was introduced in the United States by Volvo (Vonkeman, 1990). The automotive three-way catalyst contains various amounts of platinum, palladium and rhodium in order to perform these three functions.

In chapter 2 the experimental set-up and the experimental procedures are described. Furthermore the preparation and characterisation of the used polycrystalline platinum are presented. Chapter 3 deals with inert gas transport in the reactor. A model is derived for Knudsen diffusion in both interstitial and intraparticle voids. In chapter 4 a reactor model is presented, which describes the transport, adsorption, desorption and reaction processes occurring within the reactor after injection of a pulse of reactants. The range of values of rate coefficients, in which quantitative determination is possible, is assessed. Chapter 5 reports on the kinetics of carbon monoxide oxidation by oxygen on platinum. The necessity of the application of surface islands of carbon monoxide and oxygen in the modelling will be shown. The developed model allows a quantitative description of the observed effects. In chapter 6 the mechanism of the simultaneous oxidation of carbon monoxide and reduction of nitric oxide over platinum is discussed. Chapter 7 deals with isotopic oxygen exchange in $^{18}\text{OO}$ on platinum.

References

2

EQUIPMENT AND PROCEDURES

2.1 Introduction

Since January 1992 the "Laboratorium voor Chemische Technologie" at the Eindhoven University of Technology has a Temporal Analysis of Products (TAP) reactor set-up at its disposal. The TAP set-up, developed by Gleaves and co-workers (Gleaves et al., 1988), is a catalyst characterisation and evaluation set-up, in which a microreactor is encased within an ultra high vacuum chamber. Gaseous reactants are either continuously fed or pulsed into the reactor and reactants and products are monitored by a quadrupole mass spectrometer. The TAP set-up allows transient experiments to be carried out on a millisecond time scale, which is two orders of magnitude faster than with conventional transient experimental set-ups for heterogeneously catalysed reactions. Therefore, reactions proceeding at higher rates can be studied.

Primarily the TAP set-up is to be used as a pulsed reactor. In a typical TAP pulse experiment a small reactant pulse is introduced into the reactor containing catalyst and the transient responses of reactants and products are measured with a quadrupole mass spectrometer. In paragraph 2.2 the TAP apparatus is described. Paragraph 2.3 deals with the types of experiment, that can be performed with the TAP set-up. The procedures to determine the absolute calibration factors of the used gases and the number of surface sites of the catalyst are described in this paragraph as well. The single- and multi-response regression analysis, applied to minimize the difference between observed and calculated responses by application of the least square criterion, is described in paragraph 2.4. Paragraph 2.5 deals with the pretreatment and characterisation of the used catalyst.
2.2 Apparatus

The TAP set-up was described in detail by Gleaves et al. (1988), Statman (1991) and Svoboda (1993), so only the aspects relevant to the present work will be considered here. The hardware of the Temporal Analysis of Products system includes seven main components:
1. a vacuum system providing ultra high vacuum (UHV) conditions in three chambers;
2. a gas manifold assembly to which are mounted two continuous flow valves, two high speed pulse valves and a microreactor;
3. a microreactor;
4. a high pressure assembly, allowing reactor pressures during continuous flow experiments up to $2 \times 10^5$ Pa;
5. a quadrupole mass spectrometer (QMS) detector;
6. a gas preparation section;
7. a computerized data acquisition and control system.

Figure 2.1 shows an overall picture of the main part of the TAP set-up. All relevant details will be discussed.
Vacuum system

The TAP set-up consists of three vacuum chambers. The reaction chamber contains the manifold assembly, the microreactor and the high pressure assembly. Vacuum is realised by a water-cooled 10" Varian VHS10 oil diffusion pump and a Varian SD700 mechanical pump. The pressure in the reactor chamber is $10^{-4}$ to $10^{-5}$ Pa as measured with a Varian #580 ion gauge. The differential chamber is located between the reaction chamber and the analytical chamber. Vacuum in the differential chamber is provided by a water-cooled 6" Varian VHS6 oil diffusion pump with a liquid nitrogen trap and a Varian SD700 mechanical pump. The trap improves the chamber's vacuum as it prevents that oil of the diffusion pump reaches the detector chamber, and removes condensable components like water vapour, carbon dioxide and other heavier molecules from the differential chamber. Vacuum in the analytical chamber, which contains the ionisation head of the UTI 100C quadrupole mass spectrometer, is provided by a Balzers TPU450H turbomolecular pump, together with a Baltzers MD4TC diaphragm pump. The pressures in the differential and analytical chambers are measured with a Balzers IKR020 cold cathode gauge head and are usually $10^{-6}$ and $10^{-7}$ Pa respectively. The differential chamber prevents molecules, that do not directly pass through to the quadrupole mass spectrometer but in some way are deflected, to reach the mass spectrometer at a later time. The deflected molecules are pumped away. In this way peak broadening after leaving the reactor is minimised. A shutter valve is present to fully isolate the reaction chamber from the differential chamber. This arrangement permits the microreactor to be removed and replaced without disturbing the UHV conditions in the differential and analytical chamber.

Manifold assembly

Figure 2.2 shows a schematic view of the manifold assembly. The stainless steel manifold assembly has six entries. Two entries are occupied by continuous flow valves, two by high speed pulse valves, one by the microreactor and one entry is not used. During experiments the temperature of the assembly and the valves is controlled by an Eurotherm 91e temperature controller at a setpoint between 298 and 363 K by two cartridge heaters. Variations in temperature would influence the performance of the valves. Manifold heating also prevents condensation, if experiments would concern condensable reactant gases. The dead volume of the intersection of all entries is less than 1 μl.

The continuous flow valves are controlled pneumatically in order to eliminate their heating due to electrical resistance. Figure 2.3 shows a high speed pulse valve. The high speed pulse valve interior is divided into two separate chambers by a small stainless steel bellow. A pressure difference of 6-13 kPa is maintained between the front chamber, filled with reactant gas, and the back chamber, filled with nitrogen gas, to ensure the valve exit is sealed when
no current goes through the coils. The high speed pulse valve is opened by an electrical current through the opening coil. The current is supplied by a New Port BV100 beam valve driver.

The ferromagnetic field moves a magnetic disc attached to the valve stem, which lifts the stem from the valve exit. A few microseconds later, the beam valve driver stops the current through the opening coil and simultaneously the closing coil is actuated. The magnetic field is reversed and the ferromagnetic disc closes the valve exit. The pulse valves can generate up to 40 pulses per second. The amount of molecules introduced per pulse, the pulse intensity, is determined by the pressure in the front chamber and the time between opening and closing the valve. This open-to-close time can be adjusted with the beam valve driver. The pulse intensity is dependent on the stem length adjustment as well. In this way, the pulse valve can introduce $10^{13}$ to $10^{19}$ molecules per pulse with a minimal pulse width on half height of about 200 µs.
Microreactor

The microreactor, shown in figure 2.4, is a hollow cylinder of inconel with an overall length of 47.2 mm and an inner diameter of 5.6 mm. The inlet of the microreactor is sealed by a Viton O-ring. The outlet of the reactor contains a sealing flange to connect the high pressure assembly with the reactor.

Figure 2.3: Schematic view of a high speed valve (from: Autoclave Engineers Group, 1991).

Figure 2.4: Schematic view of the TAP microreactor (from: Svoboda, 1993).
The radiant furnace, see figure 2.2, provides reactor heating. The inconel reactor can be operated from ambient to 1273 K. The radiant furnace covers only the major middle part of the microreactor. A thermocouple in the reactor wall, as shown in figure 2.4, controls the reactor temperature. A thermocouple, sealed with an inconel ferrule, is positioned through the side wall to measure the catalyst bed temperature. The Viton O-ring at the inlet is cooled. When the high pressure assembly is used, the outlet is also sealed with a Viton O-ring and is therefore also cooled. As a result a temperature profile over the microreactor is established, as shown in figure 2.5a. In figures 2.5a and 2.5b the results are shown of temperature measurements, in which two bare thermocouples were entered through the exit of the microreactor. In figure 2.5a the reactor outlet was water-cooled, while in figure 2.5b no water-cooling was used. The high pressure assembly was not in use during the experiments, described in this thesis. Therefore, it was not necessary to cool the outlet of the reactor, resulting in the flatter temperature profile, as shown in figure 2.5b. Figure 2.5b shows that the middle part of the reactor, in the range of 10-23 mm from the inlet, is isothermal within 3 K at temperatures from ambient to 1000 K.

![Temperature profiles in the microreactor with water-cooling (a) and without water-cooling (b) at the reactor outlet with a temperature of the reactor wall of: 298 (+), 373 (△), 473 (○), 573 (□), 673 (■), 773 (●), 873 (▼) and 973 K (○).](image)

**Figure 2.5**: Temperature profiles in the microreactor with water-cooling (a) and without water-cooling (b) at the reactor outlet with a temperature of the reactor wall of: 298 (+), 373 (△), 473 (○), 573 (□), 673 (■), 773 (●), 873 (▼) and 973 K (○).

**High pressure assembly**

The high pressure assembly allows experiments to be carried out at pressures up to 2 $10^5$ Pa. The assembly seals the outlet of the microreactor and gases coming out of the microreactor.
are led through a vent valve. It is possible to link the vent valve to a gas chromatograph, in order to analyze the outlet gases. The high pressure assembly also contains a pinhole leak valve, which allows a small fraction of the outlet gases to reach the quadrupole mass spectrometer for time-resolved analysis. Again, the high pressure assembly was not used for the work presented in this thesis.

**Quadrupole mass spectrometer**

Detection of the molecules, coming out of the microreactor, is carried out with a UTI 100C quadrupole mass spectrometer, located in the analytical chamber with its axis mounted perpendicular to the axis of the microreactor. The mass spectrometer measures the molar flow rate of a component in amperes. Absolute calibration is possible and is described in paragraph 2.3.2. The mass spectrometer produces analog signals, which can be directly observed with an oscilloscope or digitized by the data acquisition system, and operates between m/e ratios, also called atomic mass units (AMU), of 1 to 300. The sensitivity of the mass spectrometer is limited by the real time analysis requirements of the TAP experiment. When the sensitivity of the electron multiplier is increased, its time constant also increases. For most experiments it is necessary to have a time constant less than 0.2 ms which limits the sensitivity of the standard UTI multiplier to \(10^{-10}\) A (UTI Instruments Co., 1990). The mass resolution, expressed as full width at half height, is 0.5 AMU.

**Gas preparation section**

Reactant gas samples are fed to the continuous flow valves and the high speed pulse valves from the gas preparation section. The preparation section allows to prepare reactant mixtures with accurate reactant ratios, and to feed them at a constant pressure to the valves. Two small vessels of about 150 cm³ are present to store the reactant gases. Gas mixtures in the storage vessels are prepared by measuring the pressure increase with two Setra Model 280E/C280E pressure indicators with a accuracy of 7 mbar. In this way, many experiments can be carried out without the need to refill. When mixtures are made, the vessels insure the mixtures to be perfectly mixed. In isotopic experiments the vessels are not used because of the high amount of gas which is needed to fill a vessel. In this case only the tubing of the gas preparation section is used, resulting in poor mixing of the gases. Mechanical vacuum pumps are present to allow operation below atmospheric pressure and evacuation of the tubing and vessels when preparing a gas mixture.
Control and data acquisition

A HP 360 workstation is attached to the HP 3865A data acquisition/control unit, a UTI 100 SpectraLink, two Newport BV100 beam valve drivers and a Eurotherm 818P temperature controller. A schematic view of the control and data acquisition system is given in figure 2.6.

![Schematic view of the control and data acquisition system](image)

**Figure 2.6:** Schematic view of the links between workstation and the TAP set-up (from: Svoboda, 1993).

With the TAP software, installed on the workstation, data from the quadrupole mass spectrometer can be stored, analyzed, plotted, etc. The data acquisition unit can gather up to 10,000 data points per 0.1 s. The workstation regulates the high speed pulse valves via the beam valve drivers. The types of experiments, which are described in detail in paragraph 2.3.1, are carried out and controlled via the software. The temperature of the microreactor can be set and the quadrupole mass spectrometer can be adjusted to monitor a specific m/e ratio. A detailed description of the possibilities is given by the Autoclave Engineers Group (1991).
2.3 Experimental procedures

In paragraph 2.3.1 all types of experiments, that can be performed with the TAP set-up, are discussed. The procedure to determine the calibration factors of the gases is described in paragraph 2.3.2. Paragraph 2.3.3 deals with the determination of the number of surface sites. In paragraph 2.3.4 curve smoothing is described.

2.3.1 Types of experiments

The design of the manifold, with two high speed valves and two continuous valves, and the high pressure assembly combined with the HP data acquisition and control system, allows for a large number of experimental formats. The mass spectrometer can be operated in two basic modes. In the scan mode, the mass spectrometer is set to scan a specified mass range. In the pulse mode, the mass spectrometer is fixed at a specific value of the mass and the intensity of the specified mass is measured during a specified time. Typical scan and pulse experimental outlet signals are depicted in figure 2.7.

Scan experiment

In a scan experiment a steady flow of the reactant gas(es) is fed to the microreactor via the continuous flow valve. The quadrupole mass spectrometer is set to scan a user-specified mass spectrum. In a scan experiment a plot of the mass intensity in ampere versus mass number is measured, as depicted in figure 2.7a. In this report, the scan experiments were carried out with pure gases in order to verify or to determine their fragmentation patterns.

![Image](a) ![Image](b)

*Figure 2.7: Typical scan (a) and pulse (b) responses at outlet.*

Single pulse experiment

In a single pulse experiment one high speed pulse valve, containing reactant gas(es), is actuated once. In these experiments the mass spectrometer is operated in the pulse mode and
one single mass peak is monitored, as depicted in figure 2.7b. The delay time between the opening of the high speed pulse valve and the detection of the outlet response in figure 2.7b is mainly caused by gas transport through the packed bed and is described in paragraph 2.3.4.2. The fast transients involved with pulse experiments do not allow a range of masses to be monitored by a quadrupole mass spectrometer. In a typical pulse experiment one single pulse containing $1 \times 10^{15}$ to $5 \times 10^{15}$ molecules was admitted, to ensure that Knudsen diffusion is the only mechanism of gas transport.

**Pulse experiment**

A pulse experiment consists of a sequence of single pulses to allow signal averaging. It can be performed as long as the catalyst surface is not changing throughout the experiment. Among other things, the repetition time between the single pulses should be sufficiently large to avoid accumulation of adsorbed species. As a result, the signal/noise ratio of the outlet signal increases. If more than one reactant or product is of interest, the experiment has to be repeated for each mass. Exceptionally, the mass spectrometer can monitor two m/e ratios in this type of experiment.

**Alternating pulse experiment**

In an alternating pulse experiment, also called pump-probe experiment (Gleaves *et al.*, 1988), two subsequent pulses are admitted, from two different high speed pulse valves with a user-specified time interval, also called pump-probe interval, between the pulses. Surface lifetimes of adsorbed species or intermediates can be analysed by varying the interval time between both pulses. The sequence is repeated for signal-averaging purposes, and the time duration of the whole cycle can be specified. The time interval between the two pulses and the cycle time are controlled by the valve trigger which has a variable offset pulse generator. As with the pulse experiments, the data are signal-averaged. The mass spectrometer is operated in the pulse mode and if more than one reactant or product is of interest, the experiment has to be repeated for each mass. One or two m/e ratios can be monitored in this type of experiment.

**Multi-pulse experiment**

In a multi-pulse experiment a specified number of single pulses is given during a specified time interval, while the mass spectrometer monitors one m/e ratio. The successive signals are not averaged but recorded separately, to observe the signal changes during the experiment, for instance because of changing surface coverages. In most cases, multi-pulse experiments
are carried out with a catalyst surface that has been precovered with an adsorbate. Either the reactant or product response is monitored. If more than one reactant or product is of interest, the experiment should be repeated for each mass.

2.3.2 Calibration factor determination

For a quantitative interpretation of the pulse responses, calibration is required with respect to the number of molecules in a pulse. The measured TAP signal, see figure 2.7b, is an electric current corresponding to a molar flow rate at the reactor outlet. The TAP software integrates the signals and provides peak surface areas, which are a measure for the amount of molecules leaving the reactor per pulse. An absolute calibration factor relates the peak surface area to this amount of molecules. Determination of the calibration factor is carried out for each reactant or reaction product by allowing a continuous flow from a vessel with known volume in the gas preparation section through the microreactor during a specific time, while monitoring the constant QMS-signal. Between vessel and valve, a pressure regulator maintains a constant flow through the valve. The molar flow rate is calculated from the pressure decrease of component i in the vessel, $\Delta p$, the vessel volume, $V$, and release time, $\Delta t$. Applying the ideal gas law, the absolute calibration factor can be calculated with the following expression:

$$C_i = \frac{\Delta p_i V}{RT \Delta t I_{QMS}}$$

where $C_i$ is the absolute calibration factor of component i [mol C$^{-1}$] and $I_{QMS}$ the electric current measured with the quadrupole mass spectrometer [C s$^{-1}$].

The absolute calibration factor of a component is dependent on the pressure in the analytical chamber. The higher the pressure in the analytical chamber, the lower the calibration factor, since the mass spectrometer measures a higher electric current at a higher pressure in the analytical chamber. In a measuring period the absolute calibration factors of all components have to be determined at a certain pressure at least once. However, the ratio of the absolute calibration factors of two different gases can be considered independent of the pressure in the analytical chamber, meaning that it is sufficient to determine every day the absolute calibration factor of one gas only. The absolute calibration factors of the other gases can then be calculated from the previously determined ratios.

The absolute calibration factor is also dependent on the reactor temperature. Due to a higher kinetic energy of the molecules arriving in the ionisation chamber, fragmentation becomes more pronounced at higher reactor temperature. The measured signal at the m/e ratio of unfragmented gas becomes smaller. However, the ratio of absolute calibration factors of two
different gases is independent of temperature. When in a measuring period the absolute calibration factors of all gases have been determined at one temperature, it is sufficient to determine the absolute calibration factor of only one component at another temperature.

The absolute calibration factors of Ar, CO₂, CO, O₂, N₂O, NO and N₂ at 374 K are listed in table 2.1. The absolute calibration factor of Ar was also determined at 676 K. The calibration factors of the other components at 676 K were calculated from the ratios of calibration factors and printed in italics in table 2.1.

Table 2.1: Absolute calibration factors at 374 and 676 K. Numbers in italics were calculated from the measured values, shown in normal script. The voltage of the multiplier was 1.5 kV and the pressure in the analytical chamber 1.2 \(10^{-7}\) mbar.

<table>
<thead>
<tr>
<th>gas</th>
<th>374 K (10^2) mol C(^{-1})</th>
<th>676 K (10^2) mol C(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>6.5</td>
<td>7.2</td>
</tr>
<tr>
<td>CO₂</td>
<td>7.2</td>
<td>8.0</td>
</tr>
<tr>
<td>CO</td>
<td>7.0</td>
<td>7.7</td>
</tr>
<tr>
<td>O₂</td>
<td>8.5</td>
<td>9.4</td>
</tr>
<tr>
<td>N₂O</td>
<td>10.2</td>
<td>11.3</td>
</tr>
<tr>
<td>NO</td>
<td>6.7</td>
<td>7.4</td>
</tr>
<tr>
<td>N₂</td>
<td>7.3</td>
<td>8.1</td>
</tr>
</tbody>
</table>

2.3.3 Curve smoothing

As in a single pulse experiment just one pulse is given, the TAP signal obviously cannot be averaged. In order to improve the signal/noise ratio, smoothing can be performed. Rothaemel (1993) wrote a smoothing routine for the HP 360 workstation which uses the Fast Fourier Transform (FFT) method for optimal filtering of the signal. The method is described in detail by Press et al. (1992). The routine allows to adjust the window size to minimize changes in the shape of the response curve due to smoothing. In figure 2.8 a part of a measured and a smoothed response of an argon single pulse experiment is depicted. As shown, the result of smoothing is quite satisfactory. Smoothing was never performed without comparison of the original and the smoothed response.
2.3.4 Signal analysis

2.3.4.1 Time resolution

The TAP set-up is designed to operate in the millisecond time range. This is accomplished by injecting an extremely narrow gas pulse into the microreactor. The minimal inlet pulse width at half height is about 200 μs and is negligible compared to the time scale of gas transport through a packed bed of about 300 ms. The sensitivity of the mass spectrometer is limited by the real time analysis requirements of the TAP experiment. For most experiments it is necessary to have a time constant of the mass spectrometer less than 0.2 ms, which limits the sensitivity of the UTI multiplier to $10^{10}$ A (UTI Instruments Co., 1990). The differential chamber prevents molecules, that do not directly pass through to the quadrupole mass spectrometer but in some way are deflected, to reach the mass spectrometer at a later time. Except for light gases such as hydrogen and helium, less than 0.1 % of the detected pulse results from scattered molecules (Gleaves et al., 1988). Below the delay times of single pulse experiments are discussed.

2.3.4.2 Delay times

In figure 2.9 the argon responses are shown for a pulse experiment (A) and a single pulse experiment (B) under identical conditions. The responses do not overlap. The response of the
single pulse experiment has a delay of about 4 ms compared to the response of the pulse experiment. Except for the delay time, both responses are identical. During pulse experiments a synchronisation signal from the valve power supply triggers the signal-averager, which then samples the quadrupole signal for an interval of time slightly longer than the observed product pulse. The signal-averager has a maximum time resolution of 5 μs per point and can collect data during time intervals ranging from 100 ms to 120 s. This means that averaging occurs over at least 2 periods of 5 μs. The single pulse experiments however are not triggered, and the delay time varies from experiment to experiment, depending on the mass and amplifier range of the mass spectrometer. Therefore the delay times of single pulse experiments are incorporated in the modelling and their values are estimated as one of the parameters in the regression analysis to obtain quantitative kinetic data, see paragraph 2.4. It was verified that the estimated delay times correspond to the values observed directly for each single pulse.

\[ \bar{v} = \sqrt{\frac{8RT}{\pi M}} \] (2.2)

**Figure 2.9:** Responses of a pulse experiment (A) and a single pulse experiment (B) with argon at identical conditions.

In a single pulse experiment two different delay times can be distinguished, namely the delay time due to transport from the reactor outlet to the quadrupole mass spectrometer and the delay time caused by gas transport through the packed bed. The contribution to the delay time as a result of the gas transport of the molecules from the exit of the microreactor to the quadrupole mass spectrometer, can be calculated with the kinetic theory of gases. If one assumes that molecules at the exit of the microreactor have the same temperature as the catalyst bed, the average molecular speed, \( \bar{v} \), is given by (Moore, 1987):
Here $M$ is the molecular mass [kg mol$^{-1}$].

The delay time for argon at room temperature, as a result of the gas transport from the exit of the microreactor to the mass spectrometer is 0.25 ms. This delay time due to transport from the reactor outlet to the mass spectrometer is small compared to the delay time caused by gas transport through the packed bed of about 5 ms observed in a pulse experiment, which should not be confused with the mean residence time as a result of gas transport through a packed bed of about 300 ms.

### 2.4 Regression analysis

The data analysis was performed as outlined by Froment and Hosten (1981), using the single- or multi-response Marquardt algorithm for non-linear regression (Marquardt, 1963). Single-response regression was used for the regression of the gas transport data. In this paragraph multi-response regression is outlined. The regression of the measured molar flow rate data to obtain maximum likelihood estimates, $\hat{\beta}$, for the parameters $\beta$, was performed by application of the least square criterion to the observed, $F$, and calculated, $\hat{F}$, molar flow rates of the components at the reactor outlet:

$$S(\beta) = \sum_{h=1}^{v} \sum_{k=1}^{v} \sum_{i=1}^{n} \sigma_{hk} (F_{ih} - \hat{F}_{ih}) (F_{ik} - \hat{F}_{ik}) \rightarrow \text{minimum,} \quad (2.3)$$

in which $S$ is the objective function, $v$ is the number of responses, $n$ is the number of observations and $\sigma_{hk}$ is an element of the inverse of the error variance-covariance matrix. The elements $\sigma_{hk}$ are estimated by the regression routine, following a regression with a unit error variance-covariance matrix. The objective function is based upon the assumption that the experimental errors are normally distributed with a zero mean. When good initial parameter estimates are provided, 5 to 15 iterations were sufficient to reach the minimum of the objective function.

The parameter estimates were tested for significance by means of their approximate individual $t$ values. As a rule of thumb these calculated $t$-values should be larger than 2. The approximate individual $t$-values were used to determine the two-sided $1-\alpha$ confidence intervals:

$$b_i - t(n - p, 1 - \frac{1}{2}\alpha) s(b_i) \leq \hat{\beta}_i \leq b_i + t(n - p, 1 - \frac{1}{2}\alpha) s(b_i) , \quad (2.4)$$

in which $p$ is the number of estimated parameters and $s(b_i)$ the estimated standard errors of the parameter estimates. The 95 % confidence intervals are reported in the present work.
Model discrimination was based on statistical significance of the individual parameters as well as of the global regression. The latter was expressed by means of the so-called F-ratio, i.e. the ratio of the mean calculated sum of squares to the mean residual sum of squares which is distributed according to F (Draper and Smith, 1966). A high value of the F-ratio corresponds to a high significance of the global regression. Discrimination among different models was based upon statistical testing, whenever it was not possible by direct observation or by physical or chemical laws.

2.5 Materials used in the experiments

2.5.1 Gases

In table 2.2 the used gases are listed with their purity and supplier. The gases were used as delivered.

In order to determine or verify fragmentation patterns of the gases, steady flow scan experiments were performed with all gases, except for $^{13}$CO and $^{18}$O$_2$. The scan experiments and the experiments to determine the calibration factors were carried out over an inert quartz bed. The fragmentation patterns are dependent of the temperature, as explained in paragraph 2.3.2. Fragmentation patterns should therefore be recorded at reaction temperature.

<table>
<thead>
<tr>
<th>gas</th>
<th>purity %</th>
<th>supplier</th>
<th>gas</th>
<th>purity %</th>
<th>supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>99.997</td>
<td>Hoekloos</td>
<td>NO</td>
<td>99.5</td>
<td>Hoekloos</td>
</tr>
<tr>
<td>$^{13}$CO</td>
<td>99.16</td>
<td>Isotec</td>
<td>N$_2$O</td>
<td>99.5</td>
<td>Hoekloos</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>99.999</td>
<td>Air Products</td>
<td>N$_2$</td>
<td>99.9999</td>
<td>Hoekloos</td>
</tr>
<tr>
<td>O$_2$</td>
<td>99.995</td>
<td>Air Products</td>
<td>Ar</td>
<td>99.9999</td>
<td>Hoekloos</td>
</tr>
<tr>
<td>$^{18}$O$_2$</td>
<td>99.5</td>
<td>Union Carbide</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.5.2 Catalyst

The catalyst used in the various experiments is a polycrystalline platinum sponge catalyst, supplied by Johnson Matthey. It consists of 99.9 mass % Pt and the sponge particles are between 250 and 350 μm. The platinum sponge particles are made up of many sintered non-
porous spheres with a diameter of approximately 5 μm. In figure 2.10 a SEM (Scanning Electron Microscopy) photograph is shown of a fresh platinum sponge particle.

![SEM photograph of a fresh platinum sponge particle.](image)

**Figure 2.10:** SEM photograph of a fresh platinum sponge particle.

The catalyst bed is placed in the isothermal part of the microreactor. Inert packing of 315-400 μm quartz particles was used as insulation upstream and downstream of the catalyst bed in the microreactor, as well as to maintain the catalyst bed at a fixed position. Experiments were done to verify the inertness of the quartz for CO oxidation by O₂ or NO. The quartz proved to be inert for both reactions.

### 2.5.2.1 Catalyst pretreatment

The major impurities reported on high purity platinum surfaces are carbon, calcium and phosphorus. Other impurities commonly observed on platinum are sulfur, silicon, chlorine and oxygen (Musket *et al.*, 1982). During an oxygen pretreatment impurities like sulfur, carbon and phosphorus are removed from the catalyst surface. After this oxygen pretreatment, the platinum surface is partially oxidized. The platinum oxides are reduced to Pt⁰ by hydrogen. Volatile components were removed by heating in UHV conditions.

The following pretreatment is performed for each batch of fresh platinum sponge. A mixture of 5 vol. % oxygen in argon is led through the microreactor for two hours via the continuous flow valve. After this treatment, the surface is treated with a mixture of 5 vol. % hydrogen in argon for two hours. The flow rate in both treatments was approximately 2 \(10^{-7}\) mol s⁻¹.
Except for the oxygen experiments, which are described in paragraph 5.2, the pretreatment temperature was 873 K.

\[ \text{Figure 2.11: The intensity of oxygen (•), argon (□) and water (○) during the oxygen pretreatment with 5 vol. % oxygen in argon at 873 K as function of the pretreatment time.} \]

In figures 2.11 and 2.12 the intensities of the most important components during the oxygen respectively hydrogen pretreatment at 873 K are depicted as function of time.

\[ \text{Figure 2.12: The intensity of hydrogen (•), argon (□) and water (○) during the hydrogen pretreatment with 5 vol. % hydrogen in argon at 873 K as function of the pretreatment time.} \]

The argon intensity is in both figures the signal of the doubly ionized fragment of argon at a m/e ratio of 20. The intensity of this signal is about 4% of the main fragment of argon at
a \textit{m/e} ratio of 40, and is of the same order of magnitude as the intensities of oxygen, hydrogen and water.

\textbf{Figure 2.13}: SEM photographs of a part of a fresh platinum sponge pellet (a) and a platinum sponge pellet pretreated at 873 K (b).
As expected, the argon intensity remained constant during both treatments. During the oxygen pretreatment the oxygen intensity increased until all sulfur, hydrocarbon and phosphorus impurities were removed. The water intensity decreased, as a result of the decreasing amount of hydrocarbons on the surface. After the oxygen pretreatment, the platinum surface was partially oxidized. During the hydrogen pretreatment the platinum oxides were reduced to Pt$^0$ by hydrogen, resulting in a decreasing water intensity and an increasing hydrogen intensity. Both figures indicate that a pretreatment time of 2 hours is sufficient.

On the SEM photographs in figures 2.13a and 2.13b, a part of a fresh respectively pretreated platinum sponge particle are shown. It was verified experimentally that the sintering of the catalyst took place during the catalyst pretreatment and not during the experiments. The reason being that the maximum temperature of the experiments was about 170 K lower than the pretreatment temperature.

2.5.2.2 Catalyst characterisation

The fresh and used platinum sponge catalyst, the latter possibly mixed with quartz, was characterised by the overall composition (AAS), the surface composition (XPS), the specific surface area (krypton BET) and the determination of the number of platinum surface sites.

**Atomic Absorption Spectroscopy (AAS)**

The overall composition of the used platinum sponge catalyst, possibly mixed with quartz, was characterised with AAS and elementary carbon analysis. The same measurements were carried out for fresh platinum sponge and quartz.

AAS was performed by TAUW Infra Consult B.V. in Deventer and the elementary carbon analysis by Caleb Brett Nederland in Hoogvliet. In table 2.3 the results of the AAS and elementary carbon measurements are listed.

The mass balances involving quartz ($\text{SiO}_2$) are not complete, because oxygen is not analyzed in the AAS measurements. The most important impurities of the fresh platinum sponge are silicon, potassium and sodium. The amount of the other impurities is less than 100 mg kg$^{-1}$. The used platinum sponge/quartz mixture contains more of these elements, which is due to the presence of quartz upstream and downstream of the catalyst bed in the reactor. Used platinum sponge and quartz also contain more carbon, nickel and iron than fresh platinum sponge or quartz. The nickel and iron probably originated from the inconel reactor, material which consists mainly of nickel and iron. The elementary carbon was probably formed during the reaction.
Table 2.3: Results of the AAS and elementary carbon measurements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fresh Platinum Sponge mg kg(^{-1})</th>
<th>Fresh Quartz mg kg(^{-1})</th>
<th>Used Platinum Sponge and Quartz Mixture mg kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>&lt; 1000</td>
<td>&lt; 1000</td>
<td>3500</td>
</tr>
<tr>
<td>Cu</td>
<td>1</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Cr</td>
<td>5</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Fe</td>
<td>90</td>
<td>60</td>
<td>140</td>
</tr>
<tr>
<td>K</td>
<td>600</td>
<td>400</td>
<td>150</td>
</tr>
<tr>
<td>Li</td>
<td>1.7</td>
<td>36</td>
<td>48</td>
</tr>
<tr>
<td>Na</td>
<td>200</td>
<td>1800</td>
<td>600</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>95</td>
</tr>
<tr>
<td>P</td>
<td>&lt; 90</td>
<td>&lt; 90</td>
<td>&lt; 90</td>
</tr>
<tr>
<td>Pd</td>
<td>4.7</td>
<td>8.7</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Pt</td>
<td>1.0 (10^6)</td>
<td>&lt; 10</td>
<td>5.6 (10^3)</td>
</tr>
<tr>
<td>S</td>
<td>&lt; 30</td>
<td>75</td>
<td>85</td>
</tr>
<tr>
<td>Si</td>
<td>2200</td>
<td>(5.1 (10^5))</td>
<td>(1.9 (10^3))</td>
</tr>
<tr>
<td>Sn</td>
<td>&lt; 8</td>
<td>&lt; 8</td>
<td>&lt; 8</td>
</tr>
<tr>
<td>Ti</td>
<td>5</td>
<td>44</td>
<td>51</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt; 1</td>
<td>24</td>
<td>9</td>
</tr>
</tbody>
</table>

X-ray photoelectron spectroscopy (XPS)

Contrary to AAS, XPS is surface sensitive, which gives quantitative information of the elements present in the first few atomic layers of the surface. The XPS experiments were performed by Niemantsverdriet at Eindhoven University of Technology, using a Al K\(\alpha\) source. The only impurities detected on the fresh and the used platinum sponge catalyst were sodium and carbon. The amounts were too low to quantify.
The binding energy of the C 1s peak was 285.0 eV, meaning that carbon was present on the surface as carbon graphite and not as carbonates. The binding energy of the Pt 4f7 peak was 71.1 eV, which indicates that platinum on the surface was present as Pt0. Silicon on the surface is present as SiO₂ (quartz), since the binding energy of the Si 2p peak was 106.7 eV.

**Krypton BET**

A standard method for the determination of the specific surface area of porous materials is the Brunauer, Emmet and Teller method, better known as the BET-method. The krypton BET measurement was performed by Carlson at the University of Trondheim in Norway. The BET surface area of the fresh platinum sponge catalyst was 0.050 m² g⁻¹. The low surface area demonstrates that the small spheres in the platinum sponge catalyst are non-porous.

**Determination of the number of platinum surface sites**

The number of platinum surface sites was determined in-situ with TAP by a carbon monoxide multi-pulse experiment over a platinum surface precovered with atomic adsorbed oxygen while the carbon dioxide response is measured. The number of platinum surface sites is dependent of the pretreatment temperature and the pretreatment time, because of sintering of the catalyst during the pretreatment. These multi-pulse experiments had to be performed between 365 and 480 K. The associative desorption of atomic adsorbed oxygen was observed at temperatures above approximately 480 K.

In the calculation of the number of platinum surface sites it was assumed that each adsorbed oxygen atom occupies one platinum surface site, so the total amount of formed carbon dioxide is equal to the total amount of platinum surface sites. The total amount of platinum surface sites of a fresh catalyst was equal to 9.93 \(10^{-7}\) mol g⁻¹, and 6.43 \(10^{-7}\) mol g⁻¹ for a pretreated catalyst. The data are average values of triplicate measurements. Assuming a face centred cubic crystal structure with a lattice constant of 0.393 nm (Smith, 1990), the number of surface atoms per square meter of the Pt(100) crystal plane is 1.295 \(10^{19}\). Therefore the surface area of a fresh and pretreated platinum sponge catalyst is 0.046 m² g⁻¹ respectively 0.030 m² g⁻¹. The value obtained with TAP for the fresh platinum sponge catalyst agrees very well with the krypton BET surface area. During the pretreatment the surface area decreases by about 35 % as a result of sintering.
References

- Rothaemel, M., FFT Curve Smoothing, Ruhr Universität Bochum, Lehrstuhl für Technische Chemie, 1993
- UTI Instruments Co., UTI 100C Operating and Service Manual, Milpitas, California, 1990
A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by O₂/NO on Pt
3.1 Introduction

An understanding of gas transport in packed beds is important in the study of TAP experiments, because the microreactor is typically operated with a packed bed. Unlike in a conventional pulsed reactor experiment, no carrier gas is used in a TAP experiment. The pulse moves as the result of a pressure gradient across the reactor. The modes of gas transport that may occur during pulsed TAP experiments include Knudsen diffusion, molecular diffusion and viscous flow (Gleaves et al., 1988). A model that incorporates these three modes of gas transport is necessary to obtain an accurate description of the gas transport. By using an appropriate constitutive model for the gas transport (Mason et al., 1967, Mason and Malinauskas (1983)), the effect of the inlet gas pulse intensity on the relative contribution to the gas flux associated with each mode of gas transport can be quantified (Svoboda, 1993). Viscous flow may occur during the period the pulse valve is open and gas/gas collisions predominate. At sufficiently low pulse intensities the gas/gas collisions become negligible and Knudsen diffusion is the controlling mechanism of gas transport. In this regime gas/solid collisions predominate. Experimental verification of the Knudsen regime is shown in paragraph 3.3.2 by using inert gases with various molecular weights and by varying temperature, pulse intensity and pellet diameter. In the Knudsen regime the equations needed to model an experiment are simplified to a large extent. In paragraph 3.3 a model is described for the Knudsen diffusion in the interstitial voids. In the model described in paragraph 3.4 Knudsen diffusion in both interstitial and intraparticle voids is considered. With this model the influence of catalyst porosity on the responses of TAP experiments can be examined. In this paragraph a criterion is derived for the occurrence of diffusion limitations in the pellet pores as well. First an overview of the different phenomena involved in gas transport in porous media is given in paragraph 3.2.
3.2 Gas transport in porous media

There are four mechanisms of gas transport in porous media that can be distinguished under isothermal conditions. These four mechanisms are: molecular diffusion, Knudsen diffusion, surface diffusion and viscous flow.

Mason and colleagues (Mason et al. (1967), Mason and Malinauskas (1983)) described a model, which incorporates these four mechanisms of gas transport. All four mechanisms are discussed briefly.

The effective molecular or Knudsen diffusion coefficient in a porous medium can be calculated from the molecular or Knudsen diffusion coefficient:

\[
D_{eff} = \frac{\varepsilon_b}{\tau_b} D_i,
\]

where \(D_{eff}\) is the effective diffusion coefficient of component \(i\) \([\text{m}^2 \text{s}^{-1}]\), \(D_i\) is the diffusion coefficient of component \(i\) \([\text{m}^2 \text{s}^{-1}]\), \(\varepsilon_b\) is the porosity \([\text{m}^3 \text{m}^{-3}]\) and \(\tau_b\) is the tortuosity of the medium \([\text{m}^2 \text{m}^{-2}]\). The tortuosity corrects for the effect of altered diffusion path length as well as changing cross-sectional areas in constrictions (Froment and Bischoff, 1990). In this paragraph only interstitial voids will be considered, i.e. a medium consisting of a bed packed with non-porous particles.

Molecular diffusion

Molecular diffusion corresponds to the net transport of molecules caused by a mole fraction gradient and hindered by mutual collisions. In this regime molecule/molecule collisions dominate over molecule/wall collisions. According to non-equilibrium thermodynamics, the true driving force for molecular diffusion at constant temperature and pressure, is a gradient of the chemical potential. For an ideal mixture with an activity coefficient of 1, the gradient of the chemical potential is equal to the mole fraction gradient. For an ideal gas mixture the mole fraction gradient is equal to the partial pressure gradient or the concentration gradient, assuming that respectively, the total pressure or total concentration is constant. The flux as a result of molecular diffusion can be described by the Maxwell transport equation. The general expression for the molecular diffusion of a component \(i\) in a mixture with \(j\) other components is for an ideal mixture:

\[
\sum_{k=1}^{j} \left( \frac{x_i N_k^m - x_k N_i^m}{D_{eff_k}} \right) = - \frac{d C_i}{dx},
\]
where $N_i^{m}$ is the flux of component $i$ by molecular diffusion [$\text{mol m}^{-2} \text{s}^{-1}$], $x_i$ is the mole fraction of component $i$, $C_i$ is the concentration of component $i$ [$\text{mol m}^{-3}$], $x$ is the axial reactor coordinate [m] and $D_{e_{ik}}^{m}$ is the effective binary molecular diffusion coefficient of component $i$ in component $k$ [$\text{m}^{2} \text{m}^{-1} \text{s}^{-1}$].

**Knudsen diffusion**

Knudsen diffusion occurs at pressures sufficiently low for the collisions of molecules with solid walls to dominate. The collisions between molecules mutually can be ignored compared to collisions with the walls. The mean free path must be much larger than the distance between the walls to ensure Knudsen diffusion. The driving force for Knudsen diffusion is again the partial pressure or concentration gradient. The resulting flux is proportional to that gradient:

$$N_i^K = -D_{e_i}^{K} \frac{dC_i}{dx}$$

Here $D_{e_i}^{K}$ is the effective Knudsen diffusion coefficient of component $i$ [$\text{m}^{2} \text{m}^{-1} \text{s}^{-1}$].

**Surface diffusion**

Surface diffusion is a transport process in which a molecule adsorbs on a solid and subsequently migrates over its surface. In case of a strong bond between the molecule and the surface, surface migration will not occur. In table 3.1 the different possibilities for surface diffusion are listed. It was verified that surface diffusion had not to be taken into account in the present work.

*Table 3.1: Description of surface migration depending upon the relative values of the adsorption activation energy, $E_a$, the surface migration activation energy, $E_s$, and the molar thermal energy, $RT$, (Uhlhorn (1990)).*

<table>
<thead>
<tr>
<th>Energy situation</th>
<th>Interaction</th>
<th>Transport situation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a &lt; RT$</td>
<td>no adsorption</td>
<td>no surface migration</td>
</tr>
<tr>
<td>$RT &lt; E_a &lt; E_s$</td>
<td>adsorption</td>
<td>no surface migration</td>
</tr>
<tr>
<td>$RT &lt; E_s &lt; E_a$</td>
<td>adsorption</td>
<td>hopping models or Fick-like models</td>
</tr>
<tr>
<td>$E_s &lt; RT &lt; E_a$</td>
<td>adsorption</td>
<td>hydrodynamic models</td>
</tr>
</tbody>
</table>
Viscous flow

The gas transport caused by a total pressure gradient is called viscous flow. If molecule/molecule collisions dominate over molecule/wall collisions, the corresponding flux is proportional to the total pressure gradient and can be expressed for component $i$ as follows:

$$\dot{N}_i^v = -x_i \frac{K_{ei}}{RT} \frac{dp}{dx}$$

(3.4)

Here $K_{ei}$ is the effective viscous flow factor [$m_k^3 m_i^{-1} s^{-1}$].

Mason and Malinauskas (1983) described the combined modes of gas transport analogous to an electrical circuit, which is shown in figure 3.1. Molecular diffusion and Knudsen diffusion are combined like resistances in series. The resultant diffusive flux is combined with the viscous flux and the surface flux like resistances in parallel:

$$\dot{N}_i = \dot{N}_i^d + \dot{N}_i^v + \dot{N}_i^s$$

(3.5)

Here $\dot{N}_i^d$ is the total diffusive flux of component $i$ by Knudsen and/or molecular diffusion and $\dot{N}_i^s$ is the flux of component $i$ by surface diffusion.

![Electrical Analogy](image)

Figure 3.1: Electrical analogy for combining different transport mechanisms (Mason and Malinauskas, 1983). Knudsen and molecular diffusion combine in series, and the total diffusive flux combines in parallel with the viscous flux and the surface flux.

As said, the transport caused by surface diffusion can be neglected in the described TAP experiments. When pressure gradients impose viscous flow, the total flux is simply the sum
of the diffusive and the viscous flux:

\[ N_j = N_j^d + N_j^v \]  \hspace{1cm} (3.6)

The concentration gradients corresponding to Knudsen and molecular diffusion are additive. Combination of equations 3.2 and 3.3 gives the general expression for the diffusive flux, also called the Maxwell-Stefan transport equation (Froment and Bischoff, 1990), for component \( i \) in a mixture with \( j \) other components:

\[ -\frac{dC_i}{dx} = \sum_{k=1}^{j} \frac{x_i N_i^d - x_k N_k^d}{D_{i,k}^m} + \frac{N_i^d}{D_{i}^v} \]  \hspace{1cm} (3.7)

### 3.2.1 Transport of single gases

For a single gas \( A \) equation 3.7 becomes:

\[ N_i^d = -D_{i}^v \frac{dC_A}{dx} \]  \hspace{1cm} (3.8)

In equation 3.8 the molecular diffusion coefficient has disappeared, because of the absence of mole fraction gradients. Substitution of equation 3.4 and 3.8 in equation 3.6 gives the following expression for the total flux of a single gas \( A \):

\[ N_A = -(D_{i}^v + K_{eA}) \frac{dC_A}{dx} \]  \hspace{1cm} (3.9)

Since both flux coefficients are now multiplied by the same gradient, their relative contributions can be calculated. The effective Knudsen diffusion coefficient can be calculated from the following familiar expression obtained from the kinetic theory of gases (Froment and Bischoff (1990) and Huizenga and Smith (1986)):

\[ D_{i}^v = \frac{\varepsilon_b d_i}{\tau_b} \frac{3}{8} \frac{RT}{\pi M_A} \]  \hspace{1cm} (3.10)

where \( d_i \) is the average diameter of the interstitial voids between the pellets of a packed bed [m], \( \varepsilon_b \) is the bed porosity [m\(^3\)/m\(^3\)], \( \tau_b \) is the bed tortuosity [m\(^2\)/m\(^2\)] and \( M_A \) is the molecular mass of component A [kg mol\(^{-1}\)].

If spherical packing is assumed, then \( d_i \) follows from (Huizenga and Smith, 1986):

\[ d_i = \frac{2 \varepsilon_b}{3(1 - \varepsilon_b)} d_r \]  \hspace{1cm} (3.11)
where \( d_p \) is the average diameter of the pellets [m].

The effective viscous flow factor is calculated from the D'Arcy constant, \( B_0 \) [\( m^2 \)] (D'Arcy, 1856), the dynamic viscosity, \( \mu \) [\( Pa \cdot s \)], the bed porosity, \( \varepsilon_b \) [\( m^3 / m^3 \)], the bed tortuosity, \( \tau_b \) [\( m^2 / m^2 \)] and the total pressure, \( p \) [\( Pa \)].

\[
K_{\varepsilon_A} = \frac{\varepsilon_b \cdot \frac{p \cdot B_0}{\tau_b}}{\mu} \tag{3.12}
\]

In a single pulse TAP experiment, the total concentration and consequently the total pressure, are place and time dependent. Therefore viscous flow is place and time dependent as well. At low pressures the viscosity does not depend on pressure (Bird et al., 1960), hence the viscous flow factor is directly proportional to the pressure.

The D'Arcy constant, \( B_0 \), for a straight channel is (Froment and Bischoff, 1990):

\[
B_0 = \frac{d_{\text{eff}}^2}{32} \tag{3.13}
\]

Figure 3.2 shows the relative contribution to the total flux of both Knudsen diffusion and viscous flow, calculated with relation 3.9, as function of the pulse intensity.

Figure 3.2: Average calculated contributions of Knudsen and viscous flow to the total flux of a single gas as a function of the pulse size (\( Ar, T = 298 K, \mu = 22 \times 10^6 \) Pa s (Coulson and Richardson, 1993), \( d_p = 230 \mu m, l_b = 35 mm \) and \( \varepsilon_b = 0.481 m^3 / m^2 \)).
The average pressure in the reactor, used for the calculation of the effective viscous flow factor, is determined by assuming that the inlet pulse is spread out over the total available gas volume in the bed. The results refer to transport of argon at 298 K through a packed bed of 35 mm with an average pellet diameter of 230 μm (interstitial diameter of 142 μm) and a bed porosity of 0.481 m₃ m⁻³.

Knudsen diffusion dominates at small pulse intensities and viscous flow at large pulse intensities. In the intermediate region both types of gas transport are important. Since a TAP experiment involves total pressures of many orders of magnitude, both contributions are important for moderate to high pulse intensities.

In Table 3.2 the effective diffusion coefficients at different pulse intensities, estimated with the model described in paragraph 3.3, are shown for the diffusion of argon at 298 K through a quartz bed of pellets with an average diameter of 230 μm and a bed porosity of 0.481 m₃ m⁻³.

**Table 3.2: Estimated effective diffusion coefficients at different pulse intensities for a single gas passing a quartz bed (Ar, T = 298 K, dₚ = 230 μm and εₚ = 0.481 m₃ m⁻³).**

<table>
<thead>
<tr>
<th>molecules/pulse</th>
<th>( D_e ) ( 10^{-3} \text{ m}^3 \text{ m}^{-1} \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.03 ( 10^{16} )</td>
<td>1.897 ± 0.004</td>
</tr>
<tr>
<td>1.97 ( 10^{16} )</td>
<td>1.503 ± 0.004</td>
</tr>
<tr>
<td>9.98 ( 10^{15} )</td>
<td>1.434 ± 0.005</td>
</tr>
<tr>
<td>5.95 ( 10^{15} )</td>
<td>1.409 ± 0.005</td>
</tr>
<tr>
<td>4.80 ( 10^{15} )</td>
<td>1.402 ± 0.006</td>
</tr>
<tr>
<td>2.26 ( 10^{15} )</td>
<td>1.386 ± 0.007</td>
</tr>
<tr>
<td>1.18 ( 10^{15} )</td>
<td>1.368 ± 0.007</td>
</tr>
<tr>
<td>4.96 ( 10^{14} )</td>
<td>1.358 ± 0.008</td>
</tr>
<tr>
<td>1.42 ( 10^{14} )</td>
<td>1.345 ± 0.008</td>
</tr>
<tr>
<td>1.09 ( 10^{13} )</td>
<td>1.357 ± 0.004</td>
</tr>
</tbody>
</table>

Below pulse intensities of 5 \( 10^{14} \) molecules per pulse, the effective diffusion coefficient is independent of the pulse size. As shown in Figure 3.2 Knudsen diffusion is here the only appearing mechanism of gas transport and the following expression for the total flux of a single gas A holds:
\[ N_A = -D_{x_A} \frac{dC_A}{dx} \]  

(3.14)

At pulse intensities above 5 \(10^{14}\) molecules per pulse, the estimated effective diffusion coefficient contains a contribution from the effective viscous flow factor, \( \kappa_A \), because viscous flow is proportional to the total gas pressure (see equation 3.12). The qualitative and quantitative similarity between the predicted and the measured contribution of the viscous flow to the gas transport mechanism is satisfactory.

### 3.2.2 Pressure profile in the microreactor

Figure 3.3 shows the pressure profile in the TAP microreactor calculated with the model described in paragraph 3.3, as function of time and axial reactor coordinate for a single argon pulse with a pulse size of \(5 \times 10^{15}\) molecules passing a quartz bed of length 35 mm with an average pellet diameter of 230 \(\mu\)m at 298 K.

![Figure 3.3: Calculated pressure profile in a TAP reactor as function of time and axial coordinate after the introduction of an argon pulse of \(5 \times 10^{15}\) molecules at \(t = 0\) s at the entrance of a quartz bed of length 35 mm with an average pellet diameter of 230 \(\mu\)m at 298 K.](image-url)
At any time the pressure is the highest at the entrance of the reactor and decreases to zero at the outlet of the reactor, because the outlet of the reactor is held at vacuum conditions. The pressure decreases monotonously in time at the entrance of the reactor only. At each other axial position there is a maximum in pressure as function of time. The pressure after a pulse of \(5 \times 10^{15}\) molecules varies from 0 to 180 Pa. As can be seen in figure 3.3 it is a misunderstanding that during a pulse a pressure wave traverses the reactor.

### 3.2.3 Molecular diffusion in gas mixtures

In figure 3.4 three normalised argon outlet signals at different pulse sizes for a gas mixture of 10 vol. % argon in nitric monoxide are shown. The pulse intensities are large enough to ensure that Knudsen diffusion is not the only appearing gas transport mechanism. The larger the pulse size, the faster the argon pulse traverses the reactor, and as a consequence the higher the effective diffusion coefficient for argon. In figure 3.5 it is shown that the same experiment with pure argon does not show this shift.

![Figure 3.4: Normalised responses of argon in a gas mixture of 10 vol. % Ar in NO at pulse sizes of A) \(1.8 \times 10^{16}\), B) \(1.3 \times 10^{16}\) and C) \(4.2 \times 10^{15}\) molecules (quartz bed of length 28.2 mm with an average pellet diameter of 340 \(\mu\)m and a bed porosity of 0.58 \(m^3/m^3\) at 373 K).](image)

The molecular effective diffusion coefficient of component A in component B can be calculated with the semi-empirical relation of Fuller-Schettler-Giddings (Reid et al. (1987), Wesselingh and Krishna (1990)).
A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by \(O_2/NO\) on Pt

\[
D_{eA,B}^m = \frac{\epsilon_b \cdot 3.2 \times 10^{-8} T^{1.75} \frac{1}{M_A} + \frac{1}{M_B}}{\tau_b \cdot p \left[ \left( \sum \nu_A \right)^{\frac{3}{2}} + \left( \sum \nu_B \right)^{\frac{3}{2}} \right]^2},
\]

(3.15)

where \(D_{eA,B}^m\) is the effective binary molecular diffusion coefficient [m\(^3\) m\(^-1\) s\(^-1\)], \(M_A\) and \(M_B\) the molecular masses of A and B [kg mol\(^{-1}\)] and \(\nu_A\) and \(\nu_B\) are the atomic and structural diffusion volume increments of A and B [m\(^3\) mol\(^{-1}\)].

**Figure 3.5:** Normalised responses of argon in pure Ar at pulse sizes of A) \(1.8 \times 10^{16}\), B) \(1.3 \times 10^{16}\) and C) \(4.2 \times 10^{15}\) molecules (quartz bed of length 28.2 mm with an average pellet diameter of 340 µm and a bed porosity of 0.58 m\(^3\) m\(^{-1}\) at 373 K).

At low pressures or small pulse sizes, the molecular diffusion coefficient is much higher than the Knudsen diffusion coefficient because the former is inversely proportional to the pressure, see equation 3.15. In this situation molecular diffusion can be neglected since both diffusive resistances should be added reciprocally. At high pressures molecular diffusion can be neglected because of the dominant viscous flow. At intermediate pressures however the contribution of molecular diffusion to the transport can be observed.

The shift of the argon signal in figure 3.4 cannot be caused by viscous flow because this shift is absent in the experiment with pure argon as shown in figure 3.5. In the mixture of 10 vol. % argon in nitric monoxide, nitric monoxide molecules move faster through the reactor by Knudsen diffusion since the molecular mass of nitric monoxide is lower than that of argon, see equation 3.10. As a consequence the nitric monoxide mole fraction increases towards the reactor outlet. Molecular diffusion tries to level-off the mole fraction gradient resulting in an extra transport contribution. As a result argon molecules move faster towards the outlet of the
reactor and vice versa for the nitric monoxide molecules. Hence argon shows a larger estimated effective diffusion coefficient than in the same experiment with pure argon. The larger the pulse size, the larger is the contribution of molecular diffusion to the diffusive flow, meaning that the effect is more easily observed at higher pressures or larger pulse sizes (compare figure 3.4 with 3.5), as long as viscous flow is not the only prevailing transport mechanism. At a pulse size of $4.2 \times 10^{15}$ molecules, the normalised signals of argon in figure 3.4 and 3.5 coincide. In this situation molecular diffusion can be neglected because the molecular diffusion coefficient is much higher than the Knudsen diffusion coefficient and diffusive resistances should be added reciprocally.

### 3.3 Knudsen diffusion in interstitial voids

In this paragraph the gas transport in the voids between the pellets, i.e. the interstitial space, is described mathematically for the situation that Knudsen diffusion is the primary mechanism of gas transport, because it was in this regime that the kinetic studies described in this thesis were performed, unless reported otherwise. Also, Knudsen diffusion was experimentally confirmed by reducing the inlet gas pulse intensity until the normalised output responses were identical. This was found to occur at intensities lower than approximately $5 \times 10^{15}$ molecules per pulse (see table 3.2). The influence of the molecular weight of the reactant, the temperature and the pellet diameter on the Knudsen diffusion coefficient were examined as well.

#### 3.3.1 Model equations

In case Knudsen diffusion is the controlling mechanism of gas transport and no reaction occurs, the continuity equation for a gas phase component $A$ in the interstitial voids is:

$$
\varepsilon_b \frac{\partial C_A}{\partial t} = D_{eA}^K \frac{\partial^2 C_A}{\partial x^2}
$$

(3.16)

where $C_A$ is the gas concentration of component $A$ in the interstitial voids [$\text{mol m}^{-3}$], $\varepsilon_b$ is the bed porosity [$\text{m}^3 \text{m}^{-3}$] and $D_{eA}^K$ is the effective Knudsen diffusion coefficient [$\text{m}^3 \text{m}^{-1} \text{s}^{-1}$].

Equation 3.16 has the following initial and boundary conditions:

$$
t = 0 \land 0 \leq x \leq l_b : \quad C_A(x) = \delta_x \frac{N_{p,A}}{\varepsilon_b A_p l_b}
$$

(3.17)
\[ t \geq 0 \land x = 0 : \quad \frac{\partial C_A}{\partial x} = 0 \quad (3.18) \]

\[ t \geq 0 \land x = l_b : \quad C_A = 0 \quad (3.19) \]

Here \( N_{p,A} \) is the inlet pulse size of component A [mol], \( A_r \) the cross section area of the reactor \([m^2]\) and \( l_b \) the bed length \([m]\). The factor \( N_{p,A} \epsilon_b^{-1} A_r^{-1} l_b^{-1} \) corresponds to the inlet concentration of component A, based on the total available gas volume.

The initial condition, given by equation 3.17, specifies that the initial gas concentration in the reactor is a delta function, meaning that the initial gas concentration is infinite at the entrance of the reactor and zero at all other reactor positions. This delta function can be used because in a TAP experiment the time scale on which the inlet pulse is admitted, is much smaller than the time scale of the experiment, as described in paragraph 2.3.4.1. The first boundary condition, given by equation 3.18, corresponds to the absence of flux at the reactor entrance when the pulse valve is closed. The second boundary condition, given by equation 3.19, specifies that the reactor outlet is held at vacuum conditions, so the concentration of all gaseous species is zero at \( x = l_b \).

### 3.3.1.1 Analytical solution

Equations 3.16 to 3.19 can be integrated analytically (de Croon, 1992). With axial coordinate \( z = \frac{x}{l_b} \) and normalised time \( \tau = D_{c,A} t \epsilon_b^{-1} l_b^{-2} \) equation 3.16 becomes:

\[ \frac{\partial C_A}{\partial \tau} = \frac{\partial^2 C_A}{\partial z^2} \quad (3.20) \]

Laplace transformation of equation 3.20 with respect to the normalised time \( \tau \) using initial condition 3.17 gives (Abramowitz and Stegun, 1970):

\[ \mathcal{L}\left( \frac{\partial C_A}{\partial \tau} \right) = s \tilde{C}_A - C_A(\tau = 0) = s \tilde{C}_A - C_A(\tau = 0) = \delta z^2 \frac{N_{p,A}}{\epsilon_b A_r l_b} = \frac{\partial^2 C_A}{\partial z^2}, \quad (3.21) \]

where \( s \) is the Laplace transform variable.

Laplace transformation of equation 3.21 to the dimensionless distance \( z \) gives (Abramowitz and Stegun, 1970):
where \( p \) is the Laplace transform variable with respect to the dimensionless distance.

Substitution of boundary condition 3.18 in equation 3.22 gives:

\[
\bar{C}_A = \frac{p}{p^2 - s} \bar{C}_A |_{z=0} = \frac{N_{p,A}}{\varepsilon_b A_s l_b} \quad (3.23)
\]

Inverse transformation to the dimensionless distance \( z \) gives:

\[
\bar{C}_A = \bar{C}_A |_{z=0} \cosh(\sqrt{s} z) - \frac{N_{p,A}}{\varepsilon_b A_s l_b} \frac{\sinh(\sqrt{s} z)}{\sqrt{s}} \quad (3.24)
\]

Substitution of boundary condition 3.19 in equation 3.24 gives the following expression for the Laplace transformed concentration of component A:

\[
\bar{C}_A = \frac{N_{p,A}}{\varepsilon_b A_s l_b} \left( \frac{\tanh(\sqrt{s} z)}{\sqrt{s}} \cosh(\sqrt{s} z) - \frac{\sinh(\sqrt{s} z)}{\sqrt{s}} \right) \quad (3.25)
\]

The Laplace transformed molar flow rate at the outlet of the reactor \((z=1)\) is then:

\[
\bar{F}_A |_{z=1} = -A_s D_{\varepsilon A} K \frac{\partial \bar{C}_A}{\partial z} |_{z=1} = \frac{D_{\varepsilon A} K N_{p,A}}{\varepsilon_b l_b^2} \frac{1}{\cosh(\sqrt{s})} \quad (3.26)
\]

Inverse transformation to the normalised time domain gives (Abramowitz and Stegun, 1970):

\[
F_A |_{z=1} = \frac{D_{\varepsilon A} K N_{p,A} \pi}{\varepsilon_b l_b^2} \sum_{n=0}^{\infty} (2n + 1)(-1)^n \exp(-\frac{(2n+1)^2 \pi^2 \tau}{4}) \quad (3.27)
\]

The molar flow rate at the outlet of the reactor as a function of time becomes:

\[
F_A |_{z=1} = \frac{D_{\varepsilon A} K N_{p,A} \pi}{\varepsilon_b l_b^2} \sum_{n=0}^{\infty} (2n + 1)(-1)^n \exp(-\frac{(2n+1)^2 \pi^2}{4} \frac{D_{\varepsilon A} t}{\varepsilon_b l_b^2}) \quad (3.28)
\]
3.3.1.2 Moment analysis

Analysis of the zeroth and first moments of a TAP response curve yields valuable information about the pulse size, the mean residence time and the effective Knudsen diffusion coefficient. The effective Knudsen diffusion coefficient is not of particular interest by itself but must be known accurately before the kinetic parameters can be determined.

The $i$th moment, $m_i$, of the outlet flow rate is defined by:

$$ m_i = \int_0^\infty F_A|_{x=x_i} t^i \, dt $$

(3.29)

The $i$th normalised moment, $\mu_i$, is defined as:

$$ \mu_i = \frac{m_i}{m_0} $$

(3.30)

The moments can be calculated from equation 3.28.

The zeroth moment is equal to:

$$ m_0 = \frac{4N_{p,A} l_b^2 \varepsilon_b}{\pi^3 D_{\epsilon_A}^k} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n + 1} = N_{p,A} $$

(3.31)

Without reaction the zeroth moment of the response curve equals the total amount of sample gas, $N_{p,A}$.

The first moment is given by:

$$ m_1 = \frac{16N_{p,A} l_b^2 \varepsilon_b}{\pi^3 D_{\epsilon_A}^k} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n + 1)^3} = \frac{N_{p,A} l_b^2 \varepsilon_b}{2 D_{\epsilon_A}^k} $$

(3.32)

The first normalised moment is equal to the mean residence time:

$$ \bar{t} = \mu_1 = \frac{l_b^2 \varepsilon_b}{2 D_{\epsilon_A}^k} $$

(3.33)

It is also of interest to calculate the peak time, the time where the molar flow rate at the outlet of the reactor is maximal, for the simple case of diffusion. The peak time is the time, where the derivative of equation 3.28 is equal to zero.
Gas Transport without Reaction

\[ t_{\text{peak}} = \frac{l_0^2 \varepsilon_0}{6 D_{eK}} \]

(3.34)

In the absence of reaction the effective Knudsen diffusion coefficient can simply be derived from the peak time. It should be remembered that in the above description \( D_{eA,K} \) applies to Knudsen diffusion through the interstitial voids, the bed being considered to consist of a packing of non-porous particles.

### 3.3.1.3 Numerical solution

It is also possible to solve equation 3.16 with initial and boundary conditions 3.17, 3.18 and 3.19 numerically using the NAG Fortran Library routine D03PGF (NAG Ltd., 1991), which integrates a system of nonlinear parabolic partial differential equations in one space variable, by the method of lines and Gear’s method. In this routine the parabolic equations are approximated by a set of ordinary differential equations, obtained by replacing the space derivatives by finite differences. This set is then integrated forwards in time using Gear’s method. The approximation applies an uniform mesh in the space direction, which can be specified by the user. In the time coordinate the interval is chosen by the routine to maintain the local accuracy specified by the user.

The NAG routine does not allow a \( \delta \)-function for the initial gas concentration distribution, which is defined by equation 3.17. Therefore the initial gas concentration at the first and second discretized space points were set equal to some value \( C_A^0 \) because there is no flux at the reactor entrance as the pulse valve is closed. The gas concentration at the third and following discretization points were taken zero. The applied initial distribution in the reactor is shown in figure 3.6.

![Figure 3.6: Initial gas concentration at the first ten mesh points in the reactor as used in the NAG routine D03PGF.](image-url)
The value of $C_A^0$ is based on the total available gas volume and is equal to the quotient of the inlet pulse size $N_{p,A}$ and the gas volume between the first and third discretization points:

$$C_A^0 = \frac{2 N_{p,A}}{3 \varepsilon A \Delta x},$$

in which $\Delta x$ is the distance between two mesh points [m].

Integrating equation 3.16 with its initial and boundary conditions leads to the axial gas phase concentration profiles in the reactor at any time. The molar flow rate at the outlet, $F_{A_{\text{out}}}$, can be calculated from the concentrations at the last and last but one mesh points, $C_{A,m}$ and $C_{A,m-1}$ respectively:

$$F_{A\,|_{x=x_n}} = -A_s D_e^R C_{A,m} - C_{A,m-1}$$

The concentration of component A at the last mesh point, $C_{A,m}$, is zero, because the reactor outlet is held at vacuum conditions. Therefore, the concentration of a component at the reactor outlet is proportional to the molar flow rate of that component at the reactor outlet. If the effective diffusion coefficients of all components are equal, the composition is directly coupled to the molar flow rates of the components.

The relative deviation between analytically and numerically calculated molar flow rates for different sets of parameters is below 0.25% at any time when at least 100 mesh points are applied.

### 3.3.2 Experimental verification of the Knudsen regime model

For the estimation of the effective diffusion coefficients with the single-response Marquardt routine (Froment and Hosten (1981), Marquardt (1963)), which is described in paragraph 2.4, was used to regress data such as those shown in figure 3.5. As initial guess for the parameter estimation the values obtained with the moment method were used. The final parameter estimates are shown in table 3.2. As mentioned already, the effective diffusion coefficient is nearly independent of the pulse size up to pulse sizes of $10^{16}$ molecules, meaning that only at lower pulse intensities the flow is caused by Knudsen diffusion alone. Figure 3.7 presents the results from experiments in which six gases with various molecular masses were pulsed over an inert quartz bed at pulse intensities of about $3 \times 10^{15}$ molecules. The estimated effective diffusion coefficients are plotted versus the reciprocal square root of the molecular mass and agree quite well with the plotted line through the origin, as expected from equation 3.10.
These results confirm the Knudsen diffusion model. For light molecules like helium, the agreement is not as close, due to a decreased pumping efficiency of the turbo molecular pump. The slow removal of light gases causes an apparently lower effective diffusion coefficient.

![Graph showing effective diffusion coefficient as a function of the inverse square root of molecular mass.](image)

**Figure 3.7:** Effective diffusion coefficient as a function of the inverse square root of molecular mass \((T = 295 \, \text{K}, \, d_p = 205 \, \mu\text{m} \, \text{and} \, \varepsilon_b = 0.47 \, \text{m}^3 \, \text{m}^{-3})\). Estimates for \(D_e\) obtained by regression of pulse experiments with 6 different gases.

Similar experiments in which argon was pulsed while the temperature was varied between 300 and 600 K, show that the effective diffusion coefficient is linearly proportional to the square root of the temperature again as expected from equation 3.10. This is shown in figure 3.8. The temperature in figure 3.8 is the mean of the temperatures at the beginning and the end of the bed. Although not shown here, the straight line goes through the origin as expected from the Knudsen relation.

Figure 3.9 presents the results of an experiment in which argon was pulsed over beds with various pellet diameters at a temperature of 295 K. The mean pellet size and its upper and lower limits are marked in figure 3.9. The results confirm once more the Knudsen relation which is plotted as the straight line through the origin resulting from equation 3.10 and 3.11.

From the slopes of the straight lines in figures 3.7, 3.8 and 3.9, the tortuosity of the bed can be determined with relation 3.10. The average diameter of the interstitial voids is calculated from the pellet diameter with relation 3.11. The following values of the bed tortuosity, \(\tau_b\), are obtained:
- molecular mass experiment: 5.62 m$^2$/m$^2$
- temperature experiment: 5.60 m$^2$/m$^2$
- pellet size experiment: 5.35 m$^2$/m$^2$

The calculated tortuosities show a good agreement.

**Figure 3.8:** Effective diffusion coefficient as a function of the square root of temperature ($\text{Ar}$, $d_p = 205 \mu$m and $\varepsilon_b = 0.47$ m$^3$/m$^3$). Estimates for $D_e$ obtained by regression of pulse experiments at 10 different temperatures.

**Figure 3.9:** Effective diffusion coefficient as a function of the pellet diameter ($\text{Ar}$, $T = 295$ K and $\varepsilon_b = 0.47$ m$^3$/m$^3$). Mean ($\blacksquare$) and upper and lower (+) pellet diameter. Estimates for $D_e$ obtained by regression of pulse experiments over beds with 4 different average pellet diameters.
All results demonstrate that at pulse intensities up to $1 \times 10^{16}$ molecules per pulse, Knudsen diffusion is the dominating mechanism of gas transport.

### 3.4 Knudsen diffusion in both interstitial and intraparticle voids

Most commercially used catalysts are porous in order to create a larger surface area. In the modelling of TAP experiments it can be necessary to take into account the influence of the transport phenomena in the pores. In paragraph 3.4.2 a model describing diffusion of a gas in both interstitial and intraparticle void space is presented. Before this model is presented, a criterion is derived in paragraph 3.4.1 which allows to assess the importance of diffusion limitations in a pore.

#### 3.4.1 Assessment of the relative importance of interstitial and intraparticle diffusion

In the derivation of criteria for internal gas transport limitations during reaction it is usually assumed that the experiment is carried out under steady-state conditions (Froment and Bischoff, 1990). For transient experiments these criteria are not applicable because in this case accumulation of mass has to be considered. Contrary to steady-state experiments where no reaction occurs, diffusion limitations are possible during transient experiments without reaction. In this paragraph a criterion is derived for the occurrence of diffusion limitations in a pore.

The criterion is derived for a semi-infinite cylindric pore, see figure 3.10. Through the entrance of the pore, gas diffuses into an empty pore from the bulk phase by Knudsen diffusion. The concentration in the bulk phase amounts to $C_A^0$. It is assumed that only diffusion occurs, hence no adsorption, desorption nor reaction is considered. With increasing time species A penetrates into the pore but will never reach the end of the pore because of its infinite length. In figure 3.10 the concentration profile in a pore at time $t$ is shown.

![Figure 3.10: Concentration profile for diffusion in a semi-infinite pore.](image-url)
The continuity equation for A becomes:
\[
\frac{\partial C_A}{\partial t} = D_{A,p} \frac{\partial^2 C_A}{\partial x^2}
\] (3.37)

Equation 3.37 has the following initial and boundary conditions:
\[
t = 0 \land x > 0 : \quad C_A = 0 \quad (3.38)
\]
\[
t \geq 0 \land x = 0 : \quad C_A = C_A^0 \quad (3.39)
\]
\[
t \geq 0 \land x = \infty : \quad C_A = 0 \quad (3.40)
\]

Laplace transformation of equation 3.37 with application of the transformed initial and boundary conditions 3.38, 3.39 and 3.40 yields an expression for the Laplace transformed concentration of A:
\[
\tilde{C}_A = \frac{C_A^0}{s} \exp\left(-\sqrt{\frac{s}{D_{A,p}}} x\right) \quad (3.41)
\]

Inverse transformation to the time gives (Abramowitz and Stegun, 1970):
\[
C_A = C_A^0 \text{erfc} \frac{x}{2 \sqrt{D_{A,p} t}} \quad (3.42)
\]

A measure for the depth of penetration in the cylindrical pore, \(l\), at any time is obtained by dividing the pore’s total content of A by the inlet concentration:
\[
l = \frac{1}{C_A^0} \int_0^\infty C_A \, dx \quad (3.43)
\]

Substitution of 3.42 in 3.43 gives:
\[
l = \int_0^{\text{erfc}} \frac{x}{2 \sqrt{D_{A,p} t}} \, dx \quad (3.44)
\]

This leads to (Abramowitz and Stegun, 1970):
Hence, the time required to penetrate up to the depth $l$ is given by:

$$t = \frac{\pi l^2}{2 \sqrt{D_{A,p}^K}} \frac{t}{\sqrt{\pi}}$$

(3.45)

The capacity is given by $l^2$, whereas $1/D_{A,p}^K$ corresponds to the resistance.

A convenient definition for the characteristic diffusion time in the pores of a pellet can now be derived from equation 3.46 and is given below for pores with length $l_p$:

$$\Theta_{df,p} = \frac{\pi}{4} \frac{\pi l_p^2}{D_{A,p}^K} = \frac{\pi}{4} \frac{\tau_p l_p^2}{D_{A,p}^K}$$

(3.47)

where $\Theta_{df,p}$ is the characteristic diffusion time in the pore [s], $D_{A,p}^K$ is the Knudsen diffusion coefficient of component A in the pellet pores $[m_g^2 s^{-1}]$, and $\tau_p$ is the tortuosity of the pellet pores $[m_b^2 m_c^{-2}]$.

The characteristic diffusion time in a bed consisting of a packed bed of non-porous pellets, $\Theta_{df,b}$, with a bed length $l_b$ can be put equal to the mean residence time of a gas in a bed, which was derived in equation 3.33:

$$\Theta_{df,b} = \frac{1}{2} \frac{e_b}{D_{A,b}^K} = \frac{1}{2} \frac{\tau_b l_b^2}{D_{A,b}^K}$$

(3.48)

where $D_{A,b}^K$ is the Knudsen diffusion coefficient of component A in the interstitial voids $[m_g^2 s^{-1}]$ and $\tau_b$ is the tortuosity of the bed $[m_b^2 m_c^{-2}]$.

Equations 3.47 and 3.48 correspond closely to the criterion put forward by Biloen (1983). Biloen (1983) assessed the occurrence of diffusion limitations in heterogeneous or homogeneous transient kinetic experiments by comparing the characteristic diffusion time defined as:

$$\Theta_{df} = \frac{I^2}{D_e}$$

(3.49)

in which $I$ is the characteristic transport distance of the transient experiment $[m]$ and $D_e$ is the effective diffusion coefficient $[m^2 s^{-1}]$ with the time scale of the experiment.
Theoretically three different situations may occur with respect to the influence of diffusion in the intraparticle pores:

1. The characteristic time of diffusion in the pellets is large compared to the characteristic time of diffusion in the bed. On the time scale of a TAP experiment, only diffusion in the interstitial voids occurs, which is equivalent to the situation dealt with in paragraph 3.3.

2. The characteristic times of diffusion in the pellets and in the bed are of the same order of magnitude. This situation will be considered in paragraph 3.4.2. It is now possible to determine the effective Knudsen diffusion coefficient in the intraparticle pores.

3. The characteristic time of diffusion in the pellets is small compared to the characteristic time of diffusion in the bed, meaning that during a TAP experiment the concentration of component A in the pellets is equal to the concentration in the bed at any time and any position. In this situation an analytical expression for the flux at the exit of the reactor is derived in paragraph 3.4.3.

To verify which of those three situations occurs, the characteristic diffusion times in the bed and the pellet should be compared.

For four different types of packing, namely quartz, α-Al₂O₃, Li/Sn/MgO and γ-Al₂O₃, the characteristic times for diffusion in the pellet and the bed were determined from diffusion coefficients derived from TAP pulse experiments. The quartz and α-Al₂O₃ pellets were non-porous; the Li/Sn/MgO and γ-Al₂O₃ pellets were porous. A sieve fraction of 210-250 μm was used for the different kinds of pellets.

The effective Knudsen diffusion coefficients, used for the calculation of the Knudsen diffusion coefficients, listed in table 3.3, were estimated with the model described in paragraph 3.3, from pulse experiments with argon at 298 K for beds of non-porous quartz and α-Al₂O₃ with a length, Lₚ, of 3.7 × 10⁻³ m. The tortuosity of the pellet pores lies between 1.5 and 10 m⁻² m⁻² (Satterfield (1970), Froment and Bischoff (1990)). The tortuosity of the pellet pores was assumed to be equal to the tortuosity of the bed, 5.5 m⁻² m⁻², as described in paragraph 3.3.2. The Knudsen diffusion coefficient in the pellets was calculated from the Knudsen diffusion coefficient in the interstitial voids of a non-porous quartz or a non-porous α-Al₂O₃ bed by applying equation 3.10, which states the dependence of the diffusion coefficient on the pore diameter. The interstitial pore diameter was calculated with equation 3.11. The mean intraparticle pore diameters of the porous Li/Sn/MgO and γ-Al₂O₃ pellets were obtained from specific surface area measurements using the BET method. The characteristic pore length, Lₚ, was assumed equal to the mean radius of the pellets, in order to be conservative. In table 3.3 the calculated characteristic diffusion times in the pellet and the bed are shown.
Table 3.3: Estimates for the characteristic diffusion times in the pellet $\Theta_{\text{diff,p}}$ and the bed $\Theta_{\text{diff,b}}$ for Ar at $T = 298 \, K$, $d_p = 210-250 \, \mu m$ and $\varepsilon_b = 0.48 \, m_g^3 \, m_r^{-3}$.

<table>
<thead>
<tr>
<th>Packing</th>
<th>$l_b$ or $l_p$ m</th>
<th>$d_i$ m</th>
<th>$D_{\text{Ar,b}} K^3$ or $D_{\text{Ar,p}} K^4$ $m_g^2 , s^{-1}$</th>
<th>$\Theta_{\text{diff,p}}$ s</th>
<th>$\Theta_{\text{diff,b}}$ s</th>
</tr>
</thead>
<tbody>
<tr>
<td>quartz</td>
<td>$3.7 \times 10^{-2}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>1 $1.9 \times 10^{-2}$ $3$</td>
<td>0.00</td>
<td>0.20</td>
</tr>
<tr>
<td>$\alpha$-$\text{Al}_2\text{O}_3$</td>
<td>$3.7 \times 10^{-2}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>1 $1.9 \times 10^{-2}$ $3$</td>
<td>0.00</td>
<td>0.20</td>
</tr>
<tr>
<td>Li/Sn/MgO</td>
<td>$1.2 \times 10^{-4}$</td>
<td>$5.0 \times 10^{-7}$</td>
<td>2 $5.6 \times 10^{-5}$ $4$</td>
<td>0.0011</td>
<td>0.20</td>
</tr>
<tr>
<td>$\gamma$-$\text{Al}_2\text{O}_3$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>$8.0 \times 10^{-9}$</td>
<td>2 $9.0 \times 10^{-7}$ $4$</td>
<td>0.071</td>
<td>0.20</td>
</tr>
</tbody>
</table>

1 calculated with equation 3.11.
2 from specific surface area measurements using the BET method.
3 $D_{\text{Ar,b}} K^3 = 1.68 \times 10^{-3} \, m_g^2 \, m_r^{-1} \, s^{-1}$ (estimated from TAP pulse experiments). $D_{\text{Ar,b}} K^3$ is calculated with equation 3.1.
4 calculated from the value of quartz via equation 3.10.

From table 3.3 it can be concluded that the characteristic diffusion time in the porous Li/Sn/MgO and $\gamma$-$\text{Al}_2\text{O}_3$ pellets is very short compared to the characteristic diffusion time in the bed. It means that at any time the concentration in the pores equals the concentration at the external surface of the pellets. If the time scale for diffusion in the pellets is of the same order of magnitude as the time scale for diffusion in the bed, the effective Knudsen diffusion coefficient in the pellet pores can be determined separately (see paragraph 3.4.2). For pellets with an average pellet diameter of 230 $\mu$m this is the case for a pore diameter of $1.8 \times 10^{-9}$ m. Such pore size is typical for zeolites.

3.4.2 Model equations

In a mass balance for component A over a differential volume element of the catalyst bed, the flux from the interstitial voids to the pellet pores provides an extra contribution, when compared to mass balance 3.16, next to the diffusive flux through the interstitial voids. It is obtained from the concentration profile inside the pellets which results from a mass balance for component A over a differential volume element of the catalyst pellet.

In case Knudsen diffusion is the primary mechanism of transport, the continuity equation for a gas phase component A in the interstitial voids now becomes:

$$\varepsilon_b \frac{\partial C_{A,b}}{\partial t} = D_{\varepsilon,\text{A,b}} \frac{\partial^2 C_{A,b}}{\partial x^2} - (1 - \varepsilon_b) \alpha_r \gamma_{A,p}$$

where $\varepsilon_b$ is the bed porosity consisting of the interstitial voids $[m_g^3 \, m_r^{-3}]$, $C_{A,b}$ is the
concentration of component A in the interstitial voids [mol $m^{-3}$], $D_{e,A,b}^K$ is the effective Knudsen diffusion coefficient in the interstitial voids [mol $m_s^3 m_r^{-1} s^{-1}$], $x$ is the axial reactor coordinate [$m$], $N_{A,b}$ is the flux of component A into the pellets [mol $m_s^3 s^{-1}$] and $a_c$ is the external catalyst surface area per unit catalyst volume [$m_c^2 m_c^{-3}$].

Equation 3.50 has initial and boundary conditions that are identical to those of equation 3.16:

$$t = 0 \wedge 0 \leq x \leq l_b : \quad C_{A,b}(x) = \delta_x \frac{N_{P,A}}{e_b A_r l_p}$$  \hspace{0.5cm} (3.51)

$$t \geq 0 \wedge x = 0 : \quad \frac{\partial C_{A,b}}{\partial x} = 0$$  \hspace{0.5cm} (3.52)

$$t \geq 0 \wedge x = l_b : \quad C_{A,b} = 0$$  \hspace{0.5cm} (3.53)

The following continuity equation for A holds in the intraparticle voids, i.e. in the pores:

$$\varepsilon_p \frac{\partial C_{A,p}}{\partial t} = D_{e,A,p}^K \frac{\partial^2 C_{A,p}}{\partial y^2},$$  \hspace{0.5cm} (3.54)

where $\varepsilon_p$ is the pellet porosity [$m_s^3 m_c^3$], $C_{A,p}$ is the concentration of component A in the intraparticle pores [mol $m_s^3$], $D_{e,A,p}^K$ is the effective Knudsen diffusion coefficient in the pellet pores [mol $m_s^3 m_r^{-1} s^{-1}$] and $y$ is the pellet coordinate [$m$].

Equation 3.54 has the following initial and boundary conditions:

$$t = 0 \wedge 0 \leq y \leq l_p : \quad C_{A,p} = 0$$  \hspace{0.5cm} (3.55)

$$t \geq 0 \wedge y = 0 : \quad C_{A,p} = C_{A,b}$$  \hspace{0.5cm} (3.56)

$$t \geq 0 \wedge y = l_p : \quad \frac{\partial C_{A,p}}{\partial y} = 0$$  \hspace{0.5cm} (3.57)

Here $l_b$ is the length of the intraparticle pores [$m$]. The initial condition, given by equation 3.55, specifies that the initial gas concentration of A in the pores is zero. The first boundary condition, equation 3.56, states that the gas concentration at the inlet of the pore is equal to the gas concentration in the interstitial voids. The second boundary condition, equation 3.57, follows from symmetry considerations. It assumes that a pore has length $2l_p$ with open ends on each side or has length $l_b$ and is closed at one end.
Laplace transformation of equation 3.54 to the time with substitution of initial condition 3.55 gives (Abramowitz and Stegun, 1970):

\[
\varepsilon_p \frac{d}{d\tau} \overline{C}_{A,p} = \frac{D_{eA,p}}{\varepsilon_p} \frac{\partial^2 \overline{C}_{A,p}}{\partial y^2} \tag{3.58}
\]

Applying the Laplace transforms of boundary conditions 3.56 and 3.57 in equation 3.58 gives the following expression for the Laplace transformed concentration of component A in the intraparticle pores.

\[
\overline{C}_{A,p} = \overline{C}_{A,b} \left[ -\tanh \left( \frac{s \varepsilon_p}{D_{eA,p}} l_p \right) \sinh \left( \frac{s \varepsilon_p}{D_{eA,p}} y \right) + \cosh \left( \frac{s \varepsilon_p}{D_{eA,p}} y \right) \right] \tag{3.59}
\]

The flux of component A into the pellet pores, \( N_{A,p} \), is:

\[
N_{A,p} = -D_{eA,p} \frac{\partial \overline{C}_{A,p}}{\partial y} \bigg|_{y=0} \tag{3.60}
\]

Laplace transformation of equation 3.60 to the time gives:

\[
\overline{N}_{A,p} = -D_{eA,p} \frac{\partial \overline{C}_{A,p}}{\partial y} \bigg|_{y=0} \tag{3.61}
\]

The Laplace transformed flux into the pores at the beginning of the pores is then:

\[
\overline{N}_{A,p} = \overline{C}_{A,b} \left( \frac{s \varepsilon_p}{D_{eA,p}} l_p \right) \frac{\tanh \left( \frac{s \varepsilon_p}{D_{eA,p}} l_p \right)}{\sqrt{\frac{s \varepsilon_p}{D_{eA,p}} l_p}} \tag{3.62}
\]

Inverse transformation to the time domain gives (de Croon, 1992):

\[
N_{A,p} = 2 \frac{D_{eA,p}}{l_p} \sum_{n=0} \exp \left( -\frac{(2n+1)^2 \pi^2 D_{eA,p} \varepsilon_p}{4 \varepsilon_p l_p^2} t \right) \left[ \varepsilon_{b,A} A_1 l_b \int_0^{\delta_x} \exp \left( \frac{(2n+1)^2 \pi^2 D_{eA,p} \varepsilon_p}{4 \varepsilon_p l_p^2} \xi \right) d\xi \right], \tag{3.63}
\]

where \( \xi \) is a dummy integration variable [s].
Substitution of 3.63 in the continuity equation for A in the interstitial phase, equation 3.50, gives a non-homogeneous parabolic differential equation with $C_{A,b}$ as independent variable:

$$
\varepsilon_b \frac{\partial C_{A,b}}{\partial t} = D_{eA,b} \frac{\partial^2 C_{A,b}}{\partial x^2} - 2(1 - \varepsilon_b) a_v l_p \frac{D_{eA,b}}{l_p^2} \sum_{n=0}^{\infty} \exp \left( \frac{(2n+1)^2 \pi^2 D_{eA,b}^K}{4 \varepsilon_p l_p^2} t \right)
$$

$$
\left[ \frac{N_{p,A}}{\varepsilon_b A_p l_b} \delta_x + \left. \frac{\partial C_{A,b}}{\partial t} \right|_0 \text{exp} \left( \frac{(2n+1)^2 \pi^2 D_{eA,b}^K}{4 \varepsilon_p l_p^2} \right) \right]
$$

(3.64)

In paragraph 3.4.3 equation 3.64 is applied for a simplified situation.

### 3.4.3 Instantaneous diffusion in the catalyst pores

In the situation of instantaneous diffusion in the pores of the pellets equation 3.64 can be simplified by substitution of equation 3.62, i.e. the Laplace transformed flux into the pellets, directly in the Laplace transform of equation 3.50:

$$
-s \bar{C}_{A,b} - \frac{N_{p,A}}{\varepsilon_b A_p l_b} \delta_x = D_{eA,b}^K \frac{\partial^2 \bar{C}_{A,b}}{\partial x^2} - s \bar{C}_{A,b} a_v l_p \frac{\varepsilon_p (1 - \varepsilon_b)}{\varepsilon_b} - s \frac{g(s)}{D_{eA,b}^K l_p}
$$

$$
\left( \varepsilon_p \frac{2 \varepsilon_p^2}{D_{eA,b}^K l_p} \right)^{1/2} \text{tanh} \left( \frac{s \varepsilon_p}{D_{eA,b}^K l_p} \right)
$$

(3.65)

Assume:

$$
g(s) = a_v l_p \frac{\varepsilon_p^2}{\varepsilon_b} \left( \frac{2 \varepsilon_p^2}{D_{eA,b}^K l_p} \right)^{1/2} \text{tanh} \left( \frac{s \varepsilon_p}{D_{eA,b}^K l_p} \right)
$$

(3.66)

Substitution of 3.66 in 3.65 and using the Laplace transform of initial and boundary conditions 3.55, 3.56 and 3.57, yields the concentration, $\bar{C}_{A,b}$, in the Laplace domain from which the following Laplace transformed molar flow rate at the outlet of the reactor is derived:
\[ \bar{F}_A \big|_{x=l_p} = A_p D_{eA,b}^K \frac{\partial \bar{C}_{A,b}}{\partial x} \big|_{x=l_p} = N_{p,A} \frac{1}{\cosh \left( \sqrt{\frac{s e_b l_p^2}{D_{eA,b}} (1 + g(s))} \right)} \]

Equation 3.67 is derived in an analogous way as equation 3.26. Inverse transformation of equation 3.67 is extremely difficult. For large times (small \( s \)) \( g(s) \) approaches the limit value:

\[ g(s) = a_p l_p \frac{\varepsilon_p (1 - \varepsilon_b)}{\varepsilon_b} \]

Substitution of equation 3.68 in 3.67 with the assumption that \( a_p l_p = 1 \), i.e. a flat plane with pores with length \( l_p \), gives the Laplace transformed molar flow rate at the outlet of the reactor:

\[ \bar{F}_A \big|_{x=l_p} = N_{p,A} \frac{1}{\cosh \left( \frac{s e_b l_p^2}{D_{eA,b}} (1 + g(s)) \right)} \]

In equation 3.26 the Laplace transformed molar flow rate at the outlet of the reactor for the situation that only Knudsen diffusion in the interstitial pores occurs, was derived for dimensionless time. When translated to terms of real time, that equation results in:

\[ \bar{F}_A \big|_{x=l_p} = N_{p,A} \frac{1}{\cosh \left( \frac{s e_b l_p^2}{D_{eA,b}} \right)} \]

Equations 3.69 and 3.70 are similar, the only difference being the term:

\[ 1 + \frac{\varepsilon_p (1 - \varepsilon_b)}{\varepsilon_b} \]

If the pellet porosity is zero, equation 3.69 and 3.70 are identical. Comparing the right hand sites gives:

\[ D_{e,pore}^K = \left( \frac{D_{e,narrow~pores}}{1 + \frac{\varepsilon_p (1 - \varepsilon_b)}{\varepsilon_b}} \right) \]

Equation 3.72 can be rearranged as:
A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by O₂/NO on Pt

\[
\frac{D_e^{K \text{ non-porous}}}{D_e^{K \text{ porous}}} = \frac{\varepsilon_{t \text{ porous}}}{\varepsilon_{b \text{ non-porous}}},
\]

(3.73)

where \(\varepsilon_{t \text{ porous}}\) is the total porosity of the bed, packed with porous pellets \([m^3\ m^{-3}]\).

Apparently the measured effective diffusion coefficient in case of diffusion in the interstitial pores and very fast diffusion in the intraparticle pores, is equal to the effective diffusion coefficient for diffusion in the bed only, adjusted for the larger available gas volume. From equation 3.73 the effective Knudsen diffusion coefficient for porous pellets can be calculated from the diffusion coefficient measured in a similar bed of non-porous pellets, when it is assumed that the bed porosity and bed tortuosity are the same in both experiments.

Equation 3.73 also means that the pellet or catalyst porosity can be calculated from the measured effective Knudsen diffusion coefficient in a porous and a non-porous bed.

### 3.4.4 Estimation of the diffusion coefficients and the catalyst porosities

In table 3.4 the estimated effective Knudsen diffusion coefficients, \(D_e^{K}\), for the four types of packing, mentioned earlier in paragraph 3.4.1, are listed. The Knudsen diffusion coefficients in table 3.4 were estimated with the model described in paragraph 3.3, from pulse experiments with argon at 298 K for beds of non-porous quartz, non-porous \(\alpha\)-Al₂O₃, porous Li/Sn/MgO and porous \(\gamma\)-Al₂O₃ with a length of \(3.7 \times 10^2\) m. The characteristic times of diffusion in the pellets and bed are listed in table 3.3.

**Table 3.4:** Estimated and measured pellet and total porosities determined from pulse experiments with argon at \(T = 298\ K\), \(d_p = 210-250\ \mu m\) and \(e_b = 0.48\ m^3\ m^{-3}\).

<table>
<thead>
<tr>
<th>packing</th>
<th>(D_e^{K}) (10^{-3}\ m^3\ m^{-1}\ s^{-1})</th>
<th>(\varepsilon_t) (m^3\ m^{-3})</th>
<th>(\varepsilon_p) (m^3\ m^{-3})</th>
<th>(\varepsilon_{\text{BET}}) (m^3\ m^{-3})</th>
<th>(\varepsilon_{\text{mic}}) (m^3\ m^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>quartz</td>
<td>1.67</td>
<td>0.48 (^1)</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\alpha)-Al₂O₃</td>
<td>1.68</td>
<td>0.48 (^1)</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Li/Sn/MgO</td>
<td>1.43</td>
<td>0.56 (^2)</td>
<td>0.15 (^3)</td>
<td>0.23</td>
<td>-</td>
</tr>
<tr>
<td>(\gamma)-Al₂O₃</td>
<td>0.93</td>
<td>0.86 (^2)</td>
<td>0.73 (^3)</td>
<td>0.66</td>
<td>0.61</td>
</tr>
</tbody>
</table>

\(^1\) porosity experimentally determined.

\(^2\) calculated with equation 3.73 with \(D_e^{K \text{ non-porous}} = 1.67 \times 10^{-3} m^3 m^{-1} s^{-1}\).

\(^3\) calculated with equation 3.72 with \(D_e^{K \text{ non-porous}} = 1.67 \times 10^{-2} m^3 m^{-1} s^{-1}\) and \(\varepsilon_b = 0.48 m^3 m^{-3}\).
Table 3.4 shows that the more porous the pellets, the lower the effective Knudsen diffusion coefficient. The diffusion coefficients of non-porous quartz and $\alpha$-Al$_2$O$_3$ are nearly the same. The total bed porosity and the pellet porosity were calculated with equation 3.73 and 3.72 respectively. The pellet porosities are compared with values obtained from mercury porosimetry and BET measurements. The agreement is quite satisfactory.

3.5 Conclusions

The modes of gas transport that may occur during TAP experiments include Knudsen diffusion, molecular diffusion and viscous flow. By using an appropriate constitutive model for the gas transport, the effect of the inlet pulse intensity on the flux associated with each mode of gas transport can be quantified. In a single gas Knudsen diffusion and viscous flow are the only mechanisms of gas transport. Knudsen diffusion dominates at pulse intensities lower than $1 \times 10^{16}$ molecules and viscous flow at larger pulse sizes. The qualitative and quantitative similarity predicted by the model and the measured contributions of Knudsen diffusion and viscous flow to the gas transport mechanism are reasonable. In gas mixtures molecular diffusion cannot be neglected at intermediate pulse sizes, i.e. containing about $1 \times 10^{16}$ molecules.

For single gases at pulse intensities below $1 \times 10^{16}$ molecules per pulse, the gas transport becomes independent of the inlet pulse size and Knudsen diffusion is the controlling mechanism of gas transport. Experimental verification of the Knudsen regime was shown by using gases with various molecular weights and by varying the system parameters like temperature, pulse intensity and pellet diameter. With the model presented for the diffusion in the interstitial voids, the diffusion coefficients can be estimated quantitatively in the Knudsen regime. In this situation it is possible to estimate the bed tortuosity as well, provided the bed porosity is determined separately.

A criterion is derived for the occurrence of diffusion limitations in transient experiments. With the model presented for diffusion in both interstitial and intraparticle voids, the gas transport can be described. In case of instantaneous diffusion in the pellet pores, their only effect is an increase of the total available gas volume. It was shown that in such situation, the Knudsen diffusion coefficient for porous particles is simply related to that for non-porous particles via a capacity term that corresponds to the intraparticle porosity.
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References

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- D'Arcy, H.P.G., Les Fontaines Publiques de la Ville de Dijon, Victor Dalmont, Paris, 1856
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4.1 Introduction

Although transient experiments can provide more information than steady-state experiments, they are also more difficult to analyse (Gleaves et al., 1988). Hence, the advantages of being able to focus the analysis on chemical kinetics only, are even more pronounced than in the case of steady-state experiments. Unfortunately, the reaction kinetics cannot be solved, without an understanding of the gas transport in the reactor. This latter has been considered extensively in chapter 3. In this chapter, the only occurring mechanism of gas transport is supposed to be Knudsen diffusion. In this regime the equations needed to model the system are simplified to a large extent. In paragraph 4.3 a model is presented which describes the transport, adsorption, desorption and reaction processes occurring within the TAP microreactor after injection of a pulse. With this model the influence of the adsorption, desorption and reaction rate coefficients on the pulse response, i.e. on the outlet molar flow rates of the reactants and products, is examined in paragraph 4.5. In some cases, a simple analytical expression can be derived which allows easy calculation of the various rate coefficients as is shown in paragraph 4.4. For first order processes the time scales of adsorption, desorption, reaction and diffusion are compared in paragraph 4.5. This indicates the circumstances that allow quantitative determination of the corresponding rate coefficients. In paragraph 4.2, the window of reaction rate coefficients, that can be measured with TAP, is discussed for the simple case of a pseudo first order reaction.

4.2 Delimitation of measurable rate coefficients

Estimation of rate coefficients can only be obtained with the TAP method, if these rate coefficients have values between a certain lower and upper limit. If the value of the reaction rate coefficient is too high, the response signal of a reactant cannot be distinguished from
noise anymore because of nearly complete conversion. In case the value of the reaction rate coefficient is too low, the injected pulse has passed the reactor by diffusion before significant reaction has occurred, meaning that the response will hardly differ from the response resulting from diffusion only. In these situations quantitative determination of reaction rate coefficients is impossible.

The minimum and maximum measurable reaction rate coefficients are discussed here for a simple homogeneous first order chemical reaction in an empty reactor as well as in a fixed bed reactor, under the assumption of simultaneous Knudsen diffusion.

Consider a homogeneous first order reaction:

\[ \text{A} \rightarrow \text{B} \]

The continuity equation for reactant A is:

\[ \epsilon_b \frac{\partial C_A}{\partial t} = D_{eA} \frac{\partial^2 C_A}{\partial x^2} - \epsilon_b k_1 C_A, \tag{4.1} \]

where \(k_1\) is the first order rate coefficient \([s^{-1}]\).

With axial coordinate \(z=x_0 l_b^{-1}\) and normalised time equation 4.1 becomes:

\[ \frac{\partial C_A}{\partial \tau} = \frac{\partial^2 C_A}{\partial z^2} - D_{aA} C_A \tag{4.2} \]

with:

\[ D_{aA} = \frac{\epsilon_b k_1 l_b^2}{D_{eA}} \tag{4.3} \]

and:

\[ \tau = \frac{D_{eA} t}{\epsilon_b l_b^2} \tag{4.4} \]

The Damköhler I number is the ratio of the time scale for transport to the time scale for reaction. The normalised time, \(\tau\), is, with the exception of the constant factor \(\frac{1}{2}\), the dimensionless form of the characteristic time of diffusion or mean residence time in a bed of inert non-porous packing with length \(l_b\), which was given by equation 3.48:

\[ \Theta_{df,b} = \frac{1}{2} \frac{\epsilon_b l_b^2}{D_{eA,b}} \tag{4.5} \]
Equation 4.2 has the following initial and boundary conditions when a TAP pulse experiment is considered. These conditions were explained in paragraph 3.3.1.

\[ C(z,0) = \delta_z \frac{N_{p,A}}{v_p A_z l_h} \]  \hspace{1cm} (4.6)

\[ \frac{\partial C}{\partial z} \bigg|_{z=0} = 0 \]  \hspace{1cm} (4.7)

\[ C(1,\tau) = 0 \]  \hspace{1cm} (4.8)

The solution of equations 4.2, 4.6, 4.7 and 4.8 is derived in a similar way as described in paragraph 3.3.1.1. The molar flow rate at the outlet of the reactor as function of \( \tau \) is in this situation (de Croon, 1992):

\[ F_{A} \bigg|_{z=1} = \frac{D_p A}{\varepsilon_b} \frac{N_{p,A} \pi}{l_b^2} \sum_{n=0}^{\infty} (2n+1)(-1)^n \exp\left(-\frac{(2n+1)^2 \pi^2 \tau}{4}\right) \]  \hspace{1cm} (4.9)

In the situation of diffusion only, \( Da_t = 0 \) and equation 4.9 reduces to equation 3.27.

In figure 4.1 the outlet molar flow rates, calculated according to equation 4.9 and relative to the situation where \( Da_t = 0 \), are shown for different values of the \( Da_t \) number. It follows from this figure that for too high reaction rate coefficients the response signal cannot be distinguished from noise. For too low values of \( Da_t \) the response is identical to the response by diffusion only.

![Figure 4.1: Molar flow rates at the outlet of the TAP microreactor, relative to the situation where \( Da_t = 0 \), for different values of the Damköhler I number: A) 0, B) 0.25, C) 2.5, D) 5.0 and E) 25.](image)
Assuming that a response signal area of approximately 1% of the inlet signal area is readily detectable, one obtains for the upper bound of the Damköhler I number a figure of about 25. For the lower bound one obtains, under the assumption that a deviation of 10% of the width at half height of the response signal is significant, a Damköhler I number of 0.25. In this case the onset response signal differs significantly from the signal without reaction, as shown in figure 4.1. Therefore, in principle, $D_{a_1} = 0.25$ and 25 set the limits for the minimum and maximum rate coefficients that can be measured to obtain the corresponding values of the rate coefficients.

The above considerations lead to the following delimitation of $D_{a_1}$ for which the response contains sufficient information:

$$0.25 \leq D_{a_1} \leq 25$$

(4.10)

In order to find a corresponding delimitation for the rate coefficient $k_1$, the different factors in the Damköhler I number have to be taken into account. The effective Knudsen diffusion coefficient and, hence, the average residence time of A in the reactor depends on the reactor diameter, the reactor length, the bed porosity, the bed length, the bed tortuosity, the pellet diameter, the molecular masses of the used gases and the reaction temperature. For given reactor dimensions and at a given reactor temperature, the values of the minimum and maximum measurable reaction rate coefficients are determined by the packing of the microreactor. Packing reduces the diameter of the interstitial voids in the reactor, causing a lower Knudsen diffusion coefficient and porosity. As a result the effective diffusion coefficient decreases, meaning that the measurable reaction rate coefficients decrease as well.

The maximum reaction rate coefficient that can be measured is obtained in an empty microreactor. For a reactor with a diameter of 5.6 mm and a length of 42.2 mm at 500 K the effective Knudsen diffusion coefficient, calculated with relation 3.10 for carbon monoxide, is $1.15 \text{ m}^3 \text{ m}_r^{-1} \text{ s}^{-1}$. From equation 4.10 it follows that a maximum reaction rate coefficient of $1.6 \times 10^4 \text{ s}^{-1}$ can be measured.

For lower rate coefficients packing should be applied in the reactor. The minimum reaction rate coefficient is measured in a packed bed with interstitial voids as small as possible. The diameter of the interstitial voids is proportional to the particle diameter, see equation 3.11. In the TAP microreactor, the smallest particles which can be used have a diameter of 200 μm. The porosity of such a bed is about $0.48 \text{ m}^3 \text{ m}_p^{-3}$. For argon at 500 K the effective Knudsen diffusion coefficient in such a bed with a length of 42.2 mm and a tortuosity of $5.5 \text{ m}_p^{-2} \text{ m}_r^{-2}$ is $2.2 \times 10^{-3} \text{ m}^3 \text{ m}_r^{-1} \text{ s}^{-1}$. The value of the minimum measurable reaction rate coefficient therefore is $0.64 \text{ s}^{-1}$ as follows from equation 4.10.
Summarising, with the TAP microreactor first order reaction rate coefficients can be determined with values between 1 s\(^{-1}\) and 1 \(10^4\) s\(^{-1}\):

\[1 \text{ s}^{-1} \leq k_i \leq 1 \times 10^4 \text{ s}^{-1}\]  

(4.11)

### 4.3 Model equations

In general when studying a catalytic reaction with TAP the microreactor will be packed with three subsequent beds: one catalytic bed enclosed by two inert beds, see figure 4.2.

![Figure 4.2: Schematic drawing of the TAP microreactor packed with a catalytic bed (bed 2) enclosed by two inert beds (bed 1 and 3).](image)

The response after the injection of a gas pulse is a function of all processes appearing in the reactor: gas transport, adsorption, desorption and reaction and can be calculated by integrating the continuity equations for all components considered. When the catalyst bed is placed in the isothermal part of the microreactor, the energy balances can be omitted. In the present analysis it is assumed that the used catalyst and inert particles are non-porous to exclude intraparticle diffusion limitations. The final mathematical form of the continuity equations depends on the specific bed that is described. In the two inert beds only gas transport is involved. The continuity equations in the catalytic bed contain an additional production term.

For simplicity these continuity equations may be summarized in one general equation:

\[
\varepsilon_b \frac{\partial C_i}{\partial t} + \frac{\partial N_i}{\partial x} = (1 - \varepsilon_b) a_c R_{ik}\]

(4.12)

with \(\varepsilon_b\) the bed porosity \([m^3]\), \(C_i\) the gas phase concentration of component \(i\) \([\text{mol} \cdot m^{-3}]\), \(N_i\) the molar flux of component \(i\) \([\text{mol} \cdot m^{-2} \cdot s^{-1}]\) and \(R_{ik}\) the net production rate of component \(i\) in bed \(k\) \([\text{mol} \cdot m^{-2} \cdot s^{-1}]\), with \(R_{ik} = 0\) if \(k = 1\) or 3. For a purely heterogeneous reaction, \(R_{ik}\) is the net result of adsorption and desorption rates.
When the experiments are carried out in the Knudsen diffusion regime, the molar flux is given by equation 4.13:

\[ N_i = -D_{\text{eff}}^K \frac{\partial C_i}{\partial x}, \]  

(4.13)

in which \( D_{\text{eff}}^K \) is the effective Knudsen diffusion coefficient of component \( i \) in the bed of concern \([m^3 m^{-3} s^{-1}]\).

With the assumption that \( D_{\text{eff}}^K \) and \( \varepsilon_b \) are independent of the axial coordinate in each bed, the continuity equation for component \( i \) becomes:

\[ \varepsilon_b \frac{\partial C_i}{\partial t} = D_{\text{eff}}^K \frac{\partial^2 C_i}{\partial x^2} + (1 - \varepsilon_b) a^*_i R_{ik}, \]  

(4.14)

The production term \( R_{ik} \) for \( k=2 \) is a function of the gas phase concentrations of the components and a function of the surface coverage of the adsorbed species. So besides equation 4.14 the continuity equations for the different surface species have to be integrated:

\[ \frac{\partial L_j \theta_j}{\partial t} = R_j, \]  

(4.15)

in which \( R_j \) is in general a function of the surface coverages of adsorbed species and the gas phase concentrations. The right hand side of equation 4.15 is determined by adsorption, desorption and all surface reactions. Since the gas phase concentrations are position dependent, the surface coverage is a function of the axial reactor coordinate as well.

The changes in the gas phase concentration of component \( i \) at the outlet of the TAP microreactor can be calculated by solving simultaneously the continuity equations for all components in each of the packed beds. The following initial and boundary conditions apply:

**Bed 1:**

The initial gas phase concentration of reactant \( i \) follows from the equation for the inlet pulse:

\[ t = 0 \land 0 \leq x < l_1: \quad C_i(x) = \delta_x \frac{N_{n,i}}{\varepsilon_{\text{bed}1} A_x l_1}, \]  

(4.16)

with \( l_1 \) the bed length of the first inert bed \([m]\), \( N_{n,i} \) the inlet pulse size of reactant \( i \) \([\text{mol}]\) and \( \varepsilon_{\text{bed}1} \) the porosity of bed 1 \([m^3 m^{-3}]\).
For any formed gas phase product i holds:

\[ t = 0 \land 0 \leq x < l_i : \quad C_i(x) = 0 \]  
(4.17)

After the introduction of the gas pulse, the pulse valve is closed meaning a zero flux at the reactor entrance:

\[ t \geq 0 \land x = 0 : \quad \frac{\partial C_i}{\partial x} = 0 \]  
(4.18)

The concentration of component i at the end of bed 1 is equal to the concentration of component i at the beginning of the catalyst bed:

\[ t \geq 0 \land x = l_1 : \quad C_i \big|_{\text{bed1}} = C_i \big|_{\text{bed2}} \]  
(4.19)

The surface coverage of all species j in the inert bed is zero:

\[ t \geq 0 \land 0 \leq x < l_i : \quad \theta_j = 0 \]  
(4.20)

**bed 2:**

At the start of the experiment, there are no gas phase components in bed 2:

\[ t = 0 \land l_i \leq x \leq (l_i + l_2) : \quad C_i(x) = 0 \]  
(4.21)

in which \( l_2 \) is the length of bed 2 [m].

The molar flux at the end of bed 1 is equal to the molar flux at the entrance of bed 2:

\[ t \geq 0 \land x = l_1 : \quad -D_{e, \text{bed1}} \frac{\partial C_i}{\partial x} \big|_{\text{bed1}} = -D_{e, \text{bed2}} \frac{\partial C_i}{\partial x} \big|_{\text{bed2}} \]  
(4.22)

The concentration of component i at the outlet of bed 2 is equal to the concentration of component i at the inlet of bed 3:

\[ t \geq 0 \land x = (l_i + l_2) : \quad C_i \big|_{\text{bed2}} = C_i \big|_{\text{bed3}} \]  
(4.23)

At the start of the experiment, the catalyst surface coverage is supposed to be uniform with an initial coverage \( \theta_j^0 \):

\[ t = 0 \land l_i \leq x \leq (l_i + l_2) : \quad \theta_j(x) = \theta_j^0 \]  
(4.24)
At the start of the experiment, there are no gas phase components in the reactor:

\[ t = 0 \land (l_1 + l_2) < x \leq (l_1 + l_2 + l_3) : \quad C_i(x) = 0 \quad \text{ (4.25)} \]

where \( l_3 \) is the length of bed 3 [m].

The molar flux at the exit of the catalyst bed is equal to the molar flux at the beginning of bed 3:

\[ t \geq 0 \land x = (l_1 + l_2) : \quad \text{\( -D_i^{\text{ac}} \frac{\partial C_i}{\partial x} \big|_{\text{bed 2}} = -D_i^{\text{ac}} \frac{\partial C_i}{\partial x} \big|_{\text{bed 3}} \) (4.26)} \]

The concentration of component \( i \) at the end of bed 3 is equal to zero because the reactor outlet is at vacuum conditions:

\[ t \geq 0 \land x = (l_1 + l_2 + l_3) : \quad C_i = 0 \quad \text{ (4.27)} \]

The surface coverage of species \( j \) in the inert bed is zero:

\[ t \geq 0 \land (l_1 + l_2) < x < (l_1 + l_2 + l_3) : \quad \theta_j = 0 \quad \text{ (4.28)} \]

The differential equations 4.14 and 4.15 with the accompanying initial and boundary conditions 4.16 to 4.28 were solved numerically with the routine D03PGF from the NAG Fortran Library. The routine itself is explained in paragraph 3.3.1.3.

If the effective diffusion coefficients in the inert and catalytic beds are different, boundary conditions 4.22 and 4.26 cause a discontinuity in the axial gas concentration profile. In figure 4.3 that profile is shown at 6 ms after the introduction of an inert argon gas pulse for the case that the effective diffusion coefficient in the catalyst bed is 10 times larger than the one in the inert beds. The concentration profile in the catalyst bed is rather flat because of the enhanced gas transport in the catalyst bed. In figure 4.4 the concentration profile is shown for the effective diffusion coefficients corresponding to the applied platinum sponge and quartz beds, see paragraph 2.5.2, at the same conditions as used in figure 4.3.

As the effective diffusion coefficient of argon for the catalyst bed is about a factor 1.3 larger than that for the inert beds, their difference is too small to observe the discontinuities.
4.4 Analytical results for first order adsorption and desorption

An analytical solution can be derived for some simplified situations in case of one bed only. The analytical solution presented below, applies to first order reactions only. Higher order reactions make the equations non-linear and numerical solutions are required. As an example the analytical solution for a pulse containing a single component A is derived, which undergoes adsorption and desorption at one type of site, assuming Knudsen diffusion and first order adsorption and desorption. The following continuity equations for A in the gas phase and on the surface apply:

\[
\frac{\partial C_A}{\partial t} = D_{fa} \frac{\partial^2 C_A}{\partial x^2} - (1 - \varepsilon_b) a_e L_e [ -k_a C_A (1 - \theta_A) + k_d \theta_A ]
\]  \hspace{1cm} (4.29)

\[
\frac{\partial \theta_A}{\partial t} = k_a C_A (1 - \theta_A) - k_d \theta_A
\]  \hspace{1cm} (4.30)

A further simplification of equation 4.29 and 4.30 is possible because the number of adsorption sites is usually much greater than the number of adsorbing molecules in a single-pulse TAP experiment. It means that the factor \((1-\theta_A)\) is about unity when the experiment starts with a clean surface. The accompanying initial and boundary conditions are:
\[ t = 0 \land 0 \leq x \leq l_b : \quad C_A(x) = \delta_x \frac{N_{p,A}}{e_b \Lambda_p l_b} \]  \hspace{1cm} (4.31)

\[ t = 0 \land 0 \leq x \leq l_b : \quad \theta_A = 0 \]  \hspace{1cm} (4.32)

\[ t \geq 0 \land x = 0 : \quad \frac{\partial C_A}{\partial x} = 0 \]  \hspace{1cm} (4.33)

\[ t \geq 0 \land x = l_b : \quad C_A = 0 \]  \hspace{1cm} (4.34)

The initial and boundary conditions were explained before.

The solution is derived in an analogous way as described in paragraph 3.3.1.1. The molar flow rate at the outlet of the reactor as function of time is in this situation (de Croon, 1992):

\[ \dot{F}_A|_{x=l_b} = \frac{D_{eA}}{e_b} \sum_{n=0}^{\infty} \frac{N_{p,A}}{l_b^2} (2n + 1)(-1)^n \left[ \frac{r_- + (1 - \varepsilon_b) \frac{a_v L_i k_a}{\varepsilon_b} + \lambda_n^2}{r_- - r_+} \exp(r_- t) \right] \]

\[ - \frac{r_- + (1 - \varepsilon_b) \frac{a_v L_i k_a}{\varepsilon_b} + \lambda_n^2}{r_- - r_+} \exp(r_+ t) \]

\hspace{1cm} (4.35)

with:

\[ \lambda_n^2 = \frac{(2n + 1)^2 D_{eA} \pi^2}{4 e_b l_b^2} \]  \hspace{1cm} (4.36)

and:

\[ r_+ = \frac{-a_v L_i k_a - k_d - \lambda_n^2 \pm \sqrt{(1 - \varepsilon_b) \frac{a_v L_i k_a + k_d + \lambda_n^2}{\varepsilon_b}}}{2k_d \lambda_n^2} \]  \hspace{1cm} (4.37)
Moment analysis

The moments of the response curves, as described in paragraph 3.3.1.2, can be calculated from the expression for the molar flow rate at the outlet of the reactor, equation 4.35. Analysis of the zeroth, first and second moment yields valuable information about the inlet pulse size, the mean residence time, the effective diffusion coefficient and the adsorption and desorption rate coefficients.

The zeroth moment is equal to the inlet pulse size:

\[
m_0 = \frac{4N_p}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n + 1} = N_p\lambda
\] (4.38)

The first normalised moment can be related to the mean residence time and is given by:

\[
\bar{\tau} = \mu_1 = \frac{l_b^2 \varepsilon_b}{2D_{eK}^b} \left( 1 + \frac{(1 - \varepsilon_b) \alpha_b L_i k_a}{k_d} \right)
\] (4.39)

The second normalised moment is given by:

\[
\mu_2 = \frac{5l_b^4 \varepsilon_b^2}{12D_{eK}^{b3/2}} \left( 1 + \frac{(1 - \varepsilon_b) \alpha_b L_i k_a}{k_d} \right)^2 + \frac{l_b^2 \varepsilon_b}{D_{eK}^b} \frac{(1 - \varepsilon_b) \alpha_b L_i k_a}{k_d^2}
\] (4.40)

The effective Knudsen diffusion coefficient can be derived simply from the mean residence time, equation 3.33, or the peak time, equation 3.34, if the experiment is carried out with an inert gas. It should be remembered that \(D_{eK}^b\) applies to Knudsen diffusion through the interstitial voids. Once \(D_{eK}^b\) is known, the adsorption and desorption rate coefficients can be determined from the first and second normalised moments.

4.5 Characteristic times for adsorption, desorption, reaction relative to diffusion

The results obtained in paragraph 4.2.1 for a first order homogeneous reaction are now extended towards a heterogeneous catalytic reaction which includes adsorption and desorption. Therefore the time scale of the various subprocesses are compared to obtain a qualitative picture of the circumstances that allow quantitative determination of certain parameters. For instance if the time scale of diffusion is much smaller than the time scale of adsorption, the gas leaves the reactor before adsorption can occur and the response signal is unaffected by adsorption. So the time scale or characteristic time of a specific phenomenon is a sound basis to compare the relevance of that phenomenon for changes in the pulse response.
The characteristic diffusion time in a bed, $\Theta_{\text{diff}}$, with length $l_b$ is given by equation 4.5. The characteristic time scale for first order adsorption, $\Theta_{\text{adv}}$, can be deduced from the first order reaction coefficient:

$$r_A = (1 - e_b) \frac{a_r L_i k_a}{e_b} \theta, C_A,$$

with $r_A$ the reaction rate of component A [mol m⁻³ s⁻¹], $k_a$ the first order adsorption rate coefficient [m⁻³ mol⁻¹ s⁻¹], $a_r$ the external catalyst area per unit catalyst volume [m⁻²], $L_i$ the maximum molar concentration of adsorbed species per square meter catalyst surface area [mol m⁻³] and $\theta$, the fractional coverage of vacant sites on the catalyst surface.

From this follows for the characteristic time for first order adsorption:

$$\Theta_{\text{adv}} = \frac{1}{(1 - e_b) \frac{a_r L_i k_a}{e_b} \theta}.$$  (4.42)

During one pulse the fractional coverage of vacant surface sites, $\theta$, remains constant, because the amount of molecules admitted per pulse is small compared to the amount of surface sites.

In similar way the characteristic times for first order desorption, $\Theta_{\text{des}}$, and reaction, $\Theta_{\text{reac}}$, can be derived:

$$\Theta_{\text{des}} = \frac{1}{k_d}.$$  (4.43)

$$\Theta_{\text{reac}} = \frac{1}{k_r}.$$  (4.44)

Here $k_d$ is the first order desorption rate coefficient [s⁻¹] and $k_r$ is the first order reaction rate coefficient [s⁻¹].

Table 4.1 lists the kinetic parameters which can be determined from a single pulse TAP experiment if besides diffusion, adsorption and desorption occur at various time scales. Reaction is not considered in this table, because the behaviour of the reaction rate coefficient is quite similar to that of the desorption rate coefficient. Table 4.1 shows that if the characteristic time for diffusion is of the same order of magnitude as the characteristic times for adsorption and desorption, all kinetic parameters can be determined accurately. In the experimental practice there are some ways to adjust within limits the characteristic times such that the desired parameters may be determined. The characteristic time of diffusion can be
adapted by changing the bed length or the pellet diameter. The characteristic time for adsorption can be adjusted by changing the number of vacant surface sites. Moreover, since the phenomena mentioned have normally different activation energies, a change of temperature may result in measurable parameters.

**Table 4.1:** Appearing phenomena and potential to determine kinetic parameters at different characteristic times of adsorption, desorption and diffusion.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Theta_{\text{ads}} \gg \Theta_{\text{diff}}$</td>
<td>No adsorption; response signal caused by diffusion and estimation of kinetic parameters impossible.</td>
</tr>
<tr>
<td>$\Theta_{\text{ads}} = \Theta_{\text{diff}}$</td>
<td>Part of reactant adsorbs; no desorption and estimation of $k_4$ possible. If the surface is totally covered, no adsorption occurs and response signal resembles the diffusion signal.</td>
</tr>
<tr>
<td>$\Theta_{\text{ads}} = \Theta_{\text{diff}}$</td>
<td>Part of reactant adsorbs; desorption and diffusion on the same time scale and estimation of $k_2$ and $k_d$ possible.</td>
</tr>
<tr>
<td>$\Theta_{\text{ads}} \ll \Theta_{\text{diff}}$</td>
<td>Instantaneous desorption (sorption equilibrium totally left); response signal resembles to diffusion signal and estimation of kinetic parameters impossible.</td>
</tr>
<tr>
<td>$\Theta_{\text{ads}} \ll \Theta_{\text{diff}}$</td>
<td>Total reactant adsorption (sorption equilibrium totally right) and estimation of parameters impossible. If the surface is totally covered, no adsorption occurs and the response signal resembles the diffusion signal.</td>
</tr>
<tr>
<td>$\Theta_{\text{ads}} = \Theta_{\text{ads}}$</td>
<td>Instantaneous adsorption/desorption equilibrium and estimation of the adsorption/desorption equilibrium coefficient, $K_p$, is possible.</td>
</tr>
<tr>
<td>$\Theta_{\text{ads}} \ll \Theta_{\text{ads}}$</td>
<td>Instantaneous desorption; response signal resembles to diffusion signal and estimation kinetic parameters impossible.</td>
</tr>
</tbody>
</table>

**4.6 Simulation results**

In this paragraph the influence of the adsorption, desorption and reaction rate coefficients on the outlet molar flow rate of the reactants and products is further examined. As specific example the reaction $A \rightarrow B$ is considered, which is already examined in paragraph 4.5. The following continuity equations in the gas phase and on the surface apply:
\[ \varepsilon_b \frac{\partial C_A}{\partial t} = D_{rA} \frac{\partial^2 C_A}{\partial x^2} + (1 - \varepsilon_b) \alpha_v L_i \left[ -k_A C_A \theta_A + k_d \theta_A \right] \] (4.45)

\[ \varepsilon_b \frac{\partial C_B}{\partial t} = D_{rB} \frac{\partial^2 C_B}{\partial x^2} + (1 - \varepsilon_b) \alpha_v L_i k_r \theta_A \] (4.46)

\[ \frac{\partial \theta_A}{\partial t} = k_d C_A \theta_A - k_d \theta_A - k_r \theta_A \] (4.47)

\[ \frac{\partial \theta_A}{\partial t} = -k_c C_A \theta_A + k_d \theta_A + k_r \theta_A \] (4.48)

Initial and boundary conditions 4.16 till 4.28 apply. In the simulations the microreactor is assumed to be packed with three beds: one isothermal catalytic bed enclosed by two inert beds. The continuity equations were solved numerically, as described in paragraph 3.3.1.3. In table 4.2 the values of the fixed parameters are listed.

**Table 4.2: Parameter values used in the simulation for the reaction \( A \to B \), with continuity equations 4.45 till 4.48 and initial and boundary equations 4.16 till 4.28.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{eA,\text{inert}} = D_{eB,\text{inert}} )</td>
<td>( 3.0 \times 10^{-3} ) m(^3) m(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>( D_{eA,\text{catalyst}} = D_{eB,\text{catalyst}} )</td>
<td>( 4.0 \times 10^{-3} ) m(^3) m(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>( \varepsilon_{\text{inert}} )</td>
<td>0.50</td>
</tr>
<tr>
<td>( \varepsilon_{B,\text{catalyst}} )</td>
<td>0.70</td>
</tr>
<tr>
<td>( l_1 = l_2 = l_3 )</td>
<td>( 10 \times 10^{3} ) m</td>
</tr>
<tr>
<td>( N_p )</td>
<td>( 8.33 \times 10^{6} ) mol</td>
</tr>
<tr>
<td>( \alpha_v L_i )</td>
<td>( 6.67 ) mol m(^{-3})</td>
</tr>
<tr>
<td>( V_{\text{catalyst}} )</td>
<td>( 7.38 \times 10^{8} ) m(^3)</td>
</tr>
<tr>
<td>( \theta_0 )</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The various phenomena which may occur during adsorption and desorption were listed in table 4.1. The characteristic diffusion time in the catalyst bed, calculated with equation 4.5, is 9 ms. The characteristic times of adsorption and diffusion are the same if the adsorption rate coefficient is \( 40 \) m\(^3\) mol\(^{-1}\) s\(^{-1}\) (see equation 4.42). In figure 4.5 and 4.6 the influence of the adsorption rate coefficient on the response signal is shown when desorption and reaction
are absent. The adsorption rate coefficient is varied around 40 m³ mol⁻¹ s⁻¹ because in this range changes have the greatest influence on the pulse response. Adsorption causes a reduction of the peak height (see figure 4.5) and a strong narrowing of the response signal. This is illustrated once more in figure 4.6, where the response curves of figure 4.5 are normalised with respect to the peak maxima. The higher the adsorption rate coefficient, the shorter the mean residence time of the reactant molecules because molecules with a larger residence time have a greater probability to adsorb, leading to less tailing.

**Figure 4.5:** TAP reactant responses for various values of \( k_a \ [m_\text{s}^3 \text{mol}^{-1} \text{s}^{-1}] \) with \( k_d=k_r=0 \): A) 0, B) 1, C) 10, D) 50, E) 100 and F) 500. The other parameter values used in the simulation are listed in table 4.2.

**Figure 4.6:** Normalised TAP reactant responses for various values of \( k_a \ [m_\text{s}^3 \text{mol}^{-1} \text{s}^{-1}] \) with \( k_d=k_r=0 \): A) 0, B) 1, C) 10, D) 50, E) 100 and F) 500. The parameter values used in the simulation are listed in table 4.2.
In figure 4.7 the influence of the desorption rate coefficient on the response signal is examined, when the adsorption rate coefficient is constant and reaction is absent. The characteristic desorption time, calculated with equation 4.43, is equal to the characteristic diffusion time for a desorption rate coefficient of 114 s\(^{-1}\). The desorption rate coefficient is varied around this value. If the desorption rate coefficient increases, the response signal increases and becomes narrower. Till desorption rate coefficients of 10 s\(^{-1}\), the peak is mainly caused by diffusion and adsorption because the characteristic time for desorption is too large to affect the response signal. At higher values of this coefficient the shape and size of the peak are affected by the desorption rate coefficient.

![Figure 4.7: TAP reactant responses for various values of k_d [s\(^{-1}\)] with k_a = 50 m\(^3\) mol\(^{-1}\) s\(^{-1}\) and k_r is zero: A) 0, B) 5, C) 10, D) 50, E) 100 and F) 500. The parameter values used in the simulation are listed in table 4.2.](image)

The reaction rate coefficient obviously affects both the reactant and the product response curve. The characteristic reaction time, calculated with equation 4.44, is equal to the characteristic diffusion time for a reaction rate coefficient of 114 s\(^{-1}\). If reactant desorption from the catalyst is absent, the response curve of the reactant is unaffected by the reaction rate coefficient, as shown in figure 4.8. In figure 4.9 the product response curves for this situation are shown. The amount of formed product is equal for all reaction rate coefficients, because all adsorbed reactant reacts, due to the absence of reactant desorption.

The higher the reaction rate coefficient, the faster the product is formed. The product response becomes higher and narrower. For k_r = 50 m\(^3\) mol\(^{-1}\) s\(^{-1}\) the reactant conversion can never reach 100% since part of the reactant molecules pass the reactor without being adsorbed.
Figure 4.8: TAP reactant responses for various values of $k_r \text{[s}^{-1}\text{]}$ with $k_a = 50 \text{m}_g \text{mol}^{-1} \text{s}^{-1}$ and $k_d=0$: A) 1, B) 5, C) 10, D) 50, E) 100 and F) 500. The parameter values used in the simulation are listed in table 4.2.

Figure 4.9: TAP product responses for various values of $k_r \text{[s}^{-1}\text{]}$ with $k_a = 50 \text{m}_g \text{mol}^{-1} \text{s}^{-1}$ and $k_d=0$: A) 1, B) 5, C) 10, D) 50, E) 100 and F) 500. The parameter values used in the simulation are listed in table 4.2.

If besides adsorption and reaction also desorption occurs, the shape and size of the product response signal depends as well on the desorption and reaction rate because of competition between both desorption and reaction. In this case the reactant response curve is also affected by the reaction rate coefficient.
4.6 Conclusions

The minimum and maximum reaction rate coefficients measurable with the TAP microreactor were determined for a first order reaction. These limits are caused because the response signal has to be larger than the noise level and has to be distinguishable from the response signal in case of diffusion only. The quantitative measurable reaction rate coefficients depend on the Damköhler number and hence on the effective Knudsen diffusion coefficient, the latter being adjustable to some extent by the packing of the microreactor. The maximum quantitative measurable rate coefficient should be determined in an empty microreactor and the minimum in a totally packed reactor. Pseudo first order reaction rate coefficients should be obtainable in a window between $1 \, \text{s}^{-1}$ and $1 \times 10^4 \, \text{s}^{-1}$.

In case the characteristic times of adsorption, desorption, reaction and diffusion all have the same order of magnitude all kinetic parameters can be determined accurately. The characteristic times may be adjusted occasionally by a proper choice of experimental conditions to conform this requirement.

A model was derived, which describes the gas transport, adsorption, desorption and reaction processes which occur in the microreactor. With the model the outlet molar flow rate of all gas phase reactants and products can be calculated as a function of time. In chapter 5 this model will be used to estimate some kinetic parameters for the CO oxidation over platinum powder, described in paragraph 2.5.2, using the multi-response Marquardt parameter estimation routine.

References

5

KINETICS OF THE OXIDATION OF CO BY O₂ ON Pt

5.1 Introduction

Dating back to the classical work by Langmuir (1922), numerous investigations on the platinum catalysed carbon monoxide oxidation have been performed. In addition to the obvious environmental significance, there is also the capability to gain fundamental insight into heterogeneous catalysis, through analysis of this reaction due to its relative chemical simplicity. The general trends, observed in the platinum catalysed carbon monoxide oxidation, have also been found on the other platinum group metals: Pd, Rh, Ir and Ru (Engel and Ertl, 1979). So far no results have been published for Os. Experiments have been performed both on single crystal surfaces and on polycrystalline samples. Under ultra-high vacuum (UHV) conditions, CO oxidation on Pt occurs via the Langmuir-Hinshelwood mechanism, including reversible CO adsorption, molecular oxygen adsorption followed by dissociation and reaction between adsorbed CO and O species, resulting in the formation of CO₂ (Engel and Ertl (1978,1979), Racine et al. (1991), Boudart and Tamaru (1991)). The apparent simplicity of the basic mechanism is misleading because the reaction often exhibits very complex behaviour: multiple steady-states in reaction rates at intermediate pressures (Hegedus et al. (1977), Haaland and Williams (1982), Golchert and White (1978)); self-sustained oscillations in the reaction rate under constant feed conditions (Lynch and Wanke (1984a,1984b), Razon et al. (1986a), Sant and Wolf (1988), Ertl et al. (1982), Cox et al. (1985)) and furthermore complex behaviour during forced dynamic operation (Cutlip (1979), Graham and Lynch (1990), Silveston (1991), Zhou et al. (1986)).

The aim of this chapter is to show the use of transient methods in the modelling of the reaction pathway of the carbon monoxide oxidation over platinum powder. Whereas steady-state experiments give an overall picture of a reaction, transient experiments give information
on the kinetics of the elementary steps of a reaction. The carbon monoxide oxidation experiments were carried out in the temperature range of 300 to 700 K at pressures in the range of 0.1 to 1 mbar. With the TAP set-up it is possible to adjust the oxygen and carbon monoxide surface coverage. By covering the surface with oxygen or carbon monoxide, it is possible to investigate a part of the reaction pathway. In paragraph 5.5 a model is presented which describes the CO single pulse measurements over a Pt surface treated with oxygen at temperatures up to 365 K. In paragraph 5.3 possible models for oxygen adsorption and dissociation are confirmed with experimental results in the temperature range of 300 to 800 K. First a literature survey is given of the reaction mechanism of CO oxidation over platinum.

5.2 Literature survey

In table 5.1 the elementary reaction steps are listed, which are possibly involved in the CO oxidation over platinum.

Table 5.1: Elementary reaction steps which are possibly involved in the CO oxidation over Pt (Engel and Ertl (1979), Razon and Schmitz (1986b), Harold and Garske (1991a, 1991b)).

<table>
<thead>
<tr>
<th>Step number</th>
<th>Elementary step</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{CO} + \ast \rightarrow \text{CO}^* $</td>
</tr>
<tr>
<td>2</td>
<td>$\text{O}_2 + 2\ast \rightarrow 2\text{O}^* $</td>
</tr>
<tr>
<td>3</td>
<td>$\text{O}_2 + \ast \rightarrow \text{O}_2^* $</td>
</tr>
<tr>
<td>4</td>
<td>$\text{O}_2^* + \ast \rightarrow 2\text{O}^* $</td>
</tr>
<tr>
<td>5</td>
<td>$\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2 + 2\ast $</td>
</tr>
<tr>
<td>6</td>
<td>$\text{CO} + \text{O}^* \rightarrow \text{CO}_2 + \ast $</td>
</tr>
<tr>
<td>7</td>
<td>$2\text{CO}^* + \text{O}_2^* \rightarrow 2\text{CO}_2 + 3\ast $</td>
</tr>
<tr>
<td>8</td>
<td>$\text{CO} + \text{O}_2^* \rightarrow \text{CO}_2 + \text{O}^* $</td>
</tr>
<tr>
<td>9</td>
<td>$2\text{CO}^* + \text{O}_2 \rightarrow 2\text{CO}_2 + 2\ast $</td>
</tr>
<tr>
<td>10</td>
<td>$\text{CO}^* + \text{O}_2^* \rightarrow \text{CO}_2 + \text{O}^* + \ast $</td>
</tr>
<tr>
<td>global</td>
<td>$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 $</td>
</tr>
</tbody>
</table>

It is assumed that all catalytic sites are identical and that each adsorbed species occupies one catalytic site. Elementary steps including more than three surface species are assumed to be unrealistic. $\text{CO}_2$ is weakly bonded at the platinum surface and will immediately desorb after...
formation above 300 K (Conrad et al. (1978), Gland and Kollin (1983), Kwasniewski and Schmidt (1992)). Thus this rapid desorption step is not mentioned explicitly but included when necessary in the other elementary steps, listed in table 5.1.

Engel and Ertl (1979) reviewed the findings of the UHV studies of the elementary reaction steps. Because there is no evidence for the participation of dissociatively adsorbed CO in the catalytic CO₂ formation on platinum, this effect will not be considered further (Engel and Ertl, 1979). Under UHV conditions CO adsorbs reversibly. Engel and Ertl (1978) and Campbell et al. (1980) observed in their experiments, respectively on Pd(111) and Pt(111), no molecular adsorbed oxygen so the reaction steps 3, 4, 7, 8 and 10, involving this type of species, can be discarded. Recombination and desorption of adsorbed atomic oxygen occurs only at temperatures above 700 K, so the backward step in reaction 2 will not be considered in the present work (Engel and Ertl, 1979). The formation of oxygen incorporated in the bulk of a Pt(100) crystal is not possible between 400 and 800 K at 1 bar (Berlowitz et al., 1988), but occurs at temperatures above 1000 K at higher oxygen partial pressures (Engel and Ertl, 1979). Therefore it will not be considered to be of importance under the conditions discussed here.

Engel and Ertl (1979) showed that the Langmuir-Hinshelwood mechanism between both reactants in the chemisorbed state is the only clearly detectable reaction pathway. They showed that the Eley-Rideal mechanism can be ruled out under UHV conditions. The Eley-Rideal mechanism assumes that one of the reactants is in its normal chemisorbed state, whereas the second reacts either directly from the gas phase or from a weakly held physisorbed state. Reaction step 9 cannot occur, because no CO₂ formation takes place if a surface, saturated with adsorbed CO, is exposed to gaseous O₂. Probably the dissociative oxygen chemisorption is a necessary requirement. This is evident because the Pt-O bond strength is 370 kJ mol⁻¹ and the O-O bond strength in molecular oxygen 500 kJ mol⁻¹. Reaction step 6 cannot occur because isothermal measurements of the CO₂ formation rate, in which a constant flux of gaseous CO suddenly strikes a Pd surface precoated with oxygen, always reveal an induction period in the CO₂ formation (Engel and Ertl, 1978). The maximum in the CO₂ formation rate occurred after a short while and not at time zero, as predicted by the Eley-Rideal mechanism, because at this time the adsorbed oxygen concentration is the highest. The absence of the Eley-Rideal step 6 is confirmed for platinum by Palmer and Smith (1974) and Campbell et al. (1980) with molecular beam techniques, by determination of the CO residence time of 6 × 10⁻⁴ seconds before reaction took place on the Pt(111) surface. In case of an Eley-Rideal mechanism, the CO residence time should have been much shorter.

Referring to the study of Engel and Ertl (1978), Boudart and Djéga-Mariadassou (1984) showed that the dissociative adsorption of oxygen, step 2, includes the adsorption of molecular oxygen, step 3, and the dissociation of molecular adsorbed oxygen, step 4. The
authors neglected the desorption of molecular adsorbed oxygen in step 3. Contrary to the mechanism postulated by Engel and Ertl (1979), a step involving adsorbed molecular oxygen is included. It is assumed that the surface coverage of adsorbed molecular oxygen is much smaller than that of atomic adsorbed oxygen. In this case the oxygen adsorption rate is proportional to the surface coverage of vacant sites, \( \theta_v \), rather than to \( \theta_{ao}^2 \), as would be expected from step 2. At temperatures below 550 K and pressures up to \( 10^6 \) mbar, the reaction rate is proportional to the \( \text{O}_2 \) partial pressure and inversely proportional to the \( \text{CO} \) partial pressure (Harold and Garske, 1991b). At this low temperature \( \text{CO} \) inhibits the chemisorption of oxygen. At these conditions the surface is almost totally covered with \( \text{CO} \), the adsorption of molecular oxygen, step 3, is the rate-determining step and the \( \text{CO}_2 \) formation rate is inversely proportional to the \( \text{CO} \) partial pressure, \( p_{\text{CO}} \). If dissociative oxygen adsorption occurs in one step, step 2, as proposed by Engel and Ertl (1979), the \( \text{CO}_2 \) formation rate should be inversely proportional to \( p_{\text{CO}}^2 \). The latter is not in agreement with the experimental observations, so the dissociative oxygen adsorption occurs in two steps as proposed by Boudart and Djéga-Mariadassou (1984).

Summarising it can be concluded that under UHV conditions, the \( \text{CO} \) oxidation on Pt occurs via the Langmuir-Hinshelwood mechanism, including reversible \( \text{CO} \) adsorption, molecular oxygen adsorption followed by dissociation and reaction between adsorbed \( \text{CO} \) and \( \text{O} \) species, resulting in the formation of \( \text{CO}_2 \). The similar kinetic behaviour at low and high pressures suggests that the sequence of elementary steps at high pressure is the same as at low pressure (Boudart and Rumf, 1987):

\[
\begin{align*}
\text{CO} + * & \xrightleftharpoons[k_{\text{co}}]{k_{\text{co}}^\text{a}} \text{CO}^* \\
\text{O}_2 + * & \xrightarrow[k_{\text{a}}} \text{O}_2^* \\
\text{O}_2^* + * & \xrightarrow[k_{\text{a}}] \text{O}^* \\
\text{CO}^* + \text{O}^* & \xrightarrow[k_{\text{a}}] \text{CO}_2 + 2* \\
\end{align*}
\]

The assumptions implicitly made in this Langmuir-Hinshelwood model are:
- All active sites are identical;
- There is no interaction between adsorbed species other than reaction;
- Adsorbed species are randomly distributed over the area of the sites;
- CO and O₂ compete for the same adsorption sites;
- Adsorbed CO and adsorbed O each take up one site, and
- CO₂ is weakly adsorbed and the surface coverage of CO₂ is negligible.

Figure 5.1 shows the potential energy during the course of the overall reaction at low coverage. An appreciable fraction of the reaction enthalpy is already liberated during the chemisorption of CO ($\Delta H_{\text{co,ads}(\theta=0)} = 140$ kJ mol$^{-1}$) and O₂ ($\Delta H_{\text{O₂,ads}(\theta=0)} = 230$ kJ mol$^{-1}$). The surface reaction itself is only weakly exothermic. With increasing surface coverage both $\Delta H_{\text{co,ads}}$ and $\Delta H_{\text{O₂,ads}}$ decrease due to repulsive interactions between the adsorbed species. In the potential energy diagram this would correspond to a lifting of the CO*+O* level, and explains the observed decrease of the activation energy of the Langmuir-Hinshelwood surface reaction, $E_{\text{a,LH}}$. This effect makes the determination of the activation energy of the reaction difficult, because the surface coverages $\theta_{\text{co}}$ and $\theta_{\text{o}}$ have to be known under reaction conditions. The activation energy of the Langmuir-Hinshelwood reaction, $E_{\text{a,LH}}$, varies from about 100 kJ mol$^{-1}$ on a surface with a low coverage (Engel and Ertl (1979), Campbell et al. (1980), Pacia et al. (1976)) to about 40 kJ mol$^{-1}$ on a highly covered surface (Campbell et al. (1980), Bonzel and Burton (1975), Engel and Ertl (1979)).

**Figure 5.1:** Potential energy diagram for the catalytic oxidation of CO at low coverage (Campbell et al., 1980).

Figure 5.2 shows the variation of the relative sticking probability as a function of the CO coverage on Pt(111). It is generally accepted that CO adsorbs non-dissociatively, initially at on-top sites up to a coverage of $3 \times 10^{18}$ molecules/m$^2$ after which bridged sites begin to fill...
until saturation is reached at $7 \times 10^{18}$ molecules/m² (Ertl et al., 1977). CO adsorption is non-activated as evidenced by a constant relative sticking coefficient in the coverage range of 0 to $3 \times 10^{18}$ molecules/m² (Kwasniewski and Schmidt, 1992).

\[ \text{Figure 5.2: Relative sticking probability as a function of the CO coverage on Pt(111) (Ertl et al., 1977).} \]

Since the Langmuir-Hinshelwood mechanism does not show sufficient complexity to describe adequately the observed behaviour, various side reactions were added to the mechanism, most of which have been reviewed by Razon and Schmitz (1986b). Although much has been discovered about this system, a comprehensive model has not been developed to explain all of the complex reaction behaviour. First the necessity of the application of surface islands of adsorbed CO and oxygen in the modelling will be shown.

**Surface island models**

Mutual interactions between oxygen and carbon monoxide on the surface form the basis of more complex models, taking into account topographic features such as island formation. At very low surface coverage, adsorbed carbon monoxide and oxygen will be randomly distributed over the surface (Conrad et al., 1978). No CO₂ formation takes place if a surface, saturated with adsorbed CO, is exposed to gaseous O₂, which means that pre-adsorbed CO inhibits the adsorption of gaseous O₂ (Engel and Ertl, 1979). At high CO surface coverage there are no pairs of vacant surface sites available to adsorb oxygen dissociatively. This was confirmed by Boudart and Rumf (1987), who ascribed the inability of a CO covered surface to chemisorb O₂ to the fact, that CO and O₂ both need high coordination sites to adsorb. On the other hand considerable amounts of CO can adsorb if the surface is saturated with adsorbed oxygen. At lower surface coverage both oxygen and CO will adsorb.
Both components form separate domains on the surface, from now on indicated as islands (Bonzel and Ku, 1972). LEED results indicate that atomic adsorbed oxygen forms islands for surface concentrations greater than $0.4 \times 10^{18}$ molecules/m$^2$, corresponding to 10% of the maximum oxygen coverage, and suggest that CO forms islands when it is adsorbed on surfaces containing adsorbed oxygen (Gland and Kollin, 1983). Shigeishi and King (1978) concluded from FTIR measurements that large CO domains were formed at room temperature and low pressures. This is confirmed by FTIR measurements of Haaland and Williams (1982) who reported the existence of large CO islands on a high surface area Pt/Al$_2$O$_3$ catalyst under steady-state conditions at a total pressure of one bar. This indicates the existence of repulsive interactions between adsorbed CO and oxygen. Because of these repulsive interactions the islands are "compressed" and the local surface coverage on the islands becomes higher than reached by exposing a clean surface to O$_2$ or CO alone. The local coverage of the oxygen islands can vary from 0.25 to 0.5 and of the CO islands from 0.33 to 0.5 (Conrad et al., 1978). Since the adsorbed oxygen atoms in the oxygen islands repel each other, their effective bond strength with the surface will be lowered, resulting in a higher reactivity with adsorbed CO. LEED observations indicated a mean diameter of the domains of at least 10 nm (Conrad et al., 1978), Engel and Ertl (1972)). Field Ion Microscope (FIM) studies of Gorodetskii et al. (1994) revealed that CO islands have diameters between 4 and 5 nm. The CO$_2$ production can in this situation only occur along the boundaries of these islands. This was experimentally demonstrated by FTIR studies of Haaland and Williams (1982).

Adsorbed oxygen atoms exhibit a much lower surface mobility than adsorbed CO, caused by the strong Pt-O bond. As a result of this, it can be postulated that the adsorbed CO molecules move within an essentially fixed matrix of O atoms (Engel and Ertl (1979), Kwasniewski and Schmidt (1992)). This is experimentally demonstrated by FTIR studies of Haaland and Williams (1982). The activation energy for CO surface diffusion on Pt(111) is about 50 kJ mol$^{-1}$ and coverage independent (Kwasniewski and Schmidt, 1992). Compared to other similar surfaces for which CO diffusion data exist, the surface diffusion of CO on Pt(111) is very slow: at 300 K about 100 times slower than on Rh(111) and more than 3 times slower than on Ru(001). This slow surface migration explains the existence of CO surface islands. At higher temperatures no CO islands exist on the Pt surface, due to the higher surface diffusion coefficient of CO.

Wicke et al. (1980) described a simple molecular level approach to show how islands may arise on a surface. Reactants adsorbing on sites do not migrate on the surface and can only react with adjacent molecules of the other type. This concept is illustrated in figure 5.3. If reactant A is initially at a site, it may only react if B is adsorbed adjacent to it. Product, P, is assumed to desorb immediately. Otherwise a cluster of two A molecules is formed.
Figure 5.3: Scheme for the formation of clusters developed by Wicke et al. (1980).

This scheme can be used in Monte Carlo simulations. Such simulations for CO oxidation predict the formation of both carbon monoxide and oxygen islands under both steady-state and transient conditions (Dumont et al. (1986), Racine and Herz (1992)).

Zhou et al. (1986) suggested that CO$_2$ can be formed on Pd via two pathways. In the first pathway CO adsorbs on sites adjacent to oxygen. The formed intermediate decomposes quickly to CO$_2$. The second pathway involves the diffusion of adsorbed CO molecules to an island containing atomic adsorbed oxygen. Linearly bonded CO on platinum is weakly held and diffuses easily on the surface. Figure 5.4 illustrates the island model and contrasts the surface conditions under steady-state and dynamic operation. The islands are consumed in a surface reaction on the island periphery. The formation of new surface structures containing highly energetic CO and O in equal surface coverage and the numerous but smaller CO islands formed during periodic operation, are believed to be responsible for the enhanced rates during periodic operation. During the steady-state, large areas of the surface are covered with CO, resulting in low reaction rates.

Figure 5.4: Schematic drawing of CO and O adatom coverage on the Pd surface, illustrating the differences between the steady-state and periodic operation (Zhou et al., 1986).
Mukesh et al. (1984) presented a Langmuir-Hinshelwood model, including reversible CO adsorption, dissociative oxygen adsorption and reaction between adsorbed CO and O species, incorporating CO surface islands formation. A constant number of CO islands was assumed to be present on the surface in the steady-state. The authors assumed that adsorbed CO migrates on the surface towards these islands. Only CO at the perimeter of the islands can react. These models were used to describe steady-state and transient data on platinum catalysts of Goodman et al. (1982). In this model the reaction rate is proportional to the perimeter of the CO surface islands, which is assumed to be proportional to the square root of the CO surface coverage, rather than to the CO surface coverage, as predicted by the Langmuir-Hinshelwood model. This CO surface island model can also predict oscillatory behaviour, although there is little agreement between predicted and observed rates (Mukesh et al., 1984).

Graham (1990) examined several simple kinetic models taking into account the formation of islands of carbon monoxide and oxygen adsorbates on the surface. Graham showed that for oxygen, which requires more than one catalytic site per molecule, the presence of surface islands enhances the rate of adsorption, compared to surfaces with uniform adsorbate concentrations, because of the increased concentration of vacant surface sites in the region of the surface which is free of islands. The formation of CO islands results not only in an increased local CO concentration in the island region, but also in an increased local oxygen and vacant site concentration in the region free of CO islands. This effect was not included in the model of Mukesh et al. (1984). A model incorporating this effect was superior to the Langmuir-Hinshelwood model and the CO island model, proposed by Mukesh et al. (1984), for the CO oxidation on supported platinum catalysts.

5.3 Kinetics of oxygen adsorption, desorption and dissociation

In this paragraph possible models for oxygen adsorption and dissociation are compared to experimental results. At temperatures above 150 K, a platinum surface, exposed to oxygen, is covered with atomic adsorbed oxygen (Luntz et al. (1988), Engel and Ertl (1979)).

Hickman and Schmidt (1993) and Engel and Ertl (1979) describe the dissociation of oxygen in one elementary step. Boudart and Rumf (1987) assume a two step sequence for the adsorption of oxygen, in which oxygen first adsorbs molecularly and then rapidly dissociates. This is required because the rate of adsorption of oxygen is proportional to the fraction of vacant surface sites, $\theta_v$, rather than $\theta^2$. Gland (1980), Luntz et al. (1988,1989) and Williams et al. (1988) describe a model where molecular adsorbed oxygen acts as a precursor for dissociative chemisorption. They also take into account the desorption of molecular adsorbed oxygen.
5.3.1 Experimental

The platinum powder, 0.8122 g, was pretreated at 1100 K with a gas mixture of 5% oxygen in argon and with a gas mixture of 5% hydrogen in argon, each treatment lasting one and a half hour.

Prior to each experiment, the platinum catalyst was saturated with oxygen at reaction temperature. After saturation, the catalyst was held 5 minutes at 10^4 Pa and then one single pulse of oxygen with 10% argon containing about 5 \times 10^{15} molecules was given. The oxygen signal was measured. After this single pulse another one was given to measure the argon signal for modelling the transport mechanism. Then the same treatment was repeated to allow a multi-pulse experiment with carbon monoxide for determination of the number of oxygen covered platinum sites by measuring the total carbon dioxide formation at this temperature. During subsequent experiments the temperature was varied from 323 to 788 K. At low temperatures, i.e. 323 and 405 K, the number of platinum sites, covered with oxygen without being held 5 minutes at 10^4 Pa after the oxygen treatment, was determined as well. The maximum number of platinum sites covered with atomic adsorbed oxygen was obtained from this measurement. ^18O_2 experiments were performed to investigate whether ^18O atoms exchange with O atoms on the platinum surface at 479 K.

In table 5.2 both effective diffusion coefficients required to describe the transport of oxygen in the three beds are listed at the three applied temperatures, together with all other fixed parameters, necessary in the modelling.

**Table 5.2: Estimates for the effective diffusion coefficients of oxygen and the corresponding 95% confidence intervals, used in the modelling of the oxygen kinetics (N_{p,02} = 7.26 \times 10^9 \text{ mol}, \epsilon_{\text{Pt}} = 0.515 \text{ m}^3 \text{ m}^{-3}; \epsilon_{\text{quartz}} = 0.519 \text{ m}^3 \text{ m}^{-3}; l_1 = 11.65 \text{ mm}, l_2 = 11.15 \text{ mm}, l_3 = 6.42 \text{ mm} and \alpha_i L_i = 4.57 \text{ mol m}^{-1})).**

<table>
<thead>
<tr>
<th>temperature K</th>
<th>D_{\text{eO2.quartz}} $10^3 \text{ m}^3 \text{ m}^{-3} \text{ s}^{-1}$</th>
<th>D_{\text{eO2.Pt}} $10^3 \text{ m}^3 \text{ m}^{-3} \text{ s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>490</td>
<td>3.34 ± 0.02</td>
<td>5.07 ± 0.07</td>
</tr>
<tr>
<td>585</td>
<td>3.65 ± 0.03</td>
<td>6.08 ± 0.10</td>
</tr>
<tr>
<td>635</td>
<td>3.80 ± 0.03</td>
<td>6.63 ± 0.15</td>
</tr>
</tbody>
</table>

The effective diffusion coefficient of oxygen in the quartz bed was determined from the argon response at 294 K in a quartz bed with pellets in the range of 315 to 400 μm, as described in paragraph 3.3.1.3 and adjusted for the molecular weight and actual temperature during the present experiments. The effective diffusion coefficients of argon in the platinum sponge bed
at the three different reaction temperatures were estimated with the single-response Marquardt routine from the measured argon response at these three temperatures as described in paragraph 4.3.

The oxygen inlet pulse size, the initial degree of coverage of atomic adsorbed oxygen and the initial fraction of vacant surface sites are known from the multi-pulse experiments with carbon monoxide, carried out at each temperature. With single-response Marquardt regression on the oxygen outlet molar flow rate, the rate coefficients for the different models were estimated at each of the three different temperatures, as described in paragraph 4.3.

5.3.2 Results

In table 5.3 the absolute oxygen coverage and the initial degree of oxygen coverage, as determined from the multi-pulse experiments, are shown, as well as the oxygen breakthrough of a single oxygen pulse.

Table 5.3: Absolute oxygen coverage and initial degree of oxygen coverage from CO multi-pulse experiments, together with the oxygen breakthrough during a single pulse experiment with oxygen. Before this experiment the platinum sponge catalyst was kept 5 minutes at $10^4$ Pa after the oxygen pretreatment.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>absolute oxygen coverage $10^{-7}$ mol g$^{-1}$</th>
<th>$\theta_0^{\circ}$</th>
<th>breakthrough single pulse $\text{O}_2$ $10^{-9}$ mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>6.86$^1$</td>
<td>100.0$^1$</td>
<td>7.24$^1$</td>
</tr>
<tr>
<td>405</td>
<td>6.86$^1$</td>
<td>100.0$^1$</td>
<td>7.35$^1$</td>
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<tr>
<td>490</td>
<td>7.02</td>
<td>102.4</td>
<td>7.20</td>
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<tr>
<td>585</td>
<td>6.12</td>
<td>89.2</td>
<td>6.50</td>
</tr>
<tr>
<td>635</td>
<td>4.58</td>
<td>66.8</td>
<td>1.51</td>
</tr>
<tr>
<td>686</td>
<td>3.82</td>
<td>55.7</td>
<td>0.55</td>
</tr>
<tr>
<td>737</td>
<td>2.83</td>
<td>41.3</td>
<td>0.00</td>
</tr>
<tr>
<td>788</td>
<td>2.67</td>
<td>38.9</td>
<td>0.00</td>
</tr>
</tbody>
</table>

$^1$ Measurements without keeping the catalyst 5 minutes at $10^4$ Pa after the oxygen pretreatment.
At 323 and 405 K no atomic adsorbed oxygen desorbed from the surface within 5 minutes after the oxygen treatment. At 405 K no oxygen adsorbed in a single pulse experiment, since the surface was totally covered with O adatoms. Therefore the absolute oxygen coverage at 323 and 405 K corresponds to the total amount of surface sites available for oxygen adsorption. In the single pulse experiments at 490, 585 and 635 K the oxygen broke through partially. No oxygen breakthrough was observed at temperatures above 686 K.

In figure 5.5 the atomic oxygen coverage on the platinum surface is shown. At temperatures above 400 K the oxygen coverage did decrease. These experiments were performed under non-isosteric reaction conditions, i.e. the oxygen coverage was not equal at different temperatures, as shown in figure 5.5. The desorption of atomic adsorbed oxygen occurred at temperatures above approximately 480 K. This temperature is much lower than the value of 650 K observed by Wilf and Dawson (1977).

As described above a measurable desorption of atomic adsorbed oxygen did not occur at temperatures till 480 K. In the $^{18}$O$_2$ experiment at 479 K, the surface was pretreated with CO to remove all possibly present O adatoms. After this, the platinum surface was saturated with O$_2$ or $^{18}$O$_2$. After both oxygen treatments, a $^{18}$O$_2$ multi-pulse experiment was performed, from which the $^{18}$OO and $^{18}$O$_2$ responses were measured. The measured responses of $^{18}$OO and $^{18}$O$_2$ were exactly the same for both treatments, meaning that no $^{18}$O atoms exchange with O atoms on the platinum surface at 479 K.

5.3.3 Modelling of the oxygen signal

It is still a question in the literature if the oxygen adsorption and dissociation occur in one
or in two elementary reaction steps. In this paragraph therefore three possible models for oxygen adsorption and dissociation will be compared. Since the desorption of atomic adsorbed oxygen is negligible on the time scale of a single pulse TAP experiment, such step was not considered in the modelling. The three models studied were:

**Model 1: Dissociative oxygen adsorption**

\[ O_2 + 2\ast k_{a,diss} \rightarrow 2O\ast \]  
(5.5)

**Model 2: Molecular oxygen adsorption followed by dissociation**

\[ O_2 + \ast \rightarrow O_2\ast \]  
(5.6)

\[ O_2\ast + \ast \rightarrow 2O\ast \]  
(5.7)

**Model 3: Molecular oxygen sorption equilibrium followed by dissociation**

\[ O_2 + \ast \overset{k_a}{\rightarrow} O_2\ast \]  
(5.8)

\[ O_2\ast + \ast \rightarrow 2O\ast \]  
(5.9)

The continuity equations for oxygen, the vacant active sites and the oxygen adatoms in the catalytic bed are, in the case of model 1, dissociative oxygen adsorption:

\[ \varepsilon_b \frac{\partial C_{O_i}}{\partial t} = D_{e_{O_i}} \frac{\partial^2 C_{O_i}}{\partial x^2} - (1 - \varepsilon_b) \alpha \gamma L_i k_{a,diss} C_{O_i} \Theta_i^2 \]  
(5.10)

\[ \frac{\partial \Theta_i}{\partial t} = -2 k_{a,diss} C_{O_i} \Theta_i^2 \]  
(5.11)

\[ \frac{\partial \Theta_{O_i}}{\partial t} = 2 k_{a,diss} C_{O_i} \Theta_i^2 \]  
(5.12)

Here \( k_{a,diss} \) is the rate coefficient for dissociative oxygen adsorption [m/s].
The initial conditions are as follows:

\[ t = 0 \land l_1 \leq x \leq (l_1 + l_2) : \quad \theta_1(x) = \theta_1^0 \]  
(5.13)

\[ t = 0 \land l_1 \leq x \leq (l_1 + l_2) : \quad \theta_0(x) = \theta_0^0 \]  
(5.14)

The boundary conditions are equal as expressed in paragraph 4.3.

In the case of model 2, molecular oxygen adsorption followed by dissociation, the continuity equations in the catalytic bed become:

\[ \varepsilon_b \frac{\partial C_o}{\partial t} = D_{\varepsilon o_b} \frac{\partial^2 C_o}{\partial x^2} - (1 - \varepsilon_b) a_s L c k_o C_o \theta_o \]  
(5.15)

\[ \frac{\partial \theta_o}{\partial t} = -k_a C_o \theta_o - k_{\text{dis}} \theta_o \theta_1. \]  
(5.16)

\[ \frac{\partial \theta_1}{\partial t} = 2 k_{\text{dis}} \theta_1 \theta_0. \]  
(5.17)

\[ \frac{\partial \theta_0}{\partial t} = k_a C_o \theta_1 - k_{\text{dis}} \theta_1 \theta_0. \]  
(5.18)

Here \( k_a \) is the adsorption rate coefficient of molecular oxygen \([\text{m}^3 \text{mol}^{-1} \text{s}^{-1}]\) and \( k_{\text{dis}} \) the dissociation rate coefficient of adsorbed molecular oxygen \([\text{s}^{-1}]\).

The initial conditions for \( \theta_1 \) and \( \theta_0 \) are identical to equations 5.13 and 5.14, but an additional condition for the coverage of molecular adsorbed oxygen is needed. The initial coverage of molecular oxygen was taken zero, in agreement with observations at temperatures above 150 K by Luntz et al. (1988), Engel and Ertl (1979):

\[ t = 0 \land l_1 \leq x \leq (l_1 + l_2) : \quad \theta_0(x) = 0 \]  
(5.19)

In the case of model 3, attempts were made to estimate the adsorption and desorption rate coefficients of molecular oxygen separately. The estimates of the adsorption and desorption coefficients showed a strong correlation indicating that sorption equilibrium of molecular oxygen is very likely. Therefore sorption equilibrium of molecular oxygen followed by dissociation was assumed in model 3. It was impossible to solve equation 5.20 numerically with the NAG routine DO3PGF, described in paragraph 3.3.1.3, because the fraction of vacant
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Surface sites in the left hand site of equation 5.20 is a function of time. For the integration of the continuity equations for model 3 it is assumed that the change in the fraction of vacant surface sites is negligible during the passage of one single pulse. In this case the continuity equations in the catalysts bed become:

\[
\left[ \varepsilon_b + (1 - \varepsilon_b) \alpha_a L_k K_a \theta \right] \frac{\partial C_{o_i}}{\partial t} = D_{e\theta_b} \frac{\partial^2 C_{o_i}}{\partial x^2} - (1 - \varepsilon_b) \alpha_a L_k k_{\text{diss}} K_a C_{o_i} \theta^2.
\]

(5.20)

\[
\frac{\partial \theta_i}{\partial t} = 0
\]

(5.21)

\[
\theta_{o_i} = K_a C_{o_i} \theta^2.
\]

(5.22)

\[
\frac{\partial \theta_o}{\partial t} = 2 k_{\text{diss}} K_a C_{o_i} \theta^2.
\]

(5.23)

Here \( K_a \) is the sorption equilibrium coefficient of molecular oxygen \([m^3 mol^{-1}]\). The initial conditions are identical as for model 2.

All models mentioned above were applied to describe the single pulse oxygen experiments at 490, 585 and 635 K, because these experiments showed a partial oxygen breakthrough.

The fixed parameters used in the modelling are listed in table 5.3. The regression results for the three different models are shown in tables 5.4, 5.5 and 5.6. For model 2 it was impossible to estimate the dissociation rate coefficient, because the size and shape of the oxygen response were totally independent of this coefficient. From a physical point of view the value of the dissociation rate coefficient should be sufficiently large to prevent the accumulation of any adsorbed molecular oxygen on the surface, which has never been observed at these experimental conditions (Luntz et al. (1988), Engel and Ertl (1979)). The rate coefficient for the dissociation of adsorbed molecular oxygen was therefore fixed at a value of \( 10^9 \text{ s}^{-1} \), as shown in table 5.5.

In figure 5.6 the measured and modelled curves are shown at 585 K with an initial oxygen coverage of 67%. Models 1 and 2 coincide in practice as shown in figure 5.6. Model 3, taking into account the sorption equilibrium of molecular oxygen followed by dissociation is the only model which describes the single pulse TAP experiments well at low and high oxygen coverages. For both other models the significance of the regression of the oxygen signal is much lower at lower oxygen coverages, as is shown by the corresponding lower F-ratios in tables 5.4 and 5.5.
Table 5.4: Kinetic parameter estimates with their approximate individual 95%-confidence intervals obtained for dissociative oxygen adsorption (model 1, equations 5.10 till 5.14 and 4.16 till 4.28). The fixed parameters used in the modelling are listed in table 5.3.

<table>
<thead>
<tr>
<th>$\theta_0^0$</th>
<th>$T$</th>
<th>$k_{a,\text{diss}}$</th>
<th>$F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>K</td>
<td>10^4 m^3 mol^-1 s^-1</td>
<td>10^4</td>
</tr>
<tr>
<td>89</td>
<td>490</td>
<td>0.54 ± 0.10</td>
<td>5.9</td>
</tr>
<tr>
<td>67</td>
<td>585</td>
<td>5.2 ± 0.2</td>
<td>0.27</td>
</tr>
<tr>
<td>56</td>
<td>635</td>
<td>23.9 ± 0.4</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table 5.5: Kinetic parameter estimates with their approximate individual 95%-confidence intervals obtained for molecular adsorption of oxygen followed by dissociation (model 2, equations 5.13 till 5.19 and 4.16 till 4.28). The fixed parameters used in the modelling are listed in table 5.3.

<table>
<thead>
<tr>
<th>$\theta_0^0$</th>
<th>$T$</th>
<th>$k_a$</th>
<th>$k_{\text{diss}}^*$</th>
<th>$F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>K</td>
<td>10^9 s^-1</td>
<td>10^9 s^-1</td>
<td>10^4</td>
</tr>
<tr>
<td>89</td>
<td>490</td>
<td>5.9 ± 1.3</td>
<td>1.0</td>
<td>5.9</td>
</tr>
<tr>
<td>67</td>
<td>585</td>
<td>167 ± 6</td>
<td>1.0</td>
<td>0.25</td>
</tr>
<tr>
<td>56</td>
<td>635</td>
<td>1047 ± 21</td>
<td>1.0</td>
<td>0.093</td>
</tr>
</tbody>
</table>

* fixed parameter

Table 5.6: Kinetic parameter estimates with their approximate individual 95%-confidence intervals obtained for sorption equilibrium of molecular oxygen followed by dissociation (model 3, equations 5.20 till 5.23, 5.13, 5.14, 5.19 and 4.16 till 4.28). The fixed parameters used in the modelling are listed in table 5.3.

<table>
<thead>
<tr>
<th>$\theta_0^0$</th>
<th>$T$</th>
<th>$K_0$</th>
<th>$k_{\text{diss}}$</th>
<th>$F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>K</td>
<td>m^3 mol^-1</td>
<td>10^2 s^-1</td>
<td>10^4</td>
</tr>
<tr>
<td>89</td>
<td>490</td>
<td>0.10 ± 0.02</td>
<td>4.2 ± 1.5</td>
<td>4.4</td>
</tr>
<tr>
<td>67</td>
<td>585</td>
<td>0.88 ± 0.04</td>
<td>5.4 ± 0.3</td>
<td>2.9</td>
</tr>
<tr>
<td>56</td>
<td>635</td>
<td>3.2 ± 0.2</td>
<td>7.0 ± 0.4</td>
<td>0.96</td>
</tr>
</tbody>
</table>

From the modelling it should be concluded that the adsorption of dioxygen occurs via an equilibrated sorption of dioxygen followed by the dissociation of molecular adsorbed oxygen as the rate-determining step.
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Figure 5.6: Comparison of measured (□) and calculated oxygen outlet flow rates for: dissociative oxygen adsorption (model 1) (······); molecular oxygen adsorption followed by dissociation (model 2) (-----), and molecular oxygen sorption equilibrium followed by dissociation (model 3) (———) at $\text{585 K}$ and an oxygen coverage of 67%. The estimates of the parameters for the different models are shown in tables 5.4, 5.5 and 5.6.

The pre-exponential factors and the enthalpy respectively activation energies of the estimated rate coefficients were determined from an Arrhenius plot, which is shown in figure 5.7:

- $K_\text{s}$: $A_0/A_{0.\text{dis}} = 2.29 \times 10^5 \text{ m}_g^3 \text{ mol}^{-1}$, $\Delta H = 59.8 \text{ kJ mol}^{-1}$
- $k_\text{dis}$: $A_{0.\text{dis}} = 3.42 \times 10^{13} \text{ s}^{-1}$, $E_{0.\text{dis}} = 8.6 \text{ kJ mol}^{-1}$

Figure 5.7: Arrhenius plot of the molecular oxygen sorption equilibrium coefficient (+) and the dissociation rate coefficient of adsorbed molecular oxygen (△). The values of these coefficients are shown in table 5.6.
The apparent positive enthalpy for the adsorption/desorption equilibrium of \(59.8 \text{ kJ mol}^{-1}\) should be ascribed to the fact that the experiments were performed at non-isosteric reaction conditions. Shustorovich (1991) calculated an adsorption enthalpy of \(-79.8 \text{ kJ mol}^{-1}\). Gland (1980) measured an adsorption enthalpy for molecular oxygen of about \(-33.5 \text{ kJ mol}^{-1}\) on a clean surface and about \(-15.9 \text{ kJ mol}^{-1}\) on a surface saturated with adsorbed atomic oxygen. This large difference is caused by the non-isosteric reaction conditions. At low oxygen coverage the heat of adsorption is higher than at high oxygen coverage, meaning that the desorption rate coefficient increases with increasing oxygen coverage. This effect is probably stronger than the influence of temperature. The value of the estimated activation energy for dissociation of adsorbed molecular oxygen of \(8.6 \text{ kJ mol}^{-1}\) is about the same as the value of \(13.3 \text{ kJ mol}^{-1}\) reported by Gland (1980). It can be concluded that the dissociation of adsorbed molecular oxygen is probably independent of the surface coverage.

5.4 Mechanistic investigation of the CO oxidation

5.4.1 Experimental

The platinum powder was pretreated at 873 K as described in paragraph 2.5.2.1. By precovering the surface with oxygen or carbon monoxide, it was possible to investigate a part of the reaction pathway by eliminating certain elementary steps. The CO\(_2\) formation over a surface covered with adsorbed CO was compared with the CO\(_2\) formation over a surface covered with atomic adsorbed oxygen. Therefore O\(_2\) was pulsed in a multi-pulse experiment over a surface covered with adsorbed CO and CO was pulsed in a multi-pulse experiment over a surface covered with O adatoms, while the CO\(_2\) and the O\(_2\) or CO outlet signals were recorded. All experiments were replicated. The multi-pulse experiments were carried out at temperatures between 295 and 700 K.

5.4.2 Results and discussion

At 295 K no CO\(_2\) was formed, when a multi-pulse experiment with O\(_2\) was carried out over a surface covered with adsorbed CO. The O\(_2\) outlet signal stayed constant, meaning that no oxygen was adsorbed. At this low temperature CO inhibits the adsorption of O\(_2\) completely, as was already reported by Engel and Ertl (1979). As adsorbed CO did not desorb, no vacant surface sites were available for O\(_2\) adsorption. This result confirms the occurrence of the Langmuir-Hinshelwood mechanism.

The same experiment was performed at 345 K. No O\(_2\) was adsorbed in the beginning of the multi-pulse experiment, as is shown in figure 5.8. After about 150 seconds the O\(_2\) adsorption...
started, resulting in a decreasing O\textsubscript{2} signal. At the moment that the O\textsubscript{2} signal decreased, the CO\textsubscript{2} signal increased as is shown in figure 5.9. Initially, no oxygen was adsorbed because the platinum surface was totally covered with CO. After about 150 seconds, sufficiently CO had desorbed to allow O\textsubscript{2} adsorption. In the figures 5.8 and 5.9 two maxima are shown, indicating the existence of at least two different domains of adsorbed CO on the surface.

![Figure 5.8: O\textsubscript{2} responses at 345 K in an O\textsubscript{2} multi-pulse experiment over Pt covered with CO.](image)

![Figure 5.9: CO\textsubscript{2} responses at 345 K in an O\textsubscript{2} multi-pulse experiment over Pt covered with CO.](image)
After about 150 seconds vacant surface sites became available for oxygen adsorption in the first domain, resulting in the formation of CO₂ and more vacant sites in this domain, until the amount of adsorbed CO became limiting and CO₂ formation and oxygen adsorption decreased. In the meantime vacant surface sites became available in a second domain of adsorbed CO, resulting once more in a decreasing O₂ outlet signal and an increasing CO₂ production. These results indicate the existence of CO surface islands. Similar observations were made at temperatures between 320 and 370 K.

The same experiment was carried out at 405 K as well. CO desorption now occurred at a higher rate, as a result of which sufficiently vacant surface sites were available on the surface for O₂ adsorption. Hence almost all pulsed O₂ adsorbed immediately, until all adsorbed CO had disappeared and the surface was totally covered with O adatoms, as is shown in figure 5.10. The CO₂ outlet signal, which is shown in figure 5.11, stayed nearly constant, meaning that an equal amount of the pulsed O₂ was converted into CO₂, until all adsorbed CO had disappeared. At temperatures above 405 K similar behaviour was observed, till the life time of adsorbed CO became too short at high temperatures.

![Figure 5.10: O₂ responses at 405 K in an O₂ multi-pulse experiment over Pt covered with CO.](image)

The opposite multi-pulse experiment in which CO was pulsed over a platinum surface covered with atomic adsorbed oxygen was even more reproducible, because no measurable oxygen desorption of atomic adsorbed oxygen occurs at temperatures till 480 K, as described in paragraph 5.3.2. As already shown by Engel and Ertl (1979) CO adsorption is even possible on a platinum surface totally covered with atomic adsorbed oxygen. Therefore CO adsorption starts with the first pulse, even at low temperatures, as shown in figure 5.12 for 344 K. The
CO outlet signal stayed constant during about 230 seconds, which means that from every CO pulse an equal amount was adsorbed.

Figure 5.11: CO\textsubscript{2} responses at 405 K in a O\textsubscript{2} multi-pulse experiment over Pt covered with CO.

Figure 5.12: CO responses at 344 K in a CO multi-pulse experiment over Pt covered with O adatoms.

In figure 5.13 the corresponding CO\textsubscript{2} outlet signal is shown, from which could be concluded that the CO\textsubscript{2} production decreased during the CO multi-pulse experiment. Combination of the results in figure 5.12 and 5.13 leads to the conclusion that CO partially reacted with O adatoms present on the platinum surface and partially adsorbed on the surface without
reacting. It means that atomic adsorbed oxygen and adsorbed CO both can be found on the surface without reacting. These results confirm the existence of islands.

![Graph](image1)

**Figure 5.13:** CO$_2$ responses at 344 K in a CO multi-pulse experiment over Pt covered with O adatoms.

When this CO multi-pulse experiment was performed at temperatures above 380 K, all pulsed CO is adsorbed and partially or totally converted with present O adatoms to CO$_2$. A typical example is shown in figures 5.14 and 5.15 at 384 K. At these temperatures it is impossible to determine kinetic parameters, because all pulsed CO is totally adsorbed.

![Graph](image2)

**Figure 5.14:** CO responses (responses at mass 28) at 384 K in a CO multi-pulse experiment over Pt covered with O adatoms.
Figure 5.15: \( \text{CO}_2 \) responses at 384 K in a CO multi-pulse experiment over Pt covered with O adatoms.

The small peaks present in figure 5.14 till about 100 seconds were not caused by CO breakthrough, but resulted from the fragmentation of \( \text{CO}_2 \) in the mass spectrometer. At the moment that \( \text{CO}_2 \) formation stopped, the pulsed CO broke through.

In figure 5.16 results are shown concerning a CO multi-pulse experiment at 700 K after a pretreatment with CO at the same temperature.

Figure 5.16: \( \text{CO}_2 \) responses at 700 K in a CO multi-pulse experiment over Pt treated with CO.
After the CO pretreatment no O adatoms were present on the Pt surface. The base line rise as well as the subsequent peaks indicate the formation of CO₂. Similar experiments at 500 and 600 K showed no CO₂ formation. At 700 K the CO₂ formation was probably caused by the Boudouard reaction:

\[ 2\text{CO} + * \rightarrow \text{CO}_2 + C* \] (5.24)

This is confirmed by A.A.S. measurements (Atomic Absorption Spectroscopy), carried out by Caleb Brett in Deventer, which showed the presence of small amounts of elementary carbon on the Pt catalyst after reaction.

5.5 Kinetics of the CO oxidation at low temperatures

The focus of this paragraph is to show the use of transient methods in the modelling of the reaction pathway of the carbon monoxide oxidation over platinum powder, as described in paragraph 4.3. At temperatures above about 380 K kinetic parameters could not be determined because of 100% conversion of both reactants. At temperatures till about 380 K the reactants were partially converted, which allowed determination of the kinetic parameters as function of the surface coverage. For this purpose, single pulse experiments were performed with carbon monoxide over a surface partially covered with atomic oxygen and carbon monoxide at temperatures up to 365 K. Two different kinetic models, taking into account CO adsorption and desorption followed by a surface reaction, were tested.

5.5.1 Experimental

Platinum powder, 0.7290 g, was pretreated at 873 K, as described in paragraph 2.5.2.1. Prior to each multi-pulse experiment, the platinum catalyst was treated with oxygen at reaction temperature, as a result of which the surface was covered with O adatoms, as described in paragraph 5.3. After the oxygen treatment a multi-pulse experiment with CO was performed at 323, 344 and 365 K, during which the CO and CO₂ responses were measured. In figure 5.12 and 5.13 the typical results of such an experiment at 344 K are shown. From the observed CO₂ response, the number of vacant surface sites at the different temperatures could be determined, as described in paragraph 2.5.2.2. At low temperature parts of the surface remain covered with adsorbed CO molecules, that cannot be removed by oxygen at that temperature.

A common multi-pulse experiment with TAP does not allow to monitor the individual responses without a drastic reduction of the number of data points. Therefore subsequent
single pulse experiments were performed over a platinum surface covered with atomic adsorbed oxygen and the individual CO and CO$_2$ responses were measured. By applying the subsequent single pulses, responses could be recorded at oxygen coverages varying from full to zero coverage. The whole experiment was done at 323, 344 and 365 K. Prior to each experiment, the platinum catalyst was treated with oxygen at reaction temperature to obtain complete oxygen coverage. All of the subsequent single pulses contained CO with 10 vol. % argon. The amount of CO adsorbed per pulse was about 1.3 % of a monolayer, meaning that after about 150 pulses the surface was totally covered with CO. Each experiment was carried out twice at every temperature. In the first one the CO$_2$ responses were measured and in the second one the CO responses.

Before and after each experiment, one single pulse containing CO with 10 vol. % argon was given to measure the argon signal for determination of the effective diffusion coefficients of argon in the catalyst bed at the three desired temperatures. At all three temperatures the absolute calibration factors of CO$_2$, CO and Ar were determined as described in paragraph 2.3.2.

The effective diffusion coefficients of CO and CO$_2$ in the quartz and platinum sponge beds have been determined separately at 323, 344 and 365 K, as described in paragraph 5.3.2. The effective diffusion coefficients of CO and CO$_2$ in the platinum sponge bed decrease slightly with increasing temperature. This is not in accordance with equation 3.10. The effective diffusion coefficients of CO and CO$_2$ in the quartz bed increase slightly with increasing temperature, according equation 3.10. In table 5.7 all fixed parameters used in the kinetic modelling are listed, except the CO inlet pulse sizes, because these values differed from experiment to experiment. These values are listed in tables 5A.1, 5A.2 and 5A.3 in appendix 5A.

**Table 5.7:** Estimates for effective diffusion coefficients of CO and CO$_2$ and the corresponding 95% confidence intervals, used in the modelling of the kinetics of the CO oxidation at low temperatures ($\varepsilon_{b,quanz} = 0.515$ m$^{-3}$ m$_c^{-1}$, $\varepsilon_{b,Pl} = 0.690$ m$^{-1}$ m$_c^{-3}$, $l_1 = 11.20$ mm, $l_2 = 10.00$ mm, $l_3 = 10.00$ mm and $a_L, L_\gamma = 6.14$ mol m$^{-1}$).

<table>
<thead>
<tr>
<th>T K</th>
<th>$D_{eCO,quanz}$ $10^3$ m$_g^3$ m$_c^{-1}$ s$^{-1}$</th>
<th>$D_{eCO_2,quanz}$ $10^3$ m$_g^3$ m$_c^{-1}$ s$^{-1}$</th>
<th>$D_{eCO,Pl}$ $10^3$ m$_g^3$ m$_c^{-1}$ s$^{-1}$</th>
<th>$D_{eO_2,Pl}$ $10^3$ m$_g^3$ m$_c^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>3.71 ± 0.03</td>
<td>2.96 ± 0.01</td>
<td>4.77 ± 0.05</td>
<td>3.80 ± 0.04</td>
</tr>
<tr>
<td>344</td>
<td>3.82 ± 0.03</td>
<td>3.05 ± 0.01</td>
<td>4.14 ± 0.04</td>
<td>3.30 ± 0.03</td>
</tr>
<tr>
<td>365</td>
<td>3.93 ± 0.03</td>
<td>3.14 ± 0.02</td>
<td>4.12 ± 0.08</td>
<td>3.29 ± 0.07</td>
</tr>
</tbody>
</table>
The value of the platinum sponge porosity in the CO oxidation experiments was higher than the corresponding value in the dissociative oxygen adsorption experiments, shown in table 5.2. The reason for this is, that the platinum catalyst in the CO oxidation experiments was pretreated at a lower temperature, which caused less sintering. This is also the reason for the higher amount of active Pt surface sites, \( a_n \), in the CO oxidation experiments.

5.5.2 Results

In figure 5.17 the maxima of the CO and \( \text{CO}_2 \) outlet molar flow rates of the CO multi-pulse experiment over a Pt surface treated with \( \text{O}_2 \) at 344 K are shown. The CO response stayed constant during about 80 pulses, meaning that from every CO pulse the same amount was adsorbed. The corresponding \( \text{CO}_2 \) outlet signal decreased. These results, which are similar as shown in figures 5.12 and 5.13 indicate the existence of surface islands.

![Figure 5.17: Maxima of the CO and CO\(_2\) outlet molar flow rates of a CO multi-pulse experiment at 344 K over a Pt surface treated with oxygen.](image)

In table 5.8 the total amount of \( \text{CO}_2 \) formed in the CO multi-pulse experiments at 323, 344 and 365 K is shown. The data are average values of triplicate measurements. From table 5.8 it is concluded, that at higher temperatures more \( \text{CO}_2 \) was formed, meaning that at low temperatures the amount of atomic adsorbed oxygen was lower. The reason is that at low temperature parts of the surface remain covered with adsorbed CO molecules, that cannot be removed by oxygen at that temperature. So at 323 K 44 % of the Pt surface sites remained covered with adsorbed CO molecules, making this part inactive for oxygen adsorption. At temperatures between 365 K and 480 K the surface can be totally covered with O adatoms,
because the same amount of CO$_2$ was always observed in a CO multi-pulse experiment over a surface treated with oxygen.

**Table 5.8: Total CO$_2$ formation over Pt sponge treated with oxygen and $\theta_0^0$ in a CO multi-pulse experiment at 323, 344 and 365 K.**

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>CO$_2$ formation $10^{-3}$ mol g$^{-1}$</th>
<th>$\theta_0^0$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>3.58</td>
<td>56</td>
</tr>
<tr>
<td>344</td>
<td>6.00</td>
<td>93</td>
</tr>
<tr>
<td>365</td>
<td>6.43</td>
<td>100</td>
</tr>
</tbody>
</table>

In table 5A.2 of appendix 5A the amounts of introduced CO, not adsorbed CO, formed CO$_2$ and permanently adsorbed CO after subsequent single CO pulses over Pt treated with oxygen at 344 K are listed. The results of the experiments at 323 and 365 K are shown in appendix 5A in tables 5A.1 and 5A.3 respectively. The total amount of permanently adsorbed CO, not converted into CO$_2$, was calculated from the measured amounts of introduced CO, not adsorbed CO and formed CO$_2$. The amount of formed CO$_2$ decreased, thus the amount of CO, which remained adsorbed on the surface, increased as a function of the number of CO pulses. During the first 10 CO pulses at 344 and 365 K no adsorbed CO remained on the surface, meaning that all adsorbed CO was converted to CO$_2$. At 323 K however, even at the first pulse a part of the adsorbed CO was not converted to CO$_2$ and remained adsorbed on the surface without reacting.

In the tables 5A.1, 5A.2 and 5A.3 in appendix 5A the CO and oxygen coverage during the subsequent single CO pulse experiments are listed as well. The initial oxygen coverage is also shown in table 5.8. The total CO$_2$ production at 365 K was equal to the total amount of platinum surface sites, because at this temperature the surface was totally covered with O adatoms. The oxygen coverage after every pulse was calculated from the oxygen consumption by that pulse which is expressed by the formed amount of CO$_2$. The CO coverage was calculated from the permanently adsorbed amount of CO. The fraction of vacant surface sites could be determined, because the total surface coverage is equal to one. The resulting coverages at 344 K as a function of the number of pulses are shown graphically in figure 5.18.
5.5.3 Modelling of the kinetics of the CO oxidation

In this paragraph a kinetic model, taking into account CO physisorption equilibrium followed by reaction, is examined for its capability to describe the observations. The measured CO response appears later than the modelled CO response for the situation that only adsorption occurs. This is an indication for the existence of the CO physisorption equilibrium. The results described above, show the possibly simultaneous existence of large amounts of atomic adsorbed oxygen and adsorbed CO on the surface, without the occurrence of reaction between both adsorbed species, which means that surface migration of adsorbed CO on the time scale of a subsequent single pulse experiment is negligible. The Langmuir-Hinshelwood mechanism, given by equations 5.1 to 5.4 cannot describe these results, because one of the assumptions in this model is, that all adsorbed species are randomly distributed over the catalyst surface. In such model it is impossible that adsorbed CO and atomic oxygen can coexist on the catalyst surface, without reacting. This is contradictory to the present observations and therefore a new model should be developed, which takes into account the formation of CO islands. The desorption of CO from the CO islands is negligible on the time scale of a subsequent single pulse experiment. Therefore, these features are not considered in the modelling.

CO is adsorbed in a physisorbed state, that may be a precursor for chemisorption. CO physisorption is in equilibrium and is followed by CO chemisorption on vacant surface sites next to O or CO islands. CO molecules which chemisorb next to O islands react at the island
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boundaries. The supposed CO physisorption equilibrium means, that CO molecules collide many times with the surface till they chemisorb on a vacant surface site. The chemisorbed CO molecules either react with O adatoms at the island boundaries to CO\textsubscript{2} or are incorporated in the CO islands. Chemisorption on a vacant surface site which does not belong to either an O or a CO island can be considered as the start of the formation of a new CO island.

\begin{align}
\text{CO} & \xrightarrow{k_p} \text{CO}_{p} \quad (5.25) \\
\text{CO}_{p} & \xrightarrow{k_c} \text{O} \xrightarrow{k_r} \text{CO}_{2} \quad (5.26)
\end{align}

\begin{align}
\text{CO}_{p} & \xrightarrow{k_c} \text{O} \xrightarrow{k_r} \text{CO}_{2} \quad (5.27)
\end{align}

Here CO\textsubscript{p} is the surface concentration of physisorbed CO [mol m\textsuperscript{-2}], K\textsubscript{p} the CO physisorption equilibrium coefficient [m\textsuperscript{3} m\textsuperscript{-2}], \*\textsubscript{o} a vacant surface site next to an O island, \*\textsubscript{co} a vacant surface site not next to an O island, CO\*\textsubscript{co} a chemisorbed CO molecule next to an O island, CO\*\textsubscript{co} a chemisorbed CO molecule not next to an O island, k\textsubscript{c} the CO chemisorption rate coefficient [s\textsuperscript{-1}] and k\textsubscript{r} the surface reaction rate coefficient [s\textsuperscript{-1}].

It seems physically realistic that the chemisorption of CO on vacant sites next to O or CO islands occur in the same way and is independent of the presence of O adatoms or CO molecules next to it. Therefore, the CO chemisorption rate coefficient, k\textsubscript{c}, was set equal in reaction step 5.26 and 5.27.

Below the continuity equations in the catalyst bed are summarised. For the two quartz beds only gas transport had to be taken into account, as described in paragraph 4.3. In deriving the continuity equations, the assumption was made that the change in the coverage of vacant surface sites next to O or CO islands and in the coverage of atomic adsorbed oxygen are negligible during the passage of one single pulse.

\begin{align}
\text{CO}_{p} & = K_p \text{C}_{co} \quad (5.29)
\end{align}
Here $\theta_0$ is the fractional coverage of vacant surface sites next to O islands, $\theta_{l_1}$ the fractional coverage of vacant surface sites not next to O islands, $\theta_{co|0}$ the fractional coverage of chemisorbed CO molecules next to O islands and $\theta_{co|l_1}$ the fractional coverage of chemisorbed CO molecules not next to CO islands.

The initial conditions are as follows:

$$t = 0 \land l_1 \leq x \leq (l_1 + l_2) : \quad C_{co}(x) = 0$$  \hspace{1cm} (5.34)

$$t = 0 \land l_1 \leq x \leq (l_1 + l_2) : \quad C_{co}(x) = 0$$  \hspace{1cm} (5.35)

$$t = 0 \land l_1 \leq x \leq (l_1 + l_2) : \quad \theta_{co|0}(x) = 0$$  \hspace{1cm} (5.36)

$$t = 0 \land l_1 \leq x \leq (l_1 + l_2) : \quad \theta_{co|co}(x) = 0$$  \hspace{1cm} (5.37)

The CO inlet pulse sizes are known from the experiments and are listed in appendix 5A in tables 5A.1, 5A.2 and 5A.3. The initial coverage of chemisorbed CO next to O islands is zero, because the reaction continues until the coverage of this component is zero. The initial coverage of chemisorbed CO next to CO islands is zero as well, because a CO molecule which chemisorbs on the boundary of a CO island is incorporated in this island.

Changes in the surface coverage and the CO and CO$_2$ gas concentrations as function of time and reactor coordinate were calculated with this model for each measurement, listed in tables 5A.1, 5A.2 and 5A.3. The numerical method to solve equations 5.29 to 5.33 with initial conditions 5.34 to 5.37 is described in 3.3.1.3. With multi-response Marquardt regression on
the measured outlet CO and CO₂ molar flow rates, the kinetic parameters for this model were estimated, as described in paragraph 4.3.

The value of the reaction rate coefficient, \( k_r \), tended to go to infinity, which blocked a proper execution of the computer routines. Therefore, the surface reaction was set instantaneously on forehand. As a result the derivative of the fractional coverage of chemisorbed CO molecules next to O islands with respect to the time, equation 5.32, became zero. In this case equation 5.31 becomes:

\[
\frac{\partial C_{CO}}{\partial t} = D_{eCO,
\rho} \frac{\partial^2 C_{CO}}{\partial x^2} + (1 - e_b) a \frac{\partial C_{CO}}{\partial x} + k_c \theta_c \rho K_p C_{CO} \quad (5.38)
\]

The parameters for this model, i.e. \( K_p \), \( k_c \), \( \theta_c |_{O} \) and \( k_c \theta_c |_{CO} \) were estimated at 323, 344 and 365 K and are shown in table 5B.1, 5B.2 and 5B.3 in appendix 5B.

In figure 5.19 typical measured and modelled CO and CO₂ molar flow rates are compared. The agreement is satisfactory.

![Figure 5.19: Measured (------) and modelled (-- ) CO (a) and CO₂ (b) outlet molar flow rates at 323 K and an O coverage of 45.4 %. The rate coefficients for the modelled curve are listed in table 5B.1, appendix 5B, at pulse number 10 and the fixed parameters are listed in table 5A.1 at pulse number 10 and in table 5.7.](image)

In figures 5.20, 5.21 and 5.22 \( K_p \), \( k_c \theta_c |_{O} \) and \( k_c \theta_c |_{CO} \) are graphically represented as function of \( \theta_o \) at 323, 344 and 365 K. The maximum oxygen coverage at 323 K was 56.7 %, as it was impossible to remove the remaining adsorbed CO with an oxygen treatment at this temperature.
A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by O₂/NO on Pt

Figure 5.20: Estimates of \( K_p \) obtained from the modelling of the subsequent single CO pulse experiments as a function of \( \theta_O \) at 323 (□), 344 (+) and 365 (○) K with equation 5.29, 5.30 and 5.33 till 5.38. The fixed parameters used in the modelling are listed in table 5.7, 5A.1, 5A.2 and 5A.3.

The physisorption equilibrium coefficient is nearly independent of oxygen coverage and temperature, as is shown in figure 5.20.

Figure 5.21: Estimate of \( k_c \theta_O \) obtained from the modelling of the subsequent single CO pulse experiments as a function of \( \theta_O \) at 323 (□), 344 (+) and 365 (○) K with equations 5.29, 5.30 and 5.34 till 5.38. The fixed parameters used in the modelling are listed in table 5.7, 5A.1, 5A.2 and 5A.3.

The products of the chemisorption rate coefficient and the fractional coverage of vacant surface sites next to O islands, \( k_c \theta_O \), as a function of \( \theta_O \) shown in figure 5.21, nearly coincide at all three temperatures, so \( k_c \theta_O \) seems independent of temperature. \( k_c \theta_O \) increases from 0 at \( \theta_O = 0 \) to 43 s⁻¹ at high \( \theta_O \). At low \( \theta_O \) the probability that a CO molecule
chemisorbs on a vacant surface site next to an O island is very low. The higher the O coverage, the higher the amount of O adatoms on the surface and the greater is the probability that a CO molecule chemisorbs on a vacant surface site next to an O adatom.

The product of the chemisorption rate coefficient and the fractional coverage of vacant surface sites not next to O islands, $k_c \theta_c \theta_{co}$, represented in figure 5.22, shows the opposite course compared to $k_c \theta \theta_{co}$. $k_c \theta \theta_{co}$ decreases from 30 s$^{-1}$ at low $\theta_o$ to about 0 at high $\theta_o$. At high $\theta_o$, $\theta_{co}$ is nearly 0, meaning that the probability that a CO molecule chemisorbs on a vacant surface site not next to an O island is very low. If $\theta_o$ decreases, i.e. $\theta_{co}$ increases, the probability to chemisorb next to a CO island increases, resulting in an increasing value of $k_c \theta \theta_{co}$. Apparently $k_c \theta \theta_{co}$ is also independent of temperature.

![Figure 5.22](image)

**Figure 5.22**: Estimates of $k_c \theta \theta_{co}$ obtained from the modelling of the subsequent single CO pulse experiments as a function of $\theta_o$ at 323 (□), 344 (+) and 365 (O) K with equations 5.29, 5.30 and 5.33 till 5.38. The fixed parameters used in the modelling are listed in table 5.7, 5A.1, 5A.2 and 5A.3.

The probability that a CO molecule chemisorbs on a vacant surface site is independent of the presence of O adatoms or adsorbed CO molecules in the neighbourhood. Therefore, the ratio $\theta \theta_{o}/(\theta \theta_{o} + \theta \theta_{co})$ is a good measure for the probability that a CO molecule chemisorbs next to an O island. This probability is graphically represented as a function of $\theta_o$ at the three investigated temperatures in figure 5.23. It results in a straight line through the origin with a slope of about 1, meaning that the probability to chemisorb on a vacant surface sites next to an O island is proportional to the total oxygen coverage. This probability is nearly independent of temperature. For the probability to chemisorb on a vacant surface site not next to an O island the opposite holds. This probability is proportional to $(1-\theta_o)$. 
**5.6 Conclusions**

At temperatures till 480 K, no measurable oxygen desorption of atomic adsorbed oxygen occurred. At temperatures above 150 K oxygen adsorbs dissociatively on platinum. The adsorption and desorption of molecular oxygen were in equilibrium and the dissociation of molecular adsorbed oxygen was the rate-determining step. It was impossible to determine the adsorption enthalpy of molecular oxygen adsorption, because the experiments were performed at non-isosteric reaction conditions. The value of the estimated activation energy for dissociation of adsorbed molecular oxygen of 8.6 kJ mol⁻¹ was about the same as the value of 13.3 kJ mol⁻¹ reported by Gland (1980). The dissociation of molecular oxygen was independent of the surface coverage.

At temperatures below 380 K large amounts of atomic adsorbed oxygen and molecular adsorbed CO could exist on the surface, without the occurrence of reaction between both adsorbed species. This is caused by the absence of surface migration of adsorbed CO and the existence of CO and O islands. A model taking into account CO physisorption equilibrium and CO chemisorption on vacant surface sites followed by surface reaction at the boundaries of the oxygen islands, described the experiments at low temperature well. The surface reaction at the boundaries of the O islands occurs instantaneously. The CO physisorption equilibrium coefficient was nearly independent of coverage and temperature as to be expected. The probability to chemisorb next to an O island was proportional to the total oxygen coverage and independent of temperature.
The results, which are described in this chapter, could be reached by quantitative modelling of the transient kinetic experiments. This method was applied to determine the kinetics of the CO oxidation on polycrystalline platinum powder with the TAP set-up, but is generally applicable for the quantitative modelling of transient kinetic experiments.

References

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- Lynch, D.T., Wanke, S.E., Oscillations during CO Oxidation over Supported Metal
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Appendix 5A Results of the subsequent single CO pulse experiments

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<th>pulse nr.</th>
<th>measured CO in $10^{-9}$ mol</th>
<th>measured CO out $10^{-9}$ mol</th>
<th>measured CO$_2$ out $10^{-9}$ mol</th>
<th>calculated CO surface $10^{-9}$ mol</th>
<th>calculated $\theta_o$</th>
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Table SA.2: Results of the subsequent single CO pulse experiment over Pt treated with oxygen at 344 K.

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<th>measured CO$_2$ out $10^9$ mol</th>
<th>calculated CO surface $10^9$ mol</th>
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$^1$ calculated from the balance assuming that no CO remained adsorbed on the surface during this pulse.
Table 5A.3: Results of the subsequent single CO pulse experiment over Pt treated with oxygen at 365 K.

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<th>measured CO out $10^{-9}$ mol</th>
<th>measured CO$_2$ out $10^{-9}$ mol</th>
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1 calculated from the balance assuming that no CO remained adsorbed on the surface during this pulse.
Appendix 5B Kinetic parameter estimates for the CO oxidation at low temperatures

Table 5B.1: Kinetic parameter estimates with their approximate individual 95% confidence intervals obtained from the modelling of the subsequent single CO pulse experiment at 323 K with equations 5.29, 5.30 and 5.33 till 5.38. The fixed parameters used in the modelling are listed in table 5.7 and 5A.1.

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<th>$k_c \theta_c l_o$ s$^{-1}$</th>
<th>$k_c \theta_c l_{co}$ s$^{-1}$</th>
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<td>1</td>
<td>$1.376 \pm 0.069$</td>
<td>$25.4 \pm 1.6$</td>
<td>$22.7 \pm 2.0$</td>
<td>$1.1$</td>
</tr>
<tr>
<td>2</td>
<td>$1.307 \pm 0.089$</td>
<td>$14.6 \pm 1.0$</td>
<td>$30.7 \pm 2.8$</td>
<td>$2.1$</td>
</tr>
<tr>
<td>3</td>
<td>$1.267 \pm 0.089$</td>
<td>$18.8 \pm 3.3$</td>
<td>$28.4 \pm 2.7$</td>
<td>$1.7$</td>
</tr>
<tr>
<td>4</td>
<td>$1.252 \pm 0.089$</td>
<td>$18.1 \pm 1.3$</td>
<td>$29.1 \pm 2.9$</td>
<td>$1.8$</td>
</tr>
<tr>
<td>5</td>
<td>$1.287 \pm 0.084$</td>
<td>$18.1 \pm 1.3$</td>
<td>$28.3 \pm 2.7$</td>
<td>$1.8$</td>
</tr>
<tr>
<td>6</td>
<td>$1.309 \pm 0.081$</td>
<td>$17.8 \pm 1.2$</td>
<td>$27.6 \pm 2.5$</td>
<td>$1.9$</td>
</tr>
<tr>
<td>7</td>
<td>$1.295 \pm 0.081$</td>
<td>$17.0 \pm 1.2$</td>
<td>$29.0 \pm 2.6$</td>
<td>$2.0$</td>
</tr>
<tr>
<td>8</td>
<td>$1.242 \pm 0.084$</td>
<td>$20.8 \pm 1.3$</td>
<td>$27.3 \pm 2.6$</td>
<td>$1.9$</td>
</tr>
<tr>
<td>9</td>
<td>$1.295 \pm 0.084$</td>
<td>$19.2 \pm 1.3$</td>
<td>$28.0 \pm 2.6$</td>
<td>$1.8$</td>
</tr>
<tr>
<td>10</td>
<td>$1.272 \pm 0.067$</td>
<td>$19.2 \pm 1.0$</td>
<td>$27.8 \pm 2.1$</td>
<td>$1.7$</td>
</tr>
<tr>
<td>19</td>
<td>$1.297 \pm 0.082$</td>
<td>$15.8 \pm 1.1$</td>
<td>$29.3 \pm 2.7$</td>
<td>$2.3$</td>
</tr>
<tr>
<td>20</td>
<td>$1.255 \pm 0.079$</td>
<td>$15.8 \pm 0.9$</td>
<td>$30.4 \pm 2.5$</td>
<td>$2.7$</td>
</tr>
<tr>
<td>29</td>
<td>$1.359 \pm 0.074$</td>
<td>$10.0 \pm 0.6$</td>
<td>$29.4 \pm 2.3$</td>
<td>$3.0$</td>
</tr>
<tr>
<td>38</td>
<td>$1.503 \pm 0.069$</td>
<td>$5.4 \pm 0.3$</td>
<td>$26.6 \pm 1.8$</td>
<td>$3.6$</td>
</tr>
<tr>
<td>47</td>
<td>$1.471 \pm 0.067$</td>
<td>$5.1 \pm 0.3$</td>
<td>$27.7 \pm 1.8$</td>
<td>$3.6$</td>
</tr>
<tr>
<td>56</td>
<td>$1.495 \pm 0.064$</td>
<td>$5.0 \pm 0.2$</td>
<td>$27.6 \pm 1.7$</td>
<td>$3.8$</td>
</tr>
<tr>
<td>65</td>
<td>$1.426 \pm 0.059$</td>
<td>$3.5 \pm 0.2$</td>
<td>$29.7 \pm 1.8$</td>
<td>$3.8$</td>
</tr>
</tbody>
</table>
Table 5B.2: Kinetic parameter estimates with their approximate individual 95% confidence intervals obtained from the modelling of the subsequent single CO pulse experiment at 344 K with equations 5.29, 5.30 and 5.33 till 5.38. The fixed parameters used in the modelling are listed in table 5.7 and 5A.2.

<table>
<thead>
<tr>
<th>pulse nr.</th>
<th>$K_p$ $10^3 \text{m}_e^3 \text{m}_e^{-2}$</th>
<th>$k_e \theta_I^o$ $\text{s}^{-1}$</th>
<th>$k_e \theta_I^{co}$ $\text{s}^{-1}$</th>
<th>F $10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.627 \pm 0.102$</td>
<td>$43.1 \pm 3.3$</td>
<td>$5.8 \pm 1.5$</td>
<td>0.9</td>
</tr>
<tr>
<td>2</td>
<td>$1.136 \pm 0.074$</td>
<td>$44.1 \pm 3.0$</td>
<td>$8.9 \pm 1.5$</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>$1.176 \pm 0.079$</td>
<td>$43.1 \pm 3.2$</td>
<td>$7.7 \pm 1.7$</td>
<td>1.1</td>
</tr>
<tr>
<td>4</td>
<td>$1.096 \pm 0.079$</td>
<td>$45.2 \pm 3.5$</td>
<td>$8.2 \pm 1.8$</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>$1.111 \pm 0.084$</td>
<td>$46.4 \pm 3.9$</td>
<td>$7.1 \pm 1.7$</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>$1.051 \pm 0.069$</td>
<td>$46.7 \pm 3.6$</td>
<td>$7.2 \pm 1.2$</td>
<td>1.0</td>
</tr>
<tr>
<td>7</td>
<td>$1.121 \pm 0.081$</td>
<td>$43.4 \pm 3.5$</td>
<td>$9.0 \pm 1.8$</td>
<td>1.0</td>
</tr>
<tr>
<td>8</td>
<td>$1.111 \pm 0.082$</td>
<td>$43.7 \pm 3.5$</td>
<td>$9.2 \pm 1.9$</td>
<td>1.0</td>
</tr>
<tr>
<td>9</td>
<td>$1.037 \pm 0.069$</td>
<td>$46.1 \pm 3.7$</td>
<td>$8.5 \pm 1.5$</td>
<td>1.0</td>
</tr>
<tr>
<td>23</td>
<td>$1.086 \pm 0.081$</td>
<td>$33.5 \pm 2.6$</td>
<td>$16.0 \pm 2.0$</td>
<td>1.1</td>
</tr>
<tr>
<td>36</td>
<td>$1.178 \pm 0.131$</td>
<td>$17.6 \pm 2.1$</td>
<td>$23.2 \pm 3.6$</td>
<td>0.7</td>
</tr>
<tr>
<td>49</td>
<td>$1.262 \pm 0.109$</td>
<td>$7.5 \pm 1.3$</td>
<td>$27.8 \pm 3.2$</td>
<td>1.2</td>
</tr>
<tr>
<td>62</td>
<td>$1.257 \pm 0.084$</td>
<td>$5.9 \pm 0.4$</td>
<td>$28.5 \pm 2.7$</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Table 5B.3: Kinetic parameter estimates with their approximate individual 95% confidence intervals obtained from the modelling of the subsequent single CO pulse experiment at 365 K with equations 5.29, 5.30 and 5.33 till 5.38. The fixed parameters used in the modelling are listed in table 5.7 and 5A.3.

| pulse nr. | $K_p \times 10^5$ m₉⁻³ mₛ⁻² | $k_c \theta_s |_O$ s⁻¹ | $k_c \theta_s |_{CO}$ s⁻¹ | $F$ 10⁴ |
|-----------|-------------------------------|----------------|----------------|---------|
| 1         | 1.652 ± 0.122                 | 45.4 ± 3.7     | 7.2 ± 1.5      | 0.9     |
| 2         | 1.431 ± 0.104                 | 42.6 ± 3.3     | 10.2 ± 1.8     | 1.1     |
| 3         | 1.436 ± 0.106                 | 42.2 ± 3.3     | 9.2 ± 1.7      | 1.1     |
| 4         | 1.376 ± 0.097                 | 43.2 ± 3.2     | 9.0 ± 1.5      | 1.1     |
| 5         | 1.401 ± 0.097                 | 42.0 ± 3.2     | 9.8 ± 1.5      | 1.1     |
| 6         | 1.324 ± 0.102                 | 43.5 ± 3.5     | 10.0 ± 1.8     | 1.1     |
| 7         | 1.386 ± 0.094                 | 41.1 ± 3.0     | 10.2 ± 1.7     | 1.1     |
| 8         | 1.374 ± 0.097                 | 41.4 ± 3.1     | 10.0 ± 1.7     | 1.1     |
| 9         | 1.327 ± 0.097                 | 41.2 ± 3.1     | 10.3 ± 1.7     | 1.1     |
| 10        | 1.312 ± 0.091                 | 40.3 ± 3.0     | 11.7 ± 1.7     | 1.1     |
| 23        | 1.386 ± 0.094                 | 29.7 ± 2.1     | 18.4 ± 2.1     | 1.3     |
| 36        | 1.510 ± 0.169                 | 18.2 ± 2.1     | 23.6 ± 4.0     | 0.8     |
| 49        | 1.438 ± 0.149                 | 6.4 ± 0.6      | 22.3 ± 2.7     | 0.9     |
| 62        | 1.934 ± 0.169                 | 3.2 ± 0.3      | 22.8 ± 3.0     | 0.8     |
| 75        | 1.704 ± 0.131                 | 0.36 ± 0.03    | 30.5 ± 3.3     | 2.0     |
A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by $O_2$/$NO$ on Pt
6

MECHANISTIC INVESTIGATION OF THE OXIDATION OF CO BY NO ON Pt

6.1 Introduction

The simultaneous oxidation of carbon monoxide and reduction of nitric oxide over noble metal catalysts is a widely used heterogeneous catalytic reaction for the removal of these pollutants from the exhaust gas of automobiles. Because of its environmental significance, it has been studied by a large number of industrial and academic researchers. In addition to the obvious environmental significance, there is also the capability to gain fundamental insight into heterogeneous catalysis through analysis of this reaction, since it is slightly more complicated than the classical oxidation reaction between CO and O₂. The automobile catalytic converter should remove three harmful pollutants simultaneously, and is therefore referred to as a three-way catalyst: carbon monoxide in the exhaust gas has to be further oxidised to carbon dioxide, nitric oxide should be reduced to nitrogen and unburned hydrocarbons need to be burned to carbon dioxide and water.

Platinum is one of the components of the three-way converter and therefore a platinum catalyst was used in the experiments, described in this study. The aim of this study was to acquire insight in the mechanisms involved in the global reactions between CO and NO:

\[
\begin{align*}
2 \text{ CO} + 2 \text{ NO} & \rightarrow \text{ N}_2 + 2 \text{ CO}_2 \\
\text{CO} + 2 \text{ NO} & \rightarrow \text{ N}_2\text{O} + \text{ CO}_2
\end{align*}
\]

(6.1) (6.2)

Experiments were performed with the TAP set-up on the CO oxidation by NO over polycrystalline platinum sponge in the temperature range from 407 to 726 K and at pressures from 0.1 to 2 mbar. In paragraph 6.3 preliminary pulse and multi-pulse experiments are
reported. The TAP experiments, performed to give more precise answers about the mechanism of CO\textsubscript{2}, N\textsubscript{2} and N\textsubscript{2}O formation, are discussed in paragraph 6.4.

6.2 Literature survey

The literature survey about the oxidation of CO by NO over platinum provided several possible mechanisms. The suggested mechanisms involve a sequence of Langmuir-Hinshelwood reactions, involving molecular adsorption, dissociative adsorption, and reaction between the various adsorbed species. In table 6.1 the elementary reaction steps, which are possibly involved in this reaction, are listed. It is assumed that all catalytic sites are identical and that each adsorbed species occupies one catalytic site.

**Table 6.1: Elementary reactions which are possibly involved in the oxidation of CO by NO over Pt (Klein et al. (1985), Scharpf and Benziger (1992), Fink et al. (1991), Miki et al. (1990), Cho et al. (1989), Cho (1992, 1994) and Ansell et al. (1994)).**

<table>
<thead>
<tr>
<th>Elementary reactions</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + * = CO*</td>
<td>(6.3)</td>
</tr>
<tr>
<td>NO + * = NO*</td>
<td>(6.4)</td>
</tr>
<tr>
<td>NO* + * = N* + O*</td>
<td>(6.5)</td>
</tr>
<tr>
<td>CO* + O* → CO\textsubscript{2} + 2*</td>
<td>(6.6)</td>
</tr>
<tr>
<td>CO* + NO* → CO\textsubscript{2} + N* + *</td>
<td>(6.7)</td>
</tr>
<tr>
<td>N* + N* → N\textsubscript{2} + 2*</td>
<td>(6.8)</td>
</tr>
<tr>
<td>NO* + N* = N\textsubscript{2}O* + *</td>
<td>(6.9)</td>
</tr>
<tr>
<td>N\textsubscript{2}O* = N\textsubscript{2}O + *</td>
<td>(6.10)</td>
</tr>
<tr>
<td>N\textsubscript{2}O* → N\textsubscript{2} + O*</td>
<td>(6.11)</td>
</tr>
<tr>
<td>NO* + N* → N\textsubscript{2} + O* + *</td>
<td>(6.12)</td>
</tr>
<tr>
<td>O* + O* = O\textsubscript{2} + 2*</td>
<td>(6.13)</td>
</tr>
</tbody>
</table>

CO adsorbs molecularly and reversibly on the surface, reaction 6.3, (Engel and Ertl (1979), Lambert and Comrie (1974)). CO will not dissociate on Pt (Nieuwenhuys et al., 1993).

NO adsorbs molecularly, reaction 6.4, on some crystal planes followed by dissociation, reaction 6.5. NO dissociation has been observed, dependent on the crystal plane type, at temperatures above 400 K. Studies were carried out on single crystal Pt, as well as on polycrystalline Pt, which consists mainly of Pt(111). The minor part of polycrystalline Pt is the Pt(100) plane. The Pt(410) plane is the most active for dissociation, followed by the
Mechanistic Investigation of the Oxidation of CO by NO on Pt

Pt(210), Pt(100), Pt(511) and Pt(110) plane (Masel, 1986). Pt(111) is reported to be inactive for NO dissociation (Masel (1986) and Gorte et al. (1981)). Gohndrone et al. (1985) investigated NO desorption on Pt(210) and Pt(410). While on Pt(210) both NO and N₂ desorb at the same temperature, only N₂ desorption is observed on Pt(410). Gorte et al. (1981) and Lesley and Schmidt (1985) found 50% dissociation of the adsorbed NO on Pt(100). NO has been observed to dissociate on Pt(111) planes in UHV, when defects such as steps are present (Wickham et al., 1989). All these results agree with the postulated activities for NO decomposition of the various crystal planes.

NO desorption on polycrystalline Pt was investigated by Miki et al. (1990). The Temperature Programmed Desorption (TPD) experiments were carried out with a reactant mixture of NO/CO at a ratio of 7. The effect of CO adsorption could be ignored. The TPD spectra for NO show two major NO desorption peaks at 330-360 K, denoted the α-NO peak, and 430-465 K, denoted the β-NO peak. The β-NO peak appears at about the same temperature as the sharp N₂ peak. Therefore, the α-NO peak may be caused by molecular desorption of NO, the backward reaction 6.4, and the β-NO peak could be caused by desorption of NO, as a result of recombination of N and O adatoms, the backward reaction 6.5. TPD experiments by Gohndrone and Masel (1989) with Pt(100), Pt(411) and Pt(211) show a sharp NO peak at 450 K, with Pt(100). Pt(411) is very active for NO decomposition. At low NO coverages N₂ desorption, reaction 6.8, and O₂ desorption, reaction 6.13, is observed. At moderate coverages NO desorbs molecularly at 430 K. NO desorption experiments starting from a monolayer coverage of CO on Pt(211) show two NO peaks at 370 and 500 K, while 66% of the adsorbed NO dissociates. XPS studies on Pt(210) by Lang and Masel (1986) revealed that NO is adsorbed molecularly and dissociates at 450 K.

Engel and Ertl (1979) report that O₂ is molecularly adsorbed below 100 K. At higher temperatures O₂ dissociates. Associative desorption of O₂, reaction 6.13, starts at temperatures above 650 K on Pt(110) (Wilf and Dawson, 1977), while the bulk of the oxygen desorbs between 750 and 800 K. O₂ desorption is observed above 700 K on Pt(411) in TPD experiments with NO (Gohndrone and Masel, 1989). A TPD study with NO on polycrystalline Pt (Miki et al., 1990) shows O₂ desorption at temperatures between 757 and 780 K.

Campbell et al. (1980) concluded, that the interaction between CO₂ and the Pt(111) surface was very weak. Therefore, CO₂ desorption can be assumed to be very fast under the experimental conditions, described in this chapter.

To a lower extent, this is also the case for N₂ desorption (Shigeishi and King (1977), Schwaha and Bechtold (1977)). TPD spectra of NO (Gohndrone and Masel, 1989) show a N₂ desorption peak at 460-475 K on Pt(100), a broad N₂ desorption peak at 450-520 K on
Pt(411) and at 450-500 K on Pt(211), resulting from associative nitrogen desorption, reaction 6.8. Similar experiments on Pt(100) show N₂ desorption between 500 and 550 K (Lesley and Schmidt (1985), Gorte et al. (1981)). Finally, Miki et al. (1990) report two N₂ peaks, denoted α-N₂ and β-N₂, in TPD experiments with NO on polycrystalline Pt, see figure 6.1. The small α-N₂ peak appears at approximately 370 K, the large β-N₂ peak appears between 445 and 450 K. The α-N₂ peak is probably caused by N₂O decomposition, reaction 6.11, while the β-N₂ peak is caused by N adatom recombination followed by nitrogen desorption, reaction 6.8. Figure 6.1 shows also two small N₂O peaks. Avery (1983) reported that the interactions between N₂O and the Pt(111) surface were very weak. N₂O desorption peaks in TPD experiments were observed between 90 and 100 K (Avery, 1983).

Mechanisms for the global reactions 6.1 and 6.2 as proposed in the literature will now be discussed. The first mechanism (Banse et al. (1989), Dath et al. (1992), Fink et al. (1991)) is based on the dissociation of NO, followed by reaction of adsorbed CO with atomic adsorbed O:

\[
\begin{align*}
\text{CO} + \text{O}^* & \rightarrow \text{CO}^* \quad (6.3) \\
\text{NO} + \text{O}^* & \rightarrow \text{NO}^* \quad (6.4) \\
\text{NO}^* + \text{O}^* & \rightarrow \text{N}^* + \text{O}_2^* \quad (6.5) \\
\text{CO}^* + \text{O}^* & \rightarrow \text{CO}_2 + 2^* \quad (6.6) \\
\text{N}^* + \text{N}^* & \rightarrow \text{N}_2 + 2^* \quad (6.8)
\end{align*}
\]

Transient kinetic studies on polycrystalline Pt were carried out by Banse et al. (1989). The temperature varied from 380 to 450 K and the total pressure was held at approximately 10⁻⁷-10⁻⁸ mbar. The results could be adequately described with reaction rate expressions, derived from the dissociative mechanism, with NO dissociation as rate-limiting step. Besides, the results could not be described by rate expressions, derived from other mechanisms. Experiments on Pt(100) and mathematical modelling of the results by Fink et al. (1991) also suggested, that the reaction follows a dissociative pathway. No evidence was found for a
bimolecular reaction between adsorbed NO and CO, which frequently had been considered as a possible alternative.

Ansell et al. (1994) found NO dissociation to be dominant in transient experiments, performed with the TAP set-up, with CO and NO over Pt/Al₂O₃ at 673 K. Little N₂O formation besides N₂ formation was observed. Steady-state experiments at 473 K showed substantial N₂O formation. They therefore conclude, that at low temperatures molecular adsorbed NO is present, while NO dissociation increases at higher temperatures. Ansell et al. (1994) pictured a mechanism for simultaneous N₂O and N₂ formation. N adatoms are generated by NO dissociation, reaction 6.5. If NO is next to a N adatom, N₂O is formed via reaction 6.9, which desorbs via reaction 6.10. N₂ formation takes place via N adatom recombination, reaction 6.8. Figure 6.2 shows these processes taking place on the Pt surface.

![Figure 6.2: Mechanism of N₂O and N₂formation on the Pt surface (from: Ansell et al., 1994).](image)

Cho and co-workers (Cho et al. (1989), Cho (1992, 1994)) proposed a mechanism where N₂O act as an intermediate for the CO/NO reaction over a Rh/Al₂O₃ catalyst, as a conclusion of a theoretical steady-state kinetic analysis. This mechanism includes NO decomposition and formation of N₂O.

\[
\begin{align*}
CO + * & \rightarrow CO^* \\
NO + * & \rightarrow NO^* \\
NO^* + * & \rightarrow N^* + O^* \\
NO^* + N^* & \rightarrow N₂O^* + * \\
N₂O^* & \rightarrow N₂ + O^* \\
N₂O^* & \rightarrow N₂ + O^* \\
N^* + N^* & \rightarrow N₂ + 2^* \\
CO^* + O^* & \rightarrow CO₂ + 2^*
\end{align*}
\]
Reactions 6.9 and 6.11 are often combined into:

$$\text{NO}^* + \text{N}^* \rightarrow \text{N}_2 + \text{O}^* + \text{*} \quad (6.12)$$

In this scheme both $\text{N}_2\text{O}$ and $\text{N}_2$, at least at low temperature, come from a common intermediate, which is formed by reaction of adsorbed $\text{NO}$ and $\text{N}$, reaction 6.9. Within the context of this mechanism the selectivity is controlled by the relative rates of dissociation to give $\text{N}_2$, reaction 6.11, and desorption to give $\text{N}_2\text{O}$ from this intermediate, reaction 6.10 (Cho et al. (1989), Cho (1992, 1994), Ng et al. (1994)). Both steady-state and transient pulse experiments conducted by Cho (1992, 1994) over supported Rh catalysts have revealed that the rate of the $\text{CO}/\text{N}_2\text{O}$ reaction, as an intermediate reaction in the $\text{CO}/\text{NO}$ reaction system, can be two or three orders of magnitude faster than the isolated $\text{CO}/\text{N}_2\text{O}$ reaction, which is known to be very slow compared to the $\text{CO}/\text{NO}$ reaction. This makes the rate of the intermediate $\text{CO}/\text{N}_2\text{O}$ reaction as fast as or even faster than the rate of the $\text{CO}/\text{NO}$ reaction, suggesting that the former reaction can make a major contribution to the kinetics of the reduction of $\text{NO}$ by $\text{CO}$.

Schmidt and co-workers (Klein et al., 1985) studied the $\text{CO}_2$ production from the $\text{CO}/\text{NO}$ reaction on polycrystalline platinum over a very broad range of pressures ($10^4$-1 mbar) and temperatures ($300-1200$ K) and were the first to suggest that the reaction could be described by a Langmuir-Hinshelwood mechanism, where the rate-limiting step was the bimolecular reaction between adsorbed $\text{CO}$ and adsorbed $\text{NO}$, reaction 6.7.

$$\text{CO} + * \rightarrow \text{CO}^* \quad (6.3)$$
$$\text{NO} + * \rightarrow \text{NO}^* \quad (6.4)$$
$$\text{NO}^* + \text{CO}^* \rightarrow \text{CO}_2 + \text{N}^* + * \quad (6.7)$$
$$\text{N}^* + \text{N}^* \rightarrow \text{N}_2 + 2* \quad (6.8)$$

The steady-state experiments were carried out with $\text{CO}/\text{NO}$ mixtures, with compositions varying between 0.0005 mol% and 0.99 mol% $\text{CO}$. Formation of $\text{N}_2\text{O}$ was found to be negligible. Scharpf and Benziger (1992) performed Dynamic Reflection Infrared Spectroscopy (DRIRS) measurements on the $\text{CO}/\text{NO}$ reaction on platinum foil at temperatures between 428 and 465 K, pressures of $10^6$ mbar and $\text{CO}/\text{NO}$ stoichiometries of 0.1 to 2. These measurements indicated that the rate of $\text{CO}$ removal during the $\text{CO}/\text{NO}$ reaction was not consistent with the dissociation of $\text{NO}$ being the rate-limiting step, but was consistent with the bimolecular reaction between adsorbed $\text{CO}$ and adsorbed $\text{NO}$, proposed by Schmidt and co-workers (Klein et al. (1985)). No $\text{N}_2\text{O}$ formation was reported.

TPD experiments give also information about the reaction mechanism. Miki et al. (1990) performed TPD experiments with polycrystalline Pt, with reactant mixtures of $\text{CO}$ and $\text{NO}$.
Mechanistic Investigation of the Oxidation of CO by NO on Pt

with NO/CO ratios of 3 and 7, as shown in figure 6.1. Desorption peaks of NO, N₂O, CO₂ and N₂ were observed in two temperature ranges. In the first range, from 330 to 370 K, all four components cause a desorption peak. When the NO/CO ratio is changed from 7 to 3, the CO₂ and N₂ formation increase, while the amount of NO desorption decreases. NO is believed to be molecularly adsorbed at this temperature. The CO₂ and N₂ formation is therefore ascribed to the occurrence of the bimolecular reaction between CO and NO, reaction 6.7. The N₂O peak at about the same temperature is caused by reaction of adsorbed NO and N adatoms, reaction 6.9 and 6.10. The N adatoms, participating in this reaction, originate from the bimolecular reaction 6.7. In the second temperature range, from 430 to 460 K, the same phenomena regarding the CO₂, N₂ and NO desorption are observed, although the increase of CO₂ and N₂ formation and the decrease of NO desorption is less than in the low temperature range. NO desorption is believed to be caused by recombination of N and O adatoms, backward reaction 6.5. Therefore, CO₂ is formed via the reaction between CO and O adatoms, reaction 6.6, and N₂ is formed via N adatom recombination, reaction 6.8. N₂O is formed in the same way as in the low temperature range. The N adatoms, however, now originate from NO decomposition.

The above studies indicate that the dissociative mechanism takes place under most experimental conditions. Some studies show that molecular adsorbed NO is present at low temperatures and as a result N₂O formation is observed. NO dissociation is both theoretically (Masel, 1986) as well as experimentally (Masel (1986), Gorte et al. (1981)) ruled out on the Pt(111) crystal plane, the major part of polycrystalline Pt. However, NO dissociation does occur on polycrystalline Pt, when defects such as steps are present (Wickham et al., 1989).

6.3 Preliminary experiments on the CO oxidation by NO

6.3.1 Experimental

The platinum sponge catalyst, 0.7428 g, used in the pulse and multi-pulse experiments, was pretreated at 873 K, as described in paragraph 2.5.2.1. Before the experiments the absolute calibration factors of all reactants and possibly formed products, i.e. CO₂, N₂O, Ar, O₂, NO, CO and N₂, were determined, as described in paragraph 2.3.2. Carbon monoxide and nitrogen both occur at mass 28 and carbon dioxide and nitrous oxide at mass 44. These species were differentiated during part of the experiments by using isotopically labelled ¹³CO as reactant instead of normal CO, which gave rise to ¹³CO at mass 29, and ¹³CO₂ at mass 45. During the experiments the responses of all reactants and possibly formed products were recorded.

The fragmentation patterns of N₂O and CO₂, listed in table 6.2, were recorded at 373 K. With these patterns their contribution to the responses of CO, NO and N₂ could be determined. The
overlapping of masses is always accounted for during the interpretation of the experiments. The fragmentation pattern of $^{13}\text{CO}_2$ was assumed to be equal to the fragmentation pattern of $\text{CO}_2$.

**Table 6.2: Fragmentation patterns of $\text{CO}_2$ and $\text{N}_2\text{O}$ at 373 K.**

<table>
<thead>
<tr>
<th>Gas</th>
<th>main fragment</th>
<th>fragment 1</th>
<th>fragment 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2$</td>
<td>$\text{CO}_2$: 100.0</td>
<td>CO: 11.7</td>
<td></td>
</tr>
<tr>
<td>$\text{N}_2\text{O}$</td>
<td>$\text{N}_2\text{O}$: 100.0</td>
<td>NO: 33.5</td>
<td>$\text{N}_2$: 13.0</td>
</tr>
</tbody>
</table>

Two series of multi-pulse experiments were carried out. In the first the cumulative $\text{CO}_2$ formation on Pt pretreated with NO was compared with the $\text{CO}_2$ formation on Pt precovered with O adatoms. Therefore CO was pulsed over Pt pretreated with NO or O$_2$ at 407, 450, 496 and 641 K, while the $\text{CO}_2$ formation was monitored.

In the second series $^{13}\text{CO}$ was pulsed over a Pt surface pretreated with NO, at the same temperatures as mentioned above, but now the responses of $^{13}\text{CO}_2$, $\text{N}_2\text{O}$, Ar, O$_2$, NO, $^{13}\text{CO}$ and $\text{N}_2$ were recorded. Argon was used as inert reference.

The procedure described below, ensured that each response was obtained under the same steady-state conditions of the platinum surface. Pulse experiments with a gas mixture containing 30 vol.% $^{13}\text{CO}$, 60 vol.% NO and 10 vol.% Ar, having a pulse size of approximately $6 \times 10^{15}$ molecules, were performed at 626, 676 and 726 K. A large number of pulses was given, while monitoring the NO response, with a frequency of 1 pulse per 2 seconds until a steady-state coverage on the surface had been created. The pulse frequency of 1 pulse per 2 seconds proved to be sufficient to record all responses completely, the NO response being the slowest one. NO was partially converted. After establishing the steady-state coverage on the surface, the responses of $^{13}\text{CO}_2$, $\text{N}_2\text{O}$, Ar, O$_2$, NO, $^{13}\text{CO}$ and $\text{N}_2$ all were recorded from subsequent pulses. The NO response was recorded before and after the measurements of the other components to verify that the steady-state was maintained during these measurements. Figure 6.3 shows these NO responses at 626 K.

The difference in the NO responses before and after recording all other masses, was never greater than approximately 2% at all temperatures. Every signal was averaged 100 times. During the time intervals that the mass spectrometer was adjusted from one mass to another, pulsing was not possible. To re-establish the steady-state on the surface before actually recording another mass, a sufficient number of pulses was given. This procedure ensured that each response was obtained under the same steady-state conditions.
Mechanistic Investigation of the Oxidation of CO by NO on Pt

Figure 6.3: NO responses before (A) and after (B) the measurements of all other components to verify that steady-state was maintained at 626 K, in pulse experiments with a mixture of 30 vol.% $^{13}$CO, 60 vol.% NO and 10 vol.% Ar.

Immediately after measurements of the last response, a multi-pulse experiment with CO was carried out at the same temperature, in which the CO$_2$ response was monitored, to determine the amount of atomic adsorbed oxygen on the surface.

6.3.2 Results and discussion

First, the results of the multi-pulse experiments, concerning the cumulative CO$_2$ formation on Pt pretreated with NO versus that on Pt precovered with O adatoms, will be discussed. Table 6.3 shows the data at 407, 450, 496 and 641 K.

Table 6.3: Cumulative CO$_2$ formation during CO multi-pulse experiments on Pt pretreated with O$_2$ or NO.

<table>
<thead>
<tr>
<th>temperature</th>
<th>CO$_2$ formation</th>
<th>CO$_2$ formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>O$_2$ pretreated</td>
<td>NO pretreated</td>
</tr>
<tr>
<td></td>
<td>mol g$^{-1}$</td>
<td>mol g$^{-1}$</td>
</tr>
<tr>
<td>407</td>
<td>7.3</td>
<td>decreasing from 2.5 to 0.6</td>
</tr>
<tr>
<td>450</td>
<td>7.2</td>
<td>4.4</td>
</tr>
<tr>
<td>496</td>
<td>6.6</td>
<td>2.3</td>
</tr>
<tr>
<td>641</td>
<td>3.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>
At 407 K the cumulative CO$_2$ formation decreases when repeating the multi-pulse experiment on Pt pretreated with NO. At higher temperatures the CO$_2$ formation remains constant, if the experiment is repeated. It means that at 407 K the number of available surface Pt atoms decreases, as the surface becomes increasingly covered with N adatoms. When the catalyst, which was partially covered with N adatoms, was heated to 673 K and cooled down to 407 K, the initial number of Pt surface atoms was measured again. This would correspond to the associative desorption of N$_2$ during heating.

As described already in paragraph 5.3.2, no measurable desorption of atomic adsorbed oxygen occurs at temperatures till 480 K. The CO$_2$ formation in experiments on Pt, pretreated with O$_2$ decreases considerably at 641 K, indicating O$_2$ desorption. The CO$_2$ formation in experiments with NO pretreatment is at all temperatures lower than in experiments with O$_2$ pretreatment, due to NO desorption and the presence of N adatoms. Nitrogen desorption starts at a lower temperature, about 450 K, than oxygen desorption.

Next the multi-pulse experiments in which $^{13}$CO was pulsed over Pt pretreated with NO are discussed. At 407 K no N$_2$O and O$_2$ were formed. An interesting result at this temperature is the NO response, shown in figure 6.4.

![Figure 6.4: NO response at 407 K in a $^{13}$CO multi-pulse experiment on Pt pretreated with NO.](image)

The NO molecules were displaced from the surface by $^{13}$CO molecules. This displacement of NO by CO was also observed by Gorte and Schmidt (1981) on Pt(111) at 300 K, and indicates the presence of molecularly adsorbed NO.

At 641 K no $^{13}$CO broke through when $^{13}$CO$_2$ was formed. Neither N$_2$ nor N$_2$O was formed during $^{13}$CO$_2$ formation, so N adatoms or adsorbed NO molecules were absent on the Pt
Mechanistic Investigation of the Oxidation of CO by NO on Pt

surface. N adatoms and/or adsorbed NO molecules had been converted already to N\textsubscript{2} during the NO pretreatment of the Pt surface, resulting in a high oxygen coverage. Because CO\textsubscript{2} was formed during the \textsuperscript{13}CO multi-pulse experiment, O adatoms were present on the surface after the pretreatment procedure. CO\textsubscript{2} formation at 641 K can only result from reaction (6.6):

\[ \text{CO}^* + \text{O}^* \rightarrow \text{CO}_2 + 2^* \]  \hspace{1cm} (6.5)

Thus, during the NO pretreatment at 641 K NO dissociates on the Pt surface to O and N adatoms. N adatoms are converted by recombination and desorption to N\textsubscript{2}, leaving just O adatoms on the surface:

\[ \text{NO}^* + * \rightarrow \text{N}^* + \text{O}^* \] \hspace{1cm} (6.5)

\[ \text{N}^* + \text{N}^* \rightarrow \text{N}_2 + 2^* \] \hspace{1cm} (6.8)

In figure 6.5 the normalised responses of all products and reactants of the pulse experiment with a mixture of 30 vol.% \textsuperscript{13}CO, 60 vol.% NO and 10 vol.% Ar are shown at 626 K.

![Figure 6.5: Normalised responses of A) Ar (x 2.9), B) N\textsubscript{2}O (x 3.6), C) N\textsubscript{2} (x 1.8), D) \textsuperscript{13}CO\textsubscript{2} and E) NO (x 3.2) at 626 K, in a pulse experiment with a mixture of 30 vol.% \textsuperscript{13}CO, 60 vol.% NO and 10 vol.% Ar.]

\textsuperscript{13}CO was totally converted to \textsuperscript{13}CO\textsubscript{2}. It should be noted that no O\textsubscript{2} formation had been observed at 626, 676 and 726 K. The Ar response appears before the other responses, indicating interactions of all reactants and products with the Pt surface. The responses of \textsuperscript{13}CO\textsubscript{2}, N\textsubscript{2}O and N\textsubscript{2} are positioned close to each other. N\textsubscript{2}O is formed before \textsuperscript{13}CO\textsubscript{2}, which appears before N\textsubscript{2}. The NO response consist of two peaks. The first peak is an artefact, i.e. is caused by fragmentation of N\textsubscript{2}O as confirmed by its coincidence with the N\textsubscript{2}O response, while the second peak of the NO response is caused by slowly desorbing NO. At 676 and 726 K, the Ar response appears before the other responses, indicating interactions of all reactants and products with the Pt surface.
the responses of all products and reactants, except NO, showed similar behaviour. NO desorption increased with increasing temperature, resulting in nearly coinciding responses of NO and N₂O at 726 K.

Table 6.4 lists the integrated responses of all formed components at the three temperatures studied. The data have been corrected for fragmentation.

Mass balances were made for carbon, nitrogen and oxygen. The amount of inlet $^{13}$CO and NO were calculated from the Ar signal. In table 6A.1, 6A.2 and 6A.3 in appendix 6A, the mass balances for carbon, nitrogen and oxygen are shown respectively. In all three mass balances, the differences between the number of molecules at the inlet and outlet are small.

Table 6.4: Integrated responses of all formed components during a single pulse with a mixture of 30 vol.% $^{13}$CO, 60 vol.% NO and 10 vol.% Ar. The amount of inlet $^{13}$CO and NO are listed in appendix 6A for all three temperatures.

<table>
<thead>
<tr>
<th>component</th>
<th>amount of each component in $10^{15}$ molecules at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>626 K</td>
</tr>
<tr>
<td>$^{13}$CO₂</td>
<td>1.84</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.51</td>
</tr>
<tr>
<td>N₂</td>
<td>1.04</td>
</tr>
</tbody>
</table>

From the data in tables 6A.1, 6A.2 and 6A.3, the conversions of $^{13}$CO and NO can be calculated with the following expression:

$$X = \frac{n_{i,\text{in}} - n_{i,\text{out}}}{n_{i,\text{in}}}$$ \hspace{1cm} (6.14)

In this equation $n_{i,\text{in}}$ stands for the number of inlet and $n_{i,\text{out}}$ for the number of outlet molecules of component $i$.

Table 6.5 shows these conversions as well as the $N_2/N_2O$ ratio. $^{13}$CO is almost completely converted at all temperatures. The NO conversion is independent of temperature and about 70%. The $N_2/N_2O$ ratio increases with increasing temperature.
Table 6.5: Conversions of $^{13}$CO and NO, and the $N_2/N_2O$ ratio during the pulse experiments with a mixture of 30 vol.% $^{13}$CO, 60 vol.% NO and 10 vol.% Ar.

<table>
<thead>
<tr>
<th>temperature (K)</th>
<th>$X_{CO}$ (%)</th>
<th>$X_{NO}$ (%)</th>
<th>$N_2/N_2O$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>626</td>
<td>97.1</td>
<td>70.6</td>
<td>2.2</td>
</tr>
<tr>
<td>676</td>
<td>96.7</td>
<td>70.4</td>
<td>4.0</td>
</tr>
<tr>
<td>726</td>
<td>96.2</td>
<td>72.4</td>
<td>10.1</td>
</tr>
</tbody>
</table>

The increasing extent of NO dissociation with increasing temperature, results in a decreasing amount of molecular adsorbed NO on the surface. Therefore, the N adatom recombination, reaction 6.8, is favoured at the expense of the reaction between adsorbed NO and N adatoms, reactions 6.9 and 6.10:

\[
N^* + N^* \rightarrow N_2 + 2* \quad (6.8)
\]

\[
NO^* + N^* \rightarrow N_2O^* + * \quad (6.9)
\]

\[
N_2O^* \rightarrow N_2O + * \quad (6.10)
\]

The results of the multi-pulse experiments with CO, carried out subsequently to determine the amount of atomic adsorbed oxygen on the surface, are listed in table 6.6.

Table 6.6: Amount of atomic adsorbed oxygen and corresponding oxygen surface coverage during the pulse experiments with a mixture of 30 vol.% $^{13}$CO, 60 vol.% NO and 10 vol.% Ar.

<table>
<thead>
<tr>
<th>temperature (K)</th>
<th>amount of O adatoms $10^{-7}$ mol g$^{-1}$</th>
<th>$\theta_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>626</td>
<td>4.0</td>
<td>0.55</td>
</tr>
<tr>
<td>676</td>
<td>4.0</td>
<td>0.55</td>
</tr>
<tr>
<td>726</td>
<td>4.7</td>
<td>0.64</td>
</tr>
</tbody>
</table>

The oxygen coverage increases with increasing temperature. This can be explained by N adatom recombination, reaction 6.8, taking place more easily at higher temperatures (Miki et al., 1990), resulting in a higher oxygen coverage. The increase of the oxygen coverage with increasing temperature also indicates more NO dissociation. As N adatoms are less strongly bound than O adatoms, more free sites are available for NO adsorption and dissociation.
Summarising it follows from the preliminary experiments, that at 407 K molecularly adsorbed NO is present on the Pt surface, while at 641 K NO dissociates completely. The increasing extent of NO dissociation with increasing temperature results in a decreasing amount of molecular adsorbed NO on the surface. Therefore, N₂ formation via N adatom recombination, reaction step 6.8, is favoured at the expense of N₂O formation via reaction between adsorbed NO and N adatoms, reaction 6.9.

6.4 Experiments on the CO₂, N₂O and N₂ formation

6.4.1 Introduction

The above results can be explained by various mechanisms from the literature, as is summarised briefly below.

CO₂ is formed either by a dissociative mechanism, in which the O adatom originates from NO dissociation (Banse et al. (1989), Dath et al. (1992), Fink et al. (1991)), or by a bimolecular mechanism, in which adsorbed CO is oxidised by molecular adsorbed NO (Klein et al. (1985), Scharpf and Benziger (1992)):

\[
\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2 + 2^* \tag{6.6}
\]

\[
\text{CO}^* + \text{NO}^* \rightarrow \text{CO}_2 + \text{N}^* + ^* \tag{6.7}
\]

N₂ is either formed from nitrogen recombination, in which nitrogen originates from NO dissociation (Banse et al. (1989), Dath et al. (1992), Fink et al. (1991)) or from dissociation of adsorbed N₂O to N₂ (Cho et al. (1989), Cho (1992, 1994), Ng et al. (1994)):

\[
\text{N}^* + \text{N}^* \rightarrow \text{N}_2 + 2^* \tag{6.8}
\]

\[
\text{NO}^* + \text{N}^* \rightarrow \text{N}_2\text{O}^* + ^* \tag{6.9}
\]

\[
\text{N}_2\text{O}^* \rightarrow \text{N}_2 + \text{O}^* \tag{6.11}
\]

Reaction 6.9 and 6.11 are often combined into one step:

\[
\text{NO}^* + \text{N}^* \rightarrow \text{N}_2 + \text{O}^* + ^* \tag{6.12}
\]

The N adatom originates either from the bimolecular reaction between adsorbed CO and NO or from NO dissociation.

Alternating pulse experiments were performed with $^{13}$CO and NO at 450, 496 and 641 K, to obtain further insight in the actual mechanisms of CO$_2$, N$_2$O and N$_2$ formation at different temperatures. The results of these experiments will be presented and discussed in section 6.4.3.

6.4.2 Experimental

The alternating pulse experiments were carried out on a platinum sponge catalyst, 0.7854 g, pretreated as described in paragraph 2.5.2.1 at 872 K, with a mixture of 90 vol.% $^{13}$CO and 10 vol.% Ar and a mixture of 90 vol.% NO and 10 vol.% Ar at 450, 496 and 641 K. During each experiment equal amounts of both mixtures were pulsed at a pulse intensity of approximately $1.7 \times 10^{16}$ molecules per pulse. The time interval between the two pulses and the cycle time were chosen in such a way, that none of the responses did overlap. The time interval between the $^{13}$CO/Ar and NO/Ar pulse was fixed at 5 seconds and the time interval between the NO/Ar and $^{13}$CO/Ar pulse was varied between 2 and 4 seconds. A large number of cycles was carried out, until a steady-state coverage on the surface had been created. During the steady-state coverage on the surface, the responses of $^{13}$CO$_2$, N$_2$O, Ar, O$_2$, NO, $^{13}$CO and N$_2$ were measured. The recorded signals were averaged 20 times. When the mass spectrometer was adjusted from one mass to another, pulsing was not possible temporarily. To re-establish the steady-state on the surface before actually recording a new mass, 20 pulses were given. This procedure ensured that each response was obtained at the same surface conditions.

6.4.3 Results and discussion

Figure 6.6 presents the $^{13}$CO$_2$ formation of the alternating pulse experiment at 450 K with a time interval between the NO and $^{13}$CO pulse of 2 and 4 seconds. Both $^{13}$CO and NO were totally converted. The $^{13}$CO$_2$ formation during the NO pulse, the first peak in figure 6.6, is independent of the time interval between the NO and $^{13}$CO pulse. However, the $^{13}$CO$_2$ formation during the $^{13}$CO pulse, the second peak in figure 6.6, is in the experiment with a time interval of 4 seconds lower than in a similar experiment with a time interval of 2 seconds.
As described already in paragraph 5.3.2, no measurable desorption of atomic adsorbed oxygen occurs at temperatures till 480 K. As a result the oxygen coverage is independent of the length of the time interval. Consequently, the CO$_2$ formation via the dissociative mechanism, in which the O adatom originates from NO dissociation, is also independent of the length of this time interval. NO desorption starts at lower temperatures than O$_2$ desorption. In the experiment with a time interval of 4 seconds between the NO pulse and the $^{13}$CO pulse, more NO desorbs than in an experiment with a time interval of 2 seconds. The decrease in CO$_2$ formation at the $^{13}$CO pulse with increasing time interval between the NO and $^{13}$CO pulses can therefore only occur via the bimolecular mechanism, reaction 6.7, and not via the dissociative mechanism, reaction 6.6.

At the $^{13}$CO pulse a small amount of N$_2$ was formed and no formation of N$_2$O, O$_2$ and NO was observed. The formation of small amounts of N$_2$ at the $^{13}$CO pulse is a second indication for the occurrence of the bimolecular mechanism. In the bimolecular reaction N adatoms are formed.

\[
\begin{align*}
\text{CO}^* + \text{O}^* & \rightarrow \text{CO}_2 + 2^* \quad (6.6) \\
\text{CO}^* + \text{NO}^* & \rightarrow \text{CO}_2 + \text{N}^* + ^* \quad (6.7)
\end{align*}
\]

During the NO pulse N$_2$O formation was independent of the time interval between both pulses. The Ar response appeared before the other responses, indicating interactions of all reactants and products with the Pt surface. The responses of N$_2$O and N$_2$ were positioned close to each other and appeared earlier than the $^{13}$CO$_2$ response, as shown in figure 6.7.

Figure 6.6: Response of $^{13}$CO$_2$ at 450 K in an alternating pulse experiment with a time interval of 2 (A) and 4 (B) seconds between the NO (first peak) and $^{13}$CO pulse (second peak). The time interval between the $^{13}$CO and NO pulses was constant at 5 s.
Figure 6.7: Normalised responses of A) Ar (x 6.2), B) N₂O (x 3.7), C) N₂ (x 1.2), and D) \(^{13}\)CO₂ at 450 K during the NO/Ar pulse in an alternating pulse experiment with a time interval of 4 seconds between the NO/Ar and \(^{13}\)CO/Ar pulse.

The formation of \(^{13}\)CO₂ at 450 K occurs mainly via the bimolecular reaction between NO and \(^{13}\)CO. N₂O is formed by reaction of N adatoms and adsorbed NO molecules:

\[
\begin{align*}
\text{NO}^* + \text{N}^* & \rightarrow \text{N}_2\text{O}^* + ^* \\
\text{N}_2\text{O}^* & \rightarrow \text{N}_2 + \text{O}^* + ^ *
\end{align*}
\]

The responses of N₂O and N₂ were positioned close to each other and because of that N₂ formation was probably caused by the dissociation of adsorbed N₂O, reaction 6.11:

\[
\text{N}_2\text{O}^* \rightarrow \text{N}_2 + \text{O}^* + ^ *
\]

At 496 K the difference in \(^{13}\)CO₂ formation during the \(^{13}\)CO pulse, for experiments with a time interval of 2 and 4 seconds between the NO and \(^{13}\)CO pulse, was smaller than at 450 K. This is shown in figure 6.8. \(^{13}\)CO and NO were both totally converted and no formation of N₂O and O₂ was observed during both pulses.

During the \(^{13}\)CO pulse, slightly more \(^{13}\)CO₂ was formed in the experiment with a time interval of 2 seconds between the NO and \(^{13}\)CO pulse compared to the experiment with a time interval of 4 seconds. During the NO pulse, slightly less \(^{13}\)CO₂ was formed in the experiment with a time interval of 2 seconds than in an experiment with a time interval of 4 seconds. Contrary to the experiments at 450 K, N₂ formation was only observed at the NO pulse.
Figure 6.8: Response of $^{13}C_2O_2$ at 496 K in an alternating pulse experiment with a time interval of 2 (A) and 4 (B) seconds between the NO (first peak) and $^{13}CO$ pulse (second peak).

The $^{13}CO_2$ formation during the $^{13}CO$ pulse, the second peak in figure 6.8, was in the experiment with a time interval of 4 seconds slightly lower than in a similar experiment with a time interval of 2 seconds. If CO$_2$ is formed only by the dissociative mechanism, CO$_2$ formation would be independent of the time interval between the NO and $^{13}CO$ pulse, because O adatoms do not desorb at this temperature. $^{13}CO_2$ formation at the $^{13}CO$ pulse was, however, dependent on the length of the time interval. Because of that CO$_2$ was still partially formed via the bimolecular mechanism but mainly via the dissociative mechanism, in which the O adatoms originate from NO dissociation. The dissociative mechanism plays a more important role at 496 K than at 450 K, because NO dissociation occurs more easily at higher temperatures. This is also indicated by the absence of N$_2$ formation during the $^{13}CO$ pulse.

The absence of N$_2$O formation during the NO pulse at 496 K, is an indication for absence of the reaction between N adatoms and adsorbed NO molecules. Therefore N$_2$ formation during the NO pulse does not occur via the dissociation of adsorbed N$_2$O, but via N adatom recombination, reaction 6.8:

$$N^* + N^* \rightarrow N_2 + 2^*$$ (6.8)

This is in agreement with the hypothesis, that the largest part of NO dissociates at this temperature.
At 641 K the $^{13}\text{CO}_2$ responses of the alternating pulse experiments with time intervals of 2 and 4 seconds between the NO and $^{13}\text{CO}$ coincide totally. $^{13}\text{CO}$ and NO were both converted completely and no formation of N$_2$O nor O$_2$ was observed during both pulses. No N$_2$ was formed during the $^{13}\text{CO}$ pulse. N$_2$ formation was observed at the NO pulse. At this temperature NO dissociates completely. CO$_2$ is formed only by the dissociative mechanism, in which adsorbed CO molecules react with O adatoms, originating from NO dissociation. Therefore the CO$_2$ formation is independent of the time interval. N$_2$ was formed by N adatom recombination. The results at 641 K agree with the mechanism, proposed by Banse et al. (1989), Dath et al. (1992) and Fink et al. (1991).

6.5 Conclusions

The mechanism of the CO/NO reaction on Pt involves several pathways of Langmuir-Hinshelwood reactions. From the CO multi-pulse experiments it follows, that NO does not dissociate at low temperatures. This is confirmed by alternating pulse experiments. The alternating pulse experiments with CO and NO reveal that at low temperatures, i.e. between 400 and 450 K, oxidation of CO mainly takes place via the bimolecular reaction between adsorbed CO and NO:

$$\text{CO}^* + \text{NO}^* \rightarrow \text{CO}_2 + \text{N}^* + *$$  \hspace{1cm} (6.7)

Only at low temperatures both N adatoms and adsorbed NO molecules are present on the surface, allowing the formation of N$_2$O according to:

$$\text{NO}^* + \text{N}^* = \text{N}_2\text{O}^* + *$$  \hspace{1cm} (6.9)

$$\text{N}_2\text{O}^* \rightarrow \text{N}_2\text{O} + *$$  \hspace{1cm} (6.10)

N$_2$ is formed due to dissociation of adsorbed N$_2$O to N$_2$:

$$\text{NO}^* + \text{N}^* = \text{N}_2\text{O}^* + *$$  \hspace{1cm} (6.9)

$$\text{N}_2\text{O}^* \rightarrow \text{N}_2 + \text{O}^*$$  \hspace{1cm} (6.11)

The N$_2$/N$_2$O ratio increases with increasing temperature. The increasing extent of NO dissociation at higher temperatures, results in a lower amount of molecular adsorbed NO on the surface. It causes that N$_2$ formation via N adatom recombination is favoured at the expense of N$_2$O formation:

$$\text{N}^* + \text{N}^* \rightarrow \text{N}_2 + 2*$$  \hspace{1cm} (6.8)
A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by \( O_2/NO \) on Pt

The alternating pulse experiments with CO and NO reveal that at high temperatures \( CO_2 \) is formed by a dissociative mechanism, i.e. a mechanism in which the O adatoms originate from NO dissociation:

\[
CO^* + O^* \rightarrow CO_2 + 2^* \quad (6.6)
\]

The results at high temperatures, 500-700 K, totally agree with the mechanism proposed by Banse et al. (1989), Dath et al. (1992) and Fink et al. (1991). At high temperatures NO dissociates completely. Hence \( N_2O \) formation is absent and \( N_2 \) is formed by nitrogen recombination, the N adatoms originating from NO dissociation. Based on the conclusions of the experiments three pathways are proposed, which describe the CO oxidation by NO on Pt at low and high temperatures. The pathways are listed in table 6.7.

Table 6.7: Parallel reaction pathways in the CO oxidation by NO on Pt at low (400-450 K) and high (500-700 K) temperatures.

<table>
<thead>
<tr>
<th>elementary reaction</th>
<th>( N_1^* )</th>
<th>( N_2^* )</th>
<th>( N_1^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400-450 K</td>
<td>500-700 K</td>
<td></td>
</tr>
<tr>
<td>(6.3) CO + * = CO*</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>(6.4) NO + * = NO*</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>(6.5) NO* + * = N* + O*</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>(6.6) CO* + O* ( \rightarrow ) CO_2 + 2*</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>(6.7) CO* + NO* ( \rightarrow ) CO_2 + N* + *</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>(6.8) N* + N* ( \rightarrow ) N_2 + 2*</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>(6.9) NO* + N* = N_2O* + *</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>(6.10) N_2O* = N_2O + *</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>(6.11) N_2O* ( \rightarrow ) N_2 + O*</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\( N_i = (\sigma_1, \sigma_2, ..., \sigma_n) \), with \( \sigma_i \) = stoichiometric number of \( i \).

Global reactions:

\[
N_1 \text{ and } N_3 : \quad 2 \text{ CO} + 2 \text{ NO} \rightarrow N_2 + 2 \text{ CO}_2 \quad (6.1)
\]
\[
N_2 : \quad \text{CO} + 2 \text{ NO} \rightarrow N_2O + \text{CO}_2 \quad (6.2)
\]
Mechanistic Investigation of the Oxidation of CO by NO on Pt

References

- Gohadrome, J.M., Masel, R.I., A TPD Study of Nitric Oxide Decomposition on Pt(100), Pt(411) and Pt(211), Surf. Sci., 209, 44, 1989
- Gohadrome, J.M., Park, Y.O., Masel, R.I., A Comparison of Nitric Oxide Decomposition on Pt(210) and Pt(410): An example Where an Increase in Steps Density has Produced a Decrease in Reactivity, J. Catal., 95, 244, 1985
- Gorte, R.J., Schmidt, L.D., Interactions between NO and CO on Pt(111), Surf. Sci., 111, 260, 1981
- Lambert, R.M., Comrie, C.M., The Oxidation of CO by NO on Pt(111) and Pt(110), Surf. Sci., 46, 61, 1974
Appendix 6A Mass balances of $^{13}$C, N and O during the pulse experiments

**Table 6A.1: Number of $^{13}$C-atoms ($10^{15}$) at the inlet and outlet.**

<table>
<thead>
<tr>
<th>Source of $^{13}$C</th>
<th>626 K</th>
<th>676 K</th>
<th>726 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In</td>
<td>Out</td>
<td>In</td>
</tr>
<tr>
<td>$^{13}$CO</td>
<td>1.89</td>
<td>0.05</td>
<td>1.85</td>
</tr>
<tr>
<td>$^{13}$CO$_2$</td>
<td>-</td>
<td>1.84</td>
<td>-</td>
</tr>
<tr>
<td>total</td>
<td>1.89</td>
<td>1.89</td>
<td>1.85</td>
</tr>
</tbody>
</table>

**Table 6A.2: Number of N-atoms ($10^{15}$) at the inlet and outlet.**

<table>
<thead>
<tr>
<th>Source of N</th>
<th>626 K</th>
<th>676 K</th>
<th>726 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In</td>
<td>Out</td>
<td>In</td>
</tr>
<tr>
<td>NO</td>
<td>3.79</td>
<td>0.57</td>
<td>3.71</td>
</tr>
<tr>
<td>N$_2$O (2x)</td>
<td>-</td>
<td>1.02</td>
<td>-</td>
</tr>
<tr>
<td>N$_2$ (2x)</td>
<td>-</td>
<td>2.08</td>
<td>-</td>
</tr>
<tr>
<td>total</td>
<td>3.79</td>
<td>3.67</td>
<td>3.71</td>
</tr>
</tbody>
</table>

**Table 6A.3: Number of O-atoms ($10^{15}$) at the inlet and outlet.**

<table>
<thead>
<tr>
<th>Source of O</th>
<th>626 K</th>
<th>676 K</th>
<th>726 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In</td>
<td>Out</td>
<td>In</td>
</tr>
<tr>
<td>NO</td>
<td>3.79</td>
<td>0.57</td>
<td>3.71</td>
</tr>
<tr>
<td>$^{13}$CO</td>
<td>1.89</td>
<td>0.05</td>
<td>1.85</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>-</td>
<td>0.51</td>
<td>-</td>
</tr>
<tr>
<td>$^{13}$CO$_2$ (2x)</td>
<td>-</td>
<td>3.68</td>
<td>-</td>
</tr>
<tr>
<td>total</td>
<td>5.68</td>
<td>4.81</td>
<td>5.56</td>
</tr>
</tbody>
</table>
7.1 Introduction

Cambell et al. (1980), Gland and Kollin (1983) and Kwasniewski and Schmidt (1992) reported that carbon dioxide is weakly bonded at the platinum surface and will immediately desorb after formation from CO and O₂ above 300 K. Hence, these authors do not mention this rapid carbon dioxide desorption step explicitly, but include it in the following elementary step:

$$\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2 + 2^*$$  \hspace{1cm} (7.1)

Aim of the TAP study reported on in this chapter was to investigate, whether carbon dioxide indeed desorbs immediately after formation or, more specifically, whether adsorbed carbon dioxide undergoes oxygen exchange on the Pt surface before desorbing.

The result of isotopic oxygen exchange would be that C¹⁸OO, formed in the CO oxidation by O₂ on Pt, is converted into CO₂ and C¹⁸O₂. Isotopic exchange can occur only, if C¹⁸OO, formed in the CO oxidation by O₂, does not immediately desorb after formation:

$$\text{CO}^* + ^{18}\text{O}^* \rightarrow \text{C}^{18}\text{OO}^* + ^*$$  \hspace{1cm} (7.2)
$$\text{C}^{18}\text{OO}^* + \text{O}^* \rightarrow \text{CO}_2^* + ^{18}\text{O}^* \rightarrow \text{CO}_2 + ^{18}\text{O}^* + ^*$$  \hspace{1cm} (7.3)
$$\text{C}^{18}\text{OO}^* + ^{18}\text{O}^* \rightarrow \text{C}^{18}\text{O}_2^* + \text{O}^* \rightarrow \text{C}^{18}\text{O}_2 + \text{O}^* + ^*$$  \hspace{1cm} (7.4)
$$\text{C}^{18}\text{OO}^* \rightarrow \text{C}^{18}\text{OO} + ^*$$  \hspace{1cm} (7.5)
It is unlikely that isotopic exchange in C$^{18}$O is caused by CO dissociation. CO adsorbs molecularly on platinum (Engel and Ertl (1979), Lambert and Comrie (1974)). CO will not dissociate on Pt (Nieuwenhuys et al., 1993).

7.2 Experimental

The platinum sponge catalyst, 0.8998 g, was pretreated at 831 K, as described in paragraph 2.5.2.1. Multi-pulse and alternating pulse experiments were performed with CO$_2$, CO and $^{18}$O$_2$ at 479 K. $^{18}$O$_2$ was used instead of normal O$_2$ to acquire insight in the mechanism of oxygen exchange. The responses of C$^{18}$O$_2$, C$^{18}$OO and CO$_2$ were recorded. Before the experiments the absolute calibration factors of CO$_2$, O$_2$ and CO were determined, as described in paragraph 2.3.2. The absolute calibration factors of C$^{18}$O$_2$, C$^{18}$OO and $^{18}$O$_2$ were not determined and assumed to be equal to the absolute calibration factor of CO$_2$ respectively O$_2$.

Two different multi-pulse experiments were performed. In the first one either CO$_2$ or CO was pulsed over Pt pretreated with $^{18}$O$_2$. In the second one $^{18}$O$_2$ was pulsed over Pt pretreated with CO. In all multi-pulse experiments the formation of C$^{18}$O$_2$, C$^{18}$OO and CO$_2$ was monitored.

In the alternating pulse experiments, the Pt surface was pretreated with CO. A small amount of $^{18}$O$_2$ was pulsed, followed by a large amount of CO. The time intervals between subsequent pulses were chosen in such a way, that none of the responses did overlap. A 3 seconds time interval between the $^{18}$O$_2$ and CO pulse, and the CO and $^{18}$O$_2$ pulse, appeared to be adequate. The responses of C$^{18}$O$_2$, C$^{18}$OO and CO$_2$ were recorded, each of them being averaged 100 times. The alternating pulse experiments were also performed the other way around: the Pt surface was pretreated with $^{18}$O$_2$ and during the alternating pulse experiment a small amount of CO was pulsed, followed by a large amount of $^{18}$O$_2$.

7.3 Results and discussion

First, the results of the CO$_2$ multi-pulse experiments over Pt covered with $^{18}$O adatoms, in which the formation of C$^{18}$O$_2$ was monitored, will be discussed. The C$^{18}$O$_2$ response is shown in figure 7.1. During this experiment $^{18}$O adatoms on the Pt surface were exchanged with O atoms of CO$_2$. This experiment shows that CO$_2$ adsorbs on a Pt surface and undergoes isotopic oxygen exchange on the Pt surface, reactions 7.3 and 7.4.
Isotopic Oxygen Exchange in C\textsuperscript{18}O\textsubscript{2} on Pt

Figure 7.1: C\textsuperscript{18}O\textsubscript{2} response at 479 K in a CO\textsubscript{2} multi-pulse experiment on Pt, covered with \textsuperscript{18}O adatoms.

In figures 7.2a, 7.2b and 7.2c the responses of respectively CO\textsubscript{2}, C\textsuperscript{18}OO and C\textsuperscript{18}O\textsubscript{2} are shown during the \textsuperscript{18}O\textsubscript{2} multi-pulse experiment over Pt, precovered with CO are shown. Besides C\textsuperscript{18}OO, that is directly formed by reaction of \textsuperscript{18}O adatoms and adsorbed CO molecules, reactions 7.2 and 7.5, C\textsuperscript{18}O\textsubscript{2} and CO\textsubscript{2} were formed by isotopic oxygen exchange on the Pt surface, reactions 7.3 and 7.4.

This experiment shows, that C\textsuperscript{18}OO does not desorb immediately after formation but undergoes isotopic oxygen exchange on the Pt surface before desorbing. In the beginning of the multi-pulse experiment mainly CO\textsubscript{2} and C\textsuperscript{18}OO were formed. At the end of the experiment mainly C\textsuperscript{18}O\textsubscript{2} and C\textsuperscript{18}OO were formed. This can be explained by the ratio of O and \textsuperscript{18}O adatoms on the Pt surface. At first, the Pt surface was mainly covered with adsorbed CO. During the experiment, the \textsuperscript{18}O adatom coverage increased by \textsuperscript{18}O\textsubscript{2} dissociation and the O adatom coverage decreased by oxygen exchange, resulting in an increasing C\textsuperscript{18}O\textsubscript{2} formation and a decreasing CO\textsubscript{2} formation.

When the opposite experiment was performed, i.e. a multi-pulse experiment with CO over a Pt surface covered with \textsuperscript{18}O adatoms, similar phenomena were observed. The total cumulative amounts of CO\textsubscript{2}, C\textsuperscript{18}OO and C\textsuperscript{18}O\textsubscript{2} are listed for both experiments in table 7.1. Table 7.1 indicates, that the primary product C\textsuperscript{18}OO scrambled almost totally, because the ratio of CO\textsubscript{2}:C\textsuperscript{18}OO:C\textsuperscript{18}O\textsubscript{2} was equal to about 1:2:1. It means, that isotopic oxygen exchange is fast compared to CO\textsubscript{2} desorption. The total amount of CO\textsubscript{2} isotopes, formed on Pt precovered with CO, was lower than formed in the experiment on Pt precovered with \textsuperscript{18}O adatoms, due to some CO desorption after the pretreatment at 479 K.
Figure 7.2: $\text{CO}_2$ (a), $\text{C}^{18}\text{O}_2$ (b) and $\text{C}^{18}\text{O}_2$ (c) responses at 479 K in an $^{18}\text{O}_2$ multi-pulse experiment on Pt, precovered with CO. Note the different scales on the y-axes.
Isotopic Oxygen Exchange in C^{18}O on Pt

Table 7.1: Cumulative amounts of CO₂, C^{18}O₀ and C^{18}O₂, formed during ^{18}O₂ and CO multipulse experiments over Pt, precovered with CO respectively ^{18}O₂ at 479 K.

<table>
<thead>
<tr>
<th>catalyst pre-coverage</th>
<th>CO₂ formation 10⁻⁷ mol g⁻¹</th>
<th>C^{18}O₀ formation 10⁻⁷ mol g⁻¹</th>
<th>C^{18}O₂ formation 10⁻⁷ mol g⁻¹</th>
<th>total formation 10⁻⁷ mol g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.4</td>
<td>2.7</td>
<td>1.8</td>
<td>5.9</td>
</tr>
<tr>
<td>^{18}O₂</td>
<td>3.2</td>
<td>4.0</td>
<td>1.9</td>
<td>9.1</td>
</tr>
</tbody>
</table>

Before starting the alternating pulse experiment, in which a ^{18}O₂ pulse of 1.3 10¹⁶ molecules was given at t=0 s, followed by a large CO pulse at t=3 s, the Pt surface was covered with CO. The responses of C^{18}O₂, C^{18}O₀ and CO₂ are shown in figure 7.3. During the experiment the Pt surface remained nearly totally covered with CO. CO₂ isotopes were formed only during the oxygen pulse, indicating that no oxygen adatoms remained on the surface after the ^{18}O₂ pulse. When pulsing in the opposite sequence over a surface precovered with ^{18}O adatoms, CO₂ isotopes were formed only during the CO pulse. In table 7.2 the percentages of CO₂, C^{18}O₀ and C^{18}O₂ are listed, which are formed during both alternating pulse experiments.

Figure 7.3: Responses of A) CO₂, B) C^{18}O₀ and C) C^{18}O₂ in an alternating pulse experiment at 479 K, in which a ^{18}O₂ pulse of 1.3 10¹⁶ molecules was given at t=0 s, followed by a large CO pulse at t=3 s.

The ratio of CO₂:C^{18}O₀:C^{18}O₂ again was near to 1:2:1, indicating that isotopic oxygen exchange is fast compared to carbon dioxide desorption.
Table 7.2: Percentages of CO₂, C¹⁸OO and C¹⁸O₂, formed during alternating pulse experiments at 479 K, in which a small pulse of C¹⁸O₂ and CO was given at t=0 s, followed by a large CO respectively C¹⁸O₂ pulse at t=3 s.

<table>
<thead>
<tr>
<th>pretreatment</th>
<th>small pulse</th>
<th>CO₂ formation</th>
<th>C¹⁸OO formation</th>
<th>C¹⁸O₂ formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>C¹⁸O₂</td>
<td>27</td>
<td>50</td>
<td>23</td>
</tr>
<tr>
<td>C¹⁸O₂</td>
<td>CO</td>
<td>27</td>
<td>46</td>
<td>27</td>
</tr>
</tbody>
</table>

7.4 Conclusions

At 479 K carbon dioxide adsorbs on a Pt surface and undergoes oxygen exchange. Carbon dioxide formed by CO oxidation desorbs sufficiently slowly to allow oxygen exchange on the Pt surface. The CO₂:C¹⁸OO:C¹⁸O₂ ratio of about 1:2:1 indicates complete scrambling, meaning that the oxygen exchange is fast compared to CO₂ desorption.

References

- Lambert, R.M., Comrie, C.M., The Oxidation of CO by NO on Pt(111) and Pt(110), Surf. Sci., 46, 61, 1974
The work presented in this thesis focused on the development of a method for the estimation of the reaction rate coefficients of individual elementary steps from transient pulse experiments. The results, which are described in this thesis, could be reached by quantitative modelling of the transient kinetic experiments. This method was applied to determine the kinetics of the oxidation of carbon monoxide on polycrystalline platinum powder with the TAP set-up, but is generally applicable for the quantitative modelling of transient kinetic experiments.

By using an appropriate constitutive model for the gas transport in the microreactor packed with catalyst pellets, the effect of the inlet gas pulse size on the relative contribution to the flux of each mode of gas transport was quantified. For a single gas Knudsen diffusion and viscous flow are the only mechanisms of transport. For fixed beds with a typical mean pellet size of 250 μm, Knudsen diffusion dominates at pulse intensities lower than $1 \times 10^{16}$ molecules, whereas viscous flow becomes important at higher pulse intensities. Moreover, when such bed consists of porous pellets with pore diameters as low as 8 nm, the Knudsen diffusion inside the pores occurs on a much smaller time scale than the diffusion inside the catalyst bed. It means that in the absence of reaction the concentration at any position in the pores is equal to the concentration at the outer surface of the pellets at any time. Therefore, intrapellet diffusion could be accounted for simply by adding in the accumulation term the capacity corresponding to the intrapellet porosity.

Based on the requirement of a clear distinction between the response and the noise level at one hand and between the response and the outlet signal in case of diffusion only at the other hand, the minimum and maximum reaction rate coefficients measurable with the TAP microreactor were determined for a pseudo first order reaction. The window of obtainable rate coefficients ranges from $1 \text{ s}^{-1}$ and $1 \times 10^{4} \text{ s}^{-1}$. The parameters corresponding to adsorption,
desorption, reaction and diffusion can be estimated simultaneously, provided the characteristic times of these processes are all of the same order of magnitude. In order to satisfy the above requirement, the characteristic times may be adjusted occasionally by a proper choice of experimental conditions.

The experiments for quantification of kinetic rate data on the carbon monoxide oxidation were performed on non-porous platinum powder to avoid transport limitations. At temperatures between 323 and 365 K migration of adsorbed carbon monoxide can be neglected on the time scale of a TAP pulse experiment. These experiments also showed the existence of islands of carbon monoxide and oxygen on the surface. The quantitative modelling of these experiments revealed a carbon monoxide physisorption equilibrium, followed by chemisorption of carbon monoxide on vacant surface sites next to carbon monoxide or oxygen islands. The reaction of chemisorbed carbon monoxide with oxygen at the periphery of the oxygen islands is potentially instantaneous. The estimated value of the carbon monoxide physisorption equilibrium coefficient is nearly independent of coverage and temperature. The probability that a carbon monoxide molecule chemisorbs on a vacant surface site next to an oxygen island is proportional to the total oxygen coverage and independent of temperature.

Quantitative modelling of oxygen chemisorption on platinum powder showed that the chemisorption consists of an equilibrated molecular adsorption followed by a rate-determining dissociation of the molecular adsorbed species. The latter is slightly activated with an activation energy of 8.6 kJ mol$^{-1}$. Desorption of oxygen adatoms is negligible up to 490 K.

TAP experiments, carried out to investigate the simultaneous oxidation of carbon monoxide and reduction of nitric oxide over platinum powder, showed that at temperatures between 400 and 450 K oxidation of carbon monoxide mainly takes place via the bimolecular reaction between adsorbed carbon monoxide and adsorbed nitric oxide. Nitric oxide does not dissociate at low temperatures. Nitrogen is mainly formed by the dissociation of adsorbed nitrous oxide. At temperatures between 500 and 700 K, carbon dioxide is formed through the reaction between adsorbed carbon monoxide and oxygen adatoms, the latter originating from nitric oxide dissociation. In this temperature range, nitrous oxide formation is absent and nitrogen is formed by recombination of two nitrogen adatoms, which are produced by nitric oxide dissociation.

Isotopic oxygen labelling experiments at 479 K showed that carbon dioxide adsorbs on the platinum surface and exchanges oxygen atoms with oxygen adatoms on the surface. The oxygen exchange is fast compared to carbon dioxide desorption.
DANKWOORD

In tegenstelling tot hetgeen de omslag doet vermoeden, is dit proefschrift allerminst het werk van één promovendus. Ik wil dan ook iedereen, die heeft bijgedragen aan de totstandkoming van dit proefschrift, zonder hen expliciet bij naam te noemen, van harte bedanken.
A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of CO by \( \text{O}_2/\text{NO} \) on Pt
Stellingen

beborende bij het proefschrift

A Quantitative Analysis of Transient Kinetic Experiments:
The Oxidation of CO by O₂/NO on Pt

van Jan Hainink

1. In tegenstellig tot hetgeen Zou et al. beweren, is het mogelijk om door een juiste interpretatie van TAP-pulsexperimenten te komen tot een eenduidig kinetisch model met twee of meer hiermee verbonden kinetische parameters.

2. De trage migratie van koolmonoxide op platina bij temperaturen tot 365 K is een voorwaarde voor het bestaan van koolmonoxide-eilanden.
Hoofdstuk 5 van dit proefschrift.

3. De dissociatieve adsorptie van zuurstof op platina verloopt via een adsorptie-evenwicht van moleculair zuurstof, gevolgd door dissociatie van geadsorbeerd zuurstof als snelheidsbepalende stap.
Hoofdstuk 5 van dit proefschrift.

4. De oxidatie van stikstofmonoxide op platina vindt, in tegenstelling tot hetgeen door Fink et al. vermeld wordt, bij lage temperaturen hoofdzakelijk plaats via de bimoleculaire oppervlakreactie tussen geadsorbeerd koolmonoxide en stikstofmonoxide.
Hoofdstuk 6 van dit proefschrift.

5. De desorptie van kooldioxide van een platina oppervlak wordt in de literatuur vaak ten onrechte verondersteld momentaan op te treden.
Hoofdstuk 7 van dit proefschrift.
6. In menig gesprek is het belangrijk te weten wat niet gezegd is.

7. Op autosnelwegen is niet zozeer de snelheid maar het verschil in snelheid de oorzaak van veel ongelukken. Snelheidslimieten zijn daarom niet het juiste middel om de verkeersveiligheid te bevorderen.

8. Als de mens de natuur bedreigt, bedreigt de natuur de mens.

9. Rookverboden leiden ertoe dat de gezonden gezonder en de ongezonden ongezonder worden.

10. Leasesystemen voor duurzame consumptiegoederen zullen op lange termijn een voorwaarde zijn voor de ontwikkeling van een milieuvriendelijke maatschappij.

11. De sociale zekerheid kan alleen overeind gehouden worden door inbreuk te maken op de privacy.