Nitrogen Catalytic Recombination on Copper Oxide in Tertiary Gas Mixtures

T. M. Cheung

April 27, 2015









Delft University of Technology



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Delft University of Technology

FACULTY OF AEROSPACE ENGINEERING

Nitrogen Catalytic Recombination on Copper Oxide in Tertiary Gas Mixtures

Master Thesis

For obtaining the degree of Master of Science in Aerospace Engineering at Delft University of Technology

TIMMY MAN-CHOUNG CHEUNG

Preface

This master thesis represents the work that I have conducted at KAIST (Republic of Korea) from July 2013 until December 2013 and August 2014 until March 2015. During these period I have studied the field of aerothermodynamics, learned the necessary steps to conduct experiments individually, explored and studied various numerical programs to fulfill the goal of this research. This thesis is the final step in the journey to acquire the degree of Master of Science in Aerospace Engineering at Delft University of Technology.

This report consists of three main parts. One part discusses the shock tube and the fabrication of heat transfer gauges. The second part introduces the numerical programs which are used to simulate the conditions inside the shock tube and around the model, whereas the third part covers the theory regarding heat flux and catalycity. These three parts together form a chain of required steps to acquire the desired results for this thesis.

I would like to express my sincere gratitude towards my two supervisors: Assistant Professor Ferry Schrijer (TU Delft) and Assistant Professor Gisu Park (KAIST). Both have guided me through this thesis with their priceless experience and knowledge concerning hypersonic flows and experimental aerodynamics. Moreover, I would like to thank Professor Chul Park (KAIST) for his valuable knowledge in the theoretical aspect of hypersonic aerothermodynamics. Without the support of these professors the achievements made in this thesis would have never been realizable.

Additionally, I would like to thank KAIST for providing me the opportunity to use their facilities for this project, while they covered for all the costs necessary to conduct the experiments. To my parents and friends, thank you for all the great support and the unforgettable moments in the Netherlands and in Korea.

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Timmy Cheung Delft, April 27th 2015





List of Symbols

Roman Symbols

A	Cross-sectional area of arc-jet nozzle throat	$[m^2]$
a	Speed of sound	[m/s]
B_e	Rotational constant	[—]
c	Average molecular speed	[m/s]
c	Thermal capacity	$[J/(kg \cdot K)]$
c	Local light speed	[m/s]
c_0	Light speed in vacuum	[m/s]
c_p	Specific heat at constant pressure	$[J/(kg \cdot K)]$
c_v	Specific heat at constant volume	$[J/(kg \cdot K)]$
D	Diffusion coefficient	$[m^2/s]$
D_A	Dissociation energy in the adsorbed phase	[J/mol]
D_e	Rotational constant	[—]
D_0	Dissociation energy	[J]
Da	Damköhler number	[—]
E	Surface activation energy	[J]
E	Electronic state energy	[J]
f	Dimensionless stream function	[—]
f	Friction factor	[—]
G	Statistical weight for molecule	[—]
g	Statistical weight for atom	[—]
$ar{g}$	Dimensionless frozen stagnation enthalpy	[—]
H	Total enthalpy	[J/kg]
h	Enthalpy	[J/kg]
$ar{h}$	Frozen enthalpy	[J/kg]
h_D	Dissociation enthalpy	[J/kg]
h_R	Heat of recombination	[J/kg]
J	Total electronic angular momentum quantum number	[—]
j	Net mass flux of diffused atoms	$[kg/(m^2 \cdot s)]$
K	Gladstone-Dale constant	$[m^3/kg]$
k	Thermal conductivity	$[W/(m \cdot K)]$
k_B	Boltzmann's constant	[J/K]
k_f	Forward reaction rate constant	$[m^3/(mol \cdot s)]$
k_w	Catalytic rate	[m/s]
Le	Lewis number	[—]
l	Length	[m]
l	Current	[A]
l	Chapman-Rubesin constant	[—]
l	Angular momentum quantum number	[—]
M	Mach number	[-]
M	Average molecular weight of gas mixture	[kg/mol]

M_i	Molecular weight of species i	[kg/mol]
m	Average mixture mass	[kg]
m	Order of catalytic reaction	[-]
m_i	Particle mass of species i	[kg]
\dot{m}	Mass flow rate in arc-jet	[kg/s]
N_A	Avogadro's constant	$[mol^{-1}]$
n	Number density	$[m^{-3}]$
n	Refractive index	[-]
n	Concentration	$[mol/m^3]$
n	Principle quantum number	[-]
Nu	Nusselt number	[_]
p	Pressure	$[N/m^2]$
Pr	Prandtl number	[-]
\overline{Pr}	Frozen Prandtl number	[-]
Q	Partition function	[-]
Q	Cumulative heat input	$[J/m^2]$
q	Heat flux	$[W/m^2]$
\overline{R}	Characteristic distance or nose radius	[m]
R	Resistance	$[\Omega]$
R	Specific gas constant for air	$[J/(K \cdot kg)]$
R_{uni}	Universal gas constant	$[J/(K \cdot mol)]$
Re	Reynolds number	[m ⁻¹]
r	Radius	[m]
r_0	Radial distance from axis of symmetry	m
r_e	Internuclear distance	$[Å = 10^{-10}m]$
S	Entropy	[J/K]
s	Reduced streamwise distance parameter	[-]
s	Spin quantum number	[-]
Sc	Schmidt number	[-]
St	Stanton number	[-]
T	Temperature	[K]
T^{\star}	Normalized temperature	[-]
T_e	Electronic energy level or molecules	$[cm^{-1}]$
t	Time	$[\mathbf{s}]$
u	Velocity along wall	[m/s]
V	Voltage	[V]
v	Velocity perpendicular to wall	[m/s]
v	Fundamental vibrational frequency	[Hz]
X_i	Molar fraction of species i	[-]
x	Distance along the wall from stagnation point	[m]
x	Distance along the shock tube	[m]
y	Distance perpendicular to wall measured from wall	[m]
z	Ratio of mass fraction	[-]
z(0)	Dimensionless atomic concentration at wall	[-]

Greek Symbols

α	Mass fraction	[—]
α	Thermal diffusivity	$[m^2/s]$
α_e	Rotational constant	[-]
β	Stream velocity gradient	$[s^{-1}]$
β_e	Rotational constant	[-]
β_R	Coefficient of resistivity	$[K^{-1}]$
χ	Variable parameter for φ_2	[-]
δ	Boundary Layer Thickness	[m]
δ	Penetration depth	[m]
γ	Catalytic efficiency	[-]
γ	Specific heat ratio	[-]
ϵ	Internal energy	[J]
ϵ	Potential parameter	[-]
η	Boundary layer coordinate normal to wall	[-]
Λ	Compressibility correction	[-]
μ	Dynamic viscosity	$[kg/(m \cdot s)]$
$\Omega_{ij}^{\star}{}^{(1,1)}$	Reduced average collision cross-section	[-]
$\bar{\Omega}_{ij}^{(2,2)}$	Average collision integral	$[m^2]$
ω_e	Vibrational constant	[-]
$\omega_e x_e$	Vibrational constant	[-]
$\omega_e y_e$	Vibrational constant	[-]
ψ	Stream function	[-]
ho	Density	$[kg/m^3]$
σ	Stefan-Boltzmann constant	$[W/(m^2 \cdot K^4)]$
σ	Collision diameter	[m]
au	Shear stress	$[N/m^2]$
$ heta_r$	Rotational constant	[-]
φ_1	Correction factor for catalytic effects of binary gas mixture	[-]
φ_2	Correction factor for catalytic effects of tertiary gas mixture	[-]
ξ	Reduced streamwise distance parameter	[-]

Superscripts

1

Derivative with respect to η

Subscripts

<i>v</i>	
C Conduction	
D Diffusion	
e Boundary layer edge (In Goulard's theory: outside the bounda	ry layer)
el Electronic	
eq Equilibrium	
i i^{th} component of mixture	
$j j^{\text{th}}$ component of mixture	
j j^{th} electronic energy level	
pre Before the standing shock	
rot Rotation	
s Stagnation	
se Boundary layer edge	
tr Translation	
vib Vibration	
w Wall	
0 Settling chamber of arc-jet	
1 Test gas prior to primary shock	
1 Nitrogen atoms	
2 Test gas after primary shock	
2 Nitrogen molecules	
3 Driver gas after expansion waves	
3 Krypton molecules	
4 Driver gas prior to expansion waves	
∞ Freestream	

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Summary

A reentry vehicle returning back to Earth experiences a significant temperature increase. This temperature increase is a result of the enormous heat flux the vehicle is exposed to, which originates from the transfer of kinetic energy to heat. Moreover, the high temperature results in the dissociation of air molecules which complicates the situation. The recombination of these atoms is an exothermic process which releases an additional amount of energy. This recombination requires a third body which can either be another air particles or the surface particles of the vehicle.

To properly design these vehicles it is essential to test them in ground facilities. One of these widely used facilities is an arc-jet, which is capable of reaching temperatures of several thousands Kelvin and relatively high velocities for an extensive period of time (i.e. in the order of seconds). The problem that arises with arc-jets is the variation of the enthalpy from the centerline towards the walls. It is this enthalpy that dictates the flow condition the model experiences, since enthalpy is a quantity that specifies energy. To determine the centerline enthalpy, the easiest and often applied method is by using copper slug calorimeters.

A copper calorimeter is essentially a slug made of copper with a connection from which the temperature is acquired. The temperature is converted to heat flux values and with the aid of stagnation heat transfer theories is the enthalpy determined. To use these stagnation heat transfer theories, a parameter called "catalytic efficiency" is required. This parameter specifies the ratio of the mass flux of formed molecules to the mass flux of the atoms hitting the surface.

The copper slug however experiences oxidation (hereby forming copper oxide) and roughens when exposed to the flow in the arc-jet. It is because of these changes that there is a large discrepancy between catalytic efficiencies in the literature. The focus of most literature is either on the catalytic effect of oxygen with respect to copper or copper oxide. Since one of the main components of air is nitrogen it is essential to also investigate this case. However, so far only copper has been covered for nitrogen.

In this thesis the catalytic efficiency of nitrogen is determined on copper and copper oxide in a tertiary gas mixture. The tertiary gas mixture is created by mixing the nitrogen with krypton which is an inert gas. This is done to be able to achieve sufficient amount of dissociation inside the shock tube.

The shock tube, that is used, is located at the hypersonic lab in KAIST (South Korea). The experiments are conducted using helium as driver gas and a test gas consisting of 65% krypton and 35% nitrogen. Three different flow conditions are covered which are denoted with the letters A, B, and C, with respectively 1%, 33.3%, and 54.3% dissociation. In the test section of the shock tube a flat-disk cylinder model with a diameter of 12 mm was used, which contains a flush-mounted thin-film gauge.

The thin-film gauges are manufactured in this thesis and contain a thin strip of platinum with a width of approximately 0.5 mm. After manufacturing these gauges they are mounted inside the models and calibrated. The probe is then coated using the electron beam method which vaporizes the source material and condensates on the sample. The probes are separated in four batches, each with a different set of coating:

- 1. 1000 nm SiO_2
- 2. 1000 nm SiO_2 and 180 nm black CuO
- 3. 1000 nm SiO_2 and 180 nm brown CuO
- 4. 1000 nm SiO_2 and 180 nm Cu

The difference between the black CuO and brown CuO is the amount of copper atoms present in the mixture, the latter being richer in copper.

Using this experimental setting the different coatings were exposed to the three flow conditions. The temperature data acquired from these experiments were converted to heat flux values with the one-dimensional heat diffusion equation.

These heat flux values were then matched with the stagnation heat transfer theories mentioned earlier to acquire the catalytic efficiencies. The necessary parameters for these theories are determined numerically, with the exception of the pitot pressure which is measured using a piezo-electric sensor. A series of numerical programs are used to acquire the flow parameters: a Lagrangian quasi-1D flow solver called "L1d2" from the CFCFD group of the University of Queensland (Australia) is used for determining the flow conditions inside the shock tube, an equilibrium composition calculator called "Eqtab" of Prof. Chul Park of KAIST to determine the flow conditions at the boundary layer edge of the model behind the standing shock, and a chemical equilibrium program called "CEA" of NASA to determine the conditions at the wall of the model.

Combining the heat flux measurements with the stagnation heat transfer theories the catalytic efficiencies were found to be between $6.10 \cdot 10^{-4}$ and $1.36 \cdot 10^{-3}$ for black CuO, $9.50 \cdot 10^{-4}$ for brown CuO, and $5.29 \cdot 10^{-2}$ for Cu. Each of these values have a relatively large uncertainty not only from the fluctuations in the heat flux measurements, but also from the changing sensitivity of the curve that relates the heat flux ratio and the catalytic efficiency. For Cu the heat flux value is located in a very insensitive region of the curve hence it is rather safer to conclude that its efficiency is between $3.07 \cdot 10^{-3}$ and $5.29 \cdot 10^{-2}$.

Additionally all the values potentially suffer from uncertainties in the numerical values. From the sensitivity analysis it was found that a 10% deviation of the measured pitot pressure changes the catalytic efficiencies of copper oxide with less than 10%. However, a 10% discrepancy in the total enthalpy results in a 50% increase of the catalytic efficiencies of copper oxide. A combination of 10% error for both parameters together can even yield a 61% error in the catalytic efficiency of copper oxide.

Further research regarding the catalytic efficiency of copper oxide should focus on the roughness effect of the model, which has been neglected here by polishing the thin-film gauges during the manufacturing process. Moreover, the wall remained at temperatures near room temperature during the shock tube experiments, which is not representative of the temperature that is reached during real flight. Although it is known that the catalytic efficiency increases with temperature, this relation has not been investigated quantitatively for copper or copper oxide.

The last recommendation for further research concerns the coupling between oxygen and nitrogen for copper and copper oxide. This requires the stagnation heat transfer theory to be rewritten for a gas mixtures consisting of five or more species. Only in this case the catalytic efficiency of air can be determined properly for copper oxide.

Introduction and Relevance

1.1 Historical Perspective

The sky has always had an important role in the history of mankind. Astonished by the beauty of the night sky, famous scientists – like Galileo Galilei, Johannes Kepler, and Isaac Newton – started to observe and study it. Not only stars, but also comets, meteoroids and meteors were observed. With the limited technology available, scientists attempted in finding patterns by approaching it mathematically.

The interest in space did not cease as time passed by. On the contrary, mankind started to fantasize about interplanetary travel by escaping from the Earth. Unfortunately the technology required for accomplishing this was still absent. It was only after the accomplishment of the Wright brothers in 1903 that the sky was within reach. Not long after that the First World War was a fact, resulting in the first large scale application of aircrafts. However, the role of these aircrafts was mere and mainly used for observations and coordinations of other weapons such as artillery.

After the First World War efforts were made to improve different aspects of aircrafts, and speed was one of these. Better aerodynamic shapes were found and larger (propeller) engines were constructed. It was only after the invention of the jet engine in 1939, that led to the first aircraft which is powered purely by a turbojet: the Heinkel He 178 (Fig. 1.1). The development of the jet engine accelerated the development of aircrafts resulting in aircrafts that could fly faster than before.

During the Second World War the air force had a more important role compared to the First World War. The outcome of the battlefield was often dependent on the strength of the air force. Nazi Germany was heavily investing in the development of long-distance rockets which could be used as weapons. The infamous V-2 rockets were used by Nazi Germany at the end of the war to attack London, cruising at 5,760 km/h (=1,600 m/s) or Mach 6.

It was only after the war that the United States and the Soviet Union started their own missile program, using the knowledge of the German scientists who fled to either one of the two countries. Their knowledge formed the foundation of the two programs. The political and the military atmosphere became coarse and the cold war was a fact where the two superpowers were involved in an competition to become the strongest and most powerful country.

This battle did not only take place on Earth. Space became another arena for their competition which is known as the Space Race. The Soviet Union won the first round on October 4 1957 by successfully launching the first artificial satellite in the history of mankind: Sputnik 1 (Fig. 1.2). The batteries only lasted until October 26 1957 and on January 4 1958 – after 92 days – the orbit of Sputnik 1 has decayed so much that it reentered the atmosphere and burned up completely. While Sputnik 1 was still orbiting the Earth, the Soviet Union was already preparing for Sputnik 2. On November 3 1957 Sputnik 2 was launched carrying a dog. Although the capsule orbited the Earth for 162 days until it reentered the Earth's atmosphere, the dog survived only for a few hours.

In the time that the Soviet Union was working on the Sputnik, the United States were attempting to launch their own satellite. Only after the launch of Sputnik 2, the United States managed to have a success on February 1 1958 with the Explorer 1.

The race continued with highlights such as the launch of the Luna 2 of the Soviet Union in 1959 which was the first probe to hit the moon, and the Soviet cosmonaut Yuri Gagarin who became the first person to orbit the Earth in April 1961. The adventure only took 108 minutes at an altitude of 327 km.

The United States were getting anxious and shocked by the rapid achievements of the Soviet Union, hence on May 25 1961 President John F. Kennedy held the famous speech where he announced that the United States had set the goal to land a man on the moon and return safely by 1970, resulting in the well-known Apollo program.







Figure 1.1: Heinkel He 178, the first turbojet aircraft. [1]

Figure 1.2: Sputnik 1, the first man-made object in space. [2]

The United States eventually succeeded with Apollo 11 where Neil Armstrong was the first person to set foot on the moon in July 20 1969. The previous Apollo missions were used to test the necessary technology and to explore the moon. The Apollo program followed up the Mercury and Gemini programs, all focused on human spaceflight. The experience and knowledge acquired from these two programs were of great value to the Apollo program.

All these three programs shared the aspect that reentry was required. The reentry vehicle was an aerodynamically stable capsule shaped as a blunt body, for example see Fig. 1.3 and 1.4. Because of this shape it had a low lift-over-drag ratio which led to a ballistic trajectory. Although this trajectory resulted in a fast reentry, the capsule had to face enormous heat loads since deceleration started to occur at lower altitudes where the air density is higher. However, due to the short reentry time it was possible to simply increase the protective layer at the blunt part of the body which would function as a heat sink.





Figure 1.3: The Mercury-Atlas 9 capsule called Faith 7. [3]

Figure 1.4: The Apollo 11 command module. [4]

The Soviet Union also developed reentry vehicles based on the same principle for manned programs. One of the vehicles was the Vostok reentry module used by Yuri Gagarin. A more famous vehicle is the Soyuz module which fourth generation is still in operation nowadays.

In the years after Apollo 11 the United States had a few more Apollo programs where they landed again on the moon. The Soviet Union dismantled its lunar program and on July 17 1975 both superpowers declared an end to the space race. Despite this the space technology continued its development although at a lower pace.

After the Second World War the National Aeronautics and Space Administration (NASA) started working on a large number of secret projects to develop new technologies and aerodynamic concepts, which



were called X-planes. A good example is the X-15 (Fig. 1.5) which had its first flight in 1959. It was the first manned hypersonic aircraft being able to fly at Mach 6.7. Another important project was the X-20 Dyna-Soar (Fig. 1.6), which introduced an revolutionary design to reentry vehicles compared with the blunt bodies.



Figure 1.5: The North American X-15. [5]



Figure 1.6: An artist impression of the X-20 Dyna-Soar. [6]

In contrast with the previously used capsule shaped bodies, the idea with these X-planes was to use a lifting body which would be able to reach high lift-over-drag ratios. This would enhance the range of the reentry vehicle hereby increasing the flexibility of missions since there would be more control over the vehicle. Moreover, the lifting body would be able to follow a gliding reentry trajectory which would significantly lower the heat loads compared to the capsule shaped bodies, because the vehicle would start to reduce its velocity at higher altitudes where the air density is lower. A disadvantage is that the heating time would be increased due to this type of trajectory.

The problem faced with this concept was that the geometry of the vehicle became more complex since lift has to be generated by the body, and control surfaces (such as flaps or rudders) were introduced. This increase of complexity raises the risk of failure of the vehicle in the harsh environment experienced during reentry. Moreover, although the overall heat load might be lower for these vehicles, locally – such as at sharper edges – the heat load could increase tremendously. These local heat loads would have to be considered carefully to prevent failure of the vehicle.

Although the X-20 has never been built, the acquired knowledge had an important role in the development of future reentry vehicles. The most famous program, the Space Transportation System, is a result of this knowledge, featuring a reusable reentry spacecraft launched for the first time on April 12 1981: the Space Shuttle Orbiter. It is considered to be the most successful spacecraft because it has been launched 135 times in total, distributed among five vehicles.

Shown in Fig. 1.7 is the Space Shuttle Atlantis from which it can be seen that it had a delta wing shape. The belly of the vehicle was covered with insulting tiles which served as a thermal protection system. By reentering the atmosphere with a high angle of attack, the effective surface area would be large, hereby slowing down the vehicle. Despite the experience and knowledge gained from the Apollo and the X-program which resulted in more accurate calculations of the heat loads, it was – according to Iliff and Shafer [7] – witnessed after the first few flights that the values were larger than initially predicted. Luckily the heat loads were still within the limits. Because replacement of the heat tiles was necessary after each flight the costs were a lot higher than initially anticipated, resulting in the end of the program in 2011 after 30 years of service.

The Space Shuttle Orbiter was capable of bringing a payload of almost 25,000 kg to low earth orbit. Not only a large number of experiments, supply, and parts were delivered to the International Space Station (ISS), also the Hubble Space Telescope was brought in orbit by the Space Shuttle.

While the Space Shuttle Orbiter was mainly used as a transportation system, there were a number of vehicles designed for the mere goal of understanding the reentry conditions better. As witnessed in the design of the Space Shuttle Orbiter, the conditions during reentry could not be calculated correctly beforehand hence validation data is necessary.

A vehicle that fits in this group is the European eXPErimental Reentry Testbed (EXPERT) vehicle of European Space Agency (ESA), shown in Fig. 1.8. Functioning as a testbed it can carry different experiments on-board to obtain aerothermodynamic data during each re-entry, which could be used for validation purposes of computer models and experiments.

14 difference experiments were chosen to be carried by the vehicle, which can be grouped in four scientific disciplines. The surface and gas-phase chemistry, and the hypersonic flow phenomena are two of these disciplines which are crucial to understand the conditions experienced during reentry. Moreover, any transition of the flow from laminar to turbulent is worthwhile to investigate since it would change the nature of the flow. And at last, different materials can be tested in the high temperature environment.





Figure 1.7: The Space Shuttle Orbiter Atlantis landing on the 121st shuttle flight. [8]

Although it was planned to be launched in 2011, it has currently still not been launched due to problems with the availability of Russian launchers.

Another project that has been launched successfully by ESA is the Intermediate eXperimental Vehicle (IXV) for the same purpose as the EXPERT. While the EXPERT has the well-known conical shape, the IXV is a lifting body with no wings but with thrusters and aerodynamic surfaces (Fig. 1.9). Not only can IXV acquire aerothermodynamic data which will eventually be used to understand the hypersonic regime better, the complex structure has thermal protection materials and complex design solutions to cope with the heat which need to be validated.



Figure 1.8: A replica of the EXPERT vehicle. [9]



Figure 1.9: An artist drawing of the IXV. [10]

1.2 Flow Conditions

Although each reentry vehicle has its own distinctive shape and features, they all have in common that they experience all flight regimes starting with the hypersonic regime and ending with the subsonic regime. An altitude-velocity diagram is shown in Fig. 1.10 where the differences between the high and low lift trajectories are shown. As can be seen, the former stays for a longer time decelerating at the higher altitudes, whereas the latter penetrates deeper into the atmosphere before it starts to decelerate.

Also the Mach numbers are indicated in this diagram. At the beginning of the reentry, the Mach number can be as large as 30 and it reduces when the altitude drops. The constant Mach number lines are however not perfectly vertical which is caused by the varying speed of sound due to the variation of the air temperature with altitude.

In Fig. 1.11 the unit Reynolds number is also shown in the altitude-velocity diagram. The Reynolds number increases from a high altitude to a lower altitude, because the density increases with decreasing altitude. Although the vehicle decelerates, this is significantly smaller than the density increase, hereby effectively increasing the Reynolds number.

The transition Reynolds number forms the boundary between the laminar and turbulent flow experienced by the vehicle. This occurs around $\frac{\text{Re}}{1} = 10^5 \text{ m}^{-1}$ as shown in Fig. 1.11. From this figure it can also seen that it would occur around an altitude of 50 km for a 1 m long vehicle.



Figure 1.10: An altitude-velocity diagram indicating the Mach numbers and the differences between a high and low lift trajectory. [11]



Figure 1.11: An altitude-velocity diagram indicating the magnitude of the Reynolds numbers. [11]

Generally the Mach number is used to split up the trajectory in different flight regimes:

- Subsonic: M < 0.8.
- Transonic: 0.8 < M < 1.2.
- Supersonic: 1.2 < M < 5.0.
- Hypersonic: 5.0 < M.

Comparing this with Fig. 1.10 it can be concluded that a reentry vehicle spends most of its flight in the hypersonic regime. Although the earlier mentioned boundary between supersonic and hypersonic flow at M = 5 seems as a hard line, this is absolutely not true. The difference between supersonic and hypersonic flow is more than just the Mach number: the temperature is another important quantity.

When a vehicle moves through the air the molecules are pushed away. This introduces an energy transfer from kinetic to internal energy, hereby increasing the temperature of the particles. During operations below a Mach number of 5 this increase in temperature can be neglected, however, in the hypersonic speed regime this temperature rise is so severe that the behavior of the air particles changes. Not only the molecules start to vibrate substantially (according to Park [12] hereby increasing the degree of freedom of the diatomic molecules from 5 to 7) which causes the air to be no longer a calorically perfect gas, also dissociation will take place in which molecules will be split up into atoms. At around 2500 K oxygen starts to dissociate, and at around 4000 K nitrogen dissociation starts, as illustrated in Fig. 1.12.



Figure 1.12: The ranges of oxygen and nitrogen dissociation for air at 1 atm pressure. [11]

These phases are shown in Fig. 1.13 from which it can be seen that a reentry vehicle is exposed to different types of flow during its descent. These changes in the flow composition are one of the many factors that make the computation for the hypersonic regime complex.







1.3 Relevance of Heat Flux

From the previous section (Section 1.2) it was elaborated that the high temperature has a serious effect on the thermodynamical properties of the flow, and thus on the flow field. Because of the high Mach number, a thermal boundary layer is present which introduces a heat transfer to the body due to the high temperature.

This heat flux causes many problems in the design of reentry vehicles. As witnessed with the Space Shuttle Orbiter where the heat flux could not be determined accurately enough. This resulted in an enormous increase of the operational costs caused by the constant replacement of the heat tiles.

The Space Shuttle Orbiter was fortunate enough that the inaccuracy of the heat flux calculations did not result in a failure of the vehicle. What could have happened was shown in the disaster of the Space Shuttle Columbia in 2003. During the launch of the shuttle a piece of foam insulation broke off and hit the leading edge of the left wing. The damage allowed the hot gases to penetrate inside the structure of the wing hereby weakening it. Since it was chosen for a cold structure philosophy for the Space Shuttle Orbiter, the structure could not cope with the loads and eventually it resulted in the destruction of the entire vehicle.

1.4 Aspects Affecting Heat Flux

The example of the Space Shuttle Columbia in the previous section shows the importance of properly determining the heat flux transferred to the vehicle. However, the heat flux dependents on many variables. In this section the aspects affecting the heat flux will be elaborated and discussed.

The shape of the vehicle has a large influence on the heat flux. A sharp nose or sharp edges on a vehicle experience a higher heat flux than blunt bodies, since in the latter case the heat can be distributed over a larger area. Fay and Riddell [13] presented the relation between the heat flux and the nose radius as: $q \propto \frac{1}{B}$. This will be discussed further in Section 2.3.

The state of the boundary layer also has a great influence on the heat flux. Not only there is a velocity boundary layer, also there is a thermal boundary layer as mentioned in Section 1.3. Whether or not these boundary layers have the same thickness depends on the Prandtl number which is a dimensionless number being the ratio of the kinematic viscosity and the thermal diffusivity.

The thickness of the boundary layer can vary depending on the Reynolds number as described by Fig. 1.11. Especially when the boundary layer has changed from laminar to turbulent the heat flux can be three times larger [11]. For this reason it is desired to know where transition occurs in the flow. However, this is a highly complex phenomenon [11] which depends on the Mach number, disturbances in the environment, Reynolds number, angle of attack, nose bluntness, wall temperature, and wall roughness.

Another aspect of the boundary layer is related to the shape of the vehicle: separation. When a flow separates and reattaches downstream, it will locally introduce a shock wave. This "shock wave boundary layer interaction" is a topic where a lot of research is conducted to truly understand and simulate that situation. This high interest is due to the enormous increase of heat flux locally where reattachment occurs. The exact location of reattachment and the magnitude of this increase of heat flux cannot be determined accurately yet, especially due to flow unsteadiness.

The third and last aspect that influences the heat flux is the surface of the body, often also referred to as the wall. The wall can partially absorb the energy of the dissociated air particles which can result in the recombination of these particles. This phenomenon is known as catalycity. Because recombination is an exothermic process there will be an additional increase of the heat to the wall which increases the heat flux.

The amount of recombination is affected by the composition of the wall material. It is known that metals have a positive effect on the amount of recombination whereas ceramics have a negative effect. [14] Moreover, the roughness of the wall also has a prominent role. A rougher wall results in a larger amount of recombination compared to a smooth one. More can be found in Section 2.2.

The increase in additional heat flux is denoted as the diffusive heat flux. It is caused by the concentration gradient near the wall that is created by the catalytic recombination. As will be seen in Section 2.3 the diffusive heat flux can have a considerable effect on the total heat flux which cannot be neglected.

1.5 Research Question and Objectives

The concept of catalycity has been mentioned at the end of Section 1.4. Although it will be further discussed in Chapter 2, it is essential to know that this principle affects the heat flux significantly. The magnitude of this effect is controlled by the amount of atoms that recombine at the wall: the catalytic recombination efficiency.

In Chapter 3 the experimental research in catalycity is introduced. An important test facilities for this purpose is discussed in this chapter: the arc-jec facility. As will be discussed in Section 3.4 the usage of copper slug calorimeters is essential to determine the total enthalpy which dictates the flow condition a sample experiences. The total enthalpy is typically measured by means of copper calorimeters which tend to oxidize when used. However, the catalytic efficiency of copper oxide is not the same as copper. It is therefore essential to know the catalytic efficiency of copper oxide to accurately determine the enthalpy.

In Section 3.4.3 the literature regarding the catalytic efficiencies of copper and copper oxide is presented. While a large number of experiments have been conducted for oxygen on copper oxide, it is noticed that values for nitrogen on copper oxide is still missing. Since one of the main components of air is nitrogen it is essential to investigate also this case.

The method of Park [15] is followed in this work using a shock tube, thin-film gauges and the theory for tertiary gas mixtures. The theory is discussed in Chapter 2 and the experimental equipment is discussed in Chapter 4.

From this the research question for this thesis project can be formulated as:

"What is the catalytic recombination efficiency of copper oxide when exposed to nitrogen?"

To answer this research question there are several sub-goals, called objectives, that need to be accomplished. These objectives are as follows:

- 1. Define the initial conditions for the shock tube such that nitrogen dissociation at varying degrees is present in the test section.
- 2. Construct and calibrate the thin-film heat transfer gauges.
- 3. Analysis of the tertiary gas mixture theory composed by Park [15] (Section 2.3.2.2), necessary to construct the diffusion-conduction heat transfer ratio vs. catalytic efficiency diagram.
- 4. Measurement of the heat transfer rate by using a heat transfer gauge which is mounted in a model with no coating.
- 5. Measurement of the heat transfer rate by using a heat transfer gauge which is mounted in a model and coated with silicon dioxide.
- 6. Measurement of the heat transfer rate by using a heat transfer gauge which is mounted in a model and coated with copper oxide.
- 7. Measurement of the heat transfer rate by using a heat transfer gauge which is mounted in a model and coated with copper.
- 8. Determination of the catalytic efficiency by combining the theory with the measured heat transfer rate.

The flow conditions used in the shock tube have to be determined using numerical programs (objective 1). Additionally, the thin-film gauges need to be manufactured and calibrated which will be used for the measurements (objective 2).

Objective 3 is the required theory to translate the heat transfer rate to the catalytic efficiency. Hence it forms a bridge between objectives 4 to 7 with objective 8. Objective 5 concerns a silicon dioxide coating only, which acts as a reference since it is considered to be a non catalytic material. Because objectives 6 and 7 are catalytic surfaces, these values can be compared with the former.

Not only different types of coating are investigated, also three different flow conditions are considered: one with almost no dissociation (around 1% dissociation), one with a moderate amount of dissociation (around 30% dissociation), and the last with a high amount of dissociation (around 50% dissociation). These flow conditions are given the letters A, B, and C respectively.

Condition A functions as a check to compare the measured heat transfer rate between no coating and silicon dioxide (objective 4 and objective 5 respectively). Theoretically the difference between the two should be negligible. Condition B and C are used to determine the catalytic efficiency and theoretically they should yield about the same value. However, to achieve a higher amount of dissociation at condition C the test time might be shorter hereby increasing the uncertainty of the results.

1.6 Report Outline

The first three chapters of this report functions as a literature review to introduce the concept of catalycity. This section closes off Chapter 1 in which the background information regarding hypersonic vehicles has been presented together with the introduction to heat flux. The next chapter continues on the heat flux and extends it to the different aspects that have an influence. This eventually leads to the discussion regarding the theory of catalycity and the flow conditions at the stagnation point. Chapter 3 focuses on the experimental research that has been conducted regarding catalycity, from which it can be concluded that measurement data on the combination of nitrogen and copper oxide is still absent.

After finishing the literature review the experimental equipment is discussed in Chapter 4 by presenting the shock tube and the entire manufacturing procedure of the thin-film gauges. Chapter 5 then presents the numerical programs used to determine the basic flow parameters around the model. It is then followed up by the discussion of the post-processing procedure, in which all the variables are presented that are required to compute the catalycity.

In Chapter 7 the heat flux and pressure results are presented together with the shadowgraph visualization images. This chapter also presents the catalytic efficiency values found from the experiments. Discrepancies between the results and the values predicted by numerical programs or theory are discussed in Chapter 8. In Chapter 9 a sensitivity analysis is conducted from which it can be concluded which parameters have the largest affect on the accuracy of the results. This report is then closed by a conclusion and recommendations shown in Chapter 10.

Heat Flux and Catalycity

In the previous chapter the concept of heat flux has been discussed. In this chapter the basic principles of heat transfer are listed (Section 2.1) from a macroscopic perspective. However, when dissociation occurs an additional heat flux mode arises: the diffusive heat flux. This heat flux originates from the diffusion of atoms which is caused by catalycity at the wall. To fully grasp the concept of catalycity the fundamentals are presented in Section 2.2.

The effect of catalycity can be expressed mathematically by the theory presented in Section 2.3, which relates the heat flux with the catalytic efficiency for both a binary and tertiary gas mixture at the stagnation point. This chapter then finishes by presenting the flow conditions at the stagnation point which requires the introduction of partition functions, which is a mathematical concept used to perform calculations based on the physical behavior of atoms and molecules.

2.1 Heat Flux

In Section 1.4 the aspects that affect the heat flux were listed. To fully understand the influence of catalycity on the heat flux it is necessary to present more details regarding the latter.

Heat flux is by definition the rate at which heat is transferred through a surface per unit area, hence the SI units are W/m^2 . There are several different modes by which the heat transfer can take place [16]:

- *Conduction:* The heat transfer between objects that have a physical contact is called conductive heat flux. It is required that a temperature gradient exists (e.g. in the form of a temperature difference between two objects) which results in a flow of energy in the form of heat from the high temperature to the lower temperature. This energy is stored in the form of translational, rotational, and vibrational motion of the molecules.
- *Convection:* The convective heat flux is caused by a physical displacement of a medium which transfers a part of its internal energy to another medium. Similar to the conductive heat transfer a temperature difference needs to exist between the two media.
- *Radiation:* An electromagnetic process where energy is transfered by means of radiation. A single medium can emit radiation without the need of a second medium.

For classical macroscopic heat transfer problems, it is sufficient to consider these three modes. However, in hypersonic applications especially in high enthalpy cases the conductive heat transfer will be larger than determined using the macroscopic method. To cover for this increase a fourth heat transfer mode has to be introduced.

• Atomic diffusion: The atoms resulting from dissociated molecules translate due to a concentration gradient. This gradient results in a net transport of these atoms to a certain direction which is also known as diffusion. The recombination of these atoms releases energy that adds on the conductive heat flux. This additional heat flux is called diffusive heat transfer.

It has been shown by Herdrich et al. [17] that this diffusive heat transfer could increase the heat flux experienced by a vehicle by a factor of 3. To fully understand this diffusive heat transfer it is necessary to explain catalycity first which will be tackled in the following section.

2.2 Fundamentals of Catalycity

This section starts with the gas surface interaction (Section 2.2.1) which covers the adsorption of the gas on the surface. These adsorbed atoms can move from one stable site to another at the surface and



collide, possibly resulting in the recombination of two atoms. The surface hereby acts as a catalyst (Section 2.2.2). The probability of a successful recombination increases when imperfections are present in the surface or when the roughness increases (Section 2.2.3). Moreover, the type of material dictates the catalytic behavior which can be categorized in three groups (Section 2.2.4).

2.2.1 Gas Surface Interaction

In a solid, the atoms are ordered in a closed-packed structure. Inside the solid the atoms have neighbors on all sides, however, in the most outer layer the atoms are missing neighbors on one side. This layer is called the surface layer.

As described by Park [12], when a gas atom is brought close to the surface there will be an attractive force felt by this particle. The gas particle will therefore have the intention to stick to the surface (i.e. adsorbed by the surface). This force can either be created by an "induced-dipole induced-dipole" interaction between atoms (also known as van der Waals interaction) which is called physisorption, or by a chemical bonding called chemisorption.

As the gas atom moves closer, the attractive force will become lower and the acceleration decreases. This principle is shown in Fig. 2.1. At a certain distance the attractive force changes to a repulsive force.

However, because the surface atom has moved by a fraction due to the force exerted by the gas atom during the attractive part, some of the energy is absorbed by the surface atom and transferred to its neighboring atoms. The gas atom has therefore a lower energy than initially before it interacted with the surface, hence it cannot reach the same velocity as before. The gas atom becomes trapped by the surface layer and vibrates until the motion damps out by slowly losing its kinetic energy to the surface. [18]



Figure 2.1: Intermolecular force as a function of the distance. [19]

This adsorbed atom will vibrate on the surface at a frequency proportional to the local temperature. Due to this vibration the kinetic energy increases which could lead to desorption (i.e. atom escaping from the surface layer) if it is larger than the adsorption energy. It should be noted that not all atoms become adsorbed when they hit the surface layer, the probability that an atom is adsorbed is expressed by the adsorption coefficient. [12]

2.2.2 Wall Recombination

Not only desorption can occur to the adsorbed atom, there is also the possibility that recombination takes place. Molecules can be formed from the adsorbed atoms by two different modes: the catalytic mode and the reactive mode. [12]

The catalytic mode follows the so called three-body atomic recombination process. When two atoms collide they first have an attractive potential, hence they move towards each other. However, after a certain point this potential will become repulsive and because during this process energy is preserved they will return back to the original conditions. Therefore, the two atoms need the aid of a third atom to recombine to one molecule. This third atom will absorb partly or all kinetic energy of the two colliding atoms when they interact.

Normally this process occurs when two gas atoms are flowing in the air and collide. The third atom is then pushed away by the two atoms, which results in an energy drop for those two respective atoms and they become trapped in each others potential fields, hereby forming a molecule.

This process can also occur with an adsorbed atom which has enough kinetic energy to move from one stable site (of having four bonds, shown in Fig. 2.2(a)) to the neighboring one (Fig. 2.2(b)). The adsorbed atom can then move freely on the surface layer and collide with another atom. The surface atoms function as a third body that transfers the energy to the neighboring atoms. However, not every collision is successful and the two atoms can just bounce off each other. [12]



(a) The initial stable site of the adsorbed atom.

(b) The neighboring stable site of the adsorbed atom.

Figure 2.2: The translation of an adsorbed atom shown in gray from one stable site to a neighboring one. [12]

In this catalytic mode the catalytic efficiency (γ) can be defined as the ratio of the mass flux of the formed molecules (J_4) to the mass flux of the atoms hitting the surface (J_1) [12]:

$$\gamma = 2\frac{J_4}{J_1} = \frac{1}{1 + 0.25\sqrt{\frac{\theta_r}{T}}e^{\frac{E-D_A}{k_BT}}}$$
(2.1)

The factor 2 is the result of two atoms combining into a single molecule. This efficiency depends on the temperature (T), the dissociation energy in the adsorbed phase (D_A) , and the surface activation energy (E). There are also two constants: a rotational constant (θ_r) , and the Boltzmann's constant (k_B) .

This catalytic efficiency is strongly related to the catalytic rate (k_w) . In order to explain this relation, the arrival rate has to be introduced which can be derived in the following way:

The number of particles crossing one particular area is the number density multiplied by the velocity, hence *nc*. But from the other side there are also particles crossing that area, hence only half of the total particles are effectively hitting one side. However, the particles do not necessarily hit the surface perpendicularly hence the normal velocity component needs to be taken of all angles which gives another factor half:

Arrival Rate =
$$\frac{nc}{4}$$
 (2.2)

The arrival rate is thus the number of atoms hitting the surface per unit time and unit area. It depends on the number density of the atoms one mean free path away from the surface (n) and the average molecular speed (c). This speed is dependent on the temperature (T) and the molar mass (m):

$$c = \sqrt{\frac{8k_BT}{\pi m}} \tag{2.3}$$

The number of molecules formed through catalytic recombination is the multiplication of the catalytic efficiency and the arrival rate. This same number of formed molecules can also be gained by multiplying the catalytic rate with the number density, hence the catalytic rate can be expressed as:

$$k_w = \gamma \frac{c}{4} \tag{2.4}$$

The reactive mode is the second mode at which molecules can be formed. In this mode a surface molecule gives up one of its atom and donates it to the adsorbed atom to form a diatomic molecule. The resulting cavity will be filled up again by adsorbing another gas atom hence the composition of the surface molecule does not change.

The molecules formed at the surface layer are in general only held at their place by physisorption using van der Waals forces, which is considered to be a relatively weak force. For this reason the formed molecules will desorb almost instantly. With this, the wall recombination process is completed.



2.2.3 Imperfections and Roughness

Until now it has been assumed that the surface layer is perfectly smooth. However, in reality the surface has a certain roughness dictated by imperfections. Gas atoms are more likely to become trapped in these imperfections. In general one can discern different types of imperfections: [20]:

- *Point imperfection:* There is a vacancy in the surface layer hence an atom is missing. Another possibility is when interstitialcy occurs hence there is an extra atom.
- *Line imperfection:* There is a line of atoms is missing in the surface, or an extra line of atoms is present in the surface.
- Surface imperfection: A portion of the surface atoms are missing, or an extra portion of surface atoms is present.
- Volume imperfection: A volume of atoms (void) is missing or there is an extra volume of atoms present.

These imperfections have an effect on the gas atoms hitting the surface layer. Especially when atoms are missing there will be a larger attractive potential to the incoming gas atom.

Not all incoming atoms will be adsorbed when they hit the surface, so a number of atoms will simply bounce back in the reversed direction (Fig. 2.3(a)). However, the roughness of the surface has an important effect on this interaction, because an atom that is bounced back will experience a few more collisions before "escaping" from the surface atoms (Fig. 2.3(b)). And with each collision there is a possibility that it will be adsorbed.



(a) A smooth surface will result in a single bounce if the (b) A rough surface will result in several bounces if the atom is not adsorbed.

Figure 2.3: The differences between a smooth and a rough surface.

2.2.4 Catalytic Materials

Materials can be distinguished by their catalytic behavior. The activation energy (E) present in Eq. (2.1) defines the tendency of the surface atoms to absorb the energy of two adsorbed atoms to make them recombine, hence they directly influence the catalytic behavior. [12]

A material that does not allow wall recombination by the catalytic mode are non-catalytic materials, and they have a catalytic efficiency (γ) of 0. These materials do not adsorb the incoming atoms nor make them recombine by absorbing their energies.

On the other hand, materials that have wall recombination only by catalytic mode are fully catalytic materials, and thus they have a catalytic efficiency of 1. They adsorb the incoming atoms very easily and make them recombine at an infinite rate.

Materials with a finite recombination rate are called catalytic materials and have a catalytic efficiency between 0 and 1. [11, 21]

2.3 Theoretical Research in Catalycity

In the previous sections the fundamentals of heat flux and catalycity were discussed, which are necessary to understand the theoretical background of catalycity. This section starts with the fundamental research done by Fay and Riddell regarding the stagnation point heat transfer. In this work the catalycity has been neglected in the sense that they only consider a fully or non-catalytic material. In the second part of this section the heat transfer theory is introduced that includes catalycity.

2.3.1 Stagnation Point Heat Transfer

In 1958 Fay and Riddell [13] introduced a theory to determine the stagnation point heat transfer in dissociated air. Starting from the momentum, species continuity, and the energy equation they managed to develop a set of boundary layer equations, where the diffusion and atomic recombination in the boundary layer are included. At the stagnation point these equations could be reduced to nonlinear ordinary differential equations. From this Fay and Riddell provided the solutions for a frozen and equilibrium boundary layer, which correspond to zero recombination rates and infinitely large recombination rates respectively.

Two of these results are presented in Fig. 2.4 for Le = 1.4 and Pr = 0.71. The Lewis number is a non-dimensional number which is defined as the ratio of thermal diffusivity and mass diffusivity:

$$Le = \frac{\alpha}{D} \tag{2.5}$$

whereas the Prandtl number is the ratio between momentum diffusivity and thermal diffusivity:

$$Pr = \frac{c_p \mu}{k} \tag{2.6}$$

It was stated by Fay and Riddell that both the Lewis and Prandtl numbers do not vary significantly with temperature. While the Prandtl number of air is often taken as 0.71, the Lewis number value was estimated as 1.4.



(a) Enthalpy profiles at the stagnation point for a frozen (b) Temperature profiles at the stagnation point for a and equilibrium boundary layer for a fully catalytic frozen and equilibrium boundary layer for a fully catwall. [13] alytic wall. [13]

Figure 2.4: Enthalpy and temperature profiles for a frozen and equilibrium boundary layer.

In Fig. 2.4(a) the enthalpy ratio $\left(g = \frac{h + \frac{u^2}{2}}{h_s}\right)$ is shown as a function of the non-dimensional y-distance (η) from the stagnation point in the direction of the flow. This is expressed by the non-dimensional coordinate system:

$$\xi = \xi(x) = \int_0^x \rho_w \mu_w u_e r^2 dx$$

$$\eta = \eta(x, y) = \frac{ru_e}{\sqrt{2\xi}} \int_0^y \rho dy$$
(2.7)

For a given value of η , g is higher for the equilibrium case than for the frozen case which matches the fundamental difference between the two cases. In case of an equilibrium boundary layer all the atoms will recombine inside the boundary layer which brings along the additional energy release during this process. For a frozen boundary layer there is no change in the species concentrations (hence it is "frozen") which results in a smaller g. This same applies to the temperature ratio shown in Fig. 2.4(b).

Moreover, in Fig. 2.4(b) also the atom mass fraction is shown for the two cases. For the equilibrium case the mass fraction changes due to the recombination of the atoms inside the boundary layer. For the frozen case this is due to the fully catalytic wal, l that forces all the atoms to recombine at the wall. There is however a change in the mass fraction away from the wall which is caused by the diffusion of the atoms in the boundary layer towards the wall.

Fay and Riddell [13] provided closed form solutions for both the equilibrium shown in Eq. (2.8a) and frozen boundary layer (with fully catalytic wall shown in Eq. (2.8b) and non-catalytic wall shown in Eq. (2.8c)) cases. It should be noted that the wall – fully catalytic or non-catalytic – has no effect for an equilibrium boundary layer since all the atoms have recombined when they reached wall.

Eq. BL:
$$q = 0.76Pr^{-0.6}(\rho_w\mu_w)^{0.1}(\rho_s\mu_s)^{0.4}\left(1 + (Le^{0.52} - 1)\frac{h_D}{h_s}\right)(h_s - h_w)\sqrt{\left(\frac{du_e}{dx}\right)_s}$$
 (2.8a)

Fr. BL, fully cat. wall : $q = 0.76 Pr^{-0.6} (\rho_w \mu_w)^{0.1} (\rho_s \mu_s)^{0.4} \left(1 + (Le^{0.63} - 1)\frac{h_D}{h_s} \right) (h_s - h_w) \sqrt{\left(\frac{du_e}{dx}\right)_s}$ (2.8b)

Fr. BL, non cat. wall:
$$q = 0.76 P r^{-0.6} (\rho_w \mu_w)^{0.1} (\rho_s \mu_s)^{0.4} \left(1 - \frac{h_D}{h_s}\right) \sqrt{\left(\frac{du_e}{dx}\right)_s}$$
 (2.8c)

Comparing Eq. (2.8a) and (2.8b) more closely, it can be seen that the only difference is in the exponential of the Lewis number. This indicates that there is almost no difference between an equilibrium and a frozen boundary layer for a fully catalytic wall. While for the latter case all the recombination occurs at the wall hereby releasing the heat, for the former most of the heat that is released inside the boundary layer is conducted to the wall.

Fay and Riddell [13] also calculated the heat transfer for both catalytic and non-catalytic walls at different recombination rates, shown in Fig. 2.5. The frozen case corresponds to a negligibly small recombination rate whereas equilibrium is at very large rates. It can be seen that for the catalytic wall the heat transfer only changes slightly when the recombination rate in the boundary layer is varied. At the far left (i.e. frozen) the diffusive heat flux is dominant since the conductive part is small, whereas at the far right (i.e. equilibrium) the opposite is shown since the conductive heat transfer curve overlaps the total heat transfer curve. This matches with the observation made earlier when comparing Eq. (2.8a) and (2.8b).



Figure 2.5: Stagnation point heat transfer for fully catalytic and non-catalytic walls at different recombination rates. [13]

The curve for the non-catalytic wall shows the dependency of the heat transfer on the recombination rate, corresponding to Eq. (2.8c). The heat transfer is substantially smaller for frozen conditions compared to the catalytic wall, while at equilibrium conditions the heat transfer is identical as identified earlier. In the region between frozen and equilibrium, called non-equilibrium, the heat transfer is still significantly smaller and cannot be ignored.

Considering Eq. (2.8a) and (2.8b) it can be seen that the enthalpy (at both the stagnation point and the wall) has the largest effect on the heat flux. The velocity gradient, which is directly related to the radius of the model, is another parameter that affects the heat flux. Additionally, the conditions at the wall and stagnation point also influence the heat flux.

2.3.2 Stagnation Point Heat Transfer With Catalycity

The theory provided by Fay and Riddell [13] was only limited to fully catalytic and non-catalytic walls. In this section the theoretical work of Goulard [14] is introduced for a binary gas mixture valid for catalytic walls. In the second part of this section an extension of Goulard's work for a tertiary gas mixture as developed by Park [15] is presented.

Binary Gas Mixture 2.3.2.1

In the same year as the publication of Fay and Riddell [13], Goulard [14] extended their theory by including the catalytic effect. It was noted by Goulard that the case of a fully catalytic wall investigated by Fay and Riddell gives a rate of recombination that is only possible with extremely active catalysts. From a more practical perspective a material with a recombination rate that is between fully catalytic and non-catalytic is more relevant for hypersonic vehicles. For this reason Goulard [14] developed the theory for stagnation heat transfer of finite catalytic recombination rates in a frozen flow.

Goulard [14] manipulated the conservation equations (i.e. atom mass, mixture mass, momentum, and energy equations) with basically the same similarity transformation as Fay and Riddell, shown by:

$$s = \int_0^x \rho_e \mu_e u_e r_0^2 dx$$

$$\eta = \frac{u_e}{\sqrt{2s}} \int_0^y r_0 \rho dy$$
(2.9)

Moreover the concept of a frozen stagnation enthalpy (\overline{h}_e) was introduced which represents the enthalpy without including the chemical energy from the recombination of the atoms. A dimensionless frozen stagnation enthalpy $(\overline{g} = \frac{\overline{h}_s}{\overline{h}_{se}})$ and a dimensionless atom concentration $(z = \frac{\alpha}{\alpha_e})$ were also introduced. Additionally, a stream function (ψ) was used:

$$\psi_y = \rho u r_0 \tag{2.10}$$
$$\psi_z = -\rho v r_o$$

The dimensionless stream function was defined as $f = \frac{\psi}{\sqrt{2s}}$ which means that $\frac{u}{u_e} = \frac{\partial f}{\partial \eta} = f'$. In Fig. 2.6 the coordinate system and flow parameters at the stagnation point are shown.



Figure 2.6: The stagnation point parameters defined by Goulard. [14]

With these parameters, the entire similarity transformation can be applied and the conservation equations can be rewritten to represent the momentum, energy, and atom mass conservation, respectively:

$$(lf'')' + ff'' + \frac{2s}{u_e} \frac{\partial u_e}{\partial s} \left(\frac{\rho_e}{\rho} - f'^2\right) = 0$$
(2.11a)

$$f\overline{g}' + \left(\frac{l}{\overline{Pr}}\overline{g}'\right)' + \frac{\mu_e^2}{2\overline{h}_{se}} \left[2l\left(1 - \frac{1}{\overline{Pr}}\right)f'f''\right]' = 0$$
(2.11b)

$$2s\frac{\partial z}{\partial s}f' - fz' - \left(\frac{l}{Sc}z'\right)' = 0$$
(2.11c)

By assuming that the wall temperature is a lot lower than the temperature at the boundary layer edge (i.e. $T_w/T_{se} \ll 1$) the boundary conditions can be introduced for both the momentum and energy equations:

$$f(0) = f'(0) = 0$$

$$f(\infty) = 1$$

$$\overline{g}(0) \ll 1$$

$$\overline{g}(\infty) = 1$$

(2.12)

Equation (2.11) is problematic to solve hence several simplifications are necessary. One of the assumption has been already shown in Eq. (2.12) as $\overline{g}(0) \ll 1$ (which corresponds to $\overline{h}_s \ll \overline{h}_{se}$), using which it can be proven that the coupling between the momentum and the energy equations can be dropped. More details can be found in Goulard's paper [14].

As a result of these simplifications, $l = \frac{\mu \rho}{\mu_e \rho_e}$ and \overline{Pr} are only dependent on the temperature. Goulard makes a further simplification by assuming that these values are relatively insensitive to the temperature, hence they can be considered to be constant (i.e. $\overline{Pr} = 0.715$ and Chapman-Rubesin constant l = 1).

With these assumptions the momentum and the energy equations are reduced to the form:

$$f''' + ff'' = 0 (2.13a)$$

$$\overline{g}'' + \overline{Pr}f\overline{g}' = 0 \tag{2.13b}$$

Solutions for this type of equations are well known and the following solutions can be found: f''(0) = 0.47and $\overline{g}'(0) = 0.47 \overline{Pr}^{1/3}$.

Regarding the atom mass conversation (Eq. (2.11c)) there is a nonsimilar term in s, which is caused by the dependency on the catalytic process at the wall. Neglecting thermal diffusion and by assuming that the catalytic reaction rate is proportional to the m^{th} power of the atom concentration at the wall, the net mass flux of atoms diffusing in the direction of the wall can be expressed by Fick's law:

$$j_w = \rho_w D_w \left(\frac{\partial \alpha}{\partial y}\right)_w = k_w (\alpha_w \rho_w)^m \tag{2.14}$$

where m is a value between 1 and 2. This is the boundary condition for Eq. (2.11c) at the wall.

Furthermore, by introducing the local approximations for the stagnation point shown by:

$$r_0(x) = x$$

$$u_e = \beta x$$
(2.15)

the nonsimilar part of the boundary condition (i.e. $\frac{\sqrt{2s}}{r_0 u_e}$) can be substituted by $\sqrt{\frac{\mu_e \rho_e}{2\beta}}$.

Because the Chapman-Rubesin constant l has been assumed to be equal to 1, the product of $\mu_e \rho_e$ can be replaced by $\mu_{se} \rho_{se}$. Moreover, since thermochemical equilibrium has been assumed the atom mass fraction is constant, and it is furthermore assumed that m = 1 for a cold wall. This results in the final boundary condition:

$$z'(0) = \sqrt{\frac{\mu_{es}\rho_{es}}{2\beta}} \frac{k_w}{\rho_w D_w} z(0)$$

$$z(\infty) = 1$$
(2.16)

By dropping the nonsimilar term in s for Eq. (2.11c) and solving this using the boundary conditions, the dimensionless concentration at the wall can be found:

$$z(0) = \frac{1}{\sqrt{\frac{\mu_{se}\rho_{se}}{2\beta} \frac{k_w}{0.47Sc^{1/3}\rho_w D_w} + 1}}$$
(2.17)

The Schmidt number is present in this equation which is a non-dimensional number defined as the ratio of momentum diffusivity and mass diffusivity.

With the expression for the dimensionless atomic concentration at the wall, Goulard gives the expression for the diffusive heat flux as:

$$q_D = 0.47 S c^{-2/3} \sqrt{2\beta \mu_{es} \rho_{es} h_R \alpha_e \varphi_1}$$
(2.18)

Some terms were clustered by Goulard in a correction factor φ_1 which is defined as:

$$\varphi_1 = \frac{1}{1 + \frac{0.47Sc^{-2/3}\sqrt{2\beta\mu_{se}\rho_{se}}}{\rho_w k_w}}$$
(2.19)

The conductive heat flux is determined using the solution for $\overline{g}'(0)$ and is given as:

$$q_C = 0.47 \sqrt{2\beta \mu_{se} \rho_{se}} \overline{Pr}_w^{-2/3} \overline{h}_{se} \tag{2.20}$$

When analyzing Eq. (2.18) together with Eq. (2.19), it can be seen that the catalytic rate (k_w) has a profound effect on the diffusive heat flux (q_D) . Since the catalytic efficiency is related to the catalytic rate by Eq. (2.4) it can be stated that the influence of the efficiency is large. The Schmidt number, defined as the ratio between the viscosity and the mass diffusivity, is not only affecting φ_1 but also q_D directly. Additionally, the atomic mass fraction is also proportional to q_D , while the effect of the viscosity, density, and the velocity gradient is relatively small due to the square roots. The majority of the variables are required at the boundary layer edge.

In Eq. (2.20) the frozen enthalpy has the largest influences on the conductive heat flux (q_C) . Similar to the diffusive heat flux, the majority of the parameters are required at the boundary layer edge. Another observation that can be made is the relatively simple structure of the equation and the low amount of necessary parameters, compared to the diffusive heat flux. Moreover, the catalytic efficiency has no influence on the conductive heat flux.

Goulard introduced several catalytic efficiencies (Fig. 2.7) for different materials which were acquired mostly from experiments conducted by Linnett and Marsden [22, 23]. He also provided some plots to indicate the effect of including the catalytic effect in the heat flux calculations. The reduced heat transfer (\bar{q}) expresses the heat flux with respect to the heat flux of an infinitely fast catalyst, for a range of catalytic rates. A representative example is shown in Fig. 2.8 which is for an altitude of 60960 m, a nose temperature of 700 K, and a nose diameter of 100 cm. Each of the curves correspond to a different flight velocity given in feet/second (indicated as fps). From this it can be seen that the heat flux varies depending on the catalytic rate which is dependent on the material type.



Figure 2.7: The catalytic efficiencies for different materials exposed to atomic oxygen or nitrogen. [14]

2.3.2.2 Tertiary Gas Mixture

In 2013 Park [15] extended Goulard's theory for a tertiary gas mixture where there is not only the atomic and molecular particles of a gas but also a third (inert) gas species. Park follows the same assumptions as Goulard which can be summarized as:

- Thermochemical equilibrium at the boundary layer edge.
- Frozen flow inside the boundary layer.



Figure 2.8: The reduced heat transfer against a range of catalytic rates. [14]

- Chapman-Rubesin constant is equal to 1 across the boundary layer, i.e. $l = \frac{\rho\mu}{\rho_e\mu_e} = 1$.
- Constant Prandtl number and Schmidt number across the boundary layer.

Moreover, the subscript convention of Goulard and Park differs slightly. Goulard denotes e as outside the boundary layer and se as the boundary layer edge at the stagnation point, whereas Park uses efor the boundary layer edge. Park also denotes the atomic particles, molecular particles, and the inert particles as 1, 2 and 3 respectively. In the derivation of Park, it has been assumed that z'_3 is equal to zero which corresponds to a chemically inert gas. Moreover, it is also assumed that the coefficient of self-diffusion D_{ii} is equal to zero which neglects the diffusive effects of each species on themselves.

By following the same assumption as Goulard [14], Park [15] derived again the dimensionless concentration at the wall:

$$z(0) = \frac{1}{\sqrt{\frac{\mu_e \rho_e}{2\beta} \frac{k_w}{\phi_{2m} \rho_w D_{w21}} + 1}}$$
(2.21)

Compared to Eq. (2.17) the difference is rather small: instead of having " $0.47Sc^{1/3}$ " there is " $\frac{m_2}{\phi_3 m}$ " where ϕ_3 is defined as:

$$\phi_3 = \int_0^\infty \left[\frac{f''(\eta)}{f''(0)}\right]^{\frac{m}{m_1}\frac{Sc_{12}Sc_{31}}{Sc_{32}}} d\eta$$
(2.22)

For a binary gas mixture a numerical value for ϕ_3 was available for air (i.e. $\frac{1}{0.47Sc^{1/3}}$) hence this value was substituted. For a tertiary gas mixture such numerical value is not available hence ϕ_3 has to be calculated using Eq. (2.22).

Using Eq. (2.21) and the assumption of a constant Schmidt number across the boundary layer, Park presented the conductive and diffusive heat flux respectively as:

$$q_C = 0.47 \sqrt{2\beta\mu_e\rho_e} \overline{Pr}_w^{-2/3} \overline{h}_e \tag{2.23a}$$

$$q_D = \chi \sqrt{2\beta \mu_e \rho_e h_R \alpha_{e1} \varphi_2} \tag{2.23b}$$

A similar correction factor as Goulard's (Eq. (2.19)) is also present in this equation defined as:

$$\varphi_2 = \frac{1}{1 + \frac{\chi\sqrt{2\beta\mu_e\rho_e}}{\rho_w k_{w1}}} \tag{2.24}$$

In addition to that, Park gathered several parameters in a variable parameter χ to ease the comparison with the equations for a binary gax mixture:

$$\chi = \frac{1}{\phi_3} \frac{m_2}{m} \frac{1}{Sc_{21}} \tag{2.25}$$

From these equations it can be seen that for a binary gas mixture χ corresponds to $0.47 Sc^{1/3}$.

Park [15] presented in his paper a comparison between the dimensionless concentration at the wall using the assumption of both a binary and tertiary gas mixture. In his work where he considered a test gas consisting of 21% oxygen and 79% argon it was concluded that the difference is small as can be seen in Fig. 2.9. At lower catalytic efficiencies there is no difference between the two theories, whereas at higher values there is a slight difference.



Figure 2.9: The comparison between the dimensionless concentration at the wall (z(0)) between a binary and tertiary gas mixture for a test gas consisting of 21% oxygen and 79% argon. [15]

2.4 The Flow Conditions at the Stagnation Point

In the previous sections the diffusive heat transfer and catalycity have been discussed. The influence of these phenomena differs per location on the hypersonic vehicle during re-entry. At the stagnation point the high-temperature effects are the most prominent since the flow technically comes to an halt there, hereby inducing all of its kinetic energy to the body. For this reason the stagnation point situation is considered here. This is also in line with the theory that has been discussed in Section 2.3.

The theory discussed in Section 2.3 requires a large number of variables which have to be determined. To accomplish this it is necessary to understand the situation at the stagnation point better which will be discussed in this section. This section consists of two parts: first the general situation at the stagnation point is discussed together with the assumptions that can be made, afterwards the method of determining the flow conditions at the boundary layer edge is presented.

2.4.1 Standing Shock and Boundary Layer

The shape of the shock wave induced by an object traveling faster than the speed of sound, depends on the geometry of the object: a sharp nose causes a sharp shock whereas a blunt body induces a bow shock. It is this shock wave that increases the enthalpy to such an extent that the air molecules dissociate. The sharp nose situation is not discussed further since it is not relevant for the present investigation.

For a blunt nose the bow shock stays at a finite distance from the wall. For spherical shapes, especially at the stagnation point, this distance is rather small, whereas for a flat-disk cylinder the distance is relatively larger. In Fig. 2.10 the bow shock is shown for both a spherical and flat-disk cylinder model. While various body diameters are investigated, the average shock stand-off distance for a spherical model (Fig. 2.10(a)) is only half of the distance corresponding to the flat-disk cylinder model (Fig. 2.10(b)).

This larger shock distance is necessary for the existing theory that has been discussed in Section 2.3. One of the main assumptions in that theory is thermochemical equilibrium at the boundary layer edge located between the standing shock and the wall, as illustrated in Fig. 2.11. This basically means that the dissociation has been completed when the particles reach the boundary layer edge. To reach this equilibrium, the distance between the standing shock and the boundary layer edge should be sufficiently large, which has a higher probability to be achieved using a flat-disk cylinder model.

In order to make sure that this distance is sufficiently large to ensure thermochemical equilibrium, the conditions between the standing shock and the wall have to be calculated. It is however challenging to determine this accurately at every location at the stagnation point. A method is introduced in Appendix A where a collection of assumptions has been made to attain some first order approximations. While this is a preliminary method it is possible to determine the variation of the flow parameters with respect to distance.



(a) The standing shock in front of a sphere at various (b) The standing shock in front of a flat-disk cylinder at body diameters indicated by the different symbols. [24] various body diameters indicated by the different symbols. [24]

Figure 2.10: The difference in standing shock distance between a sphere and a flat-disk cylinder at the same flow condition.



Figure 2.11: The standing shock wave and the boundary layer around the model.

There is however a more accurate method to determine the conditions at the boundary layer edge. This method relies on the thermochemical equilibrium assumption and cannot show the variation of the flow parameters with respect to the distance. The bow shock is interpreted as a normal shock wave at the stagnation point. Through this shock wave the total enthalpy is assumed to be constant since the flow is adiabatic. Using the known quantities before the standing shock (called region 2) this total enthalpy can be determined:

$$H_2 = h_2 + \frac{1}{2}u_2^2 \tag{2.26}$$

The boundary layer is assumed to be frozen, which means that the reaction rates within this layer is zero which corresponds to a constant chemical composition. This assumption implies that the recombination of the atoms occurs at the wall. A catalytic wall will result in a higher number of successful recombinations compared to a non-catalytic wall.

Since the static enthalpy (h_2) and the flow velocity (u_2) can be determined using numerical programs (for shock tubes), it is possible to determine the total enthalpy. Moreover, since the pitot pressure can also be determined by such numerical programs, the total pressure is known. It is however necessary to assume that the total pressure through the boundary layer is constant.

2.4.2 Conditions at the Boundary Layer Edge

At the boundary layer edge there is a gas mixture between atoms and molecules of all the present gas species. The exact composition of this gas is necessary to determine the remaining flow parameters, since until this stage only the total enthalpy and the total pressure are known (as discussed at the end of the previous section).

Traditional perfect gas relations will yield inaccurate results since the fundamental assumption of a perfect gas has been violated. To acquire the remaining thermodynamic gas properties such as temperature, density, and the composition of the gas, the concept of partition functions is used which originates from the field of statistical mechanics. To understand this concept the theory of quantum numbers is discussed.

2.4.2.1 Quantum Numbers

The basic structure of an atom is well known: it consists of a nucleus and electrons orbiting around it. For such a seemingly simple structure it is however challenging to determine the location of a electron at a certain moment, hence it is more common to express it in a probability by means of a wave function. The differential equation which governs this wave function and is derived from energy conservation is called the Schrödinger equation. The exact form and derivation of this equation is beyond the scope of this thesis, however in summary it makes sure that the sum of kinetic and potential energies of all particles is preserved.

There are three sets of eigenvalues of the Schrödinger equation [12]:

- 1. Principal quantum number, n: The orbit of the electron around the nucleus. The first orbit (n = 1) is denoted as K-shell followed by L-shell (n = 2) etc.
- 2. Angular momentum quantum number, l: The angular momentum of the electron which is numbered with integers starting from zero. These orbits can also be referred to by the letters s, p, d, f, g, h, etc. While the principal quantum number dictates the distance between the electron and the nucleus, the angular momentum quantum number controls the shape and the orientation of the orbit.
- 3. Spin quantum number, s: The spin of the electron which can either be 0.5 (the spin is aligned with the angular momentum) or -0.5 (the spin is opposite to the angular momentum).

Each electron has its own combination of these quantum numbers. According to the Pauli exclusion principle it is impossible to have two electrons in an atom or molecule with the same combination of these three quantum numbers; hence they cannot occupy the same orbit. [19]

For all atoms the energy levels are known and available in the NIST Atomic Spectra Database. [25] The first four levels of atomic nitrogen are shown as an example in Table 2.1. The first level is the ground state and functions as a reference for all the other levels. In Fig. 2.12 the nomenclature of the configuration is explained. As can be seen the number before the letter refers to the principal quantum number and the superscript refers to the number of electrons. Since the most inner electrons $(1s^2)$ never changes, they are omitted by NIST from the table. [12]

Combining Table 2.1 with Fig. 2.12 it is clear that the electrons occupy the first and second orbits for the first three levels; only at the fourth level an electron has moved for the 2p orbit to the 3s orbit. To reach this state, energy has to be applied to the electron hereby increasing its energy level.

Configuration	Term	J_i [-]	Level $[\mathrm{cm}^{-1}]$
$\frac{2s^22p^3}{2p^3}$	$^4S^{\circ}$	$\frac{3/2}{3/2}$	0.000
$2s^2 2p^3$	$^{2}D^{\circ}$	5/2	$19\ 224.464$
1		3/2	19 233.177
$2s^22p^3$	$^{2}P^{\circ}$	1/2	28 838.920
1		3'/2	28 839.306
$2s^22p^23s$	^{4}P	1/2	83 284.070
1		3'/2	83 317.830
		5/2	83 364.620
		/	
		C (2) (2) (2) (2) (2) (2)	

Table 2.1: NIST Atomic Spectra Database levels data for the first four levels of atomic nitrogen. [25]



Figure 2.12: The meaning of the electron configuration.

The second column in the table represents the angular momentum quantum number together with the spin and is not essential for the overall understanding of this thesis topic. For this reason it will not be further discussed.

What is essential to understand is the third column which consists of values for the total electronic angular momentum quantum number (J). This is used to determine the statistical weight (g) which has an important role in the computation of partition functions. [12]

The configurations with more than one total electronic angular momentum quantum number (J) have to be combined. The energy values (denoted by i) are averaged using the statistical weight and the total statistical weight is simply the summation:

$$g = \sum_{i} (2J_i + 1) \tag{2.27}$$

Hence for the second energy level this would result in g = 10 and an energy of 19227.95 cm⁻¹.

For molecules there is a similar system. However, instead of covering the atomic behavior, this data covers the vibrational and rotational behavior of the molecule. From the NIST Chemistry WebBook [26] the parameters of molecular nitrogen have been presented in Table 2.2 for the first three levels. The electronic states of L=1, 2, 3, etc. have changed from s, p, d to Σ , Π , Δ , etc. The superscript in front of this is an indication of the statistical weight (g). For Σ states the indicated number is equal to the statistical weight, for all other states this number has to be doubled.

Moreover, the letter in front of this symbol is an designator for the most famous states. The remaining super- and subscripts are not of importance for this thesis topic hence will not be discussed.

Table 2.2 shows the parameters that are essential to determine the partition functions for molecules. The second column (T_e) represents the energy of that particular level. Moverover, three vibrational constants are shown as ω_e , $\omega_e x_e$, and $\omega_e y_e$, together with four other parameters $-B_e$, α_e , D_e , $and\beta_e$ – representing the rotational constants. The last entry is the internuclear distance (r_e) . [26] To understand how these variables are used, it is necessary to present the theory and equations of partition functions.

Table 2.2: The NIST Chemistry WebBook data for the first three levels of molecular nitrogen. [26]

State	$T_e [\mathrm{cm}^{-1}]$	ω_e [-]	$\omega_e x_e$ [-]	$\omega_e y_e$ [-]	B_e [-]	α_e [-]	D_e [-]	r_e [Å]	β_e [-]
$X^1\Sigma_q^+$	0	2358.57	· 14.324	$-2.26 \cdot 10^{-3}$	1.99824	0.017318	$5.76 \cdot 10^{-6}$	1.09768	0
$A^3 \Sigma_u^{+}$	50203.6	1460.64	13.87	0.0103	1.4546	0.0180	$6.15 \cdot 10^{-6}$	1.2866	0
$B^3\Pi_g$	59619.3	1733.39	14.122	-0.0569	1.6374	0.0179	$5.9 \cdot 10^{-6}$	1.2126	0



2.4.2.2 Partition Functions

Having discussed the quantum numbers it is now possible to focus on the concept of partition functions. Partition functions are used to determine how the particles are partitioned among the energy groups. [12] Electrons do not necessarily have to stay in the lowest orbits but can be excited to higher orbits or to an orbit with a different shape or orientation.

There are in total four groups of partition functions: electronic, translational, vibrational, and rotational. [12, 19]

• *Electronic partition function:* This focuses on the internal energy of a particle. The mathematical expression is given by:

$$Q_{el} = \sum_{j} g_j e^{-\frac{E_j}{kT}} \tag{2.28}$$

From this equation several parameters can be recognized: the statistical weight (g) and the energy of each electronic state (E). By summing this for all the energy levels the electronic partition function can be determined.

• *Translational partition function:* The translational energy of a particle is covered by this partition function which is mathematically expressed as:

$$Q_{tr} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \tag{2.29}$$

In this equation the only value that depends on the type of particle is the mass.

• Vibrational partition function: The vibrational energy of a particle is included in this partition function which is only present in molecules. For atoms this value is equal to zero. Using the three vibrational constants (ω_e , $\omega_e x_e$, $\omega_e y_e$) shown in Table 2.2 the vibrational energy level can be computed depending on the fundamental vibrational frequency (v) using:

$$G(v) = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \omega_e y_e \left(v + \frac{1}{2}\right)^3$$
(2.30)

These energy levels can then be used to determine the vibrational partition function as shown by:

$$Q_{vib} = \sum_{v} e^{-\frac{G(v)}{kT}} \tag{2.31}$$

• Rotational partition function: The rotational energy of a particle is taken care of by this partition function which is also only present in molecules. Part of the entry values shown in Table 2.2 is required for the computation of this partition function (i.e. B_e , α_e , D_e , β_e). As can be seen in Eq. (2.32) the vibrational frequency is required, which indicates the coupling between the vibrational and rotational energy, to determine the rotational energy. Please note that the J is the rotational quantum number in this equation.

$$F(J) = BJ(J+1) - DJ^{2}(J+1)^{2}$$

where $B = B_{e} - \alpha_{e}(v + \frac{1}{2}); D = D_{e} + \beta_{e}(v + \frac{1}{2})$ (2.32)

The rotational partition function can then be determined using:

$$Q_{rot} = (2J+1)e^{-\frac{F(J)}{kT}}$$
(2.33)

The vibrational and rotational partition functions are tackled together due to their entanglement. The maximum rotational quantum number, depending on the potential curve of a energy level of the molecule, is hereby determined. The vibrational-rotational partition number can then be determined:

$$Q_{vib,rot} = \sum_{v} \left(Q_{vib} \sum_{J} Q_{rot} \right)$$
(2.34)

The translational and electronic partition numbers can also be included in a similar way as expressed by:

$$Q_{molecule,tot} = Q_{tr} \sum_{j} Q_{el} \left[\sum_{v} \left(Q_{vib} \sum_{J} Q_{rot} \right) \right]$$
(2.35)
The resulting partition function of a molecule is dependent on the temperature. By taking the derivative of the total partition function with respect to temperature, the internal energy can be determined [12, 19]:

$$\epsilon = kT^2 \frac{d}{dT} \left[\ln(Q_{molecule,tot}) \right]$$
(2.36)

For an atom the electronic and translational partition functions are multiplied in the same form as Eq. (2.35) and the total internal energy can also be determined as in Eq. (2.36). Adding the internal energy of all these particles together results in the internal energy of the whole gas mixture. This can then be used to acquire the specific heat at constant volume [19]:

$$c_v = \left(\frac{\partial e}{\partial T}\right) \tag{2.37}$$

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In case of dissociation the number density can also be determined using partition functions [12] as expressed by:

$$\frac{n_{atom1}n_{atom2}}{n_{molecule}} = \frac{Q_{atom1,tot}Q_{atom2,tot}}{Q_{molecule,tot}} e^{-\frac{D_0}{kT}}$$
(2.38)

In this expression the molecule consists of atom 1 and atom 2 which are separated due to dissociation.

At this point it is clear that the concept of partition functions tackles a problem from a real gas perspective. The specific heat ratio (γ) is not constant and is changing depending on the temperature and the gas composition.

By applying this to the situation at the boundary layer edge, and together with the known total enthalpy and total pressure (Section 2.4.1), it is possible to determine the temperature, density, and other flow parameters.

Experimental Research in Catalycity

In Chapter 2 the effect of catalycity on the heat flux has been explored. This was followed by the theories that are available regarding catalycity. To utilize these theories the catalytic efficiency has to be known. In the past this has been determined by different researchers using a variety of experimental facilities for a wide range of materials and gases.

The first three sections will discuss the facilities that are typically used: the side-arm reactor, shock tube/tunnel, and arc-jet. Section 3.4 then focuses on the application of copper slug calorimeters in arc-jets. In this section the current problems and uncertainties of these calorimeters are discussed which forms the direct motivation for this thesis project.

3.1 Side-arm Reactor

The side-arm reactor is one of the first facilities used to study the catalytic behavior of different materials and was widely used in the 1950s and 1960s. This facility consists of a quartz tube which is connected to a gas supply at one side and a vacuum pump at the other end. A "side-arm" (i.e. a second tube) is connected perpendicular to the quartz tube near the vacuum pump. A plasma generator (e.g. high frequency coils) is attached to the quartz tube which dissociates and ionizes the gas into a plasma.

When this plasma passes the side-arm, it diffuses towards the specimen that is located inside. By measuring the amount of dissociated atoms before and after the specimen, the amount of recombined atoms is determined from which the catalytic efficient is calculated. Several methods can be used to measure the amount of dissociated atoms: mass spectroscopy, laser induced fluorescence, Piranimanometer, and more. [17]

In Fig. 3.1 the side-arm reactor is shown that was used by Greaves and Linnett in 1959 [27, 28] and a similar configuration was used by Linnett and Marsden in 1956 [22, 23]. Greaves and Linnett [27, 28] experimentally determined the catalytic efficiency of a large number of materials when exposed to oxygen. A selection is shown in Table 3.1. A lot of these values from Linnett et al. have been used by Goulard [14] to make Fig. 2.7.



Figure 3.1: The side-arm reactor used by Greaves and Linnett in 1959. [27]

Material	γ [-]
Gold	$5.2 \cdot 10^{-3}$
Silver	$2.4 \cdot 10^{-1}$
Magnesium	$2.6 \cdot 10^{-3}$
Nickel	$2.8 \cdot 10^{-2}$
Iron	$3.6 \cdot 10^{-2}$
Copper	$1.7 \cdot 10^{-1}$
Boric oxide	$6.3 \cdot 10^{-5}$
Aluminium oxide	$2.1 \cdot 10^{-3}$
Lead oxide	$6.3 \cdot 10^{-4}$
Magnesium oxide	$2.5 \cdot 10^{-2}$
Ferric oxide	$5.2 \cdot 10^{-3}$
Nickel oxide	$8.9 \cdot 10^{-3}$
Cupric oxide (CuO)	$4.3 \cdot 10^{-2}$
Zinc oxide	$4.4 \cdot 10^{-4}$
Silicon oxide	$1.6 \cdot 10^{-4}$

Table 3.1: Catalytic efficiencies for various materials at room temperature exposed to oxygen. [27, 29]

On the other hand, Linnett and Marsden [22, 23] investigated the catalytic efficiency for a glass surface at elevated temperatures. Using heating elements the temperature of the sample could be increased which showed an increase in the catalytic efficiency, as presented in Fig. 3.2. For this reason it is important to know the temperature of the material when comparing catalytic efficiencies.



Figure 3.2: Catalytic efficiency variation with wall temperature. [22]

Although the focus of most research has been done using oxygen, also nitrogen has been used in side-arm reactors. In 1971 Rahman and Linnett [30] did research on a range of metal surfaces which results are summarized in Table 3.2. The same setup as for the oxygen cases has been used.

Table 3.2: Catalytic efficiencies for various metals at room temperature exposed to nitrogen. [30]

Material	γ [-]
Silver	$2.4 \cdot 10^{-1}$
Nickel	$6.7 \cdot 10^{-5}$
Iron	$2.1 \cdot 10^{-3}$
Copper	$6.8 \cdot 10^{-2}$

Another very similar facility to the side-arm reactor is the diffusion tube. Instead of having a side-arm the diffusion simply takes place in the main tube. This will not be further discussed since it works on the same principle as the side-arm reactor.

The use of side-arm reactors however brings significant uncertainties that may affect the results. This is caused by the side-arm through which the dissociated flow diffuses. When the flow turns around the corner it is prone to become less steady. Increasing the length of the side-arm could solve this problem but due to the added length a lot of the atoms will be recombined.

To investigate catalytic materials it is important to have a sufficient amount of dissociated atoms in order to be able to measure the differences in front and behind the specimen. In order to achieve a high amount of dissociation some researchers, such as Dickens and Sutcliffe [31], added traces of water vapor to the gas. It is suspected that the increase of molecular weight due to the water vapor is causing this increase in dissociation. However, a disadvantage of this method is the contamination of the test gas.



3.2 Shock Tube/Tunnel

During the 1960s not only side-arm reactors were utilized for catalycity research. In 1966 Reddy [32] used catalytic probes to measure the atom concentration in a hypersonic flow using a shock tunnel. A shock tunnel consists of a driver and driven section which is connected by a nozzle and a test section (and a dump tank). With this facility Reddy was able to reach high enthalpies. Shown in Fig. 3.3(a) are the driver and driven sections. The driven section is then connected to a nozzle system illustrated in Fig. 3.3(b).



(a) The driver and driven tube of the shock tunnel.

(b) The nozzle system connected to the driven tube of the shock tunnel.

Figure 3.3: The shock tunnel used by Reddy [32] for his catalytic research of oxygen on silver oxide.

The shock tunnel used by Reddy is fired using an active way. The driver section is filled with a stoichiometric mixture of hydrogen and oxygen which is diluted with helium. A tungsten wire suspended along the centerline of the tube is heated instantaneously to ignite the gas mixture. Different types of stainless steel diaphragms were used to control the bursting pressure. After bursting, a primary shock wave travels from the diaphragm into the driven section.

Inside the driven section the test gas (i.e. oxygen) is located. After the primary shock hits the test gas, the temperature and pressure increase instantaneously. Moreover, the gas propagates in the same direction as the shock. Thereafter, the gas enters the nozzle and accelerates to a Mach number between 15 and 17. Then it enters a test section with a probe that holds thin-film gauges using which the temperature change resulting from the stagnation heat flux is measured.

The thin-film gauges used by Reddy had a small strip of platinum with a known resistance. This resistance changes as a function of temperature, hence by flowing a constant current through the platinum the voltage change is measured which represents the temperature change. Reddy derived a relation between the heat transfer and this voltage change to acquire the heat flux.

The gauges were first coated with a 1000 nm thick layer of silicon monoxide followed by a 200 nm layer of silver. This silver was converted to silver oxide by running the shock tunnel several times so it would be exposed to oxygen. It was believed that silver oxide is responsible for the surface recombination of oxygen rather than silver.

The catalytic efficiency determined by Reddy was 0.81 for a axisymmetric probe and 0.89 for a two-dimensional probe, which are shown in Fig. 3.4.

Not only for oxygen the shock tunnel was used. In 2008 Maclean and Holden [33] performed experiments using nitrogen, air and carbon dioxide on stainless steel. The enthalpy was varied from 5 to 15 MJ/kg and a variety of test models were used: axisymmetric spherical capsule, axisymmetric spherical cone, and a two-dimensional cylinder. The catalytic efficiency found for nitrogen was in the order of 10^{-3} whereas for both air and carbon dioxide the catalytic efficiency was found to be infinitely large (i.e. super-catalytic). It was acknowledged by Maclean and Holden that the excessive catalytic efficiencies are not correct and are caused by the lack of sufficient understanding of the freestream and shock-layer state of the gas.

The result and conclusion of Maclean and Holden [33] is a clear example of a large disadvantage of using a shock tunnel. The dissociated flow in the driven section is further accelerated to higher Mach numbers in the nozzle. During this acceleration recombination can occur which alters the species concentration that reaches the model. Due to the many unknowns in the process, it is complicated and therefore inaccurate to determine the exact amount of recombination.

Reddy [32] tried to minimize this effect by having a flow condition such that the gas would have a low pressure and a high temperature, after it is being hit by the primary shock wave. In this condition the gas is assumed to be frozen when it travels through the nozzle, hence a significant amount of dissociated species reaches the test section.

In order to overcome the problem of dissociation in the nozzle, a shock tube can be used. Consisting of only a driver and driven tube (and potentially a dump tank) it is however not able to reach as





Figure 3.4: The axisymmetric (upper) and two-dimensional probe (lower) used by Reddy. [32]

high Mach number and enthalpies as using a shock tunnel. However, the simplicity of this facility makes it possible to more accurately control the flow the model experiences.

In 2013 Park [15] utilized a shock tube for this purpose. The goal of the research was to find the catalytic efficiency of oxygen on copper oxide (and copper). The enthalpy of the flow ranged from 1.92 to 4.24 MJ/kg, which is significantly lower than for the shock tunnel used by Maclean and Holden [33]. In order to achieve a high amount of dissociation in the flow the oxygen was mixed with argon which is an inert gas. Since argon does not dissociate, less energy is needed to elevate its temperature. Moreover, the inert gas increases the molecular weight of the gas mixture which slows down the shock speed, hereby having a slightly positive effect on the test time. Also, the total pressure increases significantly – while the total enthalpy drops slightly – which increases the amount of dissociation.

The consequence of this change from a binary gas mixture (O - O₂) to a tertiary gas mixture (O - O₂ - Ar) was that the theory had to be rewritten which was presented in Section 2.3.2.2. The heat flux is measured using a similar method as Reddy [32]. With the aid of thin-film gauges coated with a 500 nm thick layer of silicon dioxide and a layer of 180 nm copper oxide the heat flux was determined experimentally. The same has been repeated for copper, however, only one shot was successful. The catalytic efficiency determined by Park [15] for copper oxide was $2.6 \cdot 10^{-3}$ to $3.2 \cdot 10^{-3}$ and for copper $1.6 \cdot 10^{-2}$.

3.3 Arc-jet Facility

The third major group of facilities that are used to investigate catalycity are arc-jets. These facilities use an electric discharge (an arc) to accelerate the flow to high velocities (i.e. supersonic freestream [34, 35]) at high temperatures (i.e. several thousands Kelvin). This is achieved using two direct current power supplies, vacuum system, cooling system, high pressure gas system, and some other additional systems to operate the arc-jet. A schematic of an arc jet complex is shown in Fig. 3.5.

The two electrodes are connected to the direct current power supply and this creates an electric discharge which converts the gas to a plasma. This plasma consists of dissociated and potentially ionized particles, which is accelerated through the nozzle towards the model. Arc-jets are capable of providing test times in the order of seconds, minutes or even as long as an hour. An illustration of a specimen being testing in an arc-jet is shown in Fig. 3.6.

In 1973 Anderson [34] utilized three different arc-jets at the NASA Ames research center, each with a different range in total enthalpy ranging from 3.2 MJ/kg to 120 MJ/kg, to investigate the catalytic



Figure 3.5: The working principle of the arc jet complex at NASA Ames Research Center. [36]



Figure 3.6: Material being tested in an arc-jet at the NASA Ames Research Center. [36]

efficiencies of several materials when exposed to nitrogen. For a limited amount of cases also air was tested.

Both flat face and hemisphere models were used, as shown in Fig. 3.7. With the aid of slug calorimeters mounted at the center of the models, the heat flux was measured. Using Goulard's theory (Section 2.3.2.1) the catalytic efficiency was determined. Different coatings were applied on top of the samples (nickel, platinum, gold, chromium, copper, and silicon dioxide).

The catalytic efficiency results of Anderson [34] are shown in Fig. 3.8. Not only the different surface materials show a different value, also increasing the temperature of the model results in a change.



Figure 3.7: The models used by Anderson for arc-jet experiments. [34]

The high enthalpy and temperature that can be reached using an arc-jet, make it possible to find catalytic efficients of thermal protection materials which is relevant for re-entry vehicles. The total enthalpy and long test time that can be reached using an arc-jet surpasses the capabilities of a side-arm reactor or shock tube/tunnel. Pidan et al. [35] used in 2005 an arc-jet to produce a 34 MJ/kg flow to test sintered silicon carbide (SSiC) when exposed to dissociated oxygen. A double probe was used to measure the heat flux using a calorimeter and the pitot pressure sensor, shown in Fig. 3.9.

While an arc-jet is a formidable facility to achieve a high temperature, a high enthalpy, a high Mach number, and a long test time, it is not capable of simulating the pressure that is experienced during re-entry. The freestream static pressure in an arc-jet is in the order of several tens or hundreds pascals (e.g. Pidan et al. [35] reported 40 Pa and one of world's most powerful arc-jet SCIROCCO [37] can reach 290 Pa). This makes it impossible to properly mimic the stagnation pressure in real flight, which results in an inaccurate catalytic efficiency when used in Goulard's theory (Eq. (2.18)-(2.20)) since the Schmidt number might be incorrect.

Facility	·Figure number	Calorimeter	Gas	Total enthalpy, H _{es} Mjoules/kg	Surface material	k _w m/sec	$^{T_w}_{^{w}}$ °K	γ,
I, II	6	Hemisphere $R/D = \frac{1}{2}$	Air, and air with	$3.2 < H_{es}$	Ni, Pt, Cr, Au	17	400 ± 100	0.09
		Blunted $R/D = 4$	1% CO ₂	$H_{es} < 20$	SiO ₂	k _w < 1.00	400±100	0.001
п	7a	Hemisphere	Nitrogen	$12 < H_{ex}$	Au	12	500 ± 150	0.06
		$R/D = \frac{1}{2}$		$H_{rs} < 42$	SiO ₂	$k_2 < 1.00$	500 ± 150	0.001
				$12 < H_{es}$	Ni, Cr, Pt, Cu	22	500 ± 150	0.10
II	7b	Blunted	Nitrogen		Au	12	500 + 150	0.06
		R/D = 4		$H_{es} < 42$	SiO ₂	$k_w < 1.00$	500 ± 150	0.001
III	8a	Blunted	Nitrogen	$42 < H_{ss}$	Ni, Cr, Pt, Cu	120	1000 ± 200	0.4
		R/D = 4		$H_{es} < 120$	SiO ₂	$k_w < 1$	1000 ± 200	0.001
III	8b	Hemisphere ^a $R/D = \frac{1}{2}$	Nitrogen	$42 < H_{es}$	Au	4	1000	0.001
		Blunted $R/D = 4$		$H_{es} < 120$	Au	13	$>1000\pm200$	0.04

Figure 3.8: A copy of Anderson's paper [34] showing his catalytic efficiency results.



Figure 3.9: The double probe used by Pidan et al. [35] to measure the heat flux and pitot pressure.

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Moreover, since the electric current that discharges the flow cannot be continuous, the flow properties are fluctuating over time. This non-uniform flow is highly undesired and gives uncertainties in the actual flow conditions. Pobst et al. [38] noted that for a 1 kW arc-jet the temperature could fluctuate between 4950 K and 6000 K.

Due to the harsh environment in which the specimen is placed the composition of the material can change. Metals may for example oxidate which changes the catalytic efficiency completely. It was noticed by Park [39] in 2006 that the surface of copper calorimeters discolored after have being used in an arc-jet.

In 2013 Nawaz et al. [40] confirmed that exposing the copper calorimeters to a flow inside an arc-jet for only 2-3 sec is sufficient to create an oxidized layer, this is shown in Fig. 3.10. The oxide layer causes the red color, hence a darker red color corresponds to a thicker layer. It was noted by Nawaz et al. [40] that even though the slug used at 5 MJ/kg does not show any color change, after XPS analysis it was found that oxidation has taken place.

Another effect that is linked to the occurrence of oxidation is the increase in roughness of the surface. As explained in Section 2.2.3 the roughness may have a significant effect on the catalytic efficiency. Since the samples are exposed to the harsh environment for a long time the surface is prone to roughen.



Figure 3.10: Copper slugs used in the calorimeters before and after arc-jet experiments. [40]

3.4 Usage and Uncertainties of Copper Calorimeters in Arc-jet Facilities

In Section 3.3 copper calorimeters have been mentioned on several occasions. In this section the concept of a slug calorimeter will be discussed together with the application in arc-jet facilities. From this the uncertainties and problems will be discussed that arises in an arc-jet. Section 3.4.3 then focuses on the catalytic efficiencies of copper and copper oxide from which the main reason for this master thesis project arises.

3.4.1 Concept of Copper Slug Calorimeter

A slug calorimeter is used to determine the heat transfer rate to the surface by measuring the time rate of the temperature change. [41] The temperature is measured using a thermocouple junction which is mounted to a slug. The voltage change across the two metals in the thermocouple is measured. [39] Typically the slug is thin to approach the thin-skin approximation where there is no significant temperature gradient across the slug. Moreover, it is also necessary to use a highly conductive material as slug to minimize the temperature gradient. The basic concept of a slug calorimeter is shown in Fig. 3.11.

Copper is a common material used for the slugs due to its highly conductive properties and its low price. Examples of copper slugs are shown in Fig. 3.10.

The temperature measurements can be converted to heat flux using [41]:

$$q_s = \rho c l \frac{dT}{dt} \tag{3.1}$$

where the density (ρ) , specific heat (c) and the length (l) of the slug are required.

Copper calorimeters are mostly applied in arc-jet facilities to determine the centerline enthalpy which will be discussed more in the next section. This is possible because arc-jets have a run time in the order of seconds, sufficient to conduct the heat through the copper slug. These calorimeters are however not suitable for impulse facilities such as shock tube or shock tunnel due to the short run time.





Figure 3.11: Copper calorimeter used by Park et al. [39] to measure the heat flux.

3.4.2 Measurement of Centerline Enthalpy of Arc-jet

In an arc-jet the enthalpy is an important parameter to properly determine the flow condition a sample experiences. Such a sample could for example be a panel of a re-entry vehicle. The enthalpy is higher at the centerline of the nozzle compared to the nozzle walls. Since the sample is exposed to the flow from the centerline of the nozzle, it is necessary to determine this accurately. In general there are several ways to determine the centerline enthalpy: [39]

- Mass-averaged enthalpy measurement, heat balance method: The total power is determined by subtracting the cooling water loss from the electrical power input. The average enthalpy can then be determined experimentally by dividing the total power by the mass flow rate of the test gas. The centerline enthalpy is then assumed to be equal to the average enthalpy.
- Mass-averaged enthalpy measurement, sonic throat method: The average enthalpy is determined for air using [39]:

$$H = \left(\frac{0.293Ap_0}{\dot{m}}\right)^{2.519}$$
(3.2)

This method is based on the principle that the flow is choked at the throat of the nozzle. Also here the centerline enthalpy is assumed to be equal to the averaged enthalpy.

- Centerline enthalpy measurement, heat transfer method: This method is used to determine the stagnation point heat flux for a cold wall. The tool that is usually used for an arc-jet is a copper slug calorimeter, which had been discussed in Section 3.4.1. Using Goulard's theory (Section 2.3.2.1, Eq. (2.18) and (2.20)) the enthalpy can be determined. Hereby the catalytic efficiency is necessary. For copper it is usually taken to be equal 0.17 (Fig. 2.7).
- Centerline enthalpy measurement, spectrometric method: Using a spectrometer the radiation emitted from the shock layer is captured. This device is able to identify the wavelengths of which this radiation consists of, hereby making a spectra. The wavelengths with high intensities can be linked with certain species.

Using CFD a theoretical spectra can be made that is depending on the centerline enthalpy. By simply matching the theoretical spectra to the measured one the enthalpy can be found.

• Mass-averaged/Centerline enthalpy measurement, CFD: Using CFD the flow in an arc-jet can be simulated. With this it is possible to calculate both the mass-averaged and the centerline enthalpy. Since this is out of the scope of this thesis, it will not be discussed further. More literature can be found in the paper of Kim et al. [42].

While the heat balance method is in practice the easiest method, it yields large errors. Shown by Park et al. [39] the centerline enthalpy can be 1.41 times larger than the average enthalpy. On the other hand, the spectrometric method is considered to be a more accurate method to determine the centerline enthalpy. However, it requires an optical setup, a spectrometer, knowledge regarding the wavelengths of the species and CFD to reproduce the spectra.

Compared to the spectrometric method it is easier to use a copper calorimeter to determine the centerline enthalpy. However, for this the catalytic efficiency has to be known accurately. It was discussed in Section 3.3 that the copper oxidizes and roughens in the harsh environment of the arc-jet. This influences the catalytic efficiency and could yield inaccurate results. It was shown by Park et al. [39] that simply using $\gamma_w = 0.4$ (Fig. 2.7) which is the value of copper determined by Greaves and Linnett [29] using a side-arm reactor, the centerline enthalpy would only be 0.75 of the spectroscopically determined value.

Hence by assuming that the calorimeter is highly catalytic (i.e. copper) instead of moderately catalytic (i.e. copper oxide) would result in a lower centerline enthalpy. This underestimation of the environment could lead to the conclusion that a certain material that is tested in an arc-jet is less resistant than it actually is. This forces the engineers to choose for a more conservative design (e.g. increasing the thickness) than necessary.

3.4.3 Copper and Copper Oxide Catalytic Efficiency

From the previous section the importance of the catalytic efficiency of copper was discussed. Not only does this value depend on the composition of the copper (i.e. the amount of oxidation), the roughness of the surface, and the temperature of the surface, also the type of gas has an effect on the catalytic efficiency.

A significant amount of research has been conducted on the catalytic efficiency of copper and copper oxide, summarized in Table 3.3 which has been based mainly on the table made by Nawaz et al. [40]. It should be noted that several authors only mentioned "room temperature" in their papers. For these a temperature of 300 K has been taken. The values in the table are also shown graphically in Fig. 3.12 with the uncertainties – if they were noted by the authors.

In this table the distinction is made between the two types of copper oxides: cupric oxide (CuO) and cuprous oxide (Cu₂O). The former is black in color whereas the latter is red. This distinction is rather important since copper can oxidize in either of the two with different catalytic behavior as discussed by Nawaz et al. [40].

		A	$Test T_{wall}$	Es silitar	Veen	Authong	
γ_{Cu}	γCuO	Cu_2O	Gas [K]	Facility	rear	Authors	
0.17	0.02	-	$O_2 \ 300$	Side-arm Reactor	1958	Greaves, Linnett [29]	
-	0.043	-	$O_2 \ 300$	Side-arm Reactor	1959	Greaves, Linnett [27]	
-	0.045	0.11	$O_2 \ 300$	Side-arm Reactor	1964	Dickens, Sutcliffe [31]	
0.15	-	-	$O_2 \ 300$	Glow Discharge Tube ¹	1965	Hartunian et al. $[43]$	
0.063	-	-	$O_2 \ 300$	Effusion $Tube^2$	1967	May, Linnett [44]	
0.015	-	-	$O_2 \ 300$	Diffusion Tube	1971	Melin, Madix [45]	
-	-	0.025	$O_2 \ 313$	Side-arm Reactor	1998	Cauquot et al. [46]	
0.016	-	0.0026 - 0.0032	$O_2 \ 350$	Shock Tube	2013	Park [15]	
-	0.01	-	$O_2 \ 300$	Side-arm Reactor	2013	Nawaz et al. [40]	
0.03	-	-	$N_2 \ 314$	Diffusion Tube	1961	Prok [47]	
0.07	-	-	$N_2 \ 300$	Glow Discharge Tube ¹	1965	Hartunian et al. $[43]$	
0.08	-	-	$N_2 \ 350$	Arc-jet	1968	Pope [48]	
0.068	-	-	$N_2 \ 300$	Side-arm Reactor	1971	Rahmann, Linnett [30]	
0.10	-	-	$N_2 \ 500$	Anoiot	1072	Andongon [24]	
0.4	-	-	N_2 1000	Arc-jet	1975	Anderson [54]	
0.03	-	-	Air 350	Arc-jet	1968	Pope [48]	
0.01	-	-	Air 480	Arc-jet	2006	Park [39]	
-	0.01 - 0.03	-	Air 373	Arc-jet	2013	Nawaz et al. [40]	

Table 3.3: Summary of catalytic efficiencies of copper and two types of copper oxide (CuO and Cu₂O).

When considering the catalytic efficiencies of copper and copper oxide for oxygen in Table 3.3, it can be seen that there is a significant variation in the values. The values for copper show a variation up to one order of magnitude (Greaves, Linnett [29] vs. Park [15]), whereas for Cu₂O the variation can be even

 $^{^1}$ A glow discharge tube creates a discharge using high voltage and translates it towards the sample, similar to a diffusion tube.

 $^{^{2}}$ An effusion tube is similar to a diffusion tube but it has an orifice with openings smaller than the mean free path of the gas through which the gas has to effuse through.

two orders of magnitude (Dickens, Sutcliffe [31] vs. Park [15]). All these values are determined around 300 K.

This difference in catalytic efficiency could be explained by several reasons. First of all, the surface activation energy (E) of copper and copper oxide differ which influences the catalytic efficiency directly, as shown by Eq. (2.1). Moreover, the roughness which has a significant effect on the catalytic efficiency, is not the same for all cases shown in the table.

The copper oxide results of Park [15] is at least an order of magnitude smaller than all the other results, which could potentially indicate the inaccuracy of the values determined using facilities different than a shock tube.

The results of Park [15] using a shock tube indicates that the copper oxide catalytic efficiency – whether it is CuO or Cu₂O – has to be determined again using a shock tube, where the uncertainty on the roughness and composition is minimum. While it is desirable to determine this for air, it brings complications regarding the number of species that are present in the flow. Covering air not only includes the dissociation of oxygen, the dissociation of nitrogen, but also the coupling between the two (e.g. NO). This results in a mixture consisting of five or more species.

An important step towards this goal is to determine the copper oxide catalytic efficiency for nitrogen which has not be done before, as can be seen in Table 3.3. Having the catalytic efficiency of both oxygen and nitrogen separately, will function as a preliminary indication of the value belonging to copper oxide in air.



(c) Oxygen catalytic Efficiency.



Experimental Equipment

4

For this project the facilities at the Korea Institute of Science and Technology (KAIST) in Daejeon (Republic of Korea) are utilized. The goal of this chapter is to introduce the principles of a shock tube (Section 4.1) and the sensors used for the experiments (Section 4.2). With the basic understanding of the shock tube it is possible to investigate the effect of various gases in the driver and driven tube, which is valuable when choosing the flow conditions in Chapter 5.

Regarding the sensors a discussion is made to consider several options to measure the heat transfer rate. The thin-film gauge proves to be the ideal sensor for the experiments in the shock tube. Not only does Section 4.2 discuss the manufacturing procedure of a thin-film gauge, also the calibration and coating of the probes are covered. The coating of copper oxide introduced some difficulties which resulted in two variations of copper oxide coatings, referred as "black CuO" and "brown CuO".

This chapter ends with the shadowgraph setup which is used to perform flow visualizations (Section 4.3). The goal of the images is to visualize the shape of the standing shock, determine the shock stand-off distance, and to measure the shock radius at the stagnation point. These parameters are necessary in further calculations which will be discussed in Chapter 6.

4.1 Shock Tube

In Section 4.1.1 the characteristics of the shock tube are presented with a qualitative discussion of the working principles. This is then followed by the introduction of the test models and the test section. In Sections 4.1.3 and 4.1.4 fundamental calculations of the shock tube are presented based on a perfect gas to fully grasp the physics behind this facility. With the analytical equations presented in Section 4.1.4 a comparison is made between various gases used as driver and driven gas.

4.1.1 Shock Tube Characteristics

This approximately 4.65 m long tube consists of several parts: a driver tube, a transition piece, and a driver tube (Fig. 4.1), having respectively a length of approximately 0.80 m, 0.25 m, and 3.60 m. The driver and the driven tube have an internal diameter of 6.8 cm and 4.75 cm respectively. As shown in Fig. 4.2(a) the driver tube and the transition piece are separated by a 0.35 mm thick diaphragm made of polyethylene. The driver pressure can be doubled using two diaphragms pressed on each other.

A rotary pump is connected to both sides of the diaphragm by which a pressure below 8 Pa can be reached inside the tube. Followed by this, the test gas is introduced in the driven tube to the desired pressure. Consecutively the driver gas is allowed into the driver tube until the diaphragm burst due to the pressure difference between the driver and driven sections. Two piezo-electric pressure sensors are flush-mounted to the wall of the shock tube to not only measure the static pressure, but also the velocity of the primary shock at 3.45 m and 3.95 m, respectively. At the end of the driven tube the test section is located which will be elaborated upon in the next section.

The situation after the bursting of the diaphragm is shown in Fig. 4.2(b). The gas from the driver tube has moved to the driven tube section and pushes the test gas towards the model. A primary shock wave propagates through the test gas and compresses the gas. This is followed by a contact surface which forms the boundary between the driver and test gases. In the ideal case the test time ranges from the moment the primary shock wave reaches the model until the arrival of the contact surface, as indicated in the x-t diagram (Fig. 4.2(c)).

Some time is required for the flow to establish and to form a standing shock in front of the model. When the primary shock wave reaches the model it reflects locally at the surface, opposite to the flow





Figure 4.1: The shock tube of KAIST.



(a) Schematic of the shock tube before the rupture of the diaphragm.



(b) Schematic of the shock tube after the rupture of the diaphragm.



(c) The x-t diagram.

Figure 4.2: Schematic of the shock tube at KAIST before and after the rupture of the diaphragm.

direction. After a finite moment this reflective wave steadies and becomes a standing shock at a certain distance (i.e. shock stand-off distance) from the model.

4.1.2 Test Models and Test Section

Two different flat disk-cylinder models are utilized for the experiments. One model is used to flushmount the thin-film gauges (presented in Section 4.2) to measure the surface heat transfer rate at the stagnation point, whereas the other one is used to flush-mount a piezo-electric sensor to measure the stagnation pressure. Both models are made of stainless steel SUS 630.

The heat transfer model is shown in Fig. 4.3(a). It has a length of 15 mm, an outer diameter of 12 mm, and the edges have a fillet of 1.5 mm. The model can be attached to a 400 mm long sting with a diameter of 9 mm. This sting is then fixed to the end wall of the shock tube.

The pressure model is shown in Fig. 4.3. It is slightly larger with a length of 40 mm, an outer diameter of 20 mm, and the edges have a fillet of 3.0 mm. The sting is slightly thicker (14 mm) and is with 383 mm slightly shorter than the previous sting. Similar to the previous sting it can be attached to the end wall of the shock tube.



(a) The dimensions of the flat disk-cylinder heat transfer (b) The flat disk-cylinder pressure model used to mount model. [15] the piezo-electric sensor. [15]

Figure 4.3: The flat disk-cylinder model used to host the heat transfer gauge and pressure sensor.

As introduced in Section 2.4.1 it is necessary to have a model that induces a standing shock with a sufficiently large stand-off distance to comply with the thermochemical equilibrium assumption. A spherical model cannot fulfill this requirement while a flat-disk cylinder model does. This is verified by an analysis discussed in Appendix A.

The corner radius of a flat disk-cylinder model influences the stagnation point velocity gradient. By increasing the radius the gradient increases which results in a larger heat transfer rate as shown by Zoby and Sullivan [49]. However, increasing the radius too much would alter the general shape of the body to such a degree that the surface is no more flat. In practice the corner radius is taken to be a quarter of the body radius [50] which is also true for the heat transfer and pressure models presented in this section.

The test section of the shock tube is shown in Fig. 4.4(a). On each side two openings are located where sapphire windows can be placed. The diameter of the window ports is approximately 14.5 mm. In Fig. 4.4(a) the port is indicated and corresponds to the location which is used in the experiments. The presence of the windows allows the use of visualization techniques to capture the flow around the model, which will be elaborated in Section 4.3. In Fig. 4.4(b) a heat transfer model is located inside the test section seen through the window.



(a) The test section of the shock tube.

(b) The heat transfer model located inside the test section.

Figure 4.4: The test section located at the end of the shock tube.



4.1.3 Riemann Problem

In this section the situation inside the shock tube will be analyzed more closely for a perfect gas. These calculations are valid for flow conditions where the temperature is low enough that the molecules are not vibrationally excited.

The diaphragm bursts in a passive way by the pressure difference between the driver and driven tube. At this moment a shock wave is created starting from this diaphragm and compresses the test gas. While the test gas was initially at rest, this compression results in an acceleration of the flow in the direction of the test section. In the opposite direction of the diaphragm an expansion wave is created.

From the x-t diagram shown in Fig. 4.2(b) it can be concluded that it is a 1-D unsteady non-linear Riemann problem. The different regions are numbered from 1 to 4. Region 4 is located in the driver tube hence the pressure is a lot higher than in region 1 which is located in the driven tube. Because of the expansion wave traveling to the left the pressure will drop in region 4, expressed by the Poisson curve as shown in Fig. 4.5. In this figure it is also shown that because of the shock wave traveling into region 1 the pressure increases, expressed by the Hugoniot curve. The intersection of the two curves forms the situation of regions 2 and 3. [51]

As can be seen from this pressure-velocity diagram, the velocity increases when the gas travels from region 1 to 2 or from 4 to 3. Hence the pressure and velocities in regions 2 and 3 are the equal, but the densities, entropies and internal energies are different. This is caused by the different gases in the two regions.



Figure 4.5: Pressure-velocity diagram with the expansion and shock wave.

4.1.4 Quantitative Analysis of Shock Tube

In the previous section the situations in regions 2 and 3 have been described qualitatively. A quantitative analysis is presented in this section which is based on the equations presented by Glass and Patterson [52] to determine the four flow conditions in the shock tube. While Glass and Patterson also present equations for the reflected shock wave and reflected expansion wave, they are omitted in this section.

The strength of the shock wave, dictated by $P_{21} = \frac{p_2}{p_1}$, depends on the initial conditions by:

$$P_{14} = \frac{1}{P_{21}} \left[1 - (P_{21} - 1)\sqrt{\frac{\beta_4 E_{14}}{\alpha_1 P_{21} + 1}} \right]^{1/\beta_4}$$
(4.1)

This equation is written explicitly for the pressure ratio between the driven and driver gas $(P_{14} = \frac{p_1}{p_4})$ and can be solved using the Newton's method to find P_{21} . As concluded in Section 4.1.3 is the pressure in region 2 identical to region 3. The internal energy across the diaphragm is dependent on the gases used in the driver and driven tube by:

$$E_{14} = \frac{C_{v_1} T_1}{C_{v_4} T_4} \tag{4.2}$$

Constants that occur frequently in shock tube equations are collected in the constants α_i and β_i :

$$\alpha_i = \frac{\gamma_i + 1}{\gamma_i - 1} \tag{4.3a}$$

$$\beta_i = \frac{\gamma_i - 1}{2\gamma_i} \tag{4.3b}$$

With the acquired P_{21} it is possible to calculate the remaining flow parameters:

• The density ratio: The density ratio $(\Gamma_{ij} = \frac{\rho_i}{\rho_j})$ can be determined using:

$$\Gamma_{34} = (P_{14}P_{21})^{1/\gamma_4} \tag{4.4a}$$

$$\Gamma_{21} = \frac{1 + \alpha_1 P_{21}}{\alpha_1 + P_{21}} \tag{4.4b}$$

• Speed of sound and temperature ratio: The speed of sound ratio $(A_{ij} = \frac{a_i}{a_j})$ and temperature ratio $(T_{ij} = \frac{T_i}{T_j})$ are related to each other and can be calculated using:

$$A_{34} = \sqrt{T_{34}} = (P_{14}P_{21})^{\beta_4} \tag{4.5a}$$

$$A_{21} = \sqrt{T_{21}} = \sqrt{\frac{P_{21}(\alpha_1 + P_{21})}{1 + \alpha_1 P_{21}}}$$
(4.5b)

• *Shock wave velocity or Mach number:* The Mach number or the velocity of the shock wave can be determined using:

$$M_{shock} = \frac{u_{shock}}{a_1} = \sqrt{\beta_1 (1 + \alpha_1 P_{21})}$$
(4.6)

• Contact surface or gas slug velocity: The velocity of the flow in regions 2 and 3 can be determined using:

$$U_{21} = \frac{P_{21} - 1}{\gamma_1 \sqrt{\beta_1 (\alpha_1 P_{21} + 1)}}$$
(4.7a)

$$U_{34} = \frac{1}{\gamma_4 \beta_4} [1 - (P_{14} P_{21})^{\beta_4}]$$
(4.7b)

where the normalization $U_{ij} = \frac{u_i}{a_j}$ has taken place. When substituted with realistic initial conditions for the shock tube it is witnessed that the difference between u_2 and u_3 is negligible which confirms the conclusion of Section 4.1.3.

• Velocity of heat and tail of expansion wave: The heat (C_{44}) and the tail (C_{34}) of the expansion wave can be determined using:

$$C_{44} = -1$$
 (4.8a)

$$C_{34} = \frac{1}{\gamma_4 \beta_4} [1 - (P_{14} P_{21})^{\beta_4}] - (P_{14} P_{21})^{\beta_4}$$
(4.8b)

where the normalization $C_{ij} = \frac{u_i}{a_j}$ has taken place.

• Local Mach numbers: The Mach number of regions 2 and 3 can be calculated using:

$$M_3 = \frac{1}{\beta_4 \gamma_4} [(P_{14} P_{21})^{-\beta_4} - 1]$$
(4.9a)

$$M_2 = \frac{P_{21} - 1}{\gamma_1 \sqrt{\beta_1 P_{21}(\alpha_1 + P_{21})}}$$
(4.9b)

The speed of sound in regions 1 and 4 can be determined using

$$a_i = \sqrt{\gamma_i R_i T_i} = \sqrt{\gamma_i \frac{R_{uni}}{M_i} T_i} \tag{4.10}$$

and the density is acquired from the perfect gas law:

$$\rho_i = \frac{p_i}{\frac{R_{uni}}{M_i}T_i} \tag{4.11}$$



With Eq. (4.1)-(4.11) all the flow parameters can be determined for regions 1, 2, 3, and 4, with the exception of the expansion wave. While the head and the tail of the expansion wave are known from Eq. (4.8), Glass and Patterson [52] presented an additional series of equations to determine the flow conditions across the expansion wave:

$$a(x,t) = \left(1 - \left[\frac{n(x,t)+1}{\alpha_4}\right]\right)a_4 \tag{4.12a}$$

$$T(x,t) = \left(1 - \left[\frac{n(x,t)+1}{\alpha_4}\right]\right)^2 T_4$$
(4.12b)

$$\rho(x,t) = \left(1 - \left[\frac{n(x,t)+1}{\alpha_4}\right]\right)^{\frac{1}{\gamma_4\beta_4}}\rho_4 \tag{4.12c}$$

$$p(x,t) = \left(1 - \left[\frac{n(x,t)+1}{\alpha_4}\right]\right)^{\frac{1}{\beta_4}} p_4$$
(4.12d)

$$u(x,t) = \frac{2(a_4 - a)}{\gamma_4 - 1} \tag{4.12e}$$

$$M(x,t) = \frac{u(x,t)}{a(x,t)}$$

$$\tag{4.12f}$$

where n(x,t) is defined as:

$$n(x,t) = \frac{x}{a_4 t} \tag{4.13}$$

In Fig. 4.6 the results are shown at two instances for a condition where the helium is used as driver gas and air as driven gas. The driver and driven pressure are 1.65 MPa and 5000 Pa respectively, and the initial temperature is 300 K for both gases. The length of the shock tube discussed in Section 4.1.1 is used to display the results, where x = 0 m corresponds to the location of the diaphragm.

The primary shock wave is not only clearly visible as a sudden drop in Fig. 4.6(a) at x = 0.21 m for t = 0.1 ms, also this abrupt change is visible in the remaining figures. The more gradually transition before the shock is the expansion wave (Fig. 4.6(a) from x = -0.13 m to x = 0.51 m, for t = 0.1 ms). The contact discontinuity is visible as a jump between the expansion wave and the shock wave (Fig. 4.6(c) at x = 0.15 m for t = 0.1 ms). The flow behind the shock wave has reached Mach 2 (Fig. 4.6(d)) and a temperature of almost 1500 K (Fig. 4.6(e)).

For the given situation the shock speed is 1576.0 m/s and the contact surface travels at 1249.6 m/s. At the location of the sample in the shock tube (presented in Section 4.1.1) the test time is 566.8 μ s.

To investigate the effect of the gases used in the driver and driven tube on the flow conditions, it is important to compare several cases. The gases that are considered are presented in Table 4.1 together with the necessary properties for the calculations. Hydrogen and helium are considered as driver gases whereas oxygen, air, nitrogen, argon and krypton are covered as driven gases. Argon and krypton are included to investigate the effect of a heavy gas particle on the results.

Gas	$\gamma [-]$	$C_v \; [\mathrm{kJ}/(\mathrm{kg}\cdot\mathrm{K})]$	M [g/mol]
Hydrogen	1.405	10.16	2.016
Helium	1.667	3.12	4.003
Nitrogen	1.4	0.743	28.014
Air	1.4	0.718	28.970
Oxygen	1.395	0.659	31.998
Argon	1.667	0.312	39.948
Krypton	1.67	0.151	83.798

Table 4.1: Properties of the gases considered in the shock tube.

The results are summarized in Table 4.2. When the driver gas is kept constant it can be seen that the static pressure, static temperature, and test time increases together with the molecular weight of the driven gas. A larger test time is advantageous since it offers more time to the flow to become steady. However, the velocity decreases which is generally also observable in the shock speed and Mach number.

The shock speed and the Mach number decrease since the larger weight of the test gas accelerates more difficultly than a lighter gas. Nonetheless, the heavier gas has a higher amount of energy stored and this is released when accelerated. The increased amount of energy is expressed by the higher temperatures that is reached. This is also expressed by the decrease of C_v with the molecular weight (Table 4.1) which



Figure 4.6: Results of the shock tube calculations at two instances using helium as driver gas and air as driven gas. High temperature effects are not included.

Driver	Driven	p_2 [kPa]	$u_2 [\mathrm{km/s}]$	$\rho_2 [\mathrm{kg/m^3}]$	$M_2 [-]$	T_2 [K]	$u_{shock} [\mathrm{km/s}]$	$t_{test} \left[\mu \mathbf{s} \right]$
Hydrogen	Nitrogen	203.59	1.692	0.295	1.721	2326.4	2.090	384.94
	Air	207.34	1.680	0.306	1.724	2363.9	2.074	386.84
	Oxygen	218.16	1.644	0.343	1.744	2449.5	2.022	389.40
	Argon	259.02	1.524	0.299	1.268	4165.1	2.082	601.52
	Krypton	365.64	1.257	0.637	1.284	5785.3	1.708	717.31
Helium	Nitrogen	116.95	1.257	0.270	1.614	1459.1	1.587	565.93
	Air	119.37	1.250	0.280	1.619	1483.4	1.576	566.81
	Oxygen	126.41	1.228	0.316	1.643	1540.8	1.541	565.73
	Argon	153.78	1.156	0.286	1.221	2585.7	1.607	828.77
	Krypton	229.70	0.987	0.619	1.255	3738.0	1.355	939.46

Table 4.2: Shock tube results for various combinations of driver and driven gas. High temperature effects are not included.

indicates that the heavier particles reaches a higher temperature when absorbing the same amount of energy.

Although the calculation become inaccurate at high temperatures because γ and C_v are considered to be constant, it is still valuable to compare the results for nitrogen and a heavy gas as krypton specifically. The molecular weight of krypton is three times larger than nitrogen which results in a reduction of the shock speed with a factor 0.85. The temperature however increase with a factor 2.5 and the test time with factor 1.66.

When comparing the driver gases it can be observed that the shock speed increases significantly which is caused by the higher speed of sound of the driver gas. Since the shock speed directly affects the remaining flow parameters, the increase of the parameters shown in Table 4.2 meets the expectations. Apart from having the risk of decreasing the test time too much which could result in measurements before the flow has completely reached a steady state, there is also some safety concern with hydrogen as driver gas.

From these results it is clear that the shock tube is able to create a high velocity field in the test section by having a large initial pressure difference between the driver and driven tube. By choosing an even higher initial pressure difference and by potentially mixing the test gas with a heavy inert gas, the temperature can rise to such values that dissociation can take place. This cannot be done using these analytical equations since they are based on the perfect gas assumption. In Chapter 5 the flow conditions in the shock tube is chosen with the aid of more powerful programs.

4.2 Heat Transfer Gauge

The heat transfer gauge – a thin-film sensor – is selected to measure the heat transfer rate. Although these sensors are very fragile they have a high sensitivity which is advantageous for the measurements. During the manufacturing process a large number of gauges failed and had to be discarded. In this chapter the steps will be presented which were followed to successfully produce a heat transfer gauge.

It should be noted that the presented steps are the result of a long iterative process where many different approaches were attempted. The main difficulties were to make sure that the wires stayed properly connected to the gold bridges during the static calibration (above 45°C the heat shrink becomes a little soft hence the connection breaks), while at the same time the gauge should be able to be flush-mounted in the model, and the model can be connected to the sting without the gauge blocking it.

This section starts with the working principles of thin-film gauges and the reasons for choosing this type of sensor are presented. It then continues with the steps to manufacture a thin-film gauge (Section 4.2.3- 4.2.4). In Section 4.2.5 the gauge has been successfully produced and is mounted in the model, hereby forming a probe which is then calibrated. The probes that survived this calibration process were coated (Section 4.2.6). The probes were split in four groups, each receiving a different type of coating. The ones that eventually also survive the coating process were used for experiments in the shock tube.

4.2.1 Working Principles and Characteristics of the Heat Transfer Gauge

It is essential to clarify the working principles of the heat transfer gauge to fully understand the application method in the shock tube. A thin-film gauge works on the principle that the resistance of the metal (in this case the platinum) rises with temperature. Since the width of the platinum bridge is approximately 0.5 mm the measurements are conducted near the stagnation point. The gold bridges

simply function as a conductor and is attached to the wires. Both the gold bridges and the wires have ideally no resistance.

These wires are connected to a resistance temperature detector (RTD) using which a constant current I_c of 9.88 mA is applied. Inside the RTD there is a Wheatstone bridge which increases the voltage during a temperature increase. This RTD is attached to an oscilloscope by which the voltage can be plotted. This oscilloscope has a trigger function which activates when a certain value is surpassed. The voltage values acquired from the oscilloscope are then post-processed. This process is discussed in Chapter 6.

One might wonder why thin-film gauges are chosen for this experiment. This is related to a useful feature of these gauges: the sensitivity. Compared to other candidates, such as a thermocouple gauge, the sensitivity is superior. Schultz and Jones [41] presented the sensitivity of some common thermocouples and some metals. The temperature sensitivity of platinum is 3.01 mV/k whereas for some common thermocouples – such as copper-constantan – is in the order of μ V/k. A larger voltage output per Kelvin is preferred since it will be easier to detect. The lower sensitivity of the thermocouples might be too low for this application.

A big disadvantage of thin-film gauges is the fragility. The platinum bridge is very thin hence any small damage could disrupt the closed circuit hereby making the gauge useless. Thermocouple gauges do not have this problem. Moreover, while the copper wires are being kept in place using heat shrink and Araldite, that connection is still sensitive. Especially during the calibration process on average half of the sensors would die due to connection failure.

There is however one more aspect that makes the thermocouple disadvantageous compared to thinfilm gauges. While thin-film gauges measure the resistance change, thermocouples measure the voltage change between the two metals. This junction between the two metals can be affected by the coatings and hereby adapting the voltage change.

Moreover, the connection between the cables and the thermocouple introduces error due to the "cold junction effect" that causes a voltage change. Those cables are also connected to a device to supply electricity which again is sensitive to the same effect. While the latter can be corrected for, the cold junction effect at the thermocouple is unknown and its effect is also not known. For this reason the KAIST Hypersonics laboratory does not use thermocouples for their measurements.

As introduced in Section 3.4 the slug calorimeter is another probe that can be used to measure the heat flux. It is based on a thin-skin principle and it requires a thermocouple connection to acquire the temperature profile at the bottom on the slug. The thermocouple connection is also prone to the "cold junction effect".

However, the major disadvantage of a thin-skin sensor is the time that is required to conduct the temperature through the slug. While in an arc-jet the test time is in the order of seconds, in a shock tube the test time is in the order of hundreds of microseconds as presented in Section 4.1.4. The test time could be too short hence the temperature rise measured at the bottom of the slug is significantly smaller than at the top surface of the slug.

Moreover, in order to determine the catalytic efficiency of copper oxide it is necessary to have a slug that is made entirely of this material since the heat has to be conducted through the entire material. Copper oxide usually occurs as an oxidation layer at the surface of copper. To have a slug made of copper oxide, oxygen has to be added to molten copper such that the oxygen is distributed evenly. Moreover, this process should be performed in a high vacuum to prevent other contamination in the copper. It is therefore extremely difficult to have a slug of pure copper oxide. Additionally, it is not possible to use silicon dioxide as the slug material due to its low thermal conductivity hence there is no reference to compare the results with.

All in all, thermocouples and slug calorimeters are not suitable sensors to measure the heat flux for this research. The advantages of thin-film gauges outweigh the disadvantages. The main disadvantage of a thin-film gauge (i.e. the fragility) can be solved by manufacturing a large number of gauges.

4.2.2 Preparation of Quartz Rod and Models

Quartz is a material that has a low thermal conductivity (approximately 1.4 W/($m \cdot K$) [41]) and a low porosity hereby suitable to be used as a substrate for the gauge. The molecular structure is a continuous repetition of SiO₄ in a shape of a tetrahedron where each connection shares an oxygen atom. The quartz is bought commercially in the form of rods with a diameter of 2 mm and a length of around 10 mm.

Since the surface roughness has a large influence on the catalytic efficiency as described in Section 2.2.3 it is essential to polish the rods. Handling them individually is not only a very tedious process it is also difficult to properly orientate them on the grinder. Using acrylic cement and an acrylic ring the rods are attached all in the same orientation to form a block. This block of quartz rods is then polished on both sides using SiC sandpaper of increasing grits: 400, 800, 1500, and 2000 which corresponds to an

average particle diameter of 35.0, 21.8, 12.6, and 10.3 μ m. At each grit the polishing machine is set at a rotational speed of 350 rpm on which the block is polished for approximately 15 minutes and using 1- μ m-particle-size filtered water, waste is removed. This step is then concluded by polishing the block using diamond suspension with an average particle diameter of 6.0 μ m for approximately 20 minutes. Afterwards acetone is used to dissolve the acrylic cement which only leaves the individual quartz rods.

The models in which the gauges will be mounted (Fig. 4.3(a)) also need to be prepared. The polishing process follows the same steps as for the quartz rods but without the grinder. Moreover, instead of 20 minutes the models are only polished by hand for a few seconds.

4.2.3 Platinum and Gold Bridge

On the rods that are evenly polished a platinum bridge can be applied. Since quartz is electrically non-conducting this bridge will make the surface conductive. The platinum paste that has been used is a platinum metallo-organic conductor. By trimming a size 0 paint brush until a single hair, the paste is applied to the upper surface with a single stroke, from one end to another through the center. Practice is required to put a consistent stroke on all rods.

A muffle furnace – with a 13x11x15 cm large chamber – is used to heat up the quartz rods with the platinum strip starting from room temperature to cure the platinum paste. By placing a steel block in the furnace, the rods can be placed vertically with the painted surface pointing upwards. The furnace is set to the desired temperature of 850° C, and is kept at this temperature for 30 minutes after which the furnace is turned off.

When the furnace is cooled down the quartz rods are taken out and the platinum bridges are tested individually using a multimeter. The desired range of resistance is between 50 and 400 Ω . A too small resistance results in a sensor which is not sensitive enough to be useful, whereas a too high resistance could lead to a failure of the bridge after one utilization in the shock tube due to a too high voltage. The ones which meet this requirement are again sorted on their lay-out. This is because the goal is to have platinum bridges with a uniform width of approximately 0.5 mm to minimize the differences between different sensors.

On the rods meeting these requirements two gold bridges are made on the side. Each of these gold bridges start at the far end of the platinum bridge, go around the corner, and continues longitudinally until the end of the rod. The gold paste used is a gold metallo-organic conductor. It should be made sure that the gold is touching the platinum bridge slightly so a connection will be established. The rods are again placed in the furnace at 850°C for 25 minutes. The rods are again tested with a multimeter to determine whether all the connections are successful. The final result is shown in Fig. 4.7.



Figure 4.7: The top view of a thin-film gauge with the platinum and gold bridges.

Those who failed are not discarded yet. A common problem was that the gold bridge was not continuous over the corner on the top surface. If the platinum bridge is still intact, then a second attempt can be made in the furnace with some additional gold paste. The temperature is lowered to 700° C and the time is set to 25 minutes, which improves the survival probability of the platinum bridge.



4.2.4 Attachment of Wires

Wires are connected to the gold bridges in order to connect them to the a power source. Prior to this the sensor length should be reduced to 6.5 mm using sandpaper to ensure that everything fits when it is installed in the model.

Two pieces of enameled copper wires with a thickness of 0.2 mm are used to connect to the gold bridges. Each wire is pressed against one of the two gold bridges at the side of the rod (near the lower part of the rod). Using heat shrink with a diameter of 2 mm which is made of flexible Polyolefin capable of shrinking to a ratio of 2:1, the wires are kept in place and it covers the entire rod.

To prevent even the slightest movement of the wire attachments, Araldite is applied to the bottom of the rod where the two wires are sticking out and until halfway the sensor so the entire region of the attachments is covered. Using a heat gun the glue is hardened immediately hereby. The result is shown in Fig. 4.8.



(a) Top view of the sensor.

(b) Front view of the sensor.



The last step to complete the sensor is by attaching golden connectors to the end of the wires. A male and female connector are shown in Fig. 4.9(a). On both wires a male connector is soldered and using a heat shrink of 3 mm the soldered region is covered.

The completed sensor is then mounted in the model with the aid of Araldite to keep it in place. It is made sure that the front face is level with the surface of the model (flush-mounted). This resulting product is referred as a probe which is shown in Fig. 4.9(b) for illustration. During this entire process the resistance is checked to make sure that the gauge is still intact.



(a) The two different connectors. The top one was used on the sensors.

(b) A finished probe.



4.2.5 Calibration

Using a convection oven the probes are calibrated. The temperature is increased starting from room temperature with increments of 5° C until 65° C. This range corresponds to the temperature increase



expected during the experiments. At each step the temperature is kept constant for about 10 minutes to ensure equilibrium. The resistance is then recorded of each probe. From this a resistance-temperature diagram is made for each probe, see for example the diagram shown in Fig. 4.10.

The relationship between the resistance and the temperature is linear as shown by Kinnear and Lu [53], hence a least square method is used to filter out uncertainties during the calibration process. This results in the dashed line shown in Fig 4.10.



Figure 4.10: An example of a resistance-temperature diagram for a probe.

The slope $\left(\frac{dR}{dT}\right)$ of each probe is required to convert the measurements to temperature. This will be further discussed in Section 6.2. It is common to plot this slope against the resistance at room temperature for all probes which should yield a linear relationship (Fig. 4.11(a)).

Having a low deviation among the probes is desired hence several outliers from the linear trend were discarded. From Fig. 4.11(a) it can be seen that the \mathbb{R}^2 value, which denotes how close the linear fit matches the data points, is 0.939. Such a value indicates that the probes can be considered to be consistent. The majority of the probes show a resistance between 40 and 120 Ω hence for clarity an enlarged version is shown in Fig. 4.11(b).

This diagram is useful to correct $\frac{dR}{dT}$ in case there is a change of the resistance at room temperature. It has been experienced that a change of less than 10% is common due to daily temperature fluctuations and especially after the coating process which will be discussed in the next section. Ideally a calibration curve should be made using the probes that have been coated. However, the risk of breaking the probe during calibration was too high hence it was assumed that the effect of the coating on the calibration curve is negligible.

The correction is done by calculating the difference using the slope (i.e. 0.0025197) of the linear fit and correct the measured value at room temperature of that particular probe.

4.2.6 Coating and SEM Analysis

The coating of the probes was performed by a company called "Thin Films and Fine Materials" (THIFINE) located in Incheon (Seoul, South Korea). The probes were taped together in a batch and the golden connectors were also covered with tape for protection. An example is shown in Fig. 4.12. Two rounds of probes were sent to the company for coating and in each round there were three batches:

- 1. 1000 nm SiO_2
- 2. 1000 nm SiO_2 and 180 nm CuO
- 3. 1000 nm SiO_2 and 180 nm Cu

On all three batches a layer of silicon dioxide is applied. Only for the second and third batch a second coating is applied on top of this SiO_2 . The SiO_2 functions as a insulator to prevent contact between the copper (oxide) and the platinum or gold. The thickness of SiO_2 , CuO, and Cu were taken from the experiments conducted by Park [15] which is also very similar to the thicknesses applied by Reddy [32] as presented in Section 3.2.

In an attempt to prevent the short-circuiting problem experienced by Park [15] with the copper coating a small amount of Araldite was applied on the gold bridge for only that particular batch.



(b) Close up of the resistance slope vs. resistance diagram between 40 and 120 $\Omega.$

Figure 4.11: Resistance slope vs. resistance diagram att room temperature (20°C) for all probes used in this thesis.



Figure 4.12: The probes are grouped together prior to the coating process.

The coating is applied using an electron beam physical vapor deposition method (E-beam) which evaporates the source material using an electron beam that has a purity higher than 99%. The vapor of this material touches the upper layer of the models and it condenses forming the desired layer. The deposition rate was around 0.3 nm/s. [54] This deposition was conducted under high vacuum conditions (i.e. $8.5 \cdot 10^{-5}$ Torr = 0.011 Pa). The accuracy of the 1000 nm SiO₂ is 50 nm whereas for the 180 nm CuO or Cu layer it is 20 nm.

While the application of the SiO_2 and Cu layers went without problems, the CuO was troublesome. During the first round THIFINE attempted to perform the E-beam method on the CuO source. However it was noticed by the coating engineer that the electron beam could not evaporate the source material. Hence, instead of using an electron beam a resistor was used to evaporate the material. The CuO layer had a black color hence it is referred as "black CuO".

After analyzing the samples from the first round it was decided to process the second round differently. By evaporating the Cu source material using the E-beam method and by injecting oxygen gas in the vacuum chamber copper oxide was formed. With this method it could not be guaranteed that the ratio between the copper and monatomic oxygen was 1:1. The CuO layer had a brown color and is referred as "brown CuO".

In Fig. 4.13 the five different types of samples are shown: uncoated, SiO_2 , black CuO, brown CuO, and Cu respectively. It can be seen in Fig. 4.13(b) that SiO_2 introduces a slight greenish glow to the surface when compared to Fig. 4.13(a). The CuO shown in Fig. 4.13(c) is significantly darker compared to SiO_2 . One might even claim that there is a blueish/greenish glow, possibly from the SiO_2 layer underneath and/or the oxygen present in the layers.

In general the color of copper oxide is either black (i.e. CuO) or red (i.e. Cu_2O). Based on inspection the black CuO (Fig. 4.13(c)) would correspond to a mixture of the black from CuO and the green/transparent color of SiO₂. The brown CuO (Fig. 4.13(d)) would correspond to a mixture of CuOand Cu_2O or Cu which corresponds to a color mixture of black and brown or red.

When comparing the brown CuO with Cu (Fig. 4.13(e)) it is clear that the latter is lighter and more orange compared to the brown of the former.



(a) Uncoated.



(c) Black CuO. (d) Brown CuO.

(e) Cu.

Figure 4.13: Five different types of surfaces.

Between the two rounds it was decided to perform a Scanning Electron Microscope (SEM) analysis on the CuO models to investigate the quality of the coating. Using an electron microscope the surface can be investigated by measuring the secondary electrons (SE), backscattered electrons (BSE), and by conducting elemental analysis X-ray spectroscopy (EDS).

With SE the contour of the surface can be made visible whereas with BSE the differences in atomic species can be made visible through contrast. A lighter color means a higher atomic number whereas a darker color corresponds to a lighter element. An example is shown in Fig. 4.14 for a probe coated with SiO_2 and another probe with black CuO.

From Fig. 4.14(a) and 4.14(c) it can be seen that the coatings applied to the platinum bridge is not perfectly smooth. Both coatings show a similar amount of irregularity. Away from the platinum bridge the amount of irregularities drops significantly, since the quartz rods were polished extensively. Therefore it can be concluded that the irregularities visible on top of the platinum bridge is caused by the roughness of the dried platinum.

From Fig. 4.14(b) and 4.14(d) it is can be observed that there is no significant contrast variation in the images which means that the coatings have a high purity. When combined with the SE contour images, it is suspected that the darker areas in the BSE images are caused by flakes on top of the coating.



(a) SE image on a heat flux probe coated with SiO₂. (b) BSE image on a heat flux probe coated with SiO₂.



(c) SE image on a heat flux probe coated with black (d) BSE image on a heat flux probe coated with black CuO.

Figure 4.14: Secondary electron method and backscattered electron method taken of a the platinum bridge of a heat flux probe coated with SiO_2 and another probe with black CuO.

With the EDS method it is possible to measure the elemental composition of the surface. The CuO models of the first round were tested using this method. A representative example is shown in Fig. 4.15. The ordinate of the figure can be interpreted as the amount of particles present at the surface while the abscissa is the wavelength corresponding to a particular species.

From this it can be seen that mainly Si and O are measured while the presence of Cu is minuscule. Since the EDS is capable of penetrating the surface for several hundreds nanometers, the presence of Si in the spectrum corresponds to the expectations. The small concentration of Cu in the spectrum indicates that the amount of Cu atoms is low which can either correspond to a very oxygen rich copper oxide coating or the thickness is a lot thinner than expected.

SEM analysis was not conducted on the brown CuO probes since it was clear from visual inspection that copper was present.



Lsec: 30.0 0 Cnts 0.000 keV Det: Octane Super Det

Figure 4.15: The EDS spectrum of the surface of a black CuO coated probe.

4.3 Shadowgraph

As mentioned before in Section 4.1.2 there are openings at the sides of the test section in which sapphire windows can be placed. Using the shadowgraph visualization method the flow – especially the standing shock – is captured. In this section a short overview is presented of this technique.

The shadowgraph technique is a non-intrusive method that has a short measurement time. It is based on the principle that light is refracted differently by different densities. Through a shock wave there is a large density change hence the jump in density can be made visible. The refraction principle is known as the Gladstone-Dale relation and is dictated by the refractive index (n):

$$n = \frac{c_0}{c} = 1 + K\rho \tag{4.14}$$

where the local density (ρ) dictates the refractive index (n). The Gladstone-Dale constant (K) is dependent on the composition of the gas and the wavelength of the light. [55]

Since different substances have a different refractive index, light is bend differently according to Snell's law:

$$n_1 \sin \alpha_1 = n_2 \sin \alpha_2 \tag{4.15}$$

As dictated by the combination of Eq. (4.14) and (4.15), light bends towards the substance with a higher density. Since the density increases through a shock wave, the light is deflected towards the region behind the shock, creating a bright spot at the recording plane. A dark spot is located upstream due to the light that has been bent (Fig. 4.16).

The shadowgraph method measures the $\left(\frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2}\right)$ which corresponds to $\nabla^2 \rho$, hence it is not possible to acquire quantitative values for the density.

The setup used at KAIST is shown in Fig. 4.17. A green colored laser with a wavelength of 532 nm is used as the light source. At a distance of 2.4 cm a biconcave lens is placed with a focus length of -30.0 mm and a diameter of 20.0 mm. This lens diverges the laser and at a distance of 81.5 cm a 15x15 cm square mirror (i.e. mirror 1) is placed which changes the orientation of the beam. 123 cm from there a converging mirror with a diameter of 20 cm is situated that changes the diverging laser to a collimated beam. This beam travels towards the model located at 261 cm from the converging mirror and passes through the two optical windows towards another 15x15 cm square mirror (i.e. mirror 2). The distance between the model and this mirror is 102 cm. At last the laser is reflected towards a high-speed camera located at 168 cm from the mirror. In the figure the path of the laser is indicated by a red dotted line.

An 80-400 mm 1:4.5-5.6D Nikkor lens has been mounted to the camera. The lens was used at its longest focal length of 400 mm with an aperture of 5.6. The focus was located at 2.3 m. The high speed camera was set at 200,000 fps.





Figure 4.16: The refraction principle of light due to a density difference. [55]

Figure 4.17: The shadow graph setup used for this thesis.

Determination of Flow Conditions

In Chapter 4 the shock tube has been introduced together with an analysis of the effect of varying the driver and driven gas. However, there are more parameters that can be changed to alter the flow condition. The pressure in the driver tube can be adjusted by changing the thickness of the diaphragm and also the pressure until which the test gas is introduced in the driven tube has to be chosen. Moreover, the composition of this test gas also has to be determined.

In this chapter the focus is on the numerical determination of the flow conditions which will be used for the actual experiments. Two sets of programs are necessary: one for determining the flow conditions inside the shock tube including the high temperature effects (Section 5.1), another one for determining the condition behind the standing shock at the boundary layer edge (Section 5.2). Only with these two programs the flow conditions and the amount of dissociation are known. Additionally a third program is introduced in Section 5.2 which is used to determine the conditions at the wall of the model. These conditions are necessary for the theory presented in Chapter 6.

At the end of this chapter the exact procedure of determining the flow conditions is presented together with the values of the chosen flow conditions.

5.1 Shock Tube Program

To numerically determine the flow conditions it is necessary to have an accurate shock tube program. Two different programs have been considered: L1d2 from the Compressible-Flow CFD group of the University of Queensland in Australia [56] and stube9 from Prof. Chul Park of KAIST. After a comparison L1d2 has been chosen to be better suited for the present application (see Appendix B). For this reason this section will focus on L1d2 only.

L1d2 is a Lagrangian quasi-1D flow solver for shock and expansion tubes. Although there is only one spatial coordinate, gradual changes of the cross-sectional area are possible. It is capable of simulating the transient part of the flow which occurs after a sudden change such as a shock wave. These changes can either be introduced by a moving piston or a bursting diaphragm. Not only the dynamics of the piston and the gas slugs are considered, also the viscous effects including the heat transfer effects are included.

Different gas slugs can be simulated which are either independent (e.g. separated by a diaphragm) or interacting (e.g. when the diaphragm bursts). It also has the option to include several pistons and diaphragms. These slugs are simulated in such a way that each of them are split up into a number of control masses of which the positions are followed. The viscous effects are simulated using the correlations for friction and heat transfer in a pipe flow to take into account the effect of compressibility. [57]

Because shock tubes are used for conditions where shock waves are created it is essential that L1d2 can simulate those. These shocks are not explicitly identified nor tracked but are included using a shock capturing scheme. This scheme functions in such a way that the same set of equations is used to compute the motion of the gas, whether or not there is a shock. This simplifies the code in cases where shocks, compression waves or contact surfaces are interacting with each other. [57]

In the core of the program the predictor-corrector method is used to propagate the values to the next

time step. [57] This scheme can be expressed as:

$$\Delta X^{(1)} = \Delta t \frac{dX^{(n)}}{dt}$$

$$X^{(1)} = X^{(n)} + \Delta X^{(1)}$$

$$\Delta X^{(2)} = \Delta t \frac{dX^{(1)}}{dt}$$

$$X^{(n+1)} = X^{(1)} + \frac{1}{2} \left(\Delta X^{(2)} - \Delta X^{(1)} \right)$$
(5.1)

The superscript (1) represents the predictor stage, and together with superscript (2) it shows the intermediate results to acquire the value at the next time step (n + 1).

X can be replaced by any variable that has to be propagated to the next time step which are: interface positions, cell momentum, cell energy, piston velocity and piston position.

To determine the position of the interfaces in both the predictor and corrector phase, the Riemann problem is solved (introduced in Section 4.1.3). The pressure and the velocity of the interface can then be determined. This method is similar to the Godunov's scheme which is a finite volume method where the Riemann problem is solved at each cell interface. [58]

In Eq. (5.1) the time derivative is necessary. This is determined using the differences of a certain variable (e.g. momentum, energy) between two adjacent cells together with the losses, hence the finite difference scheme.

After the corrector step the chemical species are updated by considering an equilibrium gas mixture because the chemical reactions are relatively fast with respect to the flow time scales. For most gases the thermodynamic constants (also know as JANAF coefficients) are stored in a table for three different temperature ranges: 200 K - 1000 K, 1000 K - 6000 K, and 6000 K - 20,000 K. It uses NASA's CEA program to determine the composition of the mixtures. This program is discussed in Section 5.2.1.

The pitot pressure is also determined by L1d2 using the Rayleigh pitot formula:

$$\frac{p_{t,2}}{p_1} = \left(\frac{(\gamma+1)^2 M_1^2}{4\gamma M_1^2 - 2(\gamma-1)}\right)^{\frac{1}{\gamma-1}} \frac{(1-\gamma) + 2\gamma M_1^2}{\gamma+1}$$
(5.2)

where subscript 1 is before the standing shock and 2 after the shock. Although with different numbers, this principle was illustrated in Fig. 2.11. Since the chemical species distribution is known the specific heat ratio is available.

5.2 Equilibrium Composition Program

The shock tube program (discussed in Section 5.1) determines the conditions behind the primary shock wave. With the exception of the pitot pressure the program does not determine the conditions behind the standing shock induced by the model such as temperature, density, enthalpy, and gas composition.

As discussed in Section 2.4.1 the total enthalpy is assumed to be constant through the standing shock (determined by L1d2) and the total pressure is assumed to be constant through the boundary layer at the stagnation point (measured using a pressure sensor and calculated by L1d2). These two quantities function as the input variables for the equilibrium composition program.

In this section two equilibrium composition programs are presented, both used for different purposes. The first program called "CEA" (Section 5.2.1) is used to determine the conditions at the wall of the model where the temperature is low. Moreover, CEA is capable of determining the frozen Prandtl number and the dynamic viscosity which are necessary parameters at the wall (Section 2.3.2.2). The second program named "Eqtab" calculates the equilibrium conditions at the boundary layer edge (Section 5.2.2).

5.2.1 CEA

Chemical Equilibrium and Applications (CEA) is a program that is not only capable of determining the chemical equilibrium compositions for the assigned thermodynamic states, it can also be used to calculate the performance of rockets and detonations. [59] The option that is used is the calculations of the chemical composition with the following thermodynamic state: temperature and pressure. These parameters are known at the wall since the temperature is measured by the heat flux probe and the pressure is measured using the piezo-electric sensor.

CEA uses empirical equations to fit the thermodynamic equations. The parameters that are determined by this method are C_p , H, and S of each species:

$$\frac{C_p}{R} = \frac{a_1}{T^2} + \frac{a_2}{T} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4$$
(5.3)



$$\frac{H}{RT} = -\frac{a_1}{T^2} + \frac{a_2}{T}\ln(T) + a_3 + a_4\frac{T}{2} + a_5\frac{T^2}{3} + a_6\frac{T^3}{4} + a_7\frac{T^4}{5} + \frac{a_8}{T}$$
(5.4)

$$\frac{S}{R} = -\frac{1}{2}\frac{a_1}{T^2} - \frac{a_2}{T} + a_3\ln(T) + a_4T + a_5\frac{T^2}{2} + a_6\frac{T^3}{3} + a_7\frac{T^4}{4} + a_9$$
(5.5)

where seven constants are necessary for $\frac{C_p}{R}$ and nine integration constants for the enthalpy and entropy. [59]

These input constants are called JANAF coefficients and are divided in three temperature ranges: 200 - 1000 K, 1000 - 6000 K, and 6000 - 20,000 K. While it is claimed by the authors of the program that it is capable of calculating the conditions accurately for high temperatures, in the past versions it has been found that starting from 6000 K the results tend to become inaccurate¹. For this reason CEA is only used at low temperatures which is at the wall.

A stripped down version of CEA, which has been improved for higher temperatures, called "Therm" has been considered for the calculation of the equilibrium composition at the boundary layer edge. It was however found that the results were less accurate compared to the results acquired by Eqtab (see next section). It was noticed that the accuracy of the JANAF coefficients for high temperatures drops significantly resulting in large errors. More details can be found in Appendix C.

5.2.2 Eqtab

"Eqtab" is the program used to determine the equilibrium composition of a gas mixture at the boundary layer edge. It is based on the concept of partition functions which has been introduced in Section 2.4.2.2. For a specific pressure and enthalpy combination, Eqtab calculates the temperature, density, internal energy, and the species composition of the gas.

The composition is given by the parameter "*spgam*" in the units [mol/kg] which can be converted to molar fractions by taking the fractions of the total amount of each species. The mass fractions can be acquired by multiplying "*spgam*" with the molecular weight.

5.3 Flow Conditions

In sections 5.1 and 5.2.2 the programs "L1d2" and "Eqtab" were introduced which are used together to determine the flow conditions inside the shock tube and behind the standing shock. Three flow conditions are chosen: an almost no dissociation case, a moderate amount of dissociation case and a high amount of dissociation case which are referred as A, B, and C respectively.

Condition C has the highest amount of dissociation hence it will be the upper limit. Therefore it is important make sure that there is a sufficient amount of dissociation for this condition. While it is preferred to have 100% dissociation it was noticed that this is not possible using a shock tube. Therefore, the aim is to have approximately 50% dissociation of nitrogen. It is believed that this is a sufficient amount of dissociation when compared to the 67% dissociation used by Park [15] for a O₂-Ar gas mixture.

During the first stage of choosing the flow conditions it was observed that dissociation cannot be reached when pure nitrogen is used as test gas. Although lowering the driven pressure results in a stronger and faster shock wave, hence it is theoretically possible to choose a pressure that would result in a high amount of dissociation, there is a physical limit of what can be achieved during the experiments. Since the shock tube could only be vacuumed until 8 Pa, it was decided that the initial pressure in the driven section should be at least 100 Pa which corresponds to an error in the pressure of less than 10%.

In Section 4.1.4 it was found that a lighter driver gas and a heavier test gas result in a stronger shock wave. Due to safety concerns the usage of hydrogen as driver gas was not considered hence helium was selected for this purpose. Therefore it was necessary to adapt the test gas to reach flow conditions were dissociation is achieved. Similar to literature (Section 3.2) the nitrogen can be mixed with an inert gas. A tertiary gas mixture is then formed when nitrogen dissociates.

At first, argon was considered in various ratios with the nitrogen. The amount of energy in the flow, expressed by the enthalpy, was not high enough to dissociate a significant amount of nitrogen. Similarly to the minimum pressure of the test gas, a minimum volume mixture ratio was selected of at least 20% nitrogen to ensure a sufficient amount of nitrogen. The amount of dissociation found with this test gas for various mixture ratio were all below 8% which is not sufficient. The calculations were also conducted for a driver pressure that is doubled by using two diaphragms pressed against each other, however, this only increased the dissociation to values below 10%.

Instead of argon it was decided to use krypton as the inert gas. It was found in Section 4.1.4 that krypton – that has a molecular weight of krypton that is twice as high compared to argon – results in a

¹Private communication with Prof. Chul Park

temperature that is a factor 1.44 larger than using argon. The increased weight by mixing nitrogen with krypton results in a higher enthalpy which causes a higher amount of dissociation.

After several iterations it was found that a mixture of 35% nitrogen and 65% krypton resulted in flow conditions with sufficient amount of dissociation when a double diaphragm is used. Flow condition B can then be selected by using one diaphragm and a driven pressure that results in approximately 30% dissociation, and flow condition A is chosen freely by varying the driven pressure to ensure almost no dissociation.

However, the flow condition cannot solely be chosen based on the amount of dissociation. In Chapter 6 the steps regarding data reduction is covered. The final goal is to generate a q_D/q_C vs. γ_w diagram which is used to read off the catalytic efficiency from the measured heat flux. The diagram made by Park [15] for a O-O₂-Ar gas mixture is shown in Fig. 5.1. This curve has an S-shape and it should be made sure that the intersection between the experimentally determined heat flux ratio (horizontal lines in Fig. 5.1) with the curve is not located in flattened regions. In Fig. 5.1 these flattened regions correspond to $\gamma_w < 10^{-3}$ and $10^{-1} < \gamma_w$. If this is poorly chosen the error in the measured heat flux would be amplified significantly when expressed as an uncertainty of the catalytic efficiency.



Figure 5.1: Heat transfer ratio vs. catalytic efficiency for the O-O₂-Ar interaction. [15]

To decrease the size of the flattened regions the q_D/q_C value at which it occurs should be increased. The increase of q_D/q_C is achieved by increasing the amount of nitrogen in the gas mixture. However, increasing the amount of nitrogen translates to a smaller amount of dissociation which is undesired. A balance has to be found between the two.

The flow conditions are summarized in Table 5.1. The values are the average within the steady regime that is chosen in Section 7.1.1. From this table it can be seen that for all flow conditions a driven gas of 35% N₂ and 65% Kr is used in combination with helium as the driver gas. Not only the driven pressure is varied for all three conditions, but for condition C the driver pressure is doubled by using two diaphragms which are pressed against each other.

Both the shock speed and the total enthalpy increase when comparing flow conditions A to C. The total enthalpy is an indication of the total amount of energy in the flow. Together with the pitot pressure it determines the amount of nitrogen that dissociates. Condition A is a case with essentially no dissociation. The temperature behind the standing shock at the boundary layer edge is calculated to be around 4800 K, whereas flow condition C has a temperature of almost 7000 K. The combination of all these results in a dissociation of 1%, 33.3%, and 54.3% respectively.

Table 5.1: The three flow conditions predicted using L1d2 and Eqtab. Shock speed and pitot pressure shown here are experimentally determined.

		Flow Condition			
		А	В	С	
Driver & Driven	Driver Gas		He		
Tube	Driven Gas	35% v	vol. $N_2 - 65\%$ v	vol. Kr	
TUDE	p_{driver} [kPa]	1650	1650	3300	
	p_{driven} [Pa]	2000	150	100	
	$u_{shock} [\rm km/s]$	1.563	2.358	2.660	
	M_2 [-]	1.69	1.85	1.89	
	T_2 [K]	3192	6175	7550	
Driven Tube	p_2 [kPa]	117.9	19.90	16.72	
Freestream	$H_2 [MJ/kg]$	2.012	4.411	5.756	
	$\rho_2 [\mathrm{kg/m^3}]$	0.286	0.025	0.017	
	$u_2 \; [\rm km/s]$	1.310	1.988	2.255	
	p_{pitot} [kPa]	446.0	100.9	94.23	
	T_e [K]	4874	6425	6874	
	$\rho_e [\mathrm{kg/m^3}]$	0.706	0.109	0.089	
Behind Standing	X_N [-]	0.007	0.209	0.319	
Shock at BL edge	X_{N_2} [-]	0.345	0.209	0.134	
	X_{Kr} [-]	0.648	0.582	0.546	
	α_N [-]	0.001	0.051	0.083	
	α_{N_2} [-]	0.151	0.102	0.070	
	α_{Kr} [-]	0.847	0.847	0.847	
	Mass fraction N_2 Dissociation	0.010	0.333	0.543	

Data Reduction

Regardless of the flow condition the raw data of the measurements has voltage as unit. For the static and pitot pressure measurements the voltage has to be converted to pressure values whereas for the heat flux measurements it has to be converted to heat flux. The steps to accomplish this are covered in Section 6.1 and 6.2.

To convert the heat flux to the catalytic efficiency it is necessary to use the theory introduced in Section 2.3.2. The theory for a tertiary gas mixture requires a large number of variables. Although part of these variables have been determined by L1d2 and Eqtab in Chapter 5, the remaining variables will be covered in Section 6.3 by introducing several theories. In Section 6.4 the comparison is made between the input variables of the binary and tertiary gas mixture theories.

6.1 Pressure Measured by Piezo-electric Sensor

As discussed in Section 4.1 two piezo-electric sensors were flush-mounted in the wall of the shock tube to measure the static pressure and shock speed, and one sensor is used in the pressure model (Fig. 4.3(b)) to measure the pitot pressure.

Since these sensors were bought commercially, a calibration sheet was provided with the corresponding sensitivity. Using this sensitivity it was possible to convert the raw data from voltage to pressure values.

6.2 Surface Heat Flux Measured By Thin-Film Gauge

Each thin-film gauge located in a probe was calibrated, as discussed in Section 4.2.5 which resulted in a resistance-temperature diagram. Since the current (I_c) applied to the sensor is constant and known (i.e. 9.88 mA) the voltage measured using the oscilloscopes $(V(t_i))$ can be translated to resistance. With the aid of the results from the static calibration the temperature can be determined [15]:

$$T(t_i) = \frac{V(t_i)}{V_{supply} \cdot \beta_R} = \frac{V(t_i)}{I_c \cdot R_0 \cdot \frac{1}{R_0} \frac{dR}{dT}} = \frac{V(t_i)}{I_c \cdot \frac{dR}{dT}}$$
(6.1)

From this equation it can be seen that the resistance variation with the temperature $\left(\frac{dR}{dT}\right)$ is required from the calibration, while the initial resistance at room temperature (R_0) cancels out. $\frac{dR}{dT}$ is corrected for any variations at room temperature as discussed in Section 4.2.5.

It was noticed that the temperature profiles acquired from the experiments had some noise instead of a smooth pattern as shown by Fig. 6.1(a). Since any noise in temperature is amplified when converted to heat flux it was decided to apply a Savitzky-Golay filtering to the temperature. This filter is a low pass filter and it fits a low degree polynomial using the linear least square method between the data points. [60] The filter has been set to a third order polynomial and a frame size of 5. It was witnessed that this would filter away the noise but not distort the original shape of the profile (Fig. 6.1(b)).



Figure 6.1: Temperature profile prior and after the Savitzky-Golay filter.

To convert this temperature to the desired output value, the heat flux, assumptions have to be made regarding the thin-film gauges. Based on the semi-infinite principle discussed by Schultz et al. [41] the assumption of one-dimensional heat transfer is made. This transfer is in the form of conduction through a thin metallic film, which is in this case the platinum bridge. It is assumed that the semi-infinite substrate (i.e. the quartz rod) defines the heat capacity of the entire sensor while the metallic film has no heat capacity. Moreover, due to the small width of the metallic film it is assumed that it does not affect the temperature of the substrate surface.

From these assumptions the substrate defines the properties of the gauge. To meet the one-dimensional theory the quartz rod has to be of sufficient length to become similar to a semi-infinite solid. Kinnear and Lu [53] investigated the substrate base temperature to surface temperature ratio for a thin-film gauge and concluded that the substrate should be at least 3.0 mm even for a long test time of 1 s. In this case the substrate base temperature to surface temperature ratio is less than 1%. Since the quartz rod has a total length of 6.5 mm it is more than sufficient.

With the temperature profile the heat flux can be determined using proper physical models. Each ot these methods give a different heat flux profile where some are more prone for noise than others. Several examples are the methods presented by Cook and Felderman [61]:

$$q_{s,Cook\&Felderman} = 2\sqrt{\frac{\rho ck}{\pi}} \sum_{i=1}^{n} \frac{T_i - T_{i-1}}{\sqrt{t_n - t_i} + \sqrt{t_n - t_{i+1}}}$$
(6.2)

or Kendall et al. [62]:

$$Q_{s,Kendall\ et\ al.} = \sqrt{\frac{\rho ck}{\pi}} \sum_{i=1}^{n} \frac{T_i + T_{i-1}}{\sqrt{t_n - t_i} + \sqrt{t_n - t_{i+1}}} \Delta t$$
(6.3a)

$$q_{s,Kendall\ et\ al.} = \frac{dQ_{s,Kendall\ et\ al.}}{dt}$$
(6.3b)

The method of Cook and Felderman [61] was selected to converted the temperature to the stagnation heat flux. [41, 61] A comparison between different heat flux conversion methods is made in Appendix D from which it was chosen to use this method.

The properties of the substrate are assumed to be constant physical properties taken at room temperature, expressed by three variables: ρ , c, and k. The root of this product ($\sqrt{\rho ck}$) is called the thermal product. According to Park [15] its value is $1510 \pm 100 \text{ Ws}^{0.5}/(\text{m}^2 \cdot \text{K})$, which is similar to the value determined by Schultz et al. [41].

6.3 Diffusive and Convective Heat Flux for Tertiary Gas Mixtures

The theory required to calculate the diffusive and convective heat flux for a tertiary gas mixtures was introduced in Section 2.3.2.2. For clarity the equations are repeated here again:

$$q_C = 0.47 \sqrt{2\beta\mu_e \rho_e} \overline{Pr}_w^{-2/3} \overline{h}_e \tag{2.23a}$$

$$q_D = \chi \sqrt{2\beta \mu_e \rho_e h_R \alpha_{e1} \varphi_2} \tag{2.23b}$$

$$\varphi_2 = \frac{1}{1 + \frac{\chi\sqrt{2\beta\mu_e\rho_e}}{\rho_w k_{w_1}}} \tag{2.24}$$

$$\chi = \frac{1}{\phi_3} \frac{m_2}{m} \frac{1}{Sc_{21}} \tag{2.25}$$

$$\phi_3 = \int_0^\infty \left[\frac{f''(\eta)}{f''(0)} \right]^{\frac{m}{m_1} \frac{Sc_{12} Sc_{31}}{Sc_{32}}} d\eta$$
(2.22)

These equations have a large number of variables that need to be determined, which will be discussed in this section. It is essential to note that some of these variables have a subscript that corresponds to one of the three gas components in the tertiary gas mixtures: 1 corresponds to N_2 , corresponds to N_2 , and 3 to Kr.

6.3.1Determination of the Dynamic Viscosity and Density

The dynamic viscosity shows up in calculations of the conductive and diffusive heat fluxes (Eq. (2.23)). The viscosity at the boundary layer edge is computed using:

$$\mu = \sum_{i=1}^{n} \frac{m_i X_i}{\sum\limits_{j \neq i}^{n} X_j \Delta_{ij}^{(2)}}$$
(6.5)

where $\Delta_{ij}^{(2)}$ is defined as [63]:

$$\Delta_{ij}^{(2)} = \frac{16}{5} \sqrt{\frac{2m_i m_j}{\pi k T(m_i + m_j)}} \pi \bar{\Omega}_{ij}^{(2,2)} \tag{6.6}$$

To use these equations the particle mass per species is required which can be derived as:

$$m_i = \frac{\rho_i}{n_i} = \frac{\alpha_i \rho}{\frac{p_i}{k_B T}} = \alpha_i \frac{\rho k_B T}{p X_i} = \frac{\alpha_i}{X_i} \frac{\rho k_B T}{p}$$
(6.7)

In this equation the mass fraction (α_i) , molar fraction (X_i) , and temperature, and pressure are known quantities given in Section 5.3. Additionally, $\Delta_{ij}^{(2)}$ requires the average collision integral $\bar{\Omega}_{ij}^{(2,2)}$ that is expressed by:

$$\bar{\Omega}_{ij}^{(2,2)} = \sum_{z=1}^{2} \frac{\sigma_{ij}^{2} \alpha_{ij} \zeta_{ij_{z}} \Gamma(4 - \xi_{ij_{z}})}{\pi(\alpha_{ij} + 1)(\alpha_{ij} + 2)} \left(\frac{k_{B}T}{\epsilon_{ij}}\right)^{\xi_{ij_{z}}}$$
(6.8)

This latter equation is a method suggested by Kim et al. [64]. In his paper five collision parameters are given for common species combinations. Since krypton is an uncommon case it was not present in this paper. After consulting for Kim's help it was suggested that the behavior of krypton is similar to argon since they are both inert gases, hence it was assumed that the values for argon could be used for krypton. The collision parameters are given in Table 6.1.

Table 6.1: Collision parameters of N, N_2 , and Kr combinations. [64]

Species Combi- nation	ζ_1	ζ_2	ξ_1	ξ_2	α
$N-N_2 / N_2-N$	$-4.2367 \cdot 10^{-1}$	7.6369	$-2.9284 \cdot 10^{-2}$	$2.4099 \cdot 10^{-1}$	1.7826
N-Kr / Kr-N	$-6.5575 \cdot 10^{-1}$	5.3756	$-4.3998 \cdot 10^{-2}$	$1.5531 \cdot 10^{-1}$	1.5596
N_2 -Kr / Kr- N_2	$-1.0200 \cdot 10^{-1}$	3.3400	$-2.9123 \cdot 10^{-1}$	$8.2679 \cdot 10^{-2}$	1.3678

The second parameter that is discussed in this section is the density at the boundary layer edge. Since the molar masses and the molar fractions of the species are known the molar mass of the entire mixture can be determined. This can be implemented in the perfect gas equation of state:

$$\rho = \frac{pM_{mix}}{R_{uni}T} = \frac{p\sum_{i=1}^{n}M_iX_i}{R_{uni}T}$$
(6.9)

which gives the density. This method is compared with the value given by Eqtab and the difference is negligible.

The equations presented for the density and dynamic viscosity were only used at the boundary layer edge. The viscosity at the wall is determined using CEA which has been introduced in Section 5.2.1. The density at the wall is determined using the Chapman-Rubesin constant which was used in the derivation of both the binary and tertiary catalytic theory (Section 2.3.2), which is expressed as $l = \frac{\rho\mu}{\rho_e\mu_e} = 1$.
6.3.2 Determination of φ_2

The factor φ_2 corrects for catalytic effects and influences the diffusive heat flux as shown by Eq. (2.23b). The correction factor depends on the variable parameter χ which will be discussed in the next section and the velocity gradient (β) (discussed in Section 6.3.4). Moreover, φ_2 also depends on the catalytic velocity k_w .

The catalytic velocity can be determined using:

$$k_{w_1} = \frac{\gamma_w}{4} \sqrt{\frac{8k_B T_w}{\pi m_1}} \tag{6.10}$$

which was shown in Section 2.2.2. [15] This equation relates the catalytic efficiency at the wall γ_w to the diffusive heat flux.

6.3.3 Determination of χ

A major difference between the equations derived by Park [15] for a tertiary gas mixtures compared to the binary case is the variable parameter χ . This parameter depends on several variables as expressed by Eq. (2.25). Since the mass per particle is known from Eq. (6.7) it is possible to acquire the average mixture mass by combining it with the mass fractions. However, the two remaining parameters – ϕ_3 and the Schmidt number Sc_{ij} – are more complicated to be determined.

6.3.3.1 Determination of ϕ_3

The mathematical expression for ϕ_3 is shown in Eq. (2.22). In this equation the reverse of the mass fraction can be recognized, as well as the Schmidt number. Since the Schmidt number will be discussed in the next section it will be considered to be known. Hence, the remaining values required to acquire ϕ_3 is expressed by the stream function $f(\eta)$. This function is used in the similarity reduced momentum equation which was first introduced by Eq. (2.13a) in Section 2.3.2.1. The boundary conditions can be included which is very similar to the well-known Blasius equation $(f''' + \frac{1}{2}ff'' = 0)$:

$$f''' + ff'' = 0$$

BC: $f(0) = f'(0) = 0; \ f'(\infty) = 1$ (6.11)

Solving Eq. (6.11) is done using the shooting method combined with the Euler method for an ordinary differential equation. By first assuming a particular value for f''(0) the values at the next time step can be determined in combination with the first two boundary conditions. What happens is that this boundary value problem changes into an initial value problem since all initial values are known. At infinity for which 10 is chosen as a sufficiently large value, the result is compared with the third boundary condition. Using the Newton's method the next guess for f''(0) is determined which requires the slope at the previous guess:

$$f''(0)_{new} = f''(0)_{old} - \frac{g(\infty)}{g'(\infty)}$$

$$g(\infty) = 1 - f'(\infty)$$
(6.12)

The progression towards the next step is done using the Euler method which can be expressed as:

$$\begin{aligned}
f_{i+1} &= f_i + f'_i \cdot \Delta \eta \\
f'_{i+1} &= f'_i + f''_i \cdot \Delta \eta \\
f''_{i+1} &= f''_i + (-f_i \cdot f''_i) \cdot \Delta \eta
\end{aligned}$$
(6.13)

It can be seen that in Eq. (6.13) the first two equations are linked using Euler method. The last expression is the rewritten form of Eq. (6.11).

Using this method Eq. (6.11) was solved for $0 \le \eta \le 10$ with step size $\Delta \eta = 10^{-6}$. The iteration was terminated when the difference between the third boundary condition and the actual value is smaller than 10^{-10} .

From this it is found that f''(0) = 0.4696. After 6 iterations of the initial condition the convergence was sufficient enough to meet the termination criterion. The convergence is shown in Fig. 6.2(a). In Fig. 6.2(b) the distribution of $f''(\eta)$ is shown. It can be seen that it drops rapidly with increasing distance normal to the wall.

Having acquired the values for this stream function all the values can be normalized which is exactly the $\frac{f''(\eta)}{f''(0)}$ part of Eq. (2.22). Using the Riemann integral method which approximates the integral by the sum of a large number of rectangles, Eq. (2.22) can be solved numerically. Since η ranges from 0 to 10, the integral is performed until 10.



Figure 6.2: Convergence and distribution of $f''(\eta)$.

6.3.3.2 Determination of the Schmidt Number

The Schmidt number is defined as the ratio between the viscosity and the mass diffusivity. Since there is a tertiary gas mixture, there are in total nine different binary mass diffusion cases which results in nine Schmidt numbers:

$$Sc_{ij} = \frac{\mu}{\rho D_{ij}} \tag{6.14}$$

However, not all combinations are required as can be seen in Eq. (2.22).

The binary diffusion coefficient is determined using [18]:

$$D_{ij} = \frac{2.628 \cdot 10^{-7} \sqrt{T^3 \frac{M_i + M_j}{2000 M_i M_j}}}{\frac{p}{101325} (\sigma_{ij} \cdot 10^{10})^2 (\Omega_{ij}^{\star}^{(1,1)} \cdot 10^{20})}$$
(6.15)

The collision diameter (σ) of each species is given in Table 6.2, and since the diffusion coefficients are considered for a combination of two species, the average has to be taken of these collision diameters:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \tag{6.16}$$

Table 6.2: Characteristics of the species. [64,

Species	σ [m]	$\frac{\epsilon}{k_B}$ [K]
Ν	$3.246 \cdot 10^{-10}$	49.43
N_2	$3.681 \cdot 10^{-10}$	102.0
Kr	$3.675 \cdot 10^{-10}$	170.0

The diffusion-collision integral $\bar{\Omega}_{ij}^{(1,1)}$ is a necessary parameters to model the collision of gas particles. When this integral is normalized by the rigid sphere collision integral it results in the reduced diffusioncollision integral $\Omega_{ij}^{\star}^{(1,1)}$ which can be computed using [18, 66]:

$$\Omega_{ij}^{\star(1,1)} = \frac{A}{T^{\star^B}} + \frac{C}{e^{DT^\star}} + \frac{E}{e^{FT^\star}} + \frac{G}{e^{HT^\star}}$$
(6.17)

This is based on the Lennard-Jones potential theory which describes the interaction between two particles with a repulsive term and an attractive term (introduced in Section 2.2.1). Depending on the distance between these two particles the repulsive or the attractive term will be dominant. The coefficients A, B, ..., H are given by Neufeld [66] as: 1.06036, 0.1561, 0.193, 0.47635, 1.03587, 1.52996, 1.76474, 3.89411.

 T^{\star} is the temperature normalized by the potential parameter:

$$T^{\star} = \frac{Tk_B}{\epsilon_{ij}} \tag{6.18}$$

These potential parameters differ for all species (Table 6.2), and since the binary diffusion coefficient is required the binary potential parameter [18] is necessary:

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \tag{6.19}$$

6.3.4 Determination of Frozen Enthalpy and Stream Velocity Gradient

The only variables that have not been discussed in this section are the frozen enthalpy at the boundary layer edge, used in Eq. (2.23a), and the stream velocity gradient, present in Eq. (2.23) and (2.24).

The total enthalpy at the boundary layer edge is used to determine the frozen enthalpy at the boundary layer edge. The summation of the frozen enthalpy and the energy that is released when all the nitrogen atoms recombine is equal to the total enthalpy:

$$\bar{h}_e = h_e - h_R \alpha_1 \tag{6.20}$$

Since the total enthalpy, the heat of recombination of nitrogen (i.e. 33844376 J/kg [14]), and the mass fraction of N are known, it is possible to determine this frozen enthalpy.

The final parameter is the stream velocity gradient $\beta = \frac{du_e}{dx}$ at the boundary layer edge. It is complicated to determine this value since it cannot be measured directly. Two different methods are used which can be compared to each other:

1. By performing shadowgraph measurements the standing shock is made visible around the model. The radius of the shock at the stagnation point is measured and the gradient is determined using:

$$\left(\frac{du}{dx}\right)_{stag} \approx \frac{1}{r_{eff}} \sqrt{\frac{2p_{stag}}{\rho_{stag}}} \tag{6.21}$$

where the pitot pressure and density at the boundary layer edge were presented in Table 5.1. [49]

This equation introduced by Zoby and Sullivan [49] is based on several important assumptions. Firstly, the theory behind the equation is based on the assumption of a Newtonian flow which is only applicable in a flow with a Mach number larger than 3.5. The flow conditions, presented in Table 5.1, have a Mach number below 2 which is significantly lower than required.

Moreover, in the equation an effective radius is required. This radius corresponds to a hemisphere that creates the same velocity gradient at the stagnation point. Zoby and Sullivan [49] presented a correction for a wide range of body radii and corner radii with respect to a hemisphere. For the flat disk-cylinder models used in this thesis (where the body radius is 6 mm, corner radius is 1.5 mm, and nose radius is infinite) the correction is: $\frac{r_B}{r_{eff}} = 0.365$. Since $r_B = 6$ mm the effective radius is known.

The equation based on modified Newtonian flow includes the freestream pressure as presented by Fay and Riddell [13]. Including this to Eq. (6.21) results in:

$$\left(\frac{du}{dx}\right)_{stag} \approx \frac{1}{r_{eff}} \sqrt{\frac{2p_{stag} - p_{\infty}}{\rho_{stag}}}$$
(6.22)

2. The second method is based on the assumption that silicon dioxide is a fully non-catalytic material. Although in reality this is not completely true, the diffusive heat flux (Eq. (2.23b)) is assumed to be zero. With this the measured heat flux is equal to the conductive heat flux (Eq. (2.23a)). Since all the remaining parameters are known using the programs discussed in Chapter 5 and the equations presented in this chapter, the velocity gradient can be calculated.

6.4 Comparison Between Binary and Tertiary Gas Mixture Theory

In Section 6.3 the focus was on the theory for a tertiary gas mixture. For a binary gas mixture, discussed in Section 2.3.2.1, the resulting equation were as follows:

$$q_D = 0.47Sc^{-2/3}\sqrt{2\beta\mu_{es}\rho_{es}}h_R\alpha_e\varphi_1 \tag{2.18}$$

$$\varphi_1 = \frac{1}{1 + \frac{0.475c^{-2/3}\sqrt{2\beta\mu_{se}\rho_{se}}}{\rho_w k_w}}$$
(2.19)

$$q_C = 0.47 \sqrt{2\beta \mu_{se} \rho_{se}} \overline{Pr}_w^{-2/3} \overline{h}_{se}$$
(2.20)

Most of these parameters were discussed in Section 6.3, while for several parameters some elaboration is required.

Since in the case of a binary mixture there is no inert gas, the mass fraction (α_e) was taken to be equal to α_1 of the tertiary mixture. Moreover, Sc_{12} was taken to be the Schmidt number for this binary case.

The values at the boundary layer edge were substituted in the density, dynamic viscosity, and frozen enthalpy with subscript se.

Results

In this chapter the results of the pressure (Section 7.1) and heat flux measurements (Section 7.2) are presented and compared to theory. A comparison is also made between the flow conditions. Explanations for the discrepancies witnessed in the comparison are discussed in Chapter 8. The chapter ends with the catalytic efficiencies for the different coatings (Section 7.3).

7.1 Pressure Measurements and Shadowgraph Visualization

In this section the pressure measurements are shown and compared to the predicted values by L1d2. This comparison is essential since L1d2 is used to simulate the flow conditions and hereby has a large influence on the theoretical calculations (presented in Chapter 6). Furthermore, in combination with the shadowgraph visualization images (presented in this section) the steady regime is determined which dictates the test time of each flow condition. This steady regime is crucial for determining the heat flux measurements in Section 7.2.

7.1.1 Pressure Measurements

Static and pitot pressure measurements are conducted for all flow conditions. These graphs are shown in Fig. 7.1. Four static measurements are shown at each flow condition in Fig. 7.1(a), 7.1(c), and 7.1(e) respectively. Two clear jumps can be seen, the first corresponds to arrival of the primary shock wave at the first pressure sensor (at $t = 0 \ \mu s$) and the second to the arrival at the second pressure sensor (e.g. around $t = 300 \ \mu s$ in Fig. 7.1(a)), which is separated by 50 cm. The shock speeds deducted from the experiments are shown in Table 7.1. Compared to L1d2 the error is less than 3%.

Table 7.1: Shock speed, static pressure and pitot pressure of flow conditions A, B, and C compared to L1d2.

		- FI	0 1111	
		Flov	v Condition	
		A	В	С
	L1d2 [m/s]	$1.632 \cdot 10^3$	$2.410 \cdot 10^3$	$2.696 \cdot 10^3$
Shock Speed	Experiment [m/s]	$1.600 \cdot 10^3$	$2.370 \cdot 10^3$	$2.625 \cdot 10^{3}$
	Relative error $[\%]$	-1.96	-1.66	-2.63
	L1d2 $[N/m^2]$	$5.286 \cdot 10^5$	$1.022 \cdot 10^5$	$8.753 \cdot 10^4$
Pitot Pressure	Experiment $[N/m^2]$	$4.460 \cdot 10^5$	$1.009 \cdot 10^{5}$	$9.423 \cdot 10^4$
	Relative error [%]	-15.64	1.27	7.66

The pitot pressure measurements are shown in Fig. 7.1(b), 7.1(d), and 7.1(f) respectively. The steady pitot pressure is shown in the corner of each figure. These values are determined by taking the mean of the average pressure of each measurement curve within the steady regime. The range of the steady regime will be discussed in more detail later in this section. The variation from the mean with a 95% confidence interval of each curve is determined. The largest value is then printed together with the mean value in the figure. The pitot pressure values are compared to L1d2 in Table 7.1 from which it can be seen that there is a relatively large error in the value of flow condition A compared to the other conditions.

The presented values are based on a steady regime that requires an additional explanation. Since a





Figure 7.1: Pressure measurements at flow conditions A, B, and C.

finite amount of time is required for the standing shock to establish which is visible as relatively large oscillations, the start of the steady regime is chosen to be after those oscillations. The regime ends right before the standing shock is perturbed. This perturbation is visible as a second peak at around 70 μ s for condition B (Fig. 7.1(d)) and 45 μ s for condition C (Fig. 7.1(f)). The shadowgraphs results (discussed in Section 7.1.2) were also used in combination with these pitot measurements to determine the steady regime. The resulting steady periods are presented in Table 7.2.

Table 7.2: Steady time periods of flow conditions A, B, and C. t = 0 s is equal to the arrival of the primary shock.

Flow Condition	Steady start $[\mu s]$	Steady end $[\mu s]$	Steady time period $[\mu s]$
A	50	125	75
В	20	60	40
\mathbf{C}	10	30	20

7.1.2 Shadowgraph Visualization Results

The shadowgraph images are taken at an interval of 5 μs . The images corresponding to flow condition B from 0 μs until 25 μs are shown in Fig. 7.2. The incoming primary shock wave travels from left to right.

Comparing the different images in a chronological order it can be seen that the incoming primary shock (Fig. 7.2(a)) causes a reflective wave when it hits the model wall (Fig. 7.2(b)). This reflective wave travels in the opposite direction of the flow and it becomes a bow shock (Fig. 7.2(c)-7.2(d)). At 20 μ s the standing shock is fully developed and moves barely, which can be concluded by comparing Fig. 7.2(e) and 7.2(f).



Figure 7.2: Shadowgraph images of flow condition B.

By overlapping several shadowgraph images of the steady regime, the bow shock can be made clearer. The resulting images are shown in Fig. 7.3 for each flow condition. The first thing that is noticeable is the stand-off distance which is the largest for condition A and it becomes smaller with the flow conditions. Since the real distance corresponding to each pixel is known this distance can be measured. The results are shown in Table 7.3.

From Fig. 7.3 also the shock radius can be determined at the stagnation point. This is done by overlapping the centerpiece of the shock with a circle of which the radius is measured. The radius of each flow condition is shown in Table. 7.3. Using Eq. (6.22) the velocity gradient is calculated which is also presented in this table. Also the velocity gradient is shown which is calculated using the heat flux values for SiO₂ as introduced in Section 6.3.4.





(a) Shadowgraph measurements of con- (b) Shadowgraph measurements of con- (c) Shadowgraph measurements of condition A. dition B. dition C.

Figure 7.3: Summation of several shadowgraph pictures of the standing shock (indicated with red line) of conditions A, B, and C.

	F	low Condition	
	A	В	С
$\delta_{shock} [\mathrm{mm}]$	4.64	2.56	2.24
$r_{shock} \; [mm]$	18.74	15.36	16.24
β [s ⁻¹] (Shadowgraph)	$1.878\cdot 10^4$	$2.898\cdot 10^4$	$2.960\cdot 10^4$
$\beta [\mathrm{s}^{-1}] (\mathrm{SiO}_2)$	$1.939\cdot 10^4$	$7.447\cdot 10^4$	$1.614\cdot 10^5$

Table 7.3: Standing shock characteristics and velocity gradient.

7.2 Heat Flux Measurements

The heat flux measurements are summarized in Table 7.4. In Appendix E all the measurements can be found. Similar to the pitot pressure, the 95% confidence region of each curve is calculated and the largest is shown as the overall uncertainty in Table. 7.4. The flow conditions are discussed separately:

	Flow Condition A		Flow Condition B		Flow Condition C	
Coating Type	$q_s \; [\mathrm{MW}/\mathrm{m}^2]$	# tests	$q_s \; [{ m MW/m^2}]$	# tests	$q_s \; [\mathrm{MW}/\mathrm{m}^2]$	# tests
Uncoated	4.375 ± 0.40	7	9.974 ± 0.56	2	-	-
SiO_2	5.200 ± 0.27	7	5.918 ± 0.36	6	8.821 ± 0.62	10
Black CuO	-	-	6.568 ± 0.33	11	9.437 ± 0.43	4
Brown CuO	-	-	6.451 ± 0.51	4	7.174 ± 1.24	2
Cu	-	-	7.203 ± 0.21	7	-	-

Table 7.4: Summary of heat flux measurements.

• Flow Condition A: As initially planned in Section 1.5 this flow condition functions as a check of the coating, since it should in principle not affect the measured heat flux. Because this flow condition is a low enthalpy case, the dissociation is very low hence experiments with the copper (oxide) coated probes were not conducted.

Comparing the heat flux values of the uncoated and SiO_2 cases, it is clear that in the latter the value is higher. This result is highly unexpected since the coating should not have an effect on the heat flux. In Section 8.1.3 several possibilities are considered to clarify these measurements.

- Flow Condition B: The heat flux values for the five different coatings vary significantly. SiO_2 shows the lowest heat flux which is expected for a non-catalytic material. Copper oxide (both black CuO and brown CuO) are around 1.5 MW/m² higher than SiO₂. And copper which is a more catalytic material than copper oxide is 2.3 MW/m² higher than SiO₂. The results corresponding to the uncoated probes show the highest heat flux, since catalytic recombination is occurring at the platinum and/or the gold.
- Flow Condition C: The heat flux experiments for only three different coatings are available. The uncoated probes were not tested at this flow condition after witnessing the results of flow condition B. Also the copper results are absent since no probes were intact after conducting the experiments at condition B.

The heat flux of SiO_2 has increased significantly when comparing conditions B and C, which is also the case for the black CuO. The latter heat flux is larger than the value of SiO_2 which meets the expectations of a catalytic material against a non-catalytic material. The brown CuO results are however significantly lower than the values of SiO_2 . Moreover, the deviation is larger than any other measurement (i.e. $1.24 \, [MW/m^2]$). When the models were visually inspected it was noticed that the brown CuO layer was damaged significantly at large portions of the surface, hereby exposing the underlying layers (Fig. 7.4). For this reason only two tests have been made with this coating. However, the surface was already damaged to such a degree that the results are not useful.



Figure 7.4: The damaged surface of a brown CuO coated probe.

7.3 q_D/q_C vs. γ_w Diagram and Catalytic Efficiency

Using the heat flux values presented in Section 7.2 and the velocity gradients calculated with the SiO₂ heat flux measurements, the diffusive and conductive heat flux ratio are expressed in a q_D/q_C vs. γ_w diagram. The two curves are calculated using the binary and tertiary gas mixture theories (presented in Section 2.3.2) and the necessary values were gathered from L1d2 (Section 5.1), CEA (Section 5.2.1), Eqtab (Section 5.2.2) and the miscellaneous theories presented in Section 6.3.

The results for flow condition B are shown in Fig. 7.5. As can be seen the binary and tertiary gas mixtures agree well at low catalytic efficiencies and both show no diffusive heat transfer and thus a zero heat transfer ratio when the wall is non-catalytic. As the catalytic efficiency increases, the ratio increases also. The rise of the binary theory is steeper than for the tertiary mixture. Eventually both curves reach a plateau at high efficiencies (around $\gamma_w = 10^{-1}$).

In Fig. 7.5 the heat transfer ratio is also shown for the different coatings by the horizontal lines. The uncertainties, that were calculated with a confidence region of 95%, are shown by the error bars. By determining the intersection of the curve for a tertiary gas mixture and the experimental values, the catalytic efficiencies are determined. These are shown in Table 7.5.

Coating	Flow Condition	γ [-]	$\gamma_{\text{lower bound}}$ [-]	$\gamma_{\text{higher bound}}$ [-]
Black CuO	В	$1.36 \cdot 10^{-3}$	$4.10 \cdot 10^{-4}$	$4.40 \cdot 10^{-3}$
Brown CuO	В	$9.50\cdot10^{-4}$	$1.00 \cdot 10^{-5}$	$6.18 \cdot 10^{-3}$
Cu	В	$5.29 \cdot 10^{-2}$	$5.75 \cdot 10^{-3}$	-
Black CuO	С	$6.10 \cdot 10^{-4}$	$1.34 \cdot 10^{-4}$	$1.30 \cdot 10^{-3}$

Table 7.5:	Surface	catalvtic	efficiency	results.

The intersections corresponding to the two copper oxides take place in a region with a high sensitivity since the curve is steep. However, the copper heat ratio intersects at a location where the curved has reach a plateau. This region has a low sensitivity and introduces a large uncertainty in the catalytic efficiency.

The q_D/q_C vs. γ_w diagram for flow condition C is shown in Fig. 7.6. Only the experimental data of black CuO is shown since experimental data for Cu is absent and the data for brown CuO have been dropped. The figure shows the same shape as Fig. 7.5 but the curves reach their plateaus at higher heat flux ratios. Using the same method as flow condition B, the catalytic efficiency has been determined and is shown in Table 7.5.





Figure 7.5: Heat transfer ratio against black CuO, brown CuO, and Cu surface catalytic efficiency for N - N_2 - Kr interaction at flow condition B.

From Table 7.5 it can be seen that the catalytic efficiency of Cu is the highest. The black and brown copper oxides give a similar catalytic efficiency and both are significantly smaller than the value for Cu. This overall phenomenon matches with the oxygen case (Fig. 3.12(c)) where in general the copper efficiencies are higher than the copper oxides.

The catalytic efficiencies for flow condition B and C of black CuO are within the same range and within each others uncertainties. This same order of magnitude was also found by Park [15] for oxygen (i.e. $\gamma_w = 2.6 \cdot 10^{-3}$ and $3.2 \cdot 10^{-3}$).

Because the Cu line intersects the tertiary gas mixture curve at a plateau there is a large uncertainty in the catalytic efficiency. When the binary curve is used for Cu it is found that the efficiency is $3.07 \cdot 10^{-3}$ which is 17 times smaller.

When the results of this thesis are put in perspective with the literature (Fig. 3.12), Fig. 7.7 is made. Since the catalytic efficiencies for copper oxide are unique there is no comparison possible. Only the efficiency for Cu acquired using the tertiary curve can be compared and it is within the same range as Prok [47], Hartunian et al. [43], Rahman and Linnett [30], and Pope [48].



Figure 7.6: Heat transfer ratio against black CuO surface catalytic efficiency for N - N₂ - Kr interaction at flow condition C.



Figure 7.7: Nitrogen catalytic efficiency including the present work.

Discussion

In the previous chapter the results of the measurements were presented and compared with each other. Some of these results (such as the pressure and heat flux) did not match with the expectations from theory or numerical programs. If these discrepancies remained undiscussed, the reliability of the experiments could be questioned. Therefore, in this chapter these discrepancies are discussed for the three flow conditions. Since flow conditions B and C both show a large number of similarities in their results, they are considered together in a section.

8.1 Flow Condition A

For flow condition A there were some discrepancies regarding the pitot pressure, velocity gradient, and the heat flux. Possible reasons for these differences are given in this section.

8.1.1 Pitot Pressure

From Table. 7.1 it can be seen that there is a 15% misalignment between the measured pitot pressure and the one predicted by L1d2, while the error is significantly smaller for the other conditions. The overestimation of L1d2 is suspected to be caused by an improper prediction of the viscous effects. It is speculated that the viscous data of krypton contains an error that causes the misalignment. This is because condition A has essentially a binary gas mixture since the presence of atomic nitrogen is negligible. On the other hand, the atomic nitrogen in conditions B and C has a much larger effect on the viscosity which hides the possible error caused by krypton. Strong conclusions however cannot be made.

8.1.2 Velocity Gradient

When the velocity gradients are compared (Table 7.3) it can be found that the values only have a 3.3% discrepancy for flow condition A between the shadowgraph visualization and the SiO₂ method. With the shadowgraph visualization method the error is caused by the modified Newtonian flow assumption which is not valid due to the low Mach number of the flow. However, in the SiO₂ method it is assumed that SiO₂ is a completely non-catalytic material hence the influence of the small amount of diffusive heat flux has been neglected. Nonetheless, because the amount of dissociation is negligible it is believed that the SiO₂ method is more accurate than the shadowgraph visualization method.

8.1.3 Heat Flux

The heat flux measured by the uncoated probe was smaller than the heat flux determined by the SiO_2 coated probe. This measurement is highly unexpected since the coating should not affect the measured heat flux. If there is an effect, it should insulate the platinum from the flow, hereby resulting in a lower heat flux compared to the uncoated probe.

One possibility that could explain the excessive heat flux at the SiO_2 surface is a chemical reaction between the SiO_2 and the nitrogen molecules. Since the coated probes are not heated up in an oven to make the transition from the amorphous SiO_2 to a strong crystalline structure of SiO_2 , there are holes within the structure of SiO_2 . By considering the chemical reaction of this coating with nitrogen molecules it was found, using the formation energies of each species, that the reaction is endothermic which would lower the heat flux. Since the measured heat flux is larger, the possibility of a chemical reaction was ruled out. The last possible theoretical explanation for the increased heat flux for SiO₂ is adsorption. This phenomenon can occur when a gas particle is trapped in the amorphous SiO₂ layer. The tendency of this phenomenon dependents on the gas species and is expressed by the liquefaction temperature. This liquefaction temperature of krypton is -153 °C and -195.8 °C for nitrogen molecules. In the experiments of Park [15] a test gas consisting of argon and oxygen was used, which resulted in identical heat flux measurements using the uncoated and SiO₂ coated probes. The liquefaction temperature of argon and oxygen are -185.8 °C and -183 °C respectively. When comparing these temperature it can be seen that krypton has the highest temperature, which means that it tends to be adsorbed easier than the others species. Since adsorption is an exothermic process, it is therefore believed that the krypton gas could have caused the increase in heat flux seen with the SiO₂ measurements.

8.2 Flow Conditions B & C

Flow conditions B and C showed similar discrepancies in the static pressure, pitot pressure, and velocity gradient. While krypton made it possible to reach flow conditions with a significant amount of dissociation (33.3% for condition B and 54.3% for condition C), it is suspected that the presence of this gas caused unexpected effects on the boundary layer of the shock tube and the stability between the driver and driven gas.

8.2.1 Static Pressure

From Fig. 7.1(c) and 7.1(e) it can be seen that there is a large disparity between the measured static pressure and L1d2. Moreover, when compared with Fig. 7.1(a) it can be seen that there is a significant increase in oscillations of the static pressure measurements. These oscillations could be caused by velocity fluctuations from a turbulent boundary layer at the wall of the shock tube, which cannot be simulated by L1d2.

A turbulent boundary layer is thicker than a laminar boundary layer. [67] Hence, it decreases the effective cross-section behind the primary shock wave which increases the velocity of the gas slug behind the shock wave. The effect of a boundary layer growth on the velocity of the contact surface has been investigated throughly by several authors [68, 69]. The increase in velocity yields a decrease in static pressure which propagates through the boundary layer (since the static pressure is constant through the boundary layer). This justification potentially explains the lower static pressure (and the oscillations) seen in the measurements.

8.2.2 Pitot Pressure

In Fig. 7.1(d) and 7.1(f) a perturbation of the standing shock is shown as a second peak starting from approximately $t = 70 \ \mu s$ and $t = 45 \ \mu s$, respectively. This second peak does not correspond to the arrival of the contact surface (predicted by L1d2) nor the reflective shock wave. Efforts were made to postpone or lower the effect of this second peak to increase the steady regime. One method was by designing and manufacturing a pressure model with the same size as the heat flux model (as introduced in Section 4.1.2). Due to some leakage problems resulting from this new model, the results were less accurate. However, it was possible to conclude that the second peak is almost unaffected by the model size. More can be found in Appendix F.

The occurrence of the second peak can be explained by a phenomenon called Rayleigh-Taylor instability. [70, 71] This happens at the interface between two gases which in this case is helium and the N_2 -Kr mixture. Since there is a normal pressure gradient from the helium to the test gas, the helium can push into the latter at the centerline, ahead of the contact surface. It was found by Youngs [70] that a large density ratio between the two gases will result in a larger mixed region. This principle is shown in Fig. 8.1. It is suspected that the second peak is the arrival of helium ahead of the contact surface and reflected shock wave.

Another possibility is the decrease in effective cross-section due to the boundary layer growth as described in Section 8.2.1. This effect could drastically decrease the test time as was found by Musgrove and Appleton [69], since the contact surface arrives significantly faster than determined in the ideal case (without the effect of a thick boundary layer).



Figure 8.1: Rayleigh-Taylor instability. [70]

8.2.3 Velocity Gradient

While the velocity gradient of flow condition A determined by the shadowgraph visualization and the SiO_2 method showed a small difference, conditions B and C show an error up to 445%. Since the modified Newtonian flow theory does not consider dissociation, it is expected that the discrepancy increases with the flow condition. Moreover, similar to flow condition A, the Mach number is not sufficient to fulfill the Newtonian flow assumption. For this reason the discrepancy for conditions B and C is expected. It is believed that the error caused by the modified Newtonian method is significantly larger than the error caused by SiO_2 method hence the velocity gradient determined using SiO_2 were used for further calculations.

Sensitivity Analysis & Uncertainties

In Chapter 7 the uncertainties of both the pitot pressure and heat flux measurements were expressed by the 95% confidence interval of the curves. While the indicated uncertainty of the catalytic efficiency in Fig. 7.5 and 7.6 only depends on the uncertainty of the heat flux measurements, this does not include the uncertainties in the tertiary gas mixture curve. To create this curve a large number of variables are required which are gathered from L1d2, Eqtab, and the theories presented in Section 6.3.

This chapter will discuss the different uncertainties of the curve corresponding to the tertiary gas mixture by performing a sensitivity analysis on various parameters. Since almost all catalytic efficiency values are from flow condition B the analysis is tuned towards this case.

In Section 9.1 the sensitivity analysis is performed on the pitot pressure and total enthalpy. These variables dictate the flow behind the primary shock wave of the shock tube. Any variation in these values causes a chain effect on the remaining calculations.

Section 9.2 covers the sensitivity analysis on the average collision integrals and the binary diffusion coefficients. These parameters have an essential role in the calculation of the heat flux ratio.

9.1 Pitot Pressure and Total Enthalpy

Both the pitot pressure and total enthalpy are input variables for Eqtab. Uncertainties in these parameters result in a different flow condition at the boundary layer edge. These parameters are necessary to create the q_D/q_C vs. γ_w curve.

The pitot pressure is used at three locations: determination of the species particle mass (Eq. (6.7)), calculation of the density at the boundary layer edge (Eq. (6.9)), and determination of the binary diffusion coefficient (Eq. (6.15)). The total enthalpy is used in the expression of the frozen enthalpy (Eq. (6.20)).

The two variables are analyzed together as a combination. In Table 9.1 the results of having a 10% variation is shown. The fluctuations experienced during the pitot measurements are well within this percentage (Fig. 7.1). The same percentage has been chosen for the total enthalpy for consistency.

	T_e	X_N	X_{N_2}	X_{Kr}	N_2 diss.	β	$\gamma_{black\ Cuo}$	$\gamma_{brown} \ Cu$	o γ_{Cu}
$10\%\uparrow p_{pitot}$	$\uparrow 0.42\%$	$\downarrow 0.62\%$	$\uparrow 0.43\%$	$\uparrow 0.07\%$	$\downarrow 0.62\%$	$\downarrow 9.86\%$	\downarrow 7.35%	\downarrow 7.37%	$\uparrow 59.78\%$
$10\%\downarrow p_{pitot}$	$\downarrow 0.47\%$	$\uparrow 0.66\%$	$\downarrow 0.44\%$	$\downarrow 0.08\%$	$\uparrow 0.82\%$	$\uparrow 12.11\%$	$\uparrow 8.82\%$	$\uparrow 9.47\%$	$\downarrow 23.97\%$
$10\%\uparrow H$	$\uparrow 2.52\%$	$\uparrow 17.89\%$	$\downarrow 12.07\%$	$\downarrow 2.09\%$	$\uparrow 20.50\%$	$\downarrow 3.22\%$	$\downarrow 24.26\%$	$\downarrow 21.05\%$	$\downarrow 85.78\%$
$10\% \downarrow H$	$\downarrow 2.74\%$	$\downarrow 18.46\%$	$\uparrow 12.46\%$	$\uparrow 2.15\%$	$\downarrow 20.11\%$	$\uparrow 3.56\%$	$\uparrow 49.26\%$	$\uparrow 38.95\%$	-
$10\%\uparrow p_{pitot} \& \uparrow H$	$\uparrow 2.97\%$	$\uparrow 17.22\%$	$\downarrow 11.62\%$	$\downarrow 2.01\%$	$\uparrow 19.72\%$	$\downarrow 12.81\%$	$\downarrow 30.15\%$	$\downarrow 27.37\%$	$\downarrow 86.16\%$
$10\%\uparrow p_{pitot} \& \downarrow H$	$\downarrow 2.35\%$	$\downarrow 19.05\%$	$\uparrow 12.87\%$	$\uparrow 2.22\%$	$\downarrow 20.75\%$	$\downarrow 6.60\%$	$\uparrow 38.97\%$	$\uparrow 29.47\%$	-
$10\%\downarrow p_{pitot} \& \downarrow H$	$\downarrow 3.18\%$	$\downarrow 17.82\%$	$\uparrow 12.03\%$	$\uparrow 2.07\%$	$\downarrow 19.43\%$	$\uparrow 16.16\%$	$\uparrow 61.03\%$	$\uparrow 51.58\%$	-
$10\%\downarrow p_{pitot} \& \uparrow H$	$\uparrow 2.02\%$	$\uparrow 18.57\%$	$\downarrow 12.52\%$	$\downarrow 2.17\%$	$\uparrow 21.28\%$	$\uparrow 8.57\%$	$\downarrow\!16.91\%$	$\downarrow\!13.68\%$	$\downarrow\!85.21\%$

Table 9.1: Sensitivity analysis on pitot pressure and total enthalpy.

When considering the individual influence of p_{pitot} and H, it is clear from Table. 9.1 that the former has a small influence on the conditions at the boundary layer edge, while the latter has a large influence. A good example is the amount of dissociation that varies less than 1% when changing p_{pitot} , whereas changing H yields a 20% change in dissociation. The catalytic efficiencies show the same pattern where changing H results in a larger variation than changing p_{pitot} . Having an increase of p_{pitot} and/or H yields a decrease of catalytic efficiencies, and vice versa. The catalytic efficiency of Cu shows at some occasions a different behavior which can be clarified by the fact that the Cu heat transfer ratio intersects the curve at a plateau. Any small changes which result in a variation of the curve result in a large change in catalytic efficiency. For this reason some values are absent when there is no intersection between the curve and the Cu heat transfer ratio.

When considering the combination of p_{pitot} and H, it can be observed that the influence of H dominates. p_{pitot} strengthens the effect of H when they both change by 10% in the opposite direction.

9.2 Collision Integral and Binary Diffusion Coefficient

While the inaccuracies in the pitot pressure is a result of the pressure experiments and the inaccuracies in the total enthalpy are caused by L1d2, there is also a source of uncertainty in the theory which is used to create the q_D/q_C vs. γ_w curve. This is mainly caused by the average collision integrals $(\bar{\Omega}_{ij}^{(2,2)})$ and the binary diffusion coefficients (D_{ij}) .

The collision integrals are used in the calculations of the dynamic viscosity (Eq. (6.6) and (6.8)). In these calculations the collision parameters of krypton were assumed to be equal to the ones of argon (Table 6.1). Moreover, Kim et al. [64] compared the average collision integrals from literature and found a large variation among them for a range of species combinations. This variation is estimated in this thesis to be 20% which is used for the sensitivity analysis.

The binary diffusion coefficients are used to calculate the Schmidt number (Eq. (6.14)). Since the Schmidt number is used directly in Eq. (2.22) and (2.25), it has a great effect on the results. To be consistent with the average collision integral variation, the same percentage of variation is taken for the sensitivity analysis on the binary diffusion coefficients. Additionally, since the Schmidt number combines the dynamic viscosity and the binary diffusion coefficient, it is relevant to investigate the coupling effect of both parameters on the results. The results of the sensitivity analysis are shown in Table 9.2.

	μ_e	Sc_{12}	Sc_{23}	Sc_{13}	β	γ_{black} Cuo	γ_{brown} Cuc	γ_{Cu}
$20\%\uparrow \bar{\Omega}_{12}^{(2,2)}$	$\downarrow 0.33\%$	$\downarrow 0.33\%$	$\downarrow 0.33\%$	$\downarrow 0.33\%$	$\uparrow 0.33\%$	0.00%	0.00%	$\downarrow 7.39\%$
$20\%\downarrow \bar{\Omega}_{12}^{(2,2)}$	$\uparrow 0.36\%$	$\uparrow 0.36\%$	$\uparrow 0.36\%$	$\uparrow 0.36\%$	$\downarrow 0.36\%$	0.00%	0.00%	$\uparrow 9.47\%$
$20\%\uparrow \bar{\Omega}_{13}^{(2,2)}$	$\downarrow 6.69\%$	$\downarrow 6.69\%$	$\downarrow 6.69\%$	$\downarrow 6.69\%$	$\uparrow 7.17\%$	$\uparrow 2.21\%$	${\uparrow}4.21\%$	$\downarrow\!60.31\%$
$20\%\downarrow \bar{\Omega}_{13}^{(2,2)}$	$\uparrow 7.85\%$	$\uparrow 7.85\%$	$\uparrow 7.85\%$	$\uparrow 7.85\%$	$\downarrow 7.28\%$	$\downarrow 2.21\%$	$\downarrow 4.21\%$	-
$20\%\uparrow \bar{\Omega}_{23}^{(2,2)}$	$\downarrow 11.00\%$	$\downarrow 11.00\%$	$\downarrow 11.00\%$	$\downarrow 11.00\%$	$\uparrow 12.36\%$	$\uparrow 4.41\%$	$\uparrow 7.37\%$	$\downarrow\!70.58\%$
$20\%\downarrow \bar{\Omega}_{23}^{(2,2)}$	$\uparrow 14.31\%$	$\uparrow 14.31\%$	$\uparrow 14.31\%$	$\uparrow 14.31\%$	$\downarrow 12.51\%$	$\downarrow 3.68\%$	$\downarrow 6.32\%$	-
$20\%\uparrow D_{12}$	0.00%	$\downarrow\!16.67\%$	0.00%	0.00%	0.00%	$\downarrow 10.29\%$	$\downarrow 7.37\%$	$\downarrow\!81.19\%$
$20\%\downarrow D_{12}$	0.00%	$\uparrow 25.00\%$	0.00%	0.00%	0.00%	$\uparrow 18.38\%$	$\uparrow 11.58\%$	-
$20\%\uparrow D_{13}$	0.00%	0.00%	0.00%	$\downarrow 16.67\%$	0.00%	$\uparrow 6.62\%$	$\uparrow 4.21\%$	-
$20\% \downarrow D_{13}$	0.00%	0.00%	0.00%	$\uparrow 25.00$	0.00%	$\downarrow 6.62\%$	$\downarrow 4.21\%$	$\downarrow 73.38\%$
$20\%\uparrow D_{23}$	0.00%	0.00%	$\downarrow 16.67\%$	0.00%	0.00%	$\downarrow 5.88\%$	$\downarrow 4.21\%$	$\downarrow 69.39\%$
$20\% \downarrow D_{23}$	0.00%	0.00%	$\uparrow 25.00\%$	0.00%	0.00%	$\uparrow 8.09\%$	$\uparrow 5.26\%$	-
$20\%\uparrow \bar{\Omega}_{23}^{(2,2)} \& \uparrow D_{12}$	$\downarrow 11.00\%$	$\downarrow\!25.84\%$	$\downarrow\!11.00\%$	$\downarrow 11.00\%$	$\uparrow 12.36\%$	$\downarrow 4.41\%$	0.00%	$\downarrow\!85.61\%$
$20\%\downarrow \bar{\Omega}_{23}^{(2,2)} \& \downarrow D_{12}$	$\uparrow 14.31\%$	$\uparrow 42.88\%$	$\uparrow 14.31\%$	$\uparrow 14.31\%$	$\downarrow 12.51\%$	$\uparrow 17.65\%$	$\uparrow 6.32\%$	-
$20\%\uparrow \bar{\Omega}_{23}^{(2,2)} \& \downarrow D_{12}$	$\downarrow 11.00\%$	$\uparrow 11.25\%$	$\downarrow 11.00\%$	$\downarrow 11.00\%$	$\uparrow 12.36\%$	$\uparrow 20.59\%$	$\uparrow 17.89\%$	-
$20\%\downarrow \bar{\Omega}_{23}^{(2,2)} \& \uparrow D_{12}$	$\uparrow 14.31\%$	$\downarrow 4.75\%$	$\uparrow 14.31\%$	$\uparrow 14.31\%$	$\downarrow 12.51\%$	$\downarrow\!15.44\%$	$\downarrow 14.74\%$	$\downarrow\!60.28\%$
$20\%\uparrow \bar{\Omega}_{12}^{(2,2)}, \bar{\Omega}_{13}^{(2,2)}, \bar{\Omega}_{23}^{(2,2)} \\ \&\downarrow D_{12}, D_{13}, D_{23} $	↓16.67%	$\uparrow 4.17\%$	$\uparrow 4.17\%$	$\uparrow 4.17\%$	$\uparrow 20.00\%$	$\uparrow 22.79\%$	$\uparrow 22.11\%$	-
$\begin{array}{l} 20\%\downarrow\ \bar{\Omega}_{12}^{(2,2)},\ \bar{\Omega}_{13}^{(2,2)},\ \bar{\Omega}_{23}^{(2,2)}\\ \&\uparrow\ D_{12},\ D_{13},\ D_{23} \end{array}$	$\uparrow 25.00\%$	$\uparrow 4.17\%$	$\uparrow 4.17\%$	$\uparrow 4.17\%$	↓20.00%	$\downarrow 17.65\%$	$\downarrow 18.95\%$	-

Table 9.2: Sensitivity analysis on the collision integrals and binary diffusion coefficients.

Three different average collision integrals are used in the calculations: $\bar{\Omega}_{12}^{(2,2)}$, $\bar{\Omega}_{13}^{(2,2)}$, and $\bar{\Omega}_{23}^{(2,2)}$. From Table 9.2 it can be found that the effect of $\bar{\Omega}_{12}^{(2,2)}$ is negligibly small, which corresponds to the collision of nitrogen atoms and nitrogen molecules. Changing $\bar{\Omega}_{13}^{(2,2)}$ affects the results more but it is $\bar{\Omega}_{23}^{(2,2)}$ that has the largest effect on the results. This average collision integral corresponds to the collision of nitrogen molecules and krypton, which concerns the heaviest particles in the mixture. It can be seen that increasing the collision integral reduces the dynamic viscosity and Schmidt numbers while the velocity gradient and catalytic efficiencies increase, and vice versa.

While the collision integrals affect all the Schmidt numbers through the dynamic viscosity, this is not the case for the binary diffusion integrals. It can be seen that increasing a binary diffusion coefficient results in a 16.67% decrease of the corresponding Schmidt number, and when decreasing the diffusion coefficient the Schmidt number increases with 25%. Moreover, when comparing the effects of the diffusion coefficients on the catalytic efficiencies, it can be found that D_{12} has the largest effect which indirectly means that Sc_{12} has the largest effect among the different Schmidt numbers.

Comparing the effect of the collision integrals with the diffusion coefficients, it can be seen that the latter has a larger effect on the catalytic efficiencies. This however does not take the coupling of the two into account.

When $\bar{\Omega}_{23}^{(2,2)}$ and D_{12} are combined it can be found that the effects on the parameters increases substantially. The Schmidt numbers and catalytic efficiencies are greatly affected by $\bar{\Omega}_{23}^{(2,2)}$ and D_{12} . In the case of increasing $\bar{\Omega}_{23}^{(2,2)}$ by 20% while D_{12} is reduced by 20% the catalytic efficiency can change with 20%.

At last, when all the collision integrals and diffusion coefficients are increased or decreased, it can be seen that not only the catalytic efficiencies are greatly affected, also the dynamic viscosity and velocity gradients changes drastically.

All in all, when comparing the influence of the average collision integrals and binary diffusion coefficient with the pitot pressure and total enthalpy, it can be concluded that the total enthalpy is the most crucial parameter for the catalytic efficiency results. This value was determined by L1d2 and is assumed to be constant at the stagnation point.

10 Conclusions

10.1 Conclusions

The research question of this thesis was stated as:

"What is the catalytic recombination efficiency of copper oxide when exposed to nitrogen?"

To obtain the answer to this research question, the shock tube located at KAIST (South Korea) has been used in combination with heat transfer gauges (i.e. thin-film gauges). These gauges were highly polished and flush-mounted in a flat-disk cylinder model with a diameter of 12 mm to form a probe. The probe was coated using the E-beam evaporation technique. The probe received one of the following coating combination:

- 1. 1000 nm ${\rm SiO}_2$
- 2. 1000 nm $\rm SiO_2$ and 180 nm black CuO
- 3. 1000 nm SiO_2 and 180 nm brown CuO
- 4. 1000 nm SiO_2 and 180 nm Cu

These coated models were used to conduct experiments at different flow conditions: flow condition A has a low enthalpy (2.0 MJ/kg) with a mass fraction dissociation of 1%, B has a moderate amount of enthalpy (4.4 MJ/kg) and a dissociation of 33.3%, whereas C has a high enthalpy (5.8 MJ/kg) and a dissociation of 54.3%. Flow conditions B and C were used to determine the catalytic efficiency. All coatings have been tested in flow condition B, whereas only SiO₂ and black CuO could be tested with successful results in condition C.

The temperature measurements acquired from each probe were first filtered using a Savitzky-Golay filter and then converted to heat flux using the Cook & Feldermann [61] method. The heat flux profiles for flow condition C showed in general more oscillations than flow condition B. Moreover, due to the brittleness of the brown CuO the coating was more prone for damage which resulted in larger fluctuations in the heat flux profile.

Using the binary and tertiary gas mixture theory, the diffusive and convective heat flux ratio was related to the catalytic efficiency in an S-shaped curve, from which it was possible to read off the value based on the experimentally determined heat flux. To create this S-curve the velocity gradient was required, which was determined using the shadowgraph measurements post-processed using the modified Newtonian theory, and using the SiO₂ measurements. The difference in velocity gradients between the two methods for condition A was insignificant hereby validating the latter method as an appropriate method. For flow conditions B and C the difference was large due to the presence of dissociation which cannot be tackled by the modified Newtonian theory.

With this the catalytic efficiency was determined to be between $6.10 \cdot 10^{-4}$ and $1.36 \cdot 10^{-3}$ for black CuO, $9.50 \cdot 10^{-4}$ for brown CuO, and $5.29 \cdot 10^{-2}$ for Cu. These values however have a relatively large error margin. This error is caused by the fluctuations of the heat flux measurements, the uncertainties in the numerical programs, and the uncertainties caused by the assumptions in the binary and tertiary theories. For both copper oxides, the difference in catalytic efficiencies between the binary and tertiary curves was small. Since Cu is a highly catalytic material, the difference between the two curves is excessive. For this reason it is more appropriate to conclude that the catalytic efficiency for Cu is between $3.07 \cdot 10^{-3}$ and $5.29 \cdot 10^{-2}$. Due to all the uncertainties, it is therefore pertinent to state that the determined efficiencies for CuO and Cu are more indications of the order of magnitude rather than very accurate values.

10.2 Recommendations

• *Roughness variation:* During reentry (and also in arc-jet facilities) the harsh environment affects the surface of the body. Chemical reaction and ablation occur simultaneously which alter the structure of the material. This increase in roughness has a great impact on the number of collisions an incoming test gas experiences as discussed in Section 2.2.3, hence a rougher surface results in a higher catalytic efficiency. The magnitude of the roughness effect is not investigated and is unknown, but is important to be known for a better determination of the catalytic efficiency.

In this thesis project the quartz rods were highly polished with an average particle diameter of 6.0 μ m. Although it is possible to, for example, omit the last step of the polishing process, it is not know what the effect of a rougher surface has on quality and survivability of the platinum paste. A rougher surface could increase the difficulty for the platinum particles to bond properly to form a continuous and uniform platinum bridge.

- Wall Temperature variation: As described by Fig. 3.2, the catalytic efficiency varies depending on the wall temperature for glass. In this thesis the wall temperature was around 320 K due to the short run time of a shock tube. Since the wall temperature increases to temperature above 1000 K in both arc-jets and real reentry flights, it is important to investigate the wall temperature effect on the catalytic efficiency of copper and copper oxide.
- Coupling of oxygen and nitrogen: Using the same shock tube, Park [15] conducted experiments in 2013 for oxygen on copper oxide. Together with the conclusions made in this thesis, the preliminary conclusion is that copper oxide (whether it is CuO or Cu₂O) has a catalytic efficiency that is significantly lower than presented in literature.

To represent real-flight conditions more, air has to be used as a test gas in the shock tube. For this reason the next step should focus on the catalytic efficiency of air on copper and copper oxide, which has not been investigated thoroughly yet as seen from Fig. 3.12(a).

However, tackling this problem for air brings an even more complicated gas mixture situation. Not only will there be O, O_2 , N, and N_2 , but a coupling exists between O and N which creates NO and possibly also NO_2 and N_2O . This results in a gas mixture with at least five species. Such theory is not available and has to be derived using the same method as for the binary and tertiary gas mixtures.

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Thermochemical Equilibrium and Boundary Layer Thickness

The theory presented in Section 2.3.2 is based on the assumption that thermochemical equilibrium is reached at the boundary layer edge. This means that the dissociation of the molecules has finished between the standing shock and the boundary layer. While the method presented in Section 2.4.2 is more accurate than the theory presented in this section, the latter gives the possibility to show the time and distance dependency of the flow conditions in the region between the standing shock and the boundary layer.

In this appendix the species concentrations are first calculated against time in Section A.1 which is necessary to determine the flow conditions which is tackled in Section A.2. In Section A.3 the final results are presented where it is computed how much distance is required to reach thermochemical equilibrium. This appendix closes off with the calculations of the boundary layer thickness in Section A.4 which functions as a final check that thermochemical equilibrium is indeed established before reaching the boundary layer edge.

A.1 Species Concentrations

Assuming that the freestream conditions before the standing shock (called region 2 in Fig. 2.11) are known it is possible to determine the flow parameters right behind the shock using normal shock relations [72]:

$$p_{after} = p_{pre} \frac{2\gamma M^2 - (\gamma - 1)}{\gamma + 1} \tag{A.1a}$$

$$T_{after} = T_{pre} \frac{[2\gamma M^2 - (\gamma - 1)][(\gamma - 1)M^2 + 2]}{(\gamma + 1)^2 M^2}$$
(A.1b)

$$\rho_{after} = \rho_{pre} \frac{(\gamma+1)M^2}{(\gamma-1)M^2+2} \tag{A.1c}$$

$$u_{after} = u_{pre} \frac{2 + (\gamma - 1)M^2}{(\gamma + 1)M^2}$$
 (A.1d)

The specific heat ratio is determined using:

$$\gamma = \frac{\sum_{i}^{n} f_i X_i}{\sum_{i}^{n} (f_i - 1) X_i} \tag{A.2}$$

This is for a gas mixture consisting of n species and f_i is a constant which is 3.5 for monotonic gases and 2.5 for diatomic molecules.

The values determined using Eq. (A.1) are only the ones directly behind the standing shock. To determine the values of each of these parameters at the next time instance, it is necessary to calculate the concentration of each species over time.

The total concentration of a gas mixture can be calculated using:

$$n = \frac{p}{k_B T N_A} \tag{A.3}$$

In this equation the Avogadro's constant (N_A) is present since *n* has the unit $\left[\frac{\text{mol}}{\text{m}^3}\right]$ instead of the usual $[\text{m}^{-3}]$. Using the molar fractions that is known before the standing shock the concentration of each species can be determined. These are then the species concentrations directly after the standing shock.

The dissociation of a gas can be determined using the rate coefficient. The equation depends on the type of gas that is considered. For nitrogen [12] this is:

$$(N_2 + N_2 \to N + N + N_2): k_f = 7 \cdot 10^{15} T^{-1.6} e^{\frac{-113200}{T}}$$
 (A.4)

It is hereby assumed that the dissociation only takes place by collision of two nitrogen molecules. This rate coefficient is then used to determine the rate at which the concentration changes for N_2 and N respectively:

$$\frac{dn_{N_2}}{dt} = -k_f \cdot n_{N_2} \tag{A.5a}$$

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$$\frac{dn_{\rm N}}{dt} = 2k_f \cdot n_{N_2} \tag{A.5b}$$

It is assumed that the concentration of N_2 decays exponentially, hence it is fitted using:

$$n_{N_2} = n_{N_{2_{t=0}}} \cdot e^{\frac{dn_{N_2}}{n_{N_{2_{t=0}}}} \cdot t}$$
(A.6)

The amount at which N_2 decreases can be used to determine the amount at which N increases. Since N_2 splits into two atoms, the increase of N is twice as large as the decrease of N_2 . For flow condition B (Table. 5.1) the results are shown in Fig. A.1. Both Fig. A.1(a) and Fig. A.1(b) show an asymptotic behavior as time passes by: N_2 asymptotically approaches 0 whereas N approaches 0.6 mol/m³.



(a) The exponential decay of N_2 over time between the (b) The increase of N over time between the standing standing shock and the wall.

Figure A.1: The decrease and increase of N_2 and N between the standing shock and the wall for flow condition B.

Because of this exponential behavior it is common to define an e-folding time which is the time that is required to grow by a factor e for N (this corresponds to $1 - \frac{1}{e}$ of the asymptotic value), and it is also common to define the 99% time which corresponds to 99% of the asymptotic value for N. For flow condition B this corresponds to $t_{e-folding} = 49.3 \ \mu s$ and $t_{99\%} = 217.8 \ \mu s$.

A.2 Flow Conditions

With the known concentration of N₂ and N over time it is possible to determine the behavior of the remaining flow parameters. At each time instance c_p is calculated:

$$c_p = \frac{2.5k_Bn_1 + 3.5k_Bn_2 + 2.5k_Bn_3}{\rho} \tag{A.7}$$

This is then used in

$$H = c_p T + h_D \alpha_N \tag{A.8}$$

where h_D is the dissociation energy of N₂ (946 J/mol) [73]. Using the initial temperature from Eq. (A.1b) the total enthalpy can be determined since at that moment there is no dissociation ($\alpha_N = 0$).

The total enthalpy stays constant hence when dissociation occurs the temperature drops. Using Eq. (A.8) the temperature is then determined at each time instance. By assuming a constant pressure the density is also calculated using:

$$\rho = \frac{p}{k_B T M} N_A \tag{A.9}$$

The resulting curves for the temperature and density for condition B are shown in Fig. A.2(a) and A.2(b), respectively.



(a) Temperature against time between the standing (b) Density against time between the standing shock and shock and the wall.

Figure A.2: The change in temperature and density between the standing shock and the wall for flow condition B.

A.3 Distance and Damköhler Number

The results calculated in the previous sections are expressed against time. Time is however a relative quantity since the velocity varies hence it is necessary to express the time as function of the distance. The distance (y) starts from the standing shock and ends at the wall and the shock stand-off distance (y_s) has been measured in Section 4.3. With these parameters the time can be computed by:

$$t = \frac{y}{u} = \frac{y}{u_s \left(\frac{y_s - y}{y_s}\right)} = \frac{y_s}{u_s} \left(\frac{y}{y_s} - 1\right) \tag{A.10}$$

Using this equation the distance and the velocity can be expressed against time, shown in Fig. A.3 for flow condition B.



(a) Distance against time between the standing shock (b) Velocity against time between the standing shock and the wall.

Figure A.3: The change in distance and velocity between the standing shock and the wall for flow condition B.

From Fig. A.3(a) it can be seen that the same asymptotic behavior occurs at large time values. Since the shock stand-off distance was determined to be 2.56 mm (Section 4.3) the curve approaches this value. This is explained by the velocity curve shown in Fig. A.3(b) where the velocity approaches zero asymptotically.

The e-folding and 99% times can be translated to distances: $y_{e-folding} = 0.049$ mm and $y_{99\%} = 0.219$ mm. These values can be expressed by the Damköhler number which is the ratio between the shock stand-off distance and the e-folding distance [12]:

$$Da = \frac{\delta_{shock}}{y_{eq}} \tag{A.11}$$

This corresponds to $Da_{e-folding} = 51.8$ and $Da_{99\%} = 11.7$, respectively.

Having such large values means that equilibrium is reached very quickly. In order to conclude whether this state is established before the boundary layer edge is reached, it is necessary to determine the boundary layer thickness.

Boundary Layer Thickness A.4

To derive the boundary layer thickness it is necessary to use the coordinate transformation (Eq. (2.9)) shown in Section 2.3.2.1. In this case the subscipt e is taken to be the boundary layer edge. Moreover, so far in this appendix the distance (y) is assumed to originate from the standing shock. This made the figures more intuitive since the flow is followed. In the remainder of the thesis the coordinate system has been taken as shown in Fig. 2.6 and the non-dimensional coordinate system is based on this. Since this latter system is necessary again, the orientation is reversed which means that x=0 corresponds to the wall.

First the s coordinates need to be rewritten:

$$s = \int_0^x \rho_e \mu_e r^2 u_e dx = \rho_e \mu_e r^2 \beta \int_0^x x dx = \frac{1}{2} \rho_e \mu_e r^2 \beta x^2$$
(A.12)

using which η can be expressed as:

$$\eta = \frac{ru_e}{\sqrt{2s}} \int_0^y \rho dy = \frac{r\beta x}{\sqrt{2\frac{1}{2}\rho_e \mu_e r^2 \beta x^2}} \int_0^y \rho dy = \sqrt{\frac{\beta}{\rho_e \mu_e}} \int_0^y \rho dy \tag{A.13}$$

To do this Eq. (2.15) has been used. Additionally, the derivative of η is calculated:

$$d\eta = \sqrt{\frac{\beta}{\rho_e \mu_e}} \rho dy \tag{A.14}$$

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At last, the following is defined: $\frac{u}{u_e} = \frac{\partial f}{\partial \eta} = f'$. The displacement boundary layer thickness can be determined using:

$$\delta = \int_0^\infty \left(1 - \frac{\rho u}{\rho_e u_e} \right) dy \tag{A.15}$$

The original equation for an incompressible flow did not include the density ratio, but since the flow is dissociated inside the boundary layer it has been included. [74] Using the definition of f' and Eq. (A.14) the boundary layer thickness can be expressed in the non-dimensional coordinate as:

$$\delta = \int_0^\infty \left(1 - \frac{\rho}{\rho_e} \frac{\partial f}{\partial \eta} \right) dy = \int_0^\infty \left(1 - \frac{\rho}{\rho_e} \frac{\partial f}{\partial \eta} \right) \sqrt{\frac{\rho_e \mu_e}{\beta}} \frac{1}{\rho} d\eta = \sqrt{\frac{\mu_e}{\rho_e \beta}} \left[\int_0^\infty \frac{\rho_e}{\rho} d\eta - \int_0^\infty f' d\eta \right] \quad (A.16)$$

The necessary values at the boundary layer edge (i.e. μ_e , ρ_e , and β) are determined using the method presented in Section 6.3. The value for β that is determined using the SiO₂ measurements is chosen over the shadowgraph measurements.

Moreover, the computation of f' has been conducted in Section 6.3.3.1. The result is shown in Fig. A.4. By choosing the boundary layer edge to be at the location where $f' = \frac{u}{u_e} = 0.99$ it is found that $\eta = 3.471$. Hence the upper limit of the two integrations corresponds to this value. The integration of f' can then be done using the trapezoidal method.

The density values first need to be transferred to y coordinates by combining Fig. A.2(b) and A.3(a). Afterwards Eq. (A.13) is used to transform it to η coordinates using the trapezoidal method to perform the integration. At the end the density ratio is integrated over η .

For flow condition B where $\mu_e = 7.16 \cdot 10^{-4} \text{ kg/(m \cdot s)}, \rho_e = 1.09 \cdot 10^{-1} \text{ kg/m}^3$, and $\beta = 7.45 \cdot 10^4 \text{ s}^{-1}$, this would result in a boundary layer thickness of 1.1 mm. Since the shock stand-off distance was determined to be 2.56 mm and thermochemical equilibrium is reached at around 2.34 mm there is still around 1.24 mm left between the moment equilibrium is reached and the boundary layer edge.

While the situation has been simplified by assumptions which introduce uncertainties in the representation of the reality, the results indicate that thermochemical equilibrium is established relatively far from the boundary layer edge. Even in the pessimistic case where the errors of this calculation influences the results negatively, it is believed that equilibrium is ensured since the velocity approaches zero asymptotically near the wall (Fig. A.3(b)).



Figure A.4: The behavior of f' against the non-dimensional coordinate $\eta.$

Shock Tube Program Comparison

In Section 5.1 the shock tube program L1d2 was introduced. However, in this thesis project another shock tube program was considered which was given by Prof. Chul Park of KAIST. This program will be introduced in Section B.1 and compared with L1d2 in Section B.2.

B.1 Stube9

The alternative shock tube program that was considered is called "stube9". It uses the equations which are based on the perfect gas assumption from Glass and Patterson [52] as estimated values which have been presented in Section 4.1.4.

These estimated values are then submitted into different subroutines which determines the real gas solution using the concept of partition function which was discussed in Section 2.4.2. It should be noted that stube9 calculates the flow conditions for a given shock speed. Moreover, this program is only capable of presenting the steady values hence the transient behavior of the flow parameters is absent.

B.2 Comparison Between L1d2 and Stube9

From Sections 5.1 and B.1 it can be understood that there is a significant difference in nature between the two shock tube programs. L1d2 uses the JANAF coefficients and stube9 is based on partition functions, which requires the data regarding the electronic states of atoms and molecules, found in the NIST Atomic Spectra Database. [25]

By comparing both programs to experimentally determined values the superior one can be chosen. Using the shock tube the following flow condition was reproduced: an absolute driver pressure of 1.65 MPa helium and an absolute driven pressure of 150 Pa with 21% volume N_2 and 79% volume Kr.

As indicated in Fig. 4.2 two piezo-electric pressure sensors are used which are exactly 0.5 m separated from each other. From these the shock speed and the static pressure behind the shock wave (p_2) can be measured. These values are then compared to numerical results from L1d2 and stube9. Since stube9 needs the shock speed as input value to calculate the remaining flow parameters, the measured shock speed has been taken while L1d2 calculates it by itself based on the initial conditions.

The results are summarized in Table B.1 from which it can be seen that there is a 10% difference between the predicted shock speed by L1d2 and the measured value. L1d2 predicts a static pressure that is around 15% higher than measured while stube9 predicts a significantly lower pressure.

	Experimer	nt	L1d2	stube9	
	Shock speed [m/s]	p_2 [Pa]	Shock speed error [%]	$p_2 \text{ error } [\%]$	$p_2 \text{ error } [\%]$
Run 1	$2.17 \cdot 10^{3}$	$2.21 \cdot 10^4$	10.08	15.88	-16.77
$\operatorname{Run} 2$	$2.16 \cdot 10^{3}$	$2.48\cdot 10^4$	11.04	16.01	-27.06

Table B.1: Validation of L1d2 and stube9 using two shock tube runs.

The first run is also shown in Fig. B.1. Since the results of L1d2 are available with respect to the time it has been shown in this figure as the circled dashed lines. The steady part of the experimental data has been chosen after the initial peak, hence this same part is taken from L1d2 to determine the steady static pressure.



Figure B.1: Static pressure vs time containing the results of the experiment, L1d2, and stube9.

It is important to note that the experiment itself has flaws which can be seen in the differences in measured static pressure between the two runs. At the moment of conducting these experiments, the shock tube has some leakage problems which means that the lowest pressure which could be reached with the rotary pump was around 10 Pa and it leaked at a rate of approximately 20 sec/Pa. Therefore, the test gas was contaminated and the driven pressure could not be exactly 150 Pa. This problem was solved in a later phase of the thesis which made it possible to pump the tube consistently below 8 Pa for the real experiments. However, at that phase the choice between L1d2 and stube9 was already made.

Taking these things into account it could explain the differences between the experimental data and the results of L1d2. However, since the differences in static pressure of stube9 are larger and the results cannot be presented against time, it is less powerful than L1d2. The error of stube9 is possibly caused by the absence of the viscous effect. At a pressure of 150 Pa the viscous effect can have an effect that cannot be neglected.

Based on this validation the choice was made to use L1d2 for the shock tube calculation rather than stube9.

Equilibrium Composition Program Comparison

In Section 5.2 the equilibrium composition program "Eqtab" was introduced which was used to determine the conditions at the boundary layer edge. Also CEA was presented which was used to calculate the conditions at the wall. The program that is presented in this appendix is called "therm" and is based on the same principles as CEA. It used to be the improved version of the old version of CEA.

In Section C.1 this program will be presented which is then followed by a comparison with CEA in Section C.2. This appendix ends with a comparison between Therm and Eqtab from which the latter was chosen.

C.1 Therm

The program "therm" can determine the equilibrium composition of a gas mixture. To use therm properly an input file is required with all the species present in the gas. Each species has (next to its molar weight) a set of six coefficients for different temperature ranges: 500 K until 3000 K, 3000 K until 6000 K, and above 6000 K. These coefficients are called JANAF thermodynamic coefficients and they represent the following variables: H_f^{298} , S_c , H_c , a_1 , a_2 , and a_3 . [75] These variables represent respectively the heat of formation at 298.13 K, the reference entropy (Eq. (C.1)), the reference enthalpy (Eq. (C.2)), and the last three values are coefficients based on the curve fits.

$$S_c = \int_0^{T_s} \frac{C_p}{T} dT \tag{C.1}$$

$$H_c = \int_{T_0}^{T_s} C_p dT \tag{C.2}$$

With these six coefficients the C_p , H, and S of each species can be determined as shown by Eq. (C.3)-(C.5). The reference temperature T_0 is set to 298.13 K whereas the split temperature T_s is 3000 K.

$$C_p = a_1 + a_2 T + \frac{a_3}{T^2} \tag{C.3}$$

$$H = H_f^{298} + \Delta H \tag{C.4a}$$

$$\Delta HT = A + BT + CT^2 + DT^3 \tag{C.4b}$$

$$A = -a_3; \ B = H_c - a_1 T_s - a_2 \frac{T_s^2}{2} + \frac{a_3}{T_s}; \ C = a_1; \ D = \frac{a_2}{2}$$
(C.4c)

$$S = S_c + a_1 \ln\left(\frac{T}{T_s}\right) + a_2(T - T_s) - \frac{a_3}{2}\left(\frac{1}{T^2} - \frac{1}{T_s^2}\right)$$
(C.5)

 C_p , H, and S describe the thermodynamic properties of the species. The species enthalpy is directly related to the species energy by:

$$\Delta H = \Delta E + (\Delta n)RT \tag{C.6}$$

which is derived by substituting the ideal gas law with the definition of enthalpy. Since the initial molar fraction between the different species and the initial temperature are all input values, the species energy can be determined.

With the given pressure and enthalpy as input values the temperature is varied to find the equilibrium state of all species. This is done by varying the species concentration with a slight amount and determine the change in the species energy. This slope has to be zero (or very near zero) to represent the equilibrium position. At the end of the iteration the species concentration, temperature and the thermodynamic properties are presented. Since the conditions are matched for the pressure and enthalpy, these are also known. Based on these the density and the molecular weight of the mixture are determined.

C.2 Comparison between CEA and Therm

In Table C.1 a comparison has been made between CEA and therm. By matching the temperature and the pressure for a certain gas mixture the differences are expressed. From this table it is clear that the differences are small. There is less than 2% discrepancy between the two enthalpies, whereas the densities and molar masses are essentially identical. This verification proves that there is basically no significant difference between the two programs since they are based on the same principles.

Table C.1: Comparison between CEA and therm for a binary gas mixture consisting of 42.8% in volume N₂ & 57.2% in volume Kr.

Variable	CEA	Therm	Difference
T [K]	500	500	
$p [\mathrm{N/m^2}]$	$9.869 \cdot 10^{-1}$	$9.869 \cdot 10^{-1}$	
$h [{ m J/kg}]$	$8.2254\cdot 10^4$	$8.375\cdot 10^4$	1.819%
$ ho [kg/m^3]$	1.4416	1.441	-0.042%
$M_{mix} [\mathrm{kg/mol}]$	$5.9931 \cdot 10^{-2}$	$5.993 \cdot 10^{-2}$	-0.002%

C.3 Comparison Between Therm and Eqtab

The performance of therm and eqtab have to be compared to see the accuracy of the JANAF coefficients for high temperatures. Since the equilibrium composition program needs to be applied at the stagnation boundary layer edge located behind the standing shock, the temperature could surpass the maximum limit of the JANAF coefficients. Moreover, for lower temperature cases eqtab can be verified using the results of therm.

Both codes give the results based on a chosen pressure and enthalpy. A total of ten different cases have been chosen where not only the aforementioned two variables are varied but also the gas mixture composition. These ten test cases are shown in Table C.2.

Test cases 1 to 3 show a possible gas mixture composition for the actual experiments of this thesis. The pressure and enthalpy are varied to such a degree that there is a no dissociation, a moderate amount of dissociation, and a high amount of dissociation, respectively. For cases 1 and 3 the differences in density and temperature between the two programs are ranging from 5 to 8%, while the differences in dissociation are small. For case 2 the differences in density and temperature are small but the dissociation differs.

From these three cases it is rather impossible to conclude whether therm or eqtab is the more accurate program. For this reason the following cases cover either an almost purely krypton mixture or an almost purely nitrogen mixture. Both programs were written for a binary gas mixture hence it was still necessary to have a very small amount of the other gas.

Cases 4 to 6 cover the almost purely krypton case. There was a suspicion that the JANAF coefficients for krypton were old and inaccurate. In the past these mistakes were reported by the users to the JANAF committee but krypton is an uncommon gas, hence it is possible that the coefficients have never been updated.

The first thing that is noticed from these three cases is that the error ranges from 5 to 15%, which is significantly larger than in cases 1 to 3. Case 4 has a low temperature hence the results between therm and eqtab should match, which is definitely not true here. The amount of dissociation differs significantly but the accuracy of both program is rather doubtful, since there is basically no nitrogen in the mixture.

Since the gas mixture mainly consists of a monatomic molecule and more importantly it is inert, the temperature can be calculated analytically. Since it is known that $\frac{c_p}{R} = 2.5$, hence multiplying this by the universal gas constant results in the heat capacity at constant pressure. However, the units are $\frac{J}{\text{mol}\cdot\text{K}}$ which can be converted to $\frac{J}{\text{kg}\cdot\text{K}}$ using the molar mass of krypton (i.e. 0.083798 kg/mol). Using this c_p value of krypton the temperature can be determined since $H = c_p T$. From this the temperature can be

determined analytically for cases 4 to 6 which results in respectively: 2051.7 K, 4031.4 K, and 8062.9 K. It can be seen that the temperatures calculated by eqtab are a lot closer to these values than therm.

Cases 7 to 10 are for an almost purely nitrogen case. The error for these four cases are ranging from 0.25 to 2%. Not only the density and temperature match very well, also the amount of dissociation is very similar. Even case 10 which has a very high amount of dissociation and a temperature of almost 8000 K, the results of therm matches well with eqtab. This means that the JANAF coefficients of nitrogen have been updated to such a degree that it is relatively accurate for the higher temperature range.

This, however, does show that both programs perform very well and give almost the same results while they are fundamentally different. Moreover, this also proves that the JANAF coefficients of krypton are inaccurate and outdated. The differences seen in the gas mixture (cases 1 to 3) are mostly caused by this accuracy of the JANAF values of krypton.

From this it is concluded that eqtab is superior relative to therm for the equilibrium composition calculations.

Case	Description	Gas composition	$p [{\rm N/m^2}]$	$H \; [{\rm J/kg}]$	Program	$\rho \; [\rm kg/m^3]$	T [K]	Mass fraction N ₂ Diss.
1	Gas mixture & no diss.	21% N ₂ 79% Kr	$1.17\cdot 10^2$	$1.00\cdot 10^6$	Therm Eqtab	$\frac{3.06 \cdot 10^{-4}}{3.32 \cdot 10^{-4}}$	$3.32 \cdot 10^3$ $3.06 \cdot 10^3$	0.00 0.00
2	Gas mixture & medium diss.	$\begin{array}{c} 21\% {\rm N}_2 \\ 79\% {\rm Kr} \end{array}$	$1.17 \cdot 10^3$	$3.88\cdot 10^6$	Therm	$1.55 \cdot 10^{-3}$	$5.66\cdot10^3$	0.73
					Eqtab	$1.57 \cdot 10^{-3}$	$5.61\!\cdot\!10^3$	0.70
3	Gas mixture & high diss.	$\begin{array}{c} 21\% {\rm N}_2 \\ 79\% {\rm Kr} \end{array}$	$1.17\cdot 10^4$	$5.88\cdot 10^6$	Therm	$9.52 \cdot 10^{-3}$	$8.81 \cdot 10^{3}$	1.00
					Eqtab	$1.00 \cdot 10^{-2}$	$8.32\!\cdot\!10^3$	0.99
4	Kr & low temp.	$\begin{array}{c} 0.03\% \ \mathrm{N_2} \\ 99.97\% \ \mathrm{Kr} \end{array}$	$1.17 \cdot 10^3$	$5.00 \cdot 10^5$	Therm	$5.10 \cdot 10^{-3}$	$2.31\!\cdot\!10^3$	0.00
					Eqtab	$5.85 \cdot 10^{-3}$	$2.02\!\cdot\!10^3$	0.00
5	Kr & medium temp.	$\begin{array}{c} 0.03\% \ {\rm N}_2 \\ 99.97\% \ {\rm Kr} \end{array}$	$1.17 \cdot 10^3$	$1.00 \cdot 10^6$	Therm	$2.73 \cdot 10^{-3}$	$4.32\!\cdot\!10^3$	0.73
					Eqtab	$2.93 \cdot 10^{-3}$	$4.02\!\cdot\!10^3$	0.40
6	Kr & high temp.	$\begin{array}{c} 0.03\% \ \mathrm{N_2} \\ 99.97\% \ \mathrm{Kr} \end{array}$	$1.17 \cdot 10^3$	$2.00 \cdot 10^6$	Therm	$1.41 \cdot 10^{-3}$	$8.34\!\cdot\!10^3$	1.00
					Eqtab	$1.49 \cdot 10^{-3}$	$7.91\!\cdot\!10^3$	0.00
7	$N_2 \&$ low diss.	99.997% N_2 0.003% Kr	$1.17 \cdot 10^{3}$	$1.00 \cdot 10^{7}$	Therm	$7.19 \cdot 10^{-4}$	$4.90\!\cdot\!10^3$	0.12
					Eqtab	$7.30 \cdot 10^{-4}$	$4.87\!\cdot\!10^3$	0.11
8	$N_2 \& medium diss.$	99.997% N_2 0.003% Kr	$1.17 \cdot 10^4$	$2.50 \cdot 10^7$	Therm	$4.21 \cdot 10^{-3}$	$6.30\!\cdot\!10^3$	0.49
					Eqtab	$4.24 \cdot 10^{-3}$	$6.29\!\cdot\!10^3$	0.48
9	N_2 & high diss.	99.997% N_2 0.003% Kr	$1.17\cdot 10^4$	$3.50 \cdot 10^7$	Therm	$3.33 \cdot 10^{-3}$	$6.80\!\cdot\!10^3$	0.74
					Eqtab	$3.35 \cdot 10^{-3}$	$6.77\!\cdot\!10^3$	0.74
10	$N_2 \& very$ high diss.	99.997% N_2 0.003% Kr	$1.17\cdot 10^4$	$4.50 \cdot 10^{7}$	Therm	$2.56 \cdot 10^{-3}$	$7.85\!\cdot\!10^3$	0.97
					Eqtab	$2.61 \cdot 10^{-3}$	$7.72\!\cdot\!10^3$	0.96

Table C.2: The ten test cases to compare the performance of therm and eqtab.

D

Heat Flux Conversion Comparison

In Section 6.2 two different heat flux conversion methods were mentioned: Cook and Feldermann [61] (Eq. (6.2)) and Kendall et al. [62] (Eq. (6.3)). The latter is less prone for noise which will be shown in this appendix using actual experimental data.

In Fig. D.1 the temperature profile is shown for a probe that was coated with black CuO and tested at flow condition B. This is analyzed by the Cook and Feldermann method and Kendall et al. method. Additionally, the method that has been used in this thesis, is shown where the Savitzky-Golay filter was used for the temperature values prior to the Cook and Feldermann method. These are shown in Fig. D.2.



Figure D.1: Temperature change with respect of time measured by the heat transfer gauge.

From Fig. D.2 it can be seen that the Cook and Feldermann method shows a large amount of fluctuations. However, the Kendall et al. method shows a significant reduction of these fluctuations while maintaining the same overall shape.

The interesting part is when the comparison is made between these methods and the current method used for this thesis. It can be seen that the Savitzky-Golay filter has cleaned the signal to such a degree that the fluctuations are very similar to the Kendall et al. method. This comparison indicates that the filter does not alter the results negatively while the Cook and Feldermann method is still used.



Figure D.2: Comparison between Cook and Feldermann method, Kendall et al. method, and the method used for this thesis.

Heat Flux Profile Measurements

In this appendix all the heat flux measurements are shown. Figures E.1-E.2 correspond to flow condition A, whereas Fig. E.3-E.7 represents condition B. The results of condition C are shown in Fig. E.8-E.10.

In the legend the name of each probe is shown which is used for identification. Also the number of run is shown. In the right upper corner of each graph the average is shown of all the results inside the steady regime. Also the largest error among all the curves with a 95% confidence interval is shown which represents the uncertainty.



Figure E.1: Heat flux profile measurements of the uncoated probes at flow condition A.



Figure E.2: Heat flux profile measurements of the SiO_2 probes at flow condition A.



Figure E.3: Heat flux profile measurements of the uncoated probes at flow condition B.



Figure E.4: Heat flux profile measurements of the SiO₂ probes at flow condition B.



Figure E.5: Heat flux profile measurements of the black CuO probes at flow condition B.


Figure E.6: Heat flux profile measurements of the brown CuO probes at flow condition B.



Figure E.7: Heat flux profile measurements of the Cu probes at flow condition B.



Figure E.8: Heat flux profile measurements of the SiO_2 probes at flow condition C.



Figure E.9: Heat flux profile measurements of the black CuO probes at flow condition C.



Figure E.10: Heat flux profile measurements of the brown CuO probes at flow condition C.

Alternative Pressure Model

From the pitot pressure experiments it was found that there is was second peak after the arrival of the standing shock, as seen in Fig. 7.1(d) and 7.1(f). Initially it was tried to prevent or lowering this second peak to increase the steady regime.

Since these experiments were conducted with the pressure model with a 20 mm diameter, it was decided to design and create a model with the same dimensions as the heat flux model (i.e. 12 mm diameter) which would fit a piezo-electric sensor. This is necessary to determine how prominent the second peak is for the smaller model, since that is eventually the model that is used to measure the heat flux to acquire the catalytic efficiency.

The engineering drawing that was made is shown in Fig. F.1(a) from which it can be seen that the front part of the model has the same dimensions as the heat flux model (Fig. 4.3(a)). Since the piezo-electric sensor has a certain length, the length of the model had to be increased. Moreover, a new sting had to be manufactured to fit the screws that were chosen for this model and also to compensate for the increase in length of the model. The final product mounted on the sting with a piezo-electric sensor inside is shown in Fig. F.1(b).





(b) Picture of the alternative pressure model.

Figure F.1: The pressure model with the same dimensions as the heat flux model.

With an o-ring around the piezo-electric sensor and also at each screw it was attempted to prevent leakages. This same method worked for the original pressure sensor with a diameter of 20 mm. Unfortunately, leakages did occur which could not be solved hence instead of pumping the shock tube to pressure values below 8 Pa only 13 Pa was possible.

The results are shown in Fig. F.2. When comparing the absolute pressure values for the different flow conditions it can be seen that they are basically the same for both models in flow condition A (Fig. F.2(a)).

However, for flow conditions B and C there is a noticeable difference as can be seen from Fig. F.2(b) and F.2(c), respectively. The pressure values for the new model is significantly lower than the ones corresponding to the previous model. This difference can be justified by the leakage problem that has relatively a larger impact on the purity of the test gas used for flow conditions B and C compared to A.

The focus is on the peak and the moment of arrival of the second peak. Both Fig. F.2(b) and F.2(c) show a slightly postponed arrival of the second peak compared to the old model, however the impact is



still the same. Since the test gas is more contaminated due to the leakages it cannot be excluded that the observed delay is caused by that.

The problem of the second peak was eventually evaded by ending the steady period before the arrival of the peaks which has been confirmed by shadowgraph measurements.



(c) Pitot pressure measurements of case C.

Figure F.2: Pitot pressure measurements of case A, B, and C for both the old (i.e. 20 mm) model and new (i.e. 12 mm) model.