
Dissertation submitted to the Department of Chemical Engineering of University of Patras by

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to obtain the Degree of Doctor of the University of Patras.

Patras May 2018

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Abstract

In the first part we explore the rotating lepton model that was first suggested by C.G. Vayenas and S. Souentie. This model has the ability to agree with many of the predictions of the Standard model but without use of adjustable parameters. Beyond the usefulness as a predicting tool, the fact that this model is based on first principles suggests that it contains a substantial amount of truth and thus warrants an in-depth review and analysis. Starting from the newtonian concepts of gravitation and space-time we explore the influence of special relativity and follow the line of thought of the model which ultimately claims that nuclear forces are the relativistic facets of gravity. Several examples are analyzed.

In the second part we study the reaction of CO2 hydrogenation in terms of its importance in the energy-management field and conduct several experiments in order to cast light in the role of metal-support interactions in the heterogeneous catalysis of the reaction.
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PART A

Investigation of the role of gravitational attraction in the structure and the catalysis of the formation of particles.
**Introduction of part A**

The scope of this part of the dissertation is to study the effects of special relativity (for the most part) as well as those of general relativity when modeling physical phenomena. In chemical engineering it is mostly electromagnetic forces that govern the molecular scale and gravitational forces that govern the macro cosmos. The relation of this study with chemical engineering is not direct as we are going to discuss some elementary principles of electromagnetic and gravitational forces as seen from a relativistic point of view. However the insight that one might gain from this research can without any doubt contribute to a holistic approach in engineering and even cast light (or doubt) on established ideas.

The short window roughly between 1905 and 1915 was the time where physicists treated gravitation with the concepts of Special Relativity. Lorentz, Poincaré, Minkowski, Somelfeld, de Sitter, and Einstein were among those Physicists. After the introduction of General Theory of Relativity those efforts were largely abandoned.
1. Introducing space, time, mass and force.

Most likely we will never be able to break free from our bodies, the consequence of this being that we will always have to perceive the universe through the way our brain processes our sensory signals.

The most fundamental perception our brain offers to us is the notion of the “object”. An object is something that can be set apart, that can be considered as a unity. It is probable that the notion of the “object” is nothing but a heuristic approximation hard-wired in our brain, a creative setting of thresholds, in order to speed up the processing of our surroundings. Complementary to the notion of the object is the notion of space and time. We perceive Objects as entities floating in space and time. That also means that space and time are properties referring to a specific reference frame of perception. Space and time are different in the way we perceive them and the way we can move in them. We cannot impose a motion of an object in time but we can definitely move it in space.

Once we have a way to measure space and time we can define the world “move” more finely using the derivative notions of velocity and acceleration.

\[ \vec{v} = \frac{d \vec{s}}{dt} \text{ and } \vec{a} = \frac{d \vec{v}}{dt} \]  

(1.1)

Both are vector quantities adequately defined by their magnitude and their direction. Because of some property specific to each object some objects are more difficult to accelerate than others and for a given object it is more difficult to achieve a large acceleration than a smaller one.

In Newton's words:

“A body, from the inert state of matter, is not without difficulty put out of its state of rest or motion.” [1].

This “difficulty” is a first coarse approach of the notion of Force. The difficulty of acceleration of an object depends on the extent of the acceleration and on another property of the object. If we use the word Force for what we have described as “difficulty” and the word Mass for that “other property” we get the simplified version of Newton's second law of motion as \( F=ma \), the general version being

\[ \vec{F} = \frac{d \vec{p}}{dt} = \frac{d (m \vec{v})}{dt} = m \frac{d \vec{v}}{dt} + \vec{v} \frac{d m}{dt} \]  

(1.2)

Of course the words mass and force existed long before Newton and have been used to describe similar notions. People knew that massive objects are harder to accelerate or to stop. Based on this law, force is the natural quantity required in order to change the kinetic state of an object. Mass is
the measure of an object’s inertia.

Mass can also be defined as the ratio of momentum $p$ to velocity which is useful since momentum is conserved even in plastic collisions, where energy is dissipated.

$$m = \frac{\vec{p}}{|\vec{v}|} = \frac{p}{v}$$

(1.3)

The above definitions may seem trivial in Newtonian engineering but in Special relativity choosing from different definitions could lead to different laws. [2]

Note that the simplified version $F=ma$ implies that $m$ is not a function of velocity, which as we will see in chapter 4 is not true.

Note that the discussion so far and the definitions presented are for the concept of “inertial mass” occasionally symbolized as $m_i$ to distinguish it from the gravitational mass which we will discuss below.
2. Equivalence Principle

For some reason the quantity of mass is tightly associated with the effect of gravitation. Gravitation is well approached by Newton's inverse square Law.

Newton showed that such a law could account for Kepler's laws of planetary motion:

“Bodies, whose forces decrease in a duplicate ratio of their differences from their centres, may move among themselves in ellipsis; and by radii drawn to the foci may describe area’s proportional to the time very nearly.” [3]

In modern form:

$$F_G = G \frac{m_1 m_2}{r^2}$$ \hspace{1cm} (2.1)

The gravitational mass $m_g$ is the “charge” of gravitational attraction. Like the electric charge it dictates the strength of the gravitational force that an object will contribute in a mutual attraction. It happens that the ratio of gravitational mass over inertial mass is constant. Setting the constant equal to 1 we have $m_g = m_i$. This is called the equivalence Principle and the first precise experimental confirmation dates back to 1889 and the work of Eötvos. [4]. Thus mass dictates at the same time how much force needs to be exerted (for a given acceleration) and how much gravitational force will be exerted (for a given interaction). This is the reason why all objects will execute free fall with the same acceleration. Heavier objects will experience stronger gravitational pull from earth but at the same time because they are heavy they need this stronger force to accelerate to 1g. This has been historically the first means to verify the equivalence principle and the relevant experiments have been conducted by Philoponus (6th century AD), Gallileo and Newton (16th century AD)

The conclusion from multiple precise experiments [5, 6] is that gravitational mass always equals inertial mass, or more precisely, their proportion is always constant and thus can be set to be 1 with a factor embedded in the gravitational constant G.

This is also called the “Weak” equivalence principle, to distinguish it from the “Einstein” equivalence principle which we will discuss in chapter 14.
3. The source of force

Forces were historically distinguished in two categories, contact forces (when objects touch each other) and forces from a distance (like gravitation and magnetism). In modern physics we consider that even contact forces are in fact forces from a distance. The concept is called exchange force: forces are exerted through the exchange of hypothetical particles. This concept is an extension of a generally agreed upon understanding of electromagnetic radiation, where the corresponding mediating particle is the photon, which can be seen as a particle with momentum but without mass, or as a traveling disturbance in a field of electromagnetic potential [7]. The key in understanding the cause of those disturbances is the fact that the exchange of the mediating particles cannot happen instantly. Electromagnetic force from an object will be felt by an other object with a time delay, dictated by the speed of light (the mediating particle). When a charged body accelerates then the information of this acceleration will spread as a disturbance in the objects electromagnetic field and create an electromagnetic wave (photons).

Similarly to electromagnetic waves, Gravitational waves have also been predicted as early as 1908 by Henry Poincaré, on the grounds that the information that a source of gravitation accelerated should spread at a finite speed.

He said:

“The acceleration of celestial bodies has consequences like electromagnetic radiation: a dissipation of energy that will make itself felt in a decrease of their velocities. I actually said, that every time an electron undergoes a sudden change of velocity, radiation appears. However, this word ‘sudden’ lacks precision. If the change is slow, if the acceleration is small, there will still be radiation, but this radiation will be very weak . . . the radiation will be imperceptible, [yet] it does exist and little by little dissipates the living force [the kinetic energy] of the planets.” [8]

Gravitational waves have also been predicted by the general theory of relativity in 1916 and Eistein's equations have been successfully employed in an attempt to identify a recently detected gravitational wave as being the result of a collapse of a binary black hole system located 1.3 billion light years away. [9]
4. Reference frames and Special Relativity

The special principle of relativity was introduced by Galileo Galilei in 1632 in his *Dialogue Concerning the Two Chief World Systems*, using the metaphor of Galileo's ship. In 20th century words, H. Poincaré offers a clear definition:

“...the laws of physical phenomena should be the same, whether for an observer fixed, or for an observer carried along in a uniform movement of translation; so that we have not and could not have any means of discerning whether or not we are carried along in such a motion.” [10]

In essence, Anybody with a watch and a measuring stick can create his own reference frame and for his own convenience he can set the space coordinates to be zero in the place where he stands. When something happens he can assign to that event three space coordinates and one time coordinate.

With so many coordinate systems can we predict what the readings on someone else’s (call him B) coordinate system will be for the same event? It is an easy task provided B moves uniformly relative to A that we know the speed. We need B’s position, speed and also to make sure A's and B's clocks are well synchronized. Then we can easily predict B’s readings for any event based on our own readings for that event, provided that we use the same units. It is a simple transformation called “Galillean Transformation” we use bare symbols for quantities measured in the laboratory reference frame and primed symbols for quantities measured in an other reference frame moving uniformly at a speed $v_t$ (translational velocity) along the x axis of the laboratory reference frame.

\[
x' = x - v_t t \\
y' = y \\
z' = z \\
t' = t
\]

Those transformations follow from the assumption that clocks and measuring sticks will retain their behaviour no mater where they go and how fast they move.

Measurements of the speed of light showed that the speed of light $c$ is invariant in any reference frame and thus the Galilean transformations do not hold [11]. Lorentz and Poincaré started developing a new theory that was finalized by Einstein, who in his Special theory of Relativity (SR) showed that if we are to consider $c$ to be a finite constant no mater what the reference system, then the Galilean transformations have to be substituted by the Lorenz transformations, which he derived.
in an alternative way [1] To put it in words if the speed of light is constant then the motion of a reference frame will cause the space-time of this frame to deform (compared to a still reference frame) in order to keep c constant. This means that clocks and measuring sticks will not retain their behavior as they move thus the Galilean assumption indeed does not hold.

The Lorentz transformations that give us the instrumentation readings of measurements performed by observers on a primed reference frame moving in the x direction are

\[ x' = \gamma (x-vt) \]  \hspace{1cm} (4.5) \\
\[ y' = y \]  \hspace{1cm} (4.6) \\
\[ z' = z \]  \hspace{1cm} (4.7) \\
\[ t' = \gamma (t - \beta x/c) \]  \hspace{1cm} (4.8) \\
where \( \beta = v/c \)  \hspace{1cm} (4.9) \\
\[ \gamma = \left(1 - (v/c)^2 \right)^{-1/2} \]  \hspace{1cm} (4.10)

and \( c \) = the speed of light in vacuum, a fundamental constant.

Using the Lorentz transformations we can start building the expressions linking the observable magnitudes from two reference frames in relative uniform motion.

The first problem that quickly arises is the definition of momentum in SR

The conservation of momentum should apply when looking at a set of events (e.g. hypothetical collisions) from any reference frame. Unfortunately the quantity \( m_o v \) will appear not to be conserved when we calculate it for different reference frames. It is rather the quantity \( \gamma m_o v \) that is conserved and thus it a suitable and generally accepted expression of relativistic momentum. [7]

Subsequently from (1.3) mass appears to be velocity dependent and equal to \( \gamma m_o \)

Poincaré points out the complication:

“\( \)The mass has two aspects: it is at the same time a coefficient of inertia and a gravitating mass that appears as a factor in the Newtonian law of attraction. If the coefficient of inertia is not constant, could the attracting mass be? This is the question.” \[10\]

The concept of a velocity dependent mass, be it inertial or gravitational, has been troubling for physicist and the majority opted for using only the concept of the mass when measured with the object at rest.[7] This mass is called the “rest mass” and symbolized by \( m_o \). It is fundamentally
constant for every object.

Starting with the space and time i.e. equations (4.5) to (4.10) we move on to transforming the velocities:

\[
v'_x = \frac{v_x - v_t}{1 - v_x v_t / c^2} \quad (4.11)
\]

\[
v'_y = \frac{v_y / \gamma}{1 - v_x v_t / c^2} \quad (4.12)
\]

\[
v'_z = \frac{v_z / \gamma}{1 - v_x v_t / c^2} \quad (4.13)
\]

And subsequently the accelerations

\[
a'_x = a_x \gamma^3 (1 + v_x v_t / c^2)^3 \quad (4.14)
\]

\[
a'_y = \gamma^2 (1 + v_x v_t / c^2)^2 (a_y + \frac{(v_x v'_y / c^2) a'_x}{\gamma^2 (1 + v'_x v_t / c^2)^3})
\]

\[
\quad (4.15)
\]

And then the forces

\[
F'_x = \frac{F_x - (v_t / c^2)(\vec{F} \cdot \vec{v})}{1 - v_x v_t / c^2} \quad (4.16)
\]

\[
F'_y = \frac{F_y / \gamma}{1 - v_x v_t / c^2} \quad (4.17)
\]

\[
F'_z = \frac{F_z / \gamma}{1 - v_x v_t / c^2} \quad (4.18)
\]

And finally we can modify the laws of attraction. Fortunately, in the case of electricity, the charge \( q \) is indisputably independent of velocity so the modified Coulomb's law follows directly from Lorentz transformations without having to answer the troubling question that Poincaré posed. The result refers to the force experienced by a resting charge, measured in said charge's reference frame (the laboratory frame), the force being due to another charge whose motion is parallel to an arbitrary x axis and its position in the laboratory frame is described by \( \vec{r} = r \hat{r} = (x^2 + y^2 + z^2)^{1/2} \hat{r} \)

\[
\vec{F} = k q_1 q_2 \frac{\gamma (x^2 + y^2 + z^2)^{1/2}}{(\gamma^2 x^2 + y^2 + z^2)^{3/2}} \hat{r}
\]

\[
\quad (4.19)
\]

For a derivation of 4.11 -4.19 see [12]

The coordinates \( x, y, z \) refer to the position of the moving charge, the static charge resting at (0,0,0)
and $\gamma$ refers to the speed of the moving charge. The vector $\hat{r}$ is a unit vector in the direction of the line that connects the two charges. The constant $k$ is of course Coulomb's constant.

The need for a modification of Coulomb's law is intuitively expected since the shape of the shells of equal electrostatic potential around a moving object will be perceived to be turning from spherical to ellipsoidal, being compressed in the direction of motion together with the space (and time) in which they are perceived to reside. This is clear from the factor $\gamma^2$ in the denominator which being squared accounts for the inverse square nature of the law and being only assigned to $x$ indicates the collinear nature of length contraction. What is more complicated is the factor $\gamma$ in the nominator which accounts for the relativistic variance of force in the $y$ and $z$ directions i.e (4.17),(4.18) and for length contraction in the $x$ direction i.e (4.5).

Let's examine two special cases. In the case where the moving charge moves directly towards (or away from) the laboratory charge (i.e. $y=z=0$) the force per-se is invariant, but the law has to be modified to account for space contraction. In the case where the line connecting the two charges is momentarily perpendicular to the direction of motion of the moving charge (i.e. $x=0$) then length contraction is irrelevant, but the force is not invariant so again the law must be modified. Equation (4.19) predicts that the electric potential of a moving charge will be weaker in front and behind the particle and stronger above and below.

The case of relativistic Coulomb's law is important as it is probably the most undeniable manifestation of the correctness of the theory of special relativity, explaining at once the singular nature of electric and magnetic forces and the generation of electromagnetic radiation.

It is very interesting that in special relativity forces collinear to velocity are invariant while perpendicular forces are reduced by a factor of $\gamma$ when we are observing from the laboratory reference frame. In the case of Coulomb's law this reduction was perceived long before SR and was given the name magnetism. H Poincaré once again pioneered and clears this up.

“Resume, then, our example of two electrified bodies; these bodies repel each other, but at the same time if all is carried along in a uniform translation, they are equivalent to two parallel currents of the same sense which attract each other. This electrodynamic attraction diminishes, therefore, the electrostatic repulsion, and the total repulsion is feebler than if the two bodies were at rest. But since to measure this repulsion we must balance it by another force, and all these other forces are reduced in the same proportion, we perceive nothing.”[10]
Let us see how our modified law describes the above situation.

If both charges are static in the laboratory frame then classical Coulomb's law applies:

\[ F = \frac{k q_1 q_2}{r^2} \]  \hspace{1cm} (4.20)

If one is static and one is moving such as the line connecting the two charges is momentarily perpendicular to the direction of motion of the moving charge then \( r = y \) and from (4.19):

\[ F = \frac{\gamma k q_1 q_2}{y^2} \]  \hspace{1cm} (4.21)

If both are moving in parallel paths then from (4.20) and (4.17):

\[ F = \frac{k q_1 q_2}{\gamma y^2} \]  \hspace{1cm} (4.22)

The difference between (4.21) and (4.22) is what is perceived as magnetic force. [12]

\[ F_{mag} = \gamma \frac{k q_1 q_2 v^2}{y^2 c^2} \] (4.23)

In the case of Newton’s gravitational law the “gravitomagnetic” forces were imperceptible and became a more concrete notion after the introduction of SR and the subsequent explanation of magnetic forces. The first important paper on Gravitomagnetic forces was by Einstein in 1912. General Relativity also predicts Gravitomagnetism and recent experiments confirm, albeit tentatively, its natural existence. [13]
Another technique of using Lorenz transformations are the “Minkowski diagrams” [14]. In those diagrams we depict events in one-dimensional space and time. Each event is depicted by a single point, but there are two reference frames with different scales, each corresponding to the instrumentation readings of each observer. Below it is shown a Minkowski diagram depicting the world line (blue) of an object that experiences a short linear acceleration (red dashes).

![Minkowski diagram for accelerating body](image)

**Figure 1**: Minkowski graph for accelerating body.

Both scales are by design completely symmetric around $x=t$ but the units on the primed scales are larger. We can see the world line of an object initially moving with a constant velocity $v=0.3c$ until $t_1$. From the primed reference frame which has a $v_r=0.3c$ this object is resting at $x'_1$ until $t'_1$. At the event A the object starts accelerating and at the event B it stops accelerating. Now if we calculate
the mean acceleration for the laboratory and for the primed reference frame we get

\[ \bar{a} = \frac{(v_{\text{final}} - v_{\text{initial}})}{t_2 - t_1} = \frac{(x_3 - x_2)}{t_3 - t_2} = 1.46 \]

and

\[ \bar{a}' = \frac{(v'_{\text{final}} - v'_{\text{initial}})}{t'_2 - t'_1} = \frac{(x' - x_2')}{t'_3 - t'_2} = 2.26 \]

As expected from (4.14), \( \bar{a} < \bar{a}' \), not exactly by a factor of \( \gamma^3 \) since this is an average acceleration.

Note that both scales are in time units. The fact that the speed of light in vacuum is constant and invariant allows us to use time units to measure distance (e.g. light-years) and conversely to use distance units to measure time e.g. light-metres \( \text{i.e.} \frac{1\text{m}}{3\cdot10^8 \text{m/s}} = 0.33\cdot10^{-8} \text{sec} \). The latter is rather unfriendly to our intuition and this is why we presented the above figure in time units. In order to help our intuition handle the concept of time as length, we introduce the following oscillator as our time measuring device: Two mirrors facing each-other, separated by the unit length (one meter) and a photon gun in one of the mirrors. When starting the clock the gun emits a photon and the time is measured by the number of trips the photon does between the mirrors. This number equals the distance \( s \) it traveled (in meters) : \( s = ct \).

Figure 2: Conceptual clock (oscillator) based on a photon and 2 mirrors.

We could redraw the Minkowsy diagram as a plane of \( ct \) vs \( x \) and nothing would change \textit{apart from replacing} \( t \) \textit{with} \( ct \) \textit{and} \( t' \) \textit{with} \( ct' \). Then the “spacetime distance” between two events could be

\[ ds = (dx^2 + c^2 dt^2)^{1/2} \]

assuming that is, that we can use the Pythagorean theorem (or that this plane is Euclidean i.e. flat). Let's try it for our example

\[ ds^2 = (0.57 - 0.39)^2 + (1.16 - 0.87)^2 = 0.12 \]

Now for the primed frame : \( ds'^2 = (0.25 - 0.14)^2 + (1.04 - 0.79)^2 = 0.08 \)
This \( ds \) is of-course is a highly derived distance (or more appropriately: interval) and has a very weak physical interpretation: although dimensionally correct, it feels like adding oranges to apples. Thus there is no reason why we shouldn't tamper with it a bit more and make it invariant for both coordinate systems. It turns out that the invariant \( s \) is remarkably similar to the Pythagorean one:

\[
ds^2 = dx^2 + (ict)^2, \ i \text{ being the imaginary unit. Let's try it for our example}
\]

\[
ds^2 = (0.57-0.39)^2 - (1.16-0.87)^2 = -0.05
\]

Now for the primed frame: \( ds'^2 = (0.25 - 0.14)^2 - (1.04 - 0.79)^2 = -0.05 \)

When the \( ds^2 \) is negative the two events have a time-like connection and this is an intuition-friendly case of events, where one event can be the cause of the other, like in normal life.

The full 4D invariant interval assuming a flat space-time is

\[
ds_M^2 = -c^2 dt^2 + dx^2 + dy^2 + dz^2 \tag{4.24}
\]

Subscript \( M \) denotes that this expression was proposed by H. Minkowski. In polar coordinates equation (4.24) becomes

\[
d s_M^2 = -c^2 dτ^2 + dr^2 + r^2 dθ^2 + r^2 sin^2 θ dϕ^2 \tag{4.25}
\]

with \( r \) being the initial radius and \( dr \) being a small difference between initial and final radius. In the following text we will omit the parentheses from the notation.

If we assume that the primed reference frame moves along an object observed from the laboratory reference frame (like it happens between events O and A in the diagram) then the object is at rest for the primed frame thus \( dx' = dy' = dz' = 0 \) and (4.24) can be written as

\[
ds'^2 = -c^2 dt'^2
\]

The physical meaning of this is the fact that the only interval that such a primed observer will perceive is the time interval. The \( ct' \) of such a reference frame is denoted by \( τ \) (proper time in units of length) thus equation (4.24) can also be found as

\[
dτ^2 = -c^2 dt^2 + dx^2 + dy^2 + dz^2
\]

Equation (4.24) is known as the Minkowski metric, metric being the equation that yields the invariant interval given the space and time coordinates, a very useful tool in relativistic mechanics. Sometimes in order to avoid the awkwardness of a squared magnitude being negative it can be written as \([12]\)

\[
-ds^2 = i^2 c^2 dt^2 + dx^2 + dy^2 + dz^2
\]

The coordinates \( x, y, z, t \), define the so-called “four-vector” of position whose magnitude is \( s \). It is
also common to find the opposite convention where the + and – signs reversed.
5. Mass and energy

Using a simple thought experiment, Einstein demonstrated that mass is equivalent to energy and the additional kinetic energy relative to a reference frame will be perceived as additional mass, the total energy of an object being \( E = mc^2 \) [15]. On the other hand when an object is at rest relatively to a reference frame then the perceived mass \( m_0 \) can be used a fundamental property of the object. From this point of view, an object has only two kinds of energy, a) Kinetic energy and b) all the rest, which is “rest energy”. The rest energy contains any potential energy stored inside the object. Kinetic energy is thus given by

\[
E_{\text{kin}} = E_{\text{total}} - E_{\text{rest}} = (m-m_0)c^2.
\] (5.1)

When using the concept of relativistic momentum and the definition (1.3) for mass the total energy of an object can be written as

\[
E_{\text{tot}} = \gamma m_0 c^2 = \sqrt{(c \ p)^2 + (m_0 c^2)^2}
\] (5.2)

Also, (5.1) can be rearranged to

\[
E_{\text{kin}} = m_0 c^2 (\gamma - 1) = m_0 c^2 \beta^2 \frac{\gamma^2}{\gamma + 1} = m_0 v^2 \frac{\gamma^2}{\gamma + 1}
\] (5.3)

which to the leading order for \( \gamma \) near 1 reduces to the Newtonian \( mv^2/2 \).

Once momentum \( \vec{p} \) has been defined as \( \gamma m_0 \vec{v} \) then it is trivial to prove (5.1) together with the mass-energy equivalence. Using the same definition of kinetic energy as in the classical Newtonian derivation of \( mv^2/2 \) we have

\[
E_{\text{kin}} = \int_0^t \vec{F} \ d \vec{x} = \int_0^t \frac{d \vec{p}}{dt} \ d \vec{x} = \int_0^t \vec{v} \ d \vec{p}
\] (5.4)

Now let us set

\[
\vec{v}(\theta, \gamma) = \hat{v}(\theta) v(\gamma)
\] (5.5)

where \( v \) is a scalar defined as the magnitude of velocity and \( \hat{v}(\theta) = \cos(\theta) \hat{i} + \sin(\theta) \hat{j} \) is a unit vector indicating the direction of velocity.

using \( \vec{p} = \gamma m_0 \vec{v} \) and \( \gamma = (1-(v/c)^2)^{1/2} \) we get from (5.4) and (5.5)

\[
E_{\text{kin}} = m_0 \int_1^\gamma \ c \ (\gamma^2 - 1)^{1/2} \ \gamma \ d \left( \gamma c \ (\gamma^2 - 1)^{1/2} \ \hat{v} \right)
\] (5.6)
since \( d\hat{v}/d\gamma=0 \), \( \hat{v}=1 \) and 
\[
\frac{d}{d\gamma} (\gamma^2 - 1)^{1/2} = \frac{\gamma}{(\gamma^2 - 1)^{1/2}},
\]
(5.6) becomes
\[
E_{\text{kin}} = m_o c^2 \int_{1}^{\gamma} \frac{1}{\gamma} \frac{d}{(\gamma^2 - 1)^{1/2}} = m_o c^2 \int_{1}^{\gamma} d\gamma = \gamma (\gamma^2 - 1)^{1/2},
\]
(5.7)

The subscript \( \tau \) has been used to denote the actual value of \( \gamma \) and distinguish it from the function \( \gamma \).

The change in potential energy \( \Delta V \) of a body associated with a conservative force is usually defined as the negative of the work done by the conservative force, \( W_{\text{cons}} \) in moving the body along any path connecting the initial position to the final position. [16]

\[
\Delta V_{A \rightarrow B} = -W_{\text{cons.}} = -\int_{A}^{B} \vec{F} \cdot d\vec{r}
\]
(5.8)

The negative sign is a first convention when defining the potential energy of an object due to a field. This convention implies that when work is done against a force field increases potential energy, while work done by the force field decreases potential energy. Under this convention, a motion within a field is spontaneous when \( \Delta V < 0 \).

In equation (5.8) \( \vec{F} = F \hat{F} \) indicates the magnitude \( F \) and the direction \( \hat{F} \) of the Force exerted by the field on the object, and \( \vec{r} = r \hat{r} \) it is the vector that points from the center of our coordinates to the object. For an attractive force that pulls objects towards the center of coordinates \( \vec{F}_{\text{at}} = c \cos(\pi) = -1 \) For linear motion \( d\hat{r} = 0 \) and for circular motion, since \( \vec{F}_{\text{at}} \) and \( d\hat{r} \) are perpendicular to each other \( \vec{F}_{\text{at}} \cdot d\hat{r} = 0 \) Thus for either linear or circular motion, (5.8) becomes

\[
\Delta V_{A \rightarrow B} = -\int_{A}^{B} F_{\text{at}} \cdot d\vec{r} = -\int_{A}^{B} F_{\text{at}} (r d\hat{r} + \hat{r} dr) = \int_{A}^{B} F_{\text{at}} dr
\]
(5.9)

Note that in (5.9) the quantity \( F_{\text{at}} \) is by definition the length of a vector and as such \( F_{\text{at}} \geq 0 \). Also for an outward motion \( dr \) is positive while for an inward it is negative.

Equation (5.9) implies that an object within the field of an attractive force will lose potential energy if it yields to the attraction, just like an object that is falling pulled by earth is losing potential energy and the \( \Delta V_{\text{spont}} \) of this spontaneous motion is negative. Intuitively we understand that a falling object is losing potential energy and gaining kinetic energy and thus the negative sign convention allows one to write the conservation of energy as follows

\[
\Delta E_{\text{tot}} = \Delta T + \Delta V + \Delta E_o = 0
\]
(5.10)
Had we not used the negative sign then the $\Delta V_{spon}$ of this spontaneous motion would have been positive and $\Delta E_{tot}=\Delta T - \Delta V + \Delta E_o = 0$.

In order to derive a function of $V(r)$ from $\Delta V(r)$, a second convention is needed: the point of zero potential. In the vast majority of the cases, the point of zero potential energy is taken at $r=\infty$. This results to the potential energies due to attractive forces being negative. However, if one was to set the point of zero potential energy at $r=0$ then this would result to the potential energies due to attractive forces being positive.

We can now summarize the above remarks regarding the selection of conventions and their implications:

<table>
<thead>
<tr>
<th>$\Delta V=W_{cons.}$</th>
<th>$V(0)=0$</th>
<th>$V(\infty)=0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{attract}&lt;0$, $\Delta V_{spon.}&gt;0$</td>
<td>$V_{attract}&gt;0$, $\Delta V_{spon.}&gt;0$</td>
<td></td>
</tr>
<tr>
<td>$\Delta V=-W_{cons.}$</td>
<td>$V_{attract}&gt;0$, $\Delta V_{spon.}&lt;0$</td>
<td>$V_{attract}&lt;0$, $\Delta V_{spon.}&lt;0$</td>
</tr>
</tbody>
</table>

**Table 1**: The sign of potential for different cases.

There is a difficulty of Special Relativity to describe potential energy in the sense of stored energy sourcing from the position of the object inside a field. In special relativity the only forms of energy a body can have are kinetic and rest energy. It has been suggested that the mass equivalent to this kind of potential energy is distributed in the field between the interacting objects.[17]

Another approach is to introduce the notion of space-time metric in Newtonian gravitation. (see chapter 14) This will yield a metric that takes into account the relativistic affects of speeding reference frames and (locally) the equivalence principle. The fact that outside small regions tidal forces begin to appear makes this metric unable to fully describe gravitation because it can't account for tidal forces. The information that is lost when omitting tidal forces is mathematically equivalent to the information that is lost when modeling a curved surface as a flat surface. This led Einstein to introduce curved geometry in order to retrieve this information. The resultant metric for a spherical mass is called Schwarzchild metric.

Another approach to incorporated gravity in relative reference frames will be described in the following chapter. It follows a rather different path, as it does not involve the use of a metric.
6. Revisiting inertial mass

Vector quantities can be described in general as functions of $\theta$ and $\gamma$ where the former indicates the direction and the latter the magnitude of each vector.

$$\vec{F}(\theta, \gamma) = \frac{d \vec{p}}{dt} \quad (6.1)$$

$$\vec{v}(\theta, \gamma) = \hat{\vec{v}}(\gamma) \quad (6.2)$$

where $v$ is a scalar defined as the magnitude of velocity and $\hat{\vec{v}}(\theta) = \cos(\theta)\hat{i} + \sin(\theta)\hat{j}$ is a unit vector indicating the direction of velocity.

$$\vec{a} = \vec{a}_\perp + \vec{a}_\parallel = \vec{v} \frac{d \hat{\vec{v}}}{dt} + \hat{\vec{v}} \frac{d v}{dt} = v \left( \frac{d \hat{\vec{v}}}{dt} \times \hat{\vec{v}} \right) + \frac{d v}{dt} \hat{\vec{v}} \quad (6.3)$$

where $\alpha_\perp$ is the component of acceleration perpendicular to the direction of the motion and $\alpha_\parallel$ is the collinear component. Note that there is a one-to-one correspondence in the terms of the second equality in equation(6.3). The third equality demonstrates that the component vectors of acceleration are indeed perpendicular to each other, as indicated by the cross-product.

$$\vec{p}(\theta, \gamma) = \gamma m_o \hat{\vec{v}} \quad (6.4)$$

$$\frac{d \gamma}{dv} = \frac{d}{dv} (1 - \frac{v^2}{c^2})^{-1/2} = \frac{v}{c^2} (1 - \frac{v^2}{c^2})^{-3/2} = \gamma^3 \frac{v}{c^2} \quad (6.5)$$

$$\frac{d \gamma}{dt} = \frac{d \gamma}{dv} \frac{dv}{dt} = \gamma^3 \frac{v}{c^2} \frac{dv}{dt} \quad (6.6)$$

$$\frac{d}{dt} (\gamma v) = \gamma \frac{d v}{dt} + v \frac{d \gamma}{dt} = \gamma \left( 1 + \frac{v^2}{c^2} \right) \frac{d v}{dt} = \gamma^3 \frac{d v}{dt} \quad (6.7)$$

$$\vec{F} = m_o \frac{d}{dt} (\gamma v \hat{\vec{v}}) = m_o \frac{d \hat{\vec{v}}}{dt} (\gamma v) + m_o \gamma v \frac{d \hat{\vec{v}}}{dt} + v \frac{d \gamma}{dt} \hat{\vec{v}} = \gamma^3 m_o \hat{\vec{v}} \frac{d \hat{\vec{v}}}{dt} + m_o \gamma v \frac{d \hat{\vec{v}}}{dt} = \gamma^3 m_o a_\parallel + \gamma m_o a_\perp \quad (6.8)$$

From (6.3) and (6.8) we can see that force and acceleration are not always parallel. Only when the perpendicular or the collinear component of acceleration is zero is acceleration parallel to the force, i.e. when the object is moving on a straight line or on a perfect circle. In the above cases we can see that the coefficient of inertia (inertial mass) will be $\gamma^3 m_o$ in the linear and $\gamma m_o$ in the circular case. Note that circular motion is a challenging topic in Special Relativity, a fact most notably demonstrated by the famous Ehrenfest paradox of the rotating disk in Special relativity which decisively shaped Einstein's ideas about General Relativity [18].

The use of $\gamma^3 m_o$, also known as longitudinal mass, has recently been explored in order to model hadrons and to account for celestial general-relativistic effects [19-24]. The validity of this
The approach was originally argued in [19] and [20]. One can also use a rigorous method introduced in [22] so as to prove that the conclusion of (6.8) is valid for any path. Here we develop a generalized version of that method.

We first consider an object moving with an instantaneous velocity \( \bar{v} \) relative to an observer in a reference frame S and we focus on an instantaneous reference frame S' moving with the object. The instantaneous reference frame S' is uniquely defined by the instantaneous vector of velocity and thus for S' \( \bar{v} \) is a constant. [12]. Let also \( \delta \bar{v} \) be a small change in the velocity.

From the definition of \( \bar{v} \) we have

\[ \bar{v} = v \hat{v} = \text{constant} \]  

(6.9)

thus

\[ \frac{d}{dt} \hat{v} = \frac{dv}{dt} = \frac{d\gamma}{dt} = 0 \]  

(6.10)

from the definition of \( \delta \bar{v} \) we can define \( \delta v, \delta \hat{v}, \delta \gamma, \delta \bar{F} \) through the following equations.

\[ \bar{v} + \delta \bar{v} \equiv (v + \delta v)(\hat{v} + \delta \hat{v}) \]  

(6.11)

\[ \gamma + \delta \gamma \equiv (1 - (v + \delta v)^2/c^2)^{-1/2} \]  

(6.12)

\[ \bar{F} + \delta \bar{F} \equiv \frac{d}{dt}(m_o(\gamma + \delta \gamma)(\bar{v} + \delta \bar{v})) \]  

(6.13)

Carrying out the calculation and neglecting \( \delta \delta \) products we get

from (6.11)

\[ \delta \bar{v} = v \delta \hat{v} + \hat{v} \delta v \]  

(6.14)

from (6.12)

\[ \delta \gamma = \gamma^3 \delta v \frac{\bar{v}}{c^2} \]  

(6.15)

from (6.13) and (6.1),(6.2),(6.4)

\[ \delta \bar{F} = m_o \frac{d}{dt}(\gamma \delta \bar{v} + \delta \gamma \bar{v}) \]  

(6.16)

from (6.14) and (6.10)

\[ \frac{d}{dt} \delta \bar{v} = v \frac{d}{dt} \delta \hat{v} + \hat{v} \frac{d}{dt} \delta v \]  

(6.17)

Now we can distinguish 2 cases. The first one is the one presented in [22] where the \( \delta \bar{v} \) is in the
same direction as the velocity $\vec{v}$. This means that the direction of $\vec{v}$ remains unchanged, thus from (6.11)

$$\delta \hat{v} = 0$$

(6.18)

and subsequently

$$\frac{d \delta \hat{v}}{dt} = 0$$

(6.19)

from (6.14)

$$\delta \hat{v} = \delta v \hat{v}$$

(6.20)

from (6.17) and (6.19)

$$\frac{d \delta \hat{v}}{dt} = \hat{v} \frac{d \delta v}{dt}$$

(6.21)

from (6.16) in view of (6.9), (6.15), (6.20) we get

$$\delta \vec{F} = m_o \frac{d}{dt} (\gamma \delta v \hat{v} + (v / c^2) \gamma^3 \delta v \delta \hat{v}) = m_o \hat{v} \frac{d}{dt} (\gamma \delta v + (v^2 / c^2) \gamma^3 \delta v)$$

(6.22)

In view of $\gamma$ and $v$ being constants i.e. equation (6.10), equation (6.22) becomes

$$\delta \vec{F} = m_o \hat{v} \frac{d}{dt} (\gamma + (v^2 / c^2) \gamma^3) = m_o \hat{v} \frac{d \delta v}{dt} \gamma^3$$

(6.23)

which combined with (6.21) yields

$$\delta \vec{F} = \gamma^3 m_o \frac{d \delta \hat{v}}{dt}$$

(6.24)

Now we will treat the second case, in which the magnitude of the velocity remains unchanged and $\delta \hat{v}$ refers to a change in the direction of $\hat{v}$ thus from (6.11)

$$\delta v = 0$$

(6.25)

which means that (6.15) becomes

$$\delta \gamma = 0$$

(6.26)

and in view of (6.26) equation (6.16) becomes

$$\delta \vec{F} = m_o \frac{d}{dt} (\gamma \delta \hat{v})$$

(6.27)

which combined with (6.10) yields
\[
\delta \vec{F} = \gamma m_o \frac{d \delta \vec{v}}{dt}
\]  \hspace{1cm} (6.28)

Since \( \delta \vec{v} \) and \( \delta \vec{F} \) can be taken to be infinitesimally small, it follows that equations (6.24) and (6.28) are valid for an arbitrary motion of the object, with \( \gamma^3 m_o \) being some times called “longitudinal mass” and \( \gamma m_o \) “transverse mass” [2].

So depending on the direction of the test force, the magnitude of the corresponding acceleration will be perceived differently. The implication of this is that the inertial mass that is perceived through the response of an object to force also depends on the angle between the applied force and the object’s velocity. The perceived inertial mass ranges from \( \gamma \) to \( \gamma^3 \). With \( \gamma = 1 \) we get the rest mass, fulfilling the correspondence principle.

Based on the requirement of force invariance (i.e. that both observers must agree on the magnitude of the force that produced an accelerated motion), longitudinal mass is to be selected over transverse mass on the grounds of longitudinal forces being invariant (see chapter 4). Thus it was argued that it is \( \gamma^3 m_o \) that has to be used in the general case when modeling massive objects.[22]

“The force is not invariant in the y [perpendicular] direction, hence, it cannot be used for computing the inertial mass.” [22]

The resulting accelerated motion can be analyzed in the context of Special Relativity with the use of instantaneous reference frames [12]. In the case of circular motion instantaneous reference frames have been used to approach the curved trajectory as a sequence of infinitely small linear parts, and the inertial mass in each of them is accordingly being defined as the longitudinal mass[20]

In essence, mass in general is being defined as the coefficient of inertia against a test force collinear to the direction of motion.

In the following chapter we will elaborate on the application of this suggested treatment of mass in circular motion under gravitational attraction.
7. Force balance in circular motion

Circular motion is of great importance in physics. It has been used to successfully describe the structure of atoms and solar systems. The characteristic of circular motion is that force does not affect the magnitude of velocity but rather its direction. In classical as well as in relativistic mechanics of circular motion force and acceleration are perpendicular to the direction of velocity at any moment. (See chapter 5).

From (6.8) simplified for circular motion we get

\[ \vec{F}_\perp = m_o \gamma v \frac{d \vec{v}}{dt} = \gamma m_o a_\perp \]  \hspace{1cm} (7.1)

from (6.3)

\[ \vec{a}_\perp = v \frac{d \vec{v}}{dt} = v \left( \frac{d \vec{\theta}}{dt} \times \vec{v} \right) \]  \hspace{1cm} (7.2)

the quantity \( \frac{d \vec{\theta}}{dt} \times \vec{v} \) frequently denoted by \( \vec{\omega} \), is a vector parallel to the axis of rotation and its magnitude is \( \omega = \frac{v}{r} \), mechanically corresponding to SI units of rad/sec. Thus the quantity

\[ \frac{d \vec{\theta}}{dt} \times \vec{v} \]

is a vector perpendicular to \( \vec{v} \) contained in the plane of rotation with magnitude \( \omega = \frac{v}{r} \) and subsequently

\[ a_\perp = \frac{v^2}{r} \]  \hspace{1cm} (7.3)

Equation (7.1) becomes

\[ \vec{F}_\perp = \frac{\gamma m_o v^2}{r} \]  \hspace{1cm} (7.4)

By defining mass as the coefficient of inertia against a test force collinear to the direction of motion and on the grounds that circular motion is momentarily indistinguishable from linear motion C.G. Vayenas and S. Souentie invoked the Equivalence Principle and suggested that Newton's Universal gravitational Law should be modified as follows [19-24]

\[ F_{RG} = \frac{G m_{o,1} \gamma_1^3 m_{o,2} \gamma_2^3}{r^2} \]  \hspace{1cm} (7.5)

The subscript RG stands for Relativistic Gravity where as \( \gamma_1 \) and \( \gamma_2 \) are the Lorentz factors as
perceived for objects 1 and 2 by the laboratory observer.

Based on the equivalence of (7.4) and (7.5), several interesting results can be obtained. One of the early successes of this force balance method was the modeling of hadrons using gravity as the attractive force confining the three constituents (also known as quarks) [20-23]. The assumption is that the three constituents rotate around a common center with gravity being the centripetal force.

This model also invokes the quantization of angular momentum $mvr$ which we will examine in the next chapter.

The relation $E=hc/\lambda$ is key in this chapter. It was well known from the work of Einstein on photoelectric effect and of Plack on the black body radiation.

In 1913 Niels Bohr modeled the Hydrogen atom under the following assumption

“...the angular momentum of the electron around the nucleus in a stationary state of the system is equal to an entire multiple of a universal value, independent of the charge on the nucleus.”[26]

more precisely:

$m v r = k B , B = h/2\pi , k = 1, 2, 3... \quad (8.1)$

Bohr's model was surprisingly successful so this assumption had to hold.

In his 1924 paper, in chapter III, Louis de Broglie, who at the time considered photons as massive particles with a tiny rest mass $m_o$ and a velocity near the limit $c$, introduces the “theorem of phase harmony”. It was a speculation that the total energy of said particle is associated with an electromagnetic frequency $f$ of a light quantum of the same momentum (which light quantum he viewed merely as a periodical phenomenon suggested by the quantum relation $E=hf$).

After a thought experiment he concluded:

“We are then inclined to admit that any moving body [with velocity near c] may be accompanied by a wave and that it is impossible to disjoin motion of body and propagation of wave.”[27]

Which was his interpretation of the wave particle duality of photons. Based on the results of A. Einstein and Sir Arthur Compton, De Broglie, calculated the wavelength $\lambda$ of this accompanying wave:

$\lambda = h / (\gamma m_o c) = h / (mc) = h/p \quad (8.2)$

$h=$Planck's constant.
We could say that his suggestion was that a light quantum is a fast \((v=c)\) moving particle of a tiny rest mass \(m_o\) and momentum \(p = \gamma m_o c = h/\lambda\) joined with a purely immaterial wave of frequency \(f = c/\lambda\).

Finally he concluded that this can be extended to particles of any rest mass \(m_o\) moving at any speed \(v\).

"It is now so simple a matter to show that the theorem of phase harmony is always valid that it seems not necessary to develop the proof".[27]

This view is actually considering any moving object to be the massive companion of a photon of the same momentum \(p = \gamma m_o v\) (in today's terms that is, as De Broglie defined the massive particle as the photon and the momentum of the particle was the only momentum involved) and joins said object with the corresponding immaterial companion i.e. a wave of wavelength \(\lambda = h/p = h/\gamma m_o v\), despite \(v\) and \(c\) being different. This difference in speed was further enlarged by the condition that the corresponding wave should travel at \(c/\beta\) so that both the particle and the wave had the same energy. That would be faster than the speed of light but since the wave was immaterial De Broglie probably didn't feel that it was a problem.

This idea was used by de Broglie to account for the stability requirement that Niels Bohr introduced in his 1913 model of the Hydrogen atom. In the words of de Broglie:

"The present theory suggests an interesting explanation of Bohr's stability conditions. [...]The motion can only be stable if the phase wave is tuned with the length of the path."

The path is \(2\pi r\) so \(\lambda\) should fit in the path an integer amount of times \(n\). De Broglie's "harmony" condition is therefore \(\lambda = 2\pi r/n\) hence the momentum of the electron will be limited to values of \(n\hbar/r\) we get the condition (8.1)

De Broglie's relation was experimentally confirmed in Bell Laboratories by C. Davisson and L. H. Germer in 1927[28] and recently it has been shown to hold even for macro-molecules[29].

De Broglie based on the wave-particle junction explained the interference pattern produced by massive particles passing through a double slit. He argued that the accompanying wave of each
particle interferes with itself as it passes through the slits and thus guides the particle according to the interference pattern of the wave and produces the observed interference pattern of the particles on the detectoring screen. This idea has been studied by David Bohm and the result was a deterministic interpretation of quantum mechanics that was published in a paper titled “Suggested Interpretation of the Quantum Theory in Terms of "Hidden" Variables.” in 1952. In that paper he postulates the existence of a quantum-mechanical field that can exert real forces on the particle which helps him drop the inherent status of the uncertainty principle and thus he attributes the uncertainty to the practical difficulties of metrology below the femtometer scale. This theory is known as “hidden variables”, “Pilot wave theory”, “Bohm-De Broglie theory”, “Bohmian mechanics”, or “Ontological interpretation”.

Recently Yves Couder has been able to test the plausibility of this hypothesis by means of a hydronamic analogy. He created oil droplets bouncing on a bath and each droplet while hitting the surface of the bath for the first time it was creating a wave pattern, then when the droplet was “landing” again on the bath its motion was determined by the wave that the droplet itself had created in the previous bounce, in a repeated feedback loop [30]. So the droplet was creating a wave and the wave was causing the droplet to move. He has been able to produce the double slit interference pattern and other quantum phenomena like tunneling.

The question remains of course, if the droplet is the analogue of the particle and the ripples are the analog of the accompanying wave, what is the analog of the rippling liquid? We shall revisit this question later.

One year before the groundbreaking paper of de Broglie, Arthur Compton had already presented a strong indication that radiation had a corpuscular character. He introduced a quantity known as the Compton wavelength. This quantity results from calculations that explained his experimental results of the phenomenon of Compton scattering i.e. scattering of electrons by radiation. The basis of the calculations is that radiation of a certain frequency $f$ should be treated as particles of energy $E=hf$ and momentum $p=E/c$. The Compton wavelength refers to a corpuscular object (originally the electron in Compton's experiments) and is a special case of de Broglie wavelength for $v=c$.

In 1927, Heisenberg discovered a mathematical consequence of his matrix mechanics: position and momentum cannot be determined with arbitrary precision. The equation that he used to describe this bears a striking similarity to de Broglie's expression. It was the Uncertainty principle, which he qualitatively formulated as

$$\Delta x \Delta p \gtrsim h$$  \hspace{1cm} (8.3)
A quantitative use of this expression has been explored in order to derive a lower limit to the proximity that two objects can have to each-other. By using $mc$ for $\Delta p$ it is concluded that it is not possible to localize a particle with a precision higher than its Compton wavelength [31]. A similar line of thinking has been employed to discuss the stabilization of microscopic black holes [25].
9. The Rotating Neutrino model.

The basic feature of the rotating neutrino model as presented in [18, 20-24] is the rotation of three identical and equidistant particles of mass $m_o$ around their common center of mass, according to the following figure:

![Figure 3: The rotating neutrino model.](image)

The force balance for this system according to the ideas developed in chapter 7 is

$$\frac{\gamma m_o v^2}{r} = \frac{G m_o^2 \gamma^6}{\sqrt{3} r^2}$$  \hspace{1cm} (9.1)$$

Note that the factor $3^{1/2}$ is due to the (Euclidean) triangular geometry of the system and the only modification to Newton's Universal Gravitational Law is the addition of the $\gamma^6$ term. Also from the condition (8.1) we have

$$\gamma m_o v r = k \hbar$$ \hspace{1cm} (9.2)
Then for the fundamental state of rotation (i.e. \( k=1 \)) we can use (4.10) to substitute \( v \) with \( \gamma \) and then solve the 2x2 system for \( r \) and \( \gamma \). The solution for \( \gamma \) is

\[
\gamma = 3^{1/12} \left( \frac{m_p}{m_o} \right)^{1/3}
\]  

(9.3)

where \( m_{pl} = (\hbar c/G)^{1/2} \).

Thus \( \gamma^6 \) i.e the ratio of the relativistic gravitational force over the classical Newtonian gravitational force is

\[
\frac{F}{F_N} = \gamma^6 = \sqrt{3} \left( \frac{m_p}{m_o} \right)^2 \approx 1.35 \times 10^{38}
\]

(9.3a)

The rest mass \( m_{o,conf} \) of the confined ring is then \( 3\gamma m_o \)

\[
m_{o,conf} = 3^{13/12} \left( \frac{m_p m_o^2}{\gamma} \right)^{1/3}
\]

(9.4)

The value of \( m_o \) for which \( m_{o,conf} \) equals the mass of the proton is 0.0437eV. This is surprisingly close to the current estimates of the rest mass of the heaviest electron neutrino.[32,33]. Also \( r=0.63 \) fm which is in the same order of magnitude as the experimental value of 0.8 fm [34]. Also we will denote the solution for \( \gamma \) as \( \gamma_{3,1} \) with 3 standing for the number of constituents and 1 for the fundamental state of rotation. After substation of the numerical values in (9.3) we get that \( \gamma_{3,1} = 7.163 \times 10^9 \). Consequently \( v \to c \).

From (9.2) it is obvious that for \( v=c \) then \( r \) equals the (relativistic) reduced Compton wavelength of the constituent particle. Using the same notation as with \( \gamma \):

\[
r_{3,1} = \frac{\hbar}{\gamma m_o c}
\]

(9.5)

This suggests an alternative explanation: The three particles want to collide in the center, but are prevented from doing so because of the Heisenberg Uncertainty Principle and the subsequent interpretation of Compton's wavelength.

Even more surprisingly, when preforming the calculations for the masses of excited states, we get \( m = m_p k^{1/6} \) where \( m_p \) the proton mass. For \( m_o = 0.0437 \text{eV} \) and \( k=3,5,7,11,19,31 \) we discover the experimental masses of \( \Lambda, \Sigma \) (and \( \Delta \)), \( \Xi, \Sigma^*, \Xi^* \) and \( \Omega \) barions respectively as multiples of the proton mass, with a 97% accuracy or better. Thus \( m_o = 0.0437 \text{eV} \) appears to be the mass of a fundamental constituent. Based on the total domination of odd \( k \)'s the authors set \( k = 2n-1, n = 1, 2, 3... \) i.e. the multiple of angular momentum in (9.2) has to be an odd multiple.
Figure 4a: Prediction of barion masses with a single quantum number.
An refined formula containing 2 quantum numbers $n_B$, $l_B$ yields even more impressive agreement with the experimental data without skipping any numbers: 

$$m = m_p \left[ n_B^2 (2l_B + 1) \right]^{1/6}$$

$n_B$ is a positive integer, $l_B$ a non-negative integer and $m_p$ the proton mass. [61]

Figure 4b: Prediction of barion masses with two quantum numbers.

The treatment is a direct replication of the Bohr model for Hydrogen. In essence, the line of thinking and the conditions employed are identical in the two models. Although Bohr's model has been criticized for using inapplicable classical physics and premature concepts, [7] the insight that it offered was priceless and earned him the 1922 Nobel Prize.

In light of the recent results from project LIGO that confirmed the ideas of Poincaré and Einstein about gravitational waves, one is inclined to add another condition to the rotating neutrino model:
When the particles rotate in the permitted orbits, they should not emit gravitational waves despite being highly accelerated masses. It is only natural to suppose then that when the neutrinos jump from one orbit to another they emit quanta of gravitational waves. This is similar to Bohr's condition that electrons should not emit electromagnetic radiation in the permitted orbits but only when they jump between orbits. According to the electrodynamic analogy such a gravitational wave would carry energy equal to $E=\hbar \omega$ [35]. The corresponding frequencies of gravitational spectral lines can be calculated by setting $E$ equal to the difference of the masses of the particles of different $n$. The corresponding energies are in the range of 0.1 -1 GeV, thus according to this model the spectral lines are expected in the order of $10^{22}$ Hz. Starting from the Schrodinger equation, a derivation of the exact energy levels and frequencies has been carried out by A. Vandroos in his diploma thesis [62] 

The results from LIGO that validated the nature of gravitational waves were based on the prediction of general relativity that gravitational waves from a rotating pair of masses will spread as a double spiral ripple in space time. This brings us back to our earlier question on the hydrodynamic analogy of Yves Couder. The bouncing droplets cause a ripple on the surface of the bath and the surface of the bath then dictates how the droplet will move. The acceleration of mass of the droplet tells to the surface of the liquid how to curve and the curvature of the liquid tells to the droplet how to move. This is the same interplay between mass, curvature and motion that the field equations of General relativity describes, as famously quoted by J.A.Wheeler in his description of the Einstein field equations. Similarly, a spinning mass, (with an uneven angular distribution of mass) will produce a spiral ripple in space time and that ripple will create interference patterns when passing through a double slit so that the space-time after the slit will have “grooves” through which the geodesic of the particle will preferentially pass, creating the corresponding interference pattern on the detecting screen. We are thus inclined to consider that the pilot waves of de Broglie could in fact be gravitational waves caused by accelerated particles. Suitable forms of acceleration seem to be a polarized vibration or a spinning rotation of the kind that Vayenas’ model assumes for hadrons. This will allow for a constant translational speed of the particle and for a co-centric or spiral wave (respectively) that resembles to the co-centric waves of the Couder double slit experiment. In the case of the spiral wave it is clear that if the distance traveled by the wave during one rotation is smaller than the distance from the barrier, then an observer at the point of the slits will be hard pressed to figure whether the waves he sees are co-centric or spiral. If the double slit pattern can be achieved by concentric waves with traveling center, as Couder has shown, then most likely it can also be achieved by spiral waves. Thus this point of view requires that all traveling particles that exhibit the double slit interference pattern, exhibit a repetitive internal motion with a frequency which is proportional to their momentum so as in any case to satisfy the experimentally observed De Broglie relation. This is a feature already built-in Vayenas’ model. Note that the gravitational
wave is assumed not to pass through the barrier but only through the slit. The barrier is assumed to either reflect it or function as a damper for gravitational waves: the relative motion of its molecules that will be caused by the gravitational ripple will dissipate (in the form of heat) the energy that the gravitational wave carries, as per the “sticky bead” argument [35,36].

In order to introduce an equation for the potential energy of such particle, Vayenas, Souentie and Fokas start by deriving an expression for the $F(r)$ under the condition that the particles rotate in a circular orbit according to the ideas presented in chapter 7. By rearranging (9.1) and (9.3) they got [19-22]

$$F = -m_o c^2 \left( \frac{2 \sqrt{3}}{r_s} \right)^{1/5} \frac{1}{R^{4/5}} , r_s = \frac{2 G m_o}{c^2}$$

Then they used (5.9) i.e. $A V_{A \rightarrow B} = \int_A^B F_{attr} \, d r$. The choice of integrating the magnitude of the vector $F$ while maintaining the negative sign has been made in order to match the attractive force with a negative value of $V$. The result is

$$V_G(r) = -\frac{5 m_o c^2 2^{1/5} 3^{1/10}}{(2 G m_o/c^2)^{1/5}} r^{1/5}$$

In the above expression the presence of $r$ raised to a positive power leads to $V(r \rightarrow 0)$ being zero, while $V$ becomes unbounded as $r$ increases, which respectively imply asymptotic freedom and confinement, two key characteristics of the strong force. In the terms of the rotating neutrino model, the confinement can be understood as a transformation of the energy that we give in order to split the confined state. This energy is transformed into kinetic energy of the particles and thus increases their gravitational mass and attraction, making it impossible to separate them.

Note that in Newtonian mechanics ($\gamma = 1$) the potential depends only on the radius and the rest masses, and as such the potential of any states, rotating or otherwise, can be described with the single formula $Gm_1m_2/r$ (which lies on the bottom right box of the table). On the other hand equation (9.7) regards only rotating states.
10. The rotating pair model

The force balance for a pair of bodies in circular motion under their mutual gravitational attraction has also been developed. The initial computation was for a pair of equal masses [19,20] and it has recently been generalized for a pair of unequal masses [37].

In order to solve the problem in the case of different masses, the condition that both particles rotate at the same angular velocity has been employed explicitly. (The same condition has been used implicitly in chapter 9 through the specification “equidistant particles”).

\[
\frac{v_1}{r_1} = \frac{v_2}{r_2} \tag{10.1}
\]

Equations (9.1) and (9.2) are generalized respectively as

\[
\frac{\gamma_1 m_{o1} v^2}{r_1} = \frac{\gamma_2 m_{o2} v^2}{r_2} = \frac{G m_o^2 \gamma_1 \gamma_2}{(r_1 + r_2)^2} \tag{10.2}
\]

\[
\gamma_1 m_{o1} v r_1 = \gamma_2 m_{o2} v r_2 = k \hbar \tag{10.3}
\]

From 10.1, 10.2, and 10.3 it is found that

\[
v_1 \approx v_2 \approx c \tag{10.4}
\]

\[
r_1 = r_2 \tag{10.5}
\]

\[
\gamma_1 m_{o1} = \gamma_2 m_{o2} \tag{10.6}
\]
Figure 4: Generation of the W boson.

If we consider an electron-neutrino pair and use the rest mass of an electron (or positron) and the rest mass of a neutrino (as precised in chapter 9) then $\gamma m_{\text{rel}} = 81.74$ GeV which is very close to the detected mass of the W boson (80.42 GeV) [7]. Given that according to the standard model the W boson decays to an electron and an anti-neutrino [7], it is possible that the detected mass is solely the mass of the relativistic electron since the anti-neutrino does not interact with the sensors. Thus the $W^{\pm}$ boson can be modeled as a relativistic rotating pair of an electron(positron) and a (anti)neutrino [37].
11. Perihelion precession.

The explanation of the anomalous motion of the perihelion of Mercury was a major field for physicists until the advent of the General theory of Relativity. The discrepancy to be explained was as little as 43” of a degree in the course of an earthly century which amounts to a tilt of \(5.02 \times 10^{-7}\) rad/rev. Several early relativists tried to apply the Special theory of relativity in order to account for this offset. The results varied around 7” : Lorenz 6.7” [38], de Sitter 7.15”[39], Wacker 7.2”[40], Poincaré 5”-7”[38,41]. Several other values sourcing from a range of theories and treatments have historically been reported [42]. The modern text-book value for the special-relativistic correction is 7.15” [43]. In 1915 the General theory of Relativity became mainstream largely thanks to Einstein's accurate prediction of 43” [44].

In an elegant generalization [45] L. Silberstein showed that if one is to use the relativistic equation of motion (e.g. eq 7.4) and a relativistic gravitational law of the general form

\[ F = \gamma^{n-1}GMmr^{-2} \]  

with \(n\) being an adjustable real number, then the calculated precession rate \(\varepsilon_p\) will be

\[ \varepsilon_p = \frac{n \pi^3 \alpha^2}{T^2 c^2 (1-e^2)} \]  

In the above equation \(\alpha\) is the large semi-axis, \(e\) the eccentricity and \(T\) the period of the orbit. Equation 11.2 with \(n=6\) is Einstein's formula [42] in which has also been suggested by Gerber in 1898 [46].

Given that \(\alpha = p/(1-e^2)\), \(p\) being the semi-latus rectum of the ellipse and that for elliptical orbits around a central mass \(M\) it holds (e.g. see [47] for a proof):

\[ GM = \frac{4 \pi^2 \alpha^3}{T^2} \]  

then equation (11.2) can take a more familiar form:

\[ \varepsilon_p = n \frac{\pi GM}{pc^2} \]  

41
Einstein's result is obtained for $n=6$. Equation (11.4) is consistent with the text-book special relativistic result of 7.15” which appears to be obtained from using the relativistic equation of motion and the classic Newtonian Gravitational law i.e. for $n=1$.

The general relativistic result for the equation of the orbit of a planet (in polar coordinates $r, \phi$) that follows from the Schwarzschild metric is:

$$\frac{d^2 U}{d\phi^2} + U = 1 + \frac{3\varepsilon}{2} U^2$$  \hspace{1cm} (11.5)

where

$$U = \frac{J^2}{GMr}, \quad J = \frac{L}{m}, \quad r_s = \frac{2GM}{c^2}, \quad \varepsilon = \frac{r_s}{c} = 2 \left(\frac{GM}{cJ}\right)^2$$

Where $L$ is the angular momentum (see chapter 13, figure 5 for a detailed definition) of the planet, $m$ is the mass of the planet and $M$ the mass of the star.

An analysis by A.S. Fokas and C.G. Vayenas suggests that the equation that follows from using the longitudinal mass for the bodies is remarkably similar. [48].

$$\frac{d^2 U}{d\phi^2} + U = 1 + \frac{3\varepsilon}{2} \left(U^2 + (\frac{dU}{d\phi})^2\right)$$  \hspace{1cm} (11.6)

The above equation when integrated numerically yields exactly the same orbit with the general relativistic solution i.e equation (11.5)e in figure 5a we can see the result of the integration of the Keplerian, General Relativistic, and “$\gamma$6” approach for the first 5 revolutions. In the enlarged section it is shown the precession of the fifth aphelion.

The equations of motion of the 2 body problem in General Relativity for the case of small masses have been developed in a Recent work by L. Blanchet and A.S. Fokas, [64]. Their result for large $\gamma$ appears to coincide with the one obtained by a gravitational law of the form $F=\gamma^6/GMmr^{-2}$ where $3 \leq n \leq 6$. 


Figure 5a: Numerical integration of the equations of planetary motion of Mercury around the Sun. The gravitational constant has been multiplied by $10^5$ in order to make the precession visible in just five revolutions.
12. The Strong Force.

The Standard Model explains the force that holds together the constituents of hadrons fine structure constant in terms of a speculated natural quantity termed “Chroma” [7]. The force itself is called “Strong Force”. The rotating neutrino model as presented in chapter 9 accounts for the confinement of the above constituents without any such ad-hoc speculations.

The strong Force is about $10^2$ times stronger than the electrostatic force, both being calculated for 2 protons in the range of an atomic nucleus [49].

Two elementary charges separated by a given distance will produce a Coulombic force $F_{C,e}$ that is $\alpha$ times stronger than the Newtonian gravitational force $F_{G,Pl}$ produced by two bodies of mass $m_{Pl}$ separated by the same distance, $\alpha$ being the fine structure constant.

$$\frac{F_{C,e}}{F_{G,Pl}} = \alpha \approx 1/137 \quad (12.1)$$

The above is a direct result of the definition of $\alpha$, i.e. $\alpha = ke^2/(c\hbar)$ and of $m_{Pl}$ and of the two force laws i.e. (4.20) and (2.1). Consequently and based on (2.1) for an arbitrary mass $m_o$ we can write

$$\frac{F_{C,e}}{F_{G,o}} = \alpha \frac{m_{Pl}^2}{m_o^2} \quad (12.2)$$

From (2.1), (7.5) and (9.3) and denoting with $F_{RG,o}$ the force of Relativistic Gravity acting between bodies with mass $m_o$

$$\frac{F_{RG,o}}{F_{G,o}} = \kappa \frac{m_{Pl}^2}{m_o^2} \quad (12.3)$$

The constant $\kappa$ depends on the geometry of the relativistic gravitational confinement and equals 4 in the case of the binary rotation and $3^{1/2}$ in the case of the rotating triplet.

By dividing (12.3) with (12.2) we get

$$\frac{F_{RG,o}}{F_{C,e}} = \alpha^{-1} \kappa \quad (12.4)$$

The above ratio is in the expected order of magnitude ($\sim 10^2$) given also that the constituents (quarks) are supposed to have less than unit charge.
13. The rotating neutrino model treated with General Relativity

Given the relative success in the prediction of mercury's perihelion precession via the use of $m_\gamma^3$ as the general case of mass, a comparison with the behaviour that GR would predict for the rotating neutrino model via the use of “Schwarzschild effective potential” will be presented below. It is thus useful to clarify the concept of the “effective potential” before the engagement of GR in the discussion.

The effective potential is a tool for treating a two-dimensional two-body problem as one-dimensional. It employs the fact that angular momentum $L$ is conserved (which is also the cause of Kepler's second law). An object moving along a straight line has zero $L$ with respect to an observer located on that line but non-zero $L$ for all other observers.

\[ L = m_o r^2 \frac{d\theta}{dt} \rightarrow \text{conserved} \]  \hspace{1cm} (13.1)

**Figure 5: Definition of angular momentum.**

Given an object of arbitrary rest mass $m_o$ that moves under the attraction of another fixed object of mass $M$, its angular momentum with respect to the second object will remain constant throughout that motion. Its total energy will be the sum of the kinetic energy and potential energy due to its position in $M$'s gravitational field.

\[ E_{\text{tot}} = E_{\text{kin}} + V + m_o c^2 = \frac{1}{2} m_o v^2 - \frac{G M m_o}{r} + m_o c^2 \]  \hspace{1cm} (13.2)
For the kinetic energy we have

\[ \hat{r}(\theta) = \cos(\theta)\hat{i} + \sin(\theta)\hat{j} \]  

(13.3)

\[ \vec{r} = r\hat{r}, \vec{v} = \frac{d\vec{r}}{dt} = \hat{r}\frac{d\hat{r}}{dt} + \hat{r}\frac{dr}{dt} = r(\frac{d\hat{\theta}}{dt} \times \hat{r}) + \hat{r}\frac{dr}{dt} \]  

(13.4)

And since the two components are perpendicular to each-other (as follows from the external product), the square of the velocity will be the sum of the square of the components.

\[ v^2 = r^2 \left( \frac{d\theta}{dt} \right)^2 + \left( \frac{dr}{dt} \right)^2 \]  

(13.5)

Given (13.1) we can write

\[ E_{kin} = \frac{1}{2} m_o v^2 = \frac{1}{2} m_o r^2 \left( \frac{d\theta}{dt} \right)^2 + \frac{1}{2} m_o \left( \frac{dr}{dt} \right)^2 = \frac{L^2}{2 m_o r^2} + \frac{1}{2} m_o \left( \frac{dr}{dt} \right)^2 \]  

(13.6)

We can call the first term of the rightmost side of (13.5) “angular kinetic energy” and the second term “radial kinetic energy”. Equation (13.2) becomes

\[ E_{tot} = \frac{1}{2} m_o \left( \frac{dr}{dt} \right)^2 + \frac{L^2}{2 m_o r^2} - \frac{G M m_o}{r} + m_o c^2 \]  

(13.7)

We can re-arrange this to

\[ E_{tot} - V_{eff} = \frac{1}{2} m_o \left( \frac{dr}{dt} \right)^2 + m_o c^2 \]  

(13.7.a)

In summary we have gathered all the angular dependence in $V_{eff}$ (hidden in $L$) and we are left with a one-dimentional (radial) problem.
The effective potential \( V_{\text{eff}} \) is the sum of the gravitational potential energy \( V \) and of the angular kinetic energy which we could call “centrifugal potential”. \( V_{\text{eff}} \) is a more complicated function than \( V \) but the upside is that \( \theta \) disappears. Thus (13.7) effectively transforms the two-dimensional problem into one-dimensional. To find how \( r \) will behave in the 2D problem we can solve the 1D problem for \( r \) using \( V_{\text{eff}} \) instead of \( V \). By 1D we mean the relation that objects B and C have in the figure: the 2 objects are always found along the same, fixed straight line, i.e. the angular component of the motion is 0. The situation is reminiscent of a roller-coaster: Depending on its initial kinetic energy, the (one dimensional projection of the) bead will move following the slope of the infrastructure. If that kinetic energy is low it will be trapped in a stable fashion inside a well (local minimum). The analogy has of-course its limitations: The bead is actually moving in the \( x \) dimension under a component of the reaction force from the infrastructure which equals roughly \( m_o \cdot g \cdot \cos(\theta) \cdot \sin(\theta) = m_o \cdot g \cdot \tan(\theta) \cdot \cos^2(\theta) \) whereas had the infrastructure been an actual potential the force would have been proportional to \( \tan(\theta) \). For \( |\theta| < 20^\circ \) we have \( \cos^2(\theta) \approx 1 \) and the roller-coaster analogy gives a good intuitive sense of the behavior.

Below is a figure showing the different kinds of potential for the Newtonian 2-body problem with the larger body fixed.
Figure 7: Effective potential of rotating body.

For example, if an object has a $V_{\text{eff}}$ corresponding to the one depicted above and a total energy $E_{\text{tot}} = -30$ then its distance $r$ from the central body of mass $M$ will oscillate between $r^-=0.08$ and $r^+=0.42$ in an elliptical orbit. For a more detailed analysis see [50]. The concept of $V_{\text{eff}}$ has itself its limitations, as the derivative does not correspond to the attractive force but rather to the sum of the attractive force and the imaginary centrifugal force. Indeed the derivative is 0 for the radius of circular orbit, but the gravitational force is not.

We can rewrite (13.6) and (13.7) on a per unit of rest mass basis. (13.6) becomes

$$E_{k\text{in},s} = \frac{1}{2} v^2 = \frac{1}{2} r^2 \left( \frac{d\theta}{dt} \right)^2 + \frac{1}{2} \left( \frac{dr}{dt} \right)^2 = \frac{L^2_s}{2 m_r r^2} + \frac{1}{2} \left( \frac{dr}{dt} \right)^2$$

(13.8)

where $E_{\text{kin},s}$ and $L_s$ are the kinetic energy per unit of rest mass and angular momentum per unit mass respectively. Equation (13.7) per unit of rest mass becomes
\[ E_{\text{tot},s} = \frac{L^2}{2r^2} + \frac{1}{2} \left( \frac{dr}{dt} \right)^2 - \frac{GM}{r} + c \]  

Then (13.7a) becomes

\[ E_{\text{tot},s} + V_{\text{eff},s} = \frac{1}{2} \left( \frac{dr}{dt} \right)^2 + c \]  

Thus the effective potential per unit (rest) mass becomes

\[ V_{\text{eff},s} = \frac{L^2}{2r^2} - \frac{GM}{r} \]  

Note however that velocity \( v \) in this analysis has been implicitly considered non-relativistic as the classic expression for kinetic energy has been used.

When it comes to including the general relativistic effects and most notably the distortion of spacetime imparted by the central mass \( M \), then we have to use the notion of the metric as described in chapter 4. According to Schwarzschild's solution of Einstein's general-relativistic equations, the metric in spherical coordinates is no longer equation (4.25) but rather [51].

\[ ds^2 = -(1 - \frac{2GM}{r c^2})d(\text{ct})^2 + (1 - \frac{2GM}{r c^2})^{-1} dr^2 + r^2 d\theta^2 + r^2 \sin^2 \theta d\phi^2 \]  

which is called “the Schwarzschild metric” or “S metric”, and it is in spherical coordinates because of the spherical symmetry of the problem. For \( r \to \infty \) it reduces to Minkowski metric i.e. (4.25).

After several mathematical manipulations we can write the equivalent of equation (13.7) for general relativity in spherical coordinates [51]

\[ \frac{E_{\text{GR}}^2}{m_o c^2} = m_o \left( \frac{dr}{d\tau} \right)^2 + (1 - \frac{2GM}{r c^2}) \left( m_o c^2 + \frac{L^2}{m_o r^2} \right) \]  

In the above equation \( E_{\text{GR}} \) is the total energy of the moving body, including potential energy due to gravitation [52]. It is tempting to think that \( E_{\text{GR}} = \gamma m_o c^2 \) but as we saw in chapter 5 that would exclude gravitational potential energy. This can be seen from equation (5.7). Also as it will be shown, the effect of speed on gravitational mass has not been included.

In equation (13.13) \( L \) is the moving object's angular momentum. Note that \( \tau \) is the time in length units for the clock on the moving object. \( E_{\text{GR}} \) and \( L \) are the two conserved parameters of the problem. Setting \( r \to \infty \) and \( L = 0 \) we get \( E_{\text{GR}} = m_o c^2 \) for the case of a free fall from far away: an initially resting body with zero potential energy (far away) that is attracted by the fixed mass. At any point during this fall \( E_{\text{GR}} \) will equal \( m_o c^2 \) and \( L \) will be 0. Thus the equation describing the progression of fall will be
\[ \frac{1}{2} m_o \left( \frac{d r}{d \tau} \right)^2 - \frac{G M m_o}{r} = 0 \]  

(13.13A)

Which is remarkably similar to the Newtonian case, where the sum of kinetic plus potential energy equals the initial energy i.e. in our case 0 (free fall from far away), except that we have \( \tau \) instead of \( t \) and (13.13A) becomes

\[ \frac{1}{2} m_o \left( \frac{d r}{d \tau} \right)^2 - \frac{G M m_o}{r} = \frac{1}{2} m_o (v \cdot d t/ d \tau)^2 - \frac{G M m_o}{r} = 0 \]  

(13.13B)

From the S metric, the derivative of \( t, r, \theta \) and \( \phi \) over \( d \tau \) can be calculated under the assumption of “minimum interval s” (i.e. geodesic) with the Euler-Lagrange method using \( \tau \) as the affine parameter. In that case \( d t/ d \tau \) is a function of \( GM \) [51] which suggests that the gravitational parameter \( GM \) has slipped into the term of “kinetic energy” and the latter cannot be solely derived from speed and inertial mass. However, the gravitational mass in the “potential energy” term is the rest mass, unaffected by speed, contrary to the special relativistic ideas of chapter 7.

In (13.13), the term \( m_o \left( \frac{d r}{d \tau} \right)^2 \) represents the radial kinetic component of energy. Subsequently, if we are to transform this problem into a one-dimensional problem using the same technique of the effective potential, then from this energy balance we should group all potential and angular terms in the Schwarzschild effective potential \( V_{S,eff} \) i.e.:

\[ V_{S,eff} = -\frac{2 GM m_o}{r} + \frac{L^2}{m_o r^2} - \frac{2 GM L^2}{c^2 m_o r^3} \]  

(13.14)

We can see that the first term is the “Newtonian gravitational potential” and the second the “centrifugal potential” just as we saw in the non relativistic \( V_{eff} \). The third term is the result of the inclusion of General Relativity. By using \( r_S = \frac{2 GM}{c^2} \) equation (13.14) can be written as:

\[ V_{S,eff} = m_o c^2 \left[ -\frac{r_S}{r} + \frac{(L/c)^2}{r^2} - \frac{r_S(L/c)^2}{r^3} \right] \]  

(13.14A)

Sometimes the \( V_{S,eff, s} \) is given for a total energy of \( E_{GR}/2 \) so it takes the form [51]

\[ V_{S,eff} = \left( m_o c^2 / 2 \right) \left( -\frac{r_S}{r} + \frac{(L/c)^2}{r^2} - \frac{r_S(L/c)^2}{r^3} \right) \]  

(13.14B)

In figure 7a we can see a plot of (13.14)
Figure 7a: Plot of \( F_s \) indicates the Schwarzschild force and \( F_{H} \) the opposing force from Heisenberg Uncertainty Principle when the radius equals the Compton wavelength. Point A indicates an unstable circular orbit. [25]

Starting from (13.14A) and considering \( d(V_{S,eff})/dr = F_{eff} \) we have

\[
F_{eff} = (m_o c^2) d \left[ -\frac{r_S}{r} + \frac{(L_s/c)^2}{r^2} - \frac{r_S (L_s/c)^2}{r^3} \right] dr = (m_o c^2) \left[ \frac{r_S}{r^2} - \frac{2(L_s/c)^2}{r^3} + \frac{3r_S (L_s/c)^2}{r^4} \right] = 0
\]

we can find the radii of the circular orbits by setting \( F_{eff} = 0 \) [25,51,52]

\[
r_c = \frac{L^2}{r_S m_o c^2} \left( 1 \pm \sqrt{1 - \frac{3r_S^2 m_o^2 c^2}{2L^2}} \right), \quad r_S = \frac{2GM}{c^2}
\]

In order to compare the findings of the rotating pair model with the insights from general-relativistic mechanics we need to transform the “triple star” problem of chapter 9 into a “sun-satellite” problem so that the Schwarzschild effective potential is applicable. We will do so on the basis of keeping the orbit and the mass of moving object identical in both versions of the problem. The problem is then to find the fixed central mass \( M \) for which the moving object \( m_o \) would have the same orbit. Since the radius \( r \) and \( m_o \) should be the same, so will have to be the central force. Based on the definition of inertial mass presented in chapter 6 and its equivalence with gravitational mass we have

\[
\frac{GM m_o y^3}{r^2} = \frac{G m_o^2 y^6}{\sqrt{3} r^2}
\]

Thus \( M = m_o y^3/3^{1/2} \) and using the values \( y_{3,1} \) and \( m_o \) from chapter 9, \( r_S = 2.4554 \times 10^{-35} \text{m} \)
for \( L = h = 1.055 \times 10^{-34} \text{ kg m}^2/\text{s} \). The fraction inside the root is very small \( (8.88 \times 10^{-59}) \) so we can use
the binomial approximation for (13.15)

\[ r_{\text{min}} = \frac{L^2}{r_s m_o^2 c^2} \frac{3 r_s^2 m_o^2 c^2}{2 L^2} = \frac{3}{2} r_s, \quad r_{\text{max}} = \frac{2 L^2}{r_s m_o^2 c^2} = 1.66 \times 10^{24} m \] (13.17)

The radius \( 3 r_s / 2 \) is the minimum allowed circular radius [52] and it is unstable as it corresponds to a maximum in \( V_{S,\text{eff}} \). It is also very small, just over two Planck lengths (with Planck length being considered the smallest conceivable unit of space). The other radius is too big as it is comparable to the radius of the observable universe which is of the order of \( 10^{26} \) m. This means that the two solutions could hardly be made any more extreme. The meaning of those radii can thus be of only philosophical value.

Another way to transform the three neutrino problem into a sun-satellite system would be by using an intermediate configuration of a binary system which would have the same radius and each planet would have the same potential energy, as shown in figure 7b.

\[ \frac{G m^* \gamma^6}{(2r)^2} = \frac{G m_o^2 \gamma^6}{\sqrt{3} r^2} \] (13.18)

from (13.18) it turns that in order to achieve this, each planet should have a mass of \( m^* = 2^{1/2} 3^{-1/4} m_o \),

\[ \approx 1.07 m_o \]

\[ \text{Figure 7b: Transformation of the three neutrino model} \]

We further transform the model into a sun-satellite system of a central mass \( M \) to be specified later.
Now we impose certain conditions on this system. First we set its fundamental angular momentum

\[ L = \hbar \]  \hspace{1cm} (13.19)

As per the Heisenberg uncertainty condition, we also set its \( r_{\text{min}} \) to be equal to the Compton wavelength \( \lambda_c = \hbar / (Mc) \)

\[ r_{\text{min}} = \lambda_c = \hbar / (Mc) \]  \hspace{1cm} (13.20)

From the classical equation \[ \frac{Gm^*M}{r^2} = \frac{m^*v^2}{r} \] for \( v < c \) we also get that

\[ r_{\text{min}} = r_s / 2 = GM/c^2 \]  \hspace{1cm} (13.21)

From (13.20) and (13.21) it follows that

\[ M = (\hbar c / G)^{1/2} = m_{Pl} \]  \hspace{1cm} (13.22)

We can assign the first term \( rs/r^2 \) as the contribution of Newtonian gravitation to the force. Then we can again calculate the ratio of \( F/F_N \) like we did using special relativity in (9.3a). Using (13.19) and (13.22) and \( m_o = 0.0437 \text{ eV} \), we find that the ratio is

\[ \frac{F_{\text{eff}}}{F_N} = 1 + \left( \frac{L_s}{r_s c} \right)^2 \left[ 3 \left( \frac{r_s}{r} \right)^2 - 2 \frac{r_s}{r} \right] \approx 1.35 \times 10^{59} \]  \hspace{1cm} (13.23)

Which is the exact same result that we got from the special relativistic treatment.

It is interesting that the Newtonian equations (1.2) and (2.1) imply a universe where time (but not space) is curved by mass. Thus the corresponding metric is not the Minkowski metric i.e. eq(4.25). Actually the “Newtonian metric” $ds_N^2$ is

$$ds_N^2 = -(1 - \frac{2GM}{rc^2})dt^2 + dr^2 + r^2 d\theta^2 + r^2 \sin^2 \theta d\phi^2$$  \hspace{1cm} (14.1)

The above metric will reproduce equation (13.7) for slowly moving bodies [53]. Equation (14.1) implies that phenomena like light bending and gravitational time dilation can be accounted for by Newtonian approach, the former in part, the latter in full.

The key in both cases is the “Einstein” equivalence Principle based on which the theory of general relativity was built. It is a more restrictive version of the “weak” equivalence principle and in addition to the gravitational and inertial masses being equal it states that the effect of a homogeneous gravitational field on a reference frame is indistinguishable from the effect of a uniform acceleration of said reference frame. [54]. Light bending can be understood as the effect of an accelerated reference frame. In the figure below we can see three cases of a reference frame and how the observer of that frame will perceive the trajectory of a light beam emitted from outside of that frame.

![Figure 8: Light trajectories in different reference frames.](image-url)
The trajectory in the case of the free-falling reference frame can be found assuming a constant acceleration $g$. For the horizontal displacement we have $x=ct$ and for the vertical displacement $y=\frac{1}{2}gt^2$. Thus $y=\frac{gx^2}{2c^2}$, which is a parabolic trajectory identical to the one we get when modeling projectile shots with a constant $g$. Equivalently, a static reference frame within a gravitational potential $GM/r^2=g$ should experience the exact same bending.

Light is known to diverge when passing near a star with mass $M$.

We can understand that when a body approaches and then leaves a star and then moves away without crashing on the star, the trajectory in both ends far away from the star of the body will approximate asymptotically a straight line as the star's gravitation will have a negligible effect, and most of the bending will happen near the planet. The corresponding trajectory is a hyperbola with the star at the focus. Using the standard equations for celestial hyperbolic trajectories we can get the Newtonian result for light bending.

The distance $r_p$ from the focus to the periastron is given by [47]

$$r_p = \frac{L_s^2}{GM(1+e)} \quad (14.2)$$

First we set $r_p = R_{\text{star}}$. This equation is conveniently written per unit mass so assuming a virtual mass $m_v$ for the photon we have $L_s = m_v c R_{\text{star}} / m_v = c R_{\text{star}}$ so now we can calculate the eccentricity of said trajectory

$$e = \frac{c^2 R_{\text{star}}}{GM} - 1 \approx \frac{c^2 R_{\text{star}}}{GM} \quad (14.3)$$

From the eccentricity $e$ we can calculate the deflection angle through the equation [47]

$$\theta_{\text{defl}} = 2 \sin^{-1}(e^{-1}) \approx \frac{2GM}{R_{\text{star}} c^2} \quad (14.4)$$

So the deviation from the straight line is exactly half of what the general theory of relativity predicts from the Swarzschild metric [52]. The reasoning of this analysis clearly violates special relativity as it would result to a total velocity greater than $c$, but since the radial component is very small compared to $c$, considering that the angular component remains $c$ is an acceptable approximation. The reason for the deviation being half of the General-relativistic prediction can roughly be attributed to the fact that in the “Newtonian” metric only time is mass-dependent while in Schwarzschild metric both time and radial dimension depend on mass [55].

Light travelling near massive objects will not only bend, but also experience frequency shift. Gravitational time dilation is the cause of the gravitational red-shift phenomenon [51]. We can
imagine that a monochromatic light emitter is in fact our clock, with its oscillator ticking at the frequency of said light. Any red-shift not caused by motion is then an indication of gravitational time dilation as the clock will tick more slowly. We note that although in non relativistic Doppler effect red shift compared to a static clock will also appear when an identical clock moves away, when the clock returns to its base for a comparison, the blue-shift while approaching will cancel out the initial red-shift and the number of pulses will appear the same i.e. both clocks will agree on the lapsed time. This is not the case in neither special relativity (see “the twins” experiment) nor gravitational red shift.

The derivation of the red-shift formula does not require the use of Einstein's General relativistic equations and in deed Einstein himself derived said formula on the basis of his equivalence principle [55]:

Imagine a uniformly accelerating (at rate $g$) space-ship of length $l$, in the middle of nowhere, for our reference frame. If a passenger shoots a beam of monochromatic light of frequency $f$ from the front of the ship to the rear, the passenger in the rear will see a different color from the passenger in the front, all because of classic Doppler effect. The light will need $l/c$ seconds to reach the rear passenger and by that time the latter will have increased his velocity by $\Delta v = gl/c$. According to classical Doppler effect the shift $\Delta f$ will be $\Delta f = \Delta v/c = gl/c^2$. Consequently the same shift must appear in a static setting inside a gravitational field from a star.
The General relativistic formula can be derived from an energy balance and the mass energy equivalence from special relativity. The total energy of a photon far away from a star is $E_o = hf_o$. As the photon approaches the planet, its speed remains constant by definition, its potential energy decreases because its distance $r$ from the star's center decreases, thus its frequency must increase in order for the total energy to be conserved. We use the virtual mass $hf/c^2$ for the photon and write the energy balance per unit mass [56-59].

$$\frac{hf_o}{hf/c^2} = \frac{GM}{r} + \frac{hf}{hf/c^2}$$  \hspace{1cm} (14.5)

Thus $\Delta f/f = GM/(r \, c^2)$ which is the exact general relativistic result [52]. The use of special relativity and quantum mechanics to obtain the general relativistic result suggests a connection of the above with “Einstein Equivalence Principle” [56].

Figure 9: Gravitational red-shift.
An approach employing classical mechanics of light diffraction has also been proposed as adequate to deduce the general-relativistic results for light bending and perihelion precession [60].
15 Mass generation as an autocatalytic process.

It is clear that in a special relativistic universe when two bodies approach each other under their gravitational attraction then the gravitational acceleration will increase their gravitational mass. The increased mass will result in stronger acceleration and thus an autocatalyzed mass generation will occur according to figure 10.

Figure 10: Autocatalysis of mass generation

Autocatalytic processes are closely related to the existence of life, as most living populations can be modeled after such reactions using for example the Lotka-Volterra cycle.

The formation of a composite particle from gravitationally attracted constituents is in essence a condensation reaction and thus it is exothermal. The kinetic energy of the constituents will increase sharply as they approach each other and the autocatalytic cycle begins. It has been shown [63] that this sharp increase will only manifest itself once the constituents reach a critical speed which is the equivalent of the Activation Energy of the reaction $2\nu \rightarrow \text{meson}$.

As exothermal reactions cannot benefit from high temperatures because of the unfavorable thermodynamic equilibrium that offsets the kinetic advantage, it is important to use a good catalyst. In this case the catalyst can be played by an electron resting between the approaching neutrinos. This electron greatly enhances the gravitational attraction and therefore lowers the required initial speed. The electron is a good catalyst in chemical reactions because it a compact carrier of charge.
and in bariogenesis reaction because it is a compact carrier of rest mass. In deed, in the two approaching neutrinos set-up (with an initial distance between them of 1mm) an electron resting in the middle can reduce the activation energy by a factor of 25, as can be seen in figure 11 [63].

**Figure 11** An electron acts as catalyst in the formation of a binary composite particle.
16. Conclusion

A new relativistic treatment of Newtonian gravity has been explored. This treatment can be used to model the strong force as gravitation. The careful application of definitions from quantum mechanics, special-relativity, and the equivalence principle can produce simple but successful deterministic models of physical phenomena in a variety of scales and challenge the necessity of several components of the standard model. The generation of mass can be modeled as an autocatalytic reaction.
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PART B

Study of the catalytic hydrogenation of CO$_2$ using supported Ruthenium catalysts on different substrates.
1 Introduction-Theory of part B

This part of the dissertation is a study of the reaction of CO$_2$ hydrogenation. The motivation has to do with the management of energy storage and CO$_2$ emissions. This reaction allows us to store hydrogen in the form of hydrocarbons while at the same time reducing the excessive emissions of CO$_2$.

1.1 Energy storage

Renewable energy sources like PV and wind turbines offer energy in the form of electricity. This electricity should preferably be consumed immediately in the grid, but one major problem is that supply and demand do not always coincide so a significant amount of renewable energy has to be stored or wasted. There are several ways to store this energy. As we can see in figure 1.1 there is a trade-off between efficiency and duration: Solutions that allow longer storage periods come at a cost of lower efficiency. As efficiency we define the so called “round-trip efficiency” i.e. the ratio of energy of retrievable energy over supplied energy.

![Figure 1.1: round-trip efficiency of energy storage methods vs duration of storage (Data from ISEA)](image)

We can distinguish energy storage methods in two large categories: mechanical methods, where electrical charge transfer is not relevant, and electrical methods

**Mechanical methods:**
- The flywheel where energy is stored as kinetic energy of a rotating wheel, suitable for small scales and short term storage
Compressed air energy storage, where air stores energy by acting as a compressed spring.

Pumped hydro storage, where energy is stored by elevating water to a higher altitude, suitable for centralised large scale storage, commonly in hydroelectric plants.

Those methods are mature and well established.

**Electrical methods:**

- Batteries, which have a very high efficiency but also limited lifetime, low energy density and power density.
- Capacitors, which have higher efficiency and power density but also orders of magnitude smaller energy density than batteries.
- Hydrogen (via water electrolysis), which has the advantage of high energy density by weight and of clean emissions. On the other hand, storage and handling of hydrogen has a number of issues. Transforming hydrogen to methane solves those issues at a conversion cost. Electricity to methane has been achieved with a 60% conversion. Converting methane back to electricity when needed will result in a “round trip efficiency” of around 35%. The advantage that offsets this low rate is the ability to store for extended periods and the possibility of using methane directly in existing infrastructures[1]. This is the ultimate goal towards which the research presented in this thesis is focused.

Another critical factor for energy storage is compactness. In the graph below we can see that there is a trade-off between energy density and power density. Power density is the rate at which energy can be dispensed from a specific form of storage. Energy is important for travelling range and power for acceleration of the vehicle. This graph is called Ragone plot and it clearly depicts the struggle of alternative energy forms to reach the performance of conventional methods in terms of energy and power density which is of great importance in automotive applications.
Figure 1.2: Ragone plot for different energy dispensing methods. (source [2])
1.2 Hydrogen as an energy carrier.

The atom of Hydrogen is nothing but an electron revolving around a proton. This ultimate simplicity allows it to participate in more compounds than any other element. [3]. In its usual form Hydrogen is bimolecular. It is colourless odourless, tasteless, extremely light and very flammable. Hydrogen is mainly used as a raw material in the industry of methanol and ammonia production, but also for the production of a wide range of other chemicals.

Hydrogen has the greatest energy content by weight than any other fuel. It releases 147 kJ/g. In terms of energy content by volume, Hydrogen suffers due to its very low density, even when liquified. The table below shows a comparison of “energy carriers” on a 1MJ basis.

<table>
<thead>
<tr>
<th>For 1 MJ</th>
<th>H₂ gas 700bar</th>
<th>H₂ Liquid 1bar</th>
<th>diesel</th>
<th>Lithium-ion battery</th>
</tr>
</thead>
<tbody>
<tr>
<td>grams</td>
<td>7</td>
<td>7</td>
<td>21</td>
<td>1250</td>
</tr>
<tr>
<td>mL</td>
<td>178</td>
<td>99</td>
<td>28</td>
<td>1000</td>
</tr>
</tbody>
</table>

*Table 1.1: Comparison of energy densities of different energy carriers*
As we can see in figure 3, there are two ways to increase the energy density of Hydrogen: cooling and pressurising. The first will result to liquid Hydrogen, the second to pressurised Hydrogen and the combination of cooling and high pressure results in transcritical Hydrogen. Liquidation of hydrogen requires a significant amount of energy to achieve. As a boiling liquid, hydrogen can remain self-cooling as any excess heat is automatically removed with evaporation, which results in a significant loss of fuel and fire hazard. To avoid that, external cooling is required at an additional energy cost. On the other hand, pressurising hydrogen also requires energy for the compression, the required cooling (to remove heat that is added from the pump) and the subsequent reheating when dispensing H\textsubscript{2} to the cell(required to avoid freezing problems). As of 2009, liquefaction processes require 30 - 40% of the liquid hydrogen volume and the theoretical energy requirements for 700 bar compression and storage range within 4-10% , assuming an initial pressure of 20 bar.[4]

The extreme pressures or fuel loss required for storing hydrogen in pressurized, cryogenic or transcritical tanks respectively make it unsuitable for many applications. Also problematic is its extreme flammability, combined with its ability to escape through the tiniest of pores due to its small size. Technological advances in materials and methods have rendered hydrogen safe to be
used in cars but the biggest challenge is the distribution network of Hydrogen which is extremely limited. Hydrogen cars are in limited production and sold only in California where there is a small network of Hydrogen fuelling stations. An alternative way of storing hydrogen is by using metal hydrides. Metal hydrides are formed under high pressures and ambient temperatures when certain metals are exposed to hydrogen and absorb it. This technology has the drawbacks of high-cost and high weight.

Also, feeding of impure hydrogen greatly reduces the storage capacity. [5]
1.3 CO₂ hydrogenation

CO₂ hydrogenation can offer two categories of products: a) fuel and b) chemicals. Products of CO₂ hydrogenation like Methanol and formic acid are widely used as raw material in the chemical industry.

Products like methanol and hydrocarbons are excellent fuel for internal combustion engines, they have high energy content per liter and are easy to store and transfer. That been said, internal combustion engines have reached maturity and their efficiency (~30%) is still significantly lower than that of electric motors (~90%).

![Figure 1.4: Thermal efficiency of heat engines. Source [6]](image)

Hydrocarbons can also fuel electric motors via Fuel Cells. The intermediate step requires an additional efficiency factor during the fuel cell reaction which ranges from 50% for PEM FC's to 70% in the case of SOFC's. If instead of a fuel cell we use a battery to power an electric motor the additional efficiency factor of the battery is much more favourable (~90%). In the case of the electric vehicle, the battle between battery and fuel cell is still uncertain. Longevity issues as well as power density and energy density requirements make the choice unclear and both technologies attracted significant support from investors.
It is worth noting however than when taking into account the emissions from the manufacturing of a car, the manufacturing emissions are around 1/3 of the total emissions in the lifecycle of the car [7]. The implication of this is that it still makes sense to use an internal combustion car if the car has enough years of service ahead, rather than scrap it and order a new electric car, because the electric car will have to offset its own production emissions.

Reactions

When co-feeding CO$_2$ and hydrogen on a hydrogenation catalyst, mainly two reactions take place:

\[ CO_2 + H_2 \leftrightarrow CO + H_2O \]
\[ xCO_2 + \left(2x-z+\frac{y}{2}\right)H_2 \leftrightarrow C_xH_yO_z + (2x-z)H_2O \]

The first reaction is called Reverse Water Gas Shift (RWGS) and it leads to co-production of water and synthesis gas. The second reaction leads to the formation of hydrocarbons and/or oxygen-containing molecules. For example when $x = 1$, $y = 4$ and $Z = 0$ we have the formation of methane and it is called Sabatier reaction. If $x = 1$, $y = 4$ and $Z = 1$ we have the formation of methanol and so on. CO$_2$ hydrogenation has been studied extensively due to the fundamental and practical importance of the reaction in the sector of catalysis, surface Science, Biology, nanotechnology and climate science. For this reaction homogeneous and heterogeneous catalysts have been studied. Homogeneous catalyst have a satisfactory activity and selectivity but they are hard to recover and reuse. alternatively, in terms of stability separation from the reactants, handling and reuse, heterogeneous catalyst are Superior when it comes to designing the reactor Which means lower costs for a larger production. The issue with heterogeneous catalysts is that they produce smaller variety of products than their homogeneous counterparts [8]. In order to combine the activity of homogeneous catalysts with the ease of handling of heterogeneous ones, several innovations have been developed, including immobilization of heterogeneous catalysts and the use of eco-friendly solvents, like ionic liquids and supercritical CO$_2$. [9].

Due to the production of CO, other reactions also take place:

- The Boudouard reaction which leads to carbon formation and poisoning:
\[2CO \rightarrow CO_2 + C\]

- The Fischer-Tropsh reaction, which leads to the formation of higher hydrocarbons
Reverse Water-Gas Shift

Catalytic conversion of CO$_2$ to CO through RWGS has been proposed as a way of managing excessive CO$_2$ emissions in order to produce “Syngas” which is a mixture of CO and H$_2$ that has a wide variety of applications in the energy and chemicals sectors.

RWGS is an endothermic reaction, releasing 41.2 kJ/mol. Common metallic heterogeneous catalysts used for “forward” WGS are naturally suitable for “reverse” WGS. [10]

Supported Noble metal catalysts for RWGS are mainly Ru, Pt, Rh. They have been found to absorb dissociatively H$_2$ and have been used in CO$_2$ hydrogenation through both reactions.[9] The kind of precursor used to create the catalyst has been found to play a role in the activity and selectivity of the catalyst,. Rh/SiO$_2$ from acid and nitric salts yielded mainly CO while when using chloric salts the main product was methane. [11]

The mechanism of RWGS has been studied mainly on Copper catalysts. Two main mechanisms have been proposed, the redox version and the formic intermediate version.

According to the redox model, CO$_2$ oxidises copper and produces CO and H$_2$ reduces the copper oxide back to metallic copper and produces water. The formic intermediate mechanism suggests that CO is produced from the dissociation of formic species that are produced when CO$_2$ is combined with water. Noble metal catalysts have been found to produce formic intermediates and to favor dissociative adsorption of Hydrogen [9,12,13,14].

Methanation

The reaction of methanation of CO$_2$ is also called Sabatier reaction. It has been studied by NASA as a way to transform the CO$_2$ of Mars’ atmosphere into fuel (methane) This reaction at room temperature is thermodynamically spontaneous (ΔG$_{298}$=−131kJ/mol) but very slow so the use of catalysts is required.

The Sabatier reaction has been studied using metals of the group VIIIB of the periodic table e.g. Ru and Rh on metal oxide supports e.g. SiO$_2$, TiO$_2$, Al$_2$O$_3$, ZrO$_2$ και CeO$_2$).

The most common metal used as a catalyst for this reaction is Ni . One major problem of Ni catalysts is their deactivation from CO which form carbon on the catalytic surface. Noble metals are
less prone to this and more active than Ni in methanation.

Metal oxides are commonly used as supports

It has been found that the TOF of Ru catalysts depends on the dispersion and the kind of the support, with Al₂O₃ being the best support and carbon being the worst. High loading of Ru on Al₂O₃ yields ten times the production rate of similar Ni catalysts. Titania nanotubes are a support with high specific surface (Pt/Tnt 287m²/g). Pt catalysts on Titania-nanotubes yielded only methane and was active from temperature as low as 450K. Addition of Yttria in Ru catalysts assists in dispersion activity and tolerance to poisoning.

In industrial applications, reactants containing traces (~20ppm) of sulphur compounds are common. Those compounds have been found to promote the reaction on Titania supported catalysts and inhibit it on zirconia supported catalysts. On the other hand when using ZrO₂ or MgO as supports, or when H₂S concentration exceeds 100ppm then the methanation rate decreases.[15] There are two general mechanisms for the methanation of CO₂. The first considers the transformation of CO₂ to CO and the production of methane from CO. The second considers the direct transformation of CO₂ to methane [16-22] From experiments on Ru/TiO₂ catalysts it has been found that CO is an intermediate product of methanation. Formic species that act as intermediate for the formation of CO are strongly absorbed on the support and are in equilibrium with active formic species on the metal/support interface. Also the activation energy and the rate of the reaction are similar to those of the production of methane from CO. It has also been found that Rh/γAl₂O₃ catalysts can yield 100% conversion of CO₂ to CO even in ambient conditions. CO₂ is adsorbed on the surface of Rh dissociatively as CO and O species. The O species oxidise the Rh atoms and the RhO-CO species are the most prone to react with Hydrogen. [23,24].

Synthesis of other Hydrocarbons.

The synthesis of other hydrocarbons is a modification of the well-known Fischer-Tropsch (F-T) process. The modification is that CO is substituted by CO₂. The metals used as catalysts for the production of other hydrocarbons are the same used in F-T processes. There are again two paths: One involves the intermediate production of methanol using mainly Cu-Zn catalysts and the subsequent conversion of methanol to hydrocarbons. The other involves the intermediate production of CO with RWGS and the subsequent production of hydrocarbons through F-T process.
Catalysts for higher hydrocarbons

Cobalt has been used extensively in F-T processes due to its high cost efficiency. When instead of syngas Co is fed with CO$_2$-H$_2$ mix it mainly acts as a methanation catalyst. [25-28]. It has been suggested that CO and CO$_2$ follow different paths to higher hydrocarbons. The former includes C-H and O-H intermediates released in the bulk while the latter includes C-O-H and O-H intermediates on the surface [27]. Those surface species are hydrogenated at a faster rate than the rate of CO$_2$ adsorption so are stabilised into methane before any new C atoms have a chance to start a carbon chain.

Iron is also used for CO$_2$ hydrogenation. The reaction path is RWGS and then F-T. Its main problem is poisoning from carbon. Potassium is frequently used as a promoting additive [29]. Meganium and copper are also used as a promoter to increase the length of carbon chain [30].

Both the Sabatier and the RWGS reactions produce water. Accumulation of water not only deactivates the catalysts but also thermodynamically reduces the rate of the reactions. Several approaches try to remove water from the products eg. using selectively permeable silica membranes.[31,32]

Methanol

Methanol is a common solvent, a promising fuel and a raw material in the chemical industry, so the production of methanol from CO$_2$ is important. Methanol from CO$_2$ is produced with reaction $=2=$ with $x=z=1$ and $y=4$. It is exothermic and it results in reduction of volume so thermodynamically it is favored by low temperatures and high pressures. The same catalysts that are used for the production of methanol from CO are used also for production from CO$_2$ [33]

Copper remains the most popular catalyst for methanol production and it is usually combined with other metals such as Zn, Zr, Ce. [34,35,36] The selection of the support is critical as it affects the formation of the active phase of the catalyst, the interaction with the promoters and the acidity of the catalyst. ZnO is a proper support as its oxygen vacancies in the crystal are active for the formation of methanol Ga$_2$O$_3$ and Si O$_2$ are used as additives for the stabilisation and the promotion of the Cu/ZnO catalyst. Noble metals are also used as promoters

Zirconia is also a good support for methanol production due to its high stability in oxidative and
reducing environments and offers good dispersion to copper. It has been suggested that CO$_2$ is absorbed on zirconia and that the required hydrogen is supplied via spillover species adsorbed on copper [37].
1.4 Promoters

Promoters are additives that improve the properties of the catalyst. There are two main kinds of promoters: Structural and functional. Structural promoters help with the dispersion and stabilisation of the active phase thus increasing the number of active sites. Functional promoters can optimise the strength of the absorption of reactants thus improving the activity and selectivity of catalysts for every active site.

Functional promoters and electrochemical promotion

An important factor for the adsorption of the reactants on the catalytic surface is their propensity to either donate or receive an electron from the catalyst. Additives that change the electronic density of the catalytic surface will also change the work function (i.e. the required energy for the electron to escape) for the shared electron that unites the reactant with the catalytic surface. If a reactant has the propensity to donate an electron, then an increase in the work function will deter this electron from going back to the reactant and thus will strengthen the absorption. If the reactant has a propensity to receive an electron then an increase in the work function will make it more difficult for the electron to go from the catalyst to said reactant and thus the latter will be more weakly adsorbed.

The additive itself has a propensity to accept or donate electrons. Donors are called electropositive and they reduce the work function of the catalyst. Acceptors are called electronegative and they increase the work function.

Thus, When the reactant and the additive have opposite propensities then the bond is strengthened.

In any case the ultimate goal of a functional promoter is that if a reactant is of negative kinetic order in the desired reaction then the promoter must change the work function of the catalyst so as to make the bond weaker. If a reactant is of positive order then we want to maximise its concentration on the catalytic surface so the promoter will have to strengthen the bond.

In the case where the support is an electrolite and has enough bulk so as to allow one to apply electrodes on it, then an electrocatalytic system can be created, in which one of the electrodes is the catalytic surface. By applying current, one can simulate the presence of promoters on the catalytic
surface. In a rather unintuitive way, sending negative charge towards the catalytic electrode does not correspond to the addition of an electropositive (donor) promoter but of an electronegative promoter. This happens because the actual mechanism of electrochemical promotion of catalysis involves an “effective double layer of charge” in which the charge that travels towards the metal reaches the exposed surface of the electrode through the triple phase boundary and then it is neutralised (by either releasing its electrons to the external circuit or absorbing electrons from it) but in the process of doing so it forms a dipole with the conductivity electrons of the metal. This can be described by the following reaction given here for the case of $\text{O}^{2-}$ ions on a YSZ supported Ru electrode:

$$\text{O}^{2-} (\text{YSZ}) \rightarrow [\text{O}^{\delta-}\delta^+](\text{Ru}) + 2e^-$$

The quantity $\delta$ denotes the amount of charge that the spilled over species attracts from the metal. The dipole is formed as the spilled over species attracts a mirroring opposite charge $\delta$ inside the metal and it is this mirroring charge that is equivalent to the charge from functional additives. [38]

In the case of CO$_2$ Hydrogenation the above observations can be seen in figure 1.4.

![Figure 1.4: Depiction of electrochemical modification of catalysis for CO2 Hydrogenation. The + or – signs are not quantitative.](image)

Hydrogen has a propensity to donate electrons and this results in an orientation where the positive part of hydrogen (the proton) stands over the metallic surface whereas the negative part of hydrogen is towards the bulk of the metal. As we can see in the above figure, this orientation is stabilised by
attractive forces from the double layer that resulted from the application of positive potential (left). We can see that the donated electron (tip of the bullet) is closer to the positive layer than the negative layer thus, in net effect, it is attracted towards the metal by the positive layer. Similarly the positive side of hydrogen is closer to the negative layer and it is also attracted. The absorbed CO\textsubscript{2} is an electron acceptor and assumes the opposite orientation which results in repulsive forces. Reversing the potential (right) reverses all the effects.

In electrochemical research, cells have usually three electrodes: the working (W) which is the catalyst in our case, the counter (C) which is the one used to apply the current and the reference (R) which is a third electrode not depicted above and it is used to measure the applied voltage (U) without interfering with the application of voltage. In the electrochemical notation the left image corresponds to a positive UWR while the right to a negative UWR. By another convention the application of negative UWR is said to be the “default” electricity through the cell, so all reactions that are enhanced with the application of negative UWR have been called “electrophilic”. In the case of CO\textsubscript{2} hydrogenation the Sabattier reaction has a higher kinetic order on hydrogen thus it is favoured in the left case (UWR>0, electrophobic) whereas the RWGS has a higher kinetic order on CO\textsubscript{2}, thus it is favoured in the right case (UWR<0, electrophilic).

[38]
1.5 Thermodynamics

The figures below were obtained with the use of software HSC Chemistry 5.11. The depict the percentage of each species on a carbon-containing molecules basis i.e. CO, CO₂, CH₄. [39]

As we can see in the figure above, in the case of the Sabattier reaction, increasing the amount of CO₂ results in a lower CH₄/(CH₄+CO₂+CO) rate. The same holds for the RWGS reaction, as we add CO₂, more CO is produced but the conversion becomes less efficient. As we can see in the case of Sabattier, production of hydrocarbons is thermodynamically favoured at low temperatures (exothermic 165 KJ/mol at 298K). The opposite holds for RWGS (-41.2KJ/mol at 298K)

The combined system that includes both reactions shows that the concentration of hydrocarbons exhibits a peak. This modeling did not include alcoholes.

The volume reduction in the formation of higher alkanes is favoured in high pressures. The stoichiometric volume reduction is 40% for methane, 44% in the case of ethane and approaches 50% for large chains. For ethanol the volume reduction is 50% and increases as the chain lengthens.

Figure 1.5: Thermodynamic calculations of equilibrium for RWGS and Sabatier reactions individually (top) and combined (bottom).
As we can see in figure 1.5, the effect is negligible at 300°C.
References of part B.1

1. Dirk Uwe Sauer et al. : Overview on the potential and on the deployment perspectives of electricity storage technologies, ISEA 2012


5. Ν. Ρωμανός. Το Αυτοκίνητο του Μέλλοντος κινούμενο με Ανανεώσιμες Πηγές Ενέργειας (Α.Π.Ε.), Ηλεκτροκίνητα μέσα μεταφοράς στην Ελλάδα – Υφιστάμενη κατάσταση και προοπτικές, TEE, 2006

7. EtoGas Gmbh, Power to Gas: Smart energy conversion and storage, 2013


40. I. Kalaitzidou, A. Kotsiras, D. Grigoriou et al. (in preparation)
2. Experimental

The general scope of the experiments included

a) Identifying catalysts that can lead to the production of higher hydrocarbons. In order to be able to trace those hydrocarbons large amounts of catalyst have been loaded in the reactor and therefore the experiments yielded a conversion rate up to 95%, suggesting that they were mass transfer controlled and unsuitable for kinetic analysis. Because of the high dilution of the reactants and the limited range of mass flow controllers, it was not possible to further increase the flowrate. Experiments were repeated with smaller amounts of catalyst in order to calculate activation energies.

b) Identifying metal-support interactions. Solid state Proton conductors have been used as supports and were compared to anionic conductors or neutral supports.
2.1 Catalyst preparation

Catalysts were prepared using the wet impregnation method. This method consists of mixing an amount of the pulverised support with a quantity of a solution of precursor molecule that contains the metal. The quantity of the precursor solution is determined by the desired loading of the support. Both substances are mixed in an amount of water much higher than the pore volume of the support and after the evaporation the loaded support is calcinated in order to remove all other atoms except the metal. The precursor compound that was used in our experiments was Ruthenium (III) nitrosyl nitrate, Ru 31.1% min (Alfa Aesar) and Cobalt (II) nitrate (Alfa)

The supports used were
- TiO$_2$ P25, Degussa
- Conductor of O$_2$: (ZrO$_2$ + Y$_2$O$_3$, YSZ, Partially Stabilised Yttria Zirconia HSY3, Zirconia Sales (U.K.) Ltd.)
- A proprietary perovskite called BZY was used as a Proton conductor
  BaZr$_{0.85}$Y$_{0.15}$O$_{2.925}$ +1 w% NiO (NorECs)

The latter was received from NorECs as a mix of pulverised compounds with the instruction to calcinate it at 1450 °C for 12 hours. After that the result was a solid ceramic lump that required a significant effort to pulverise again. Pulverising of baked BZY was carried out with a glass mortar and pestle which resulted in a wide distribution of particle sizes.

Below is the detailed process that was followed for wet impregnation

Weighing of 5 grams of support
Weighing of the calculated amount of precursor compound
Dilution of precursor in 80 mL of distilled (3D) water in a spherical bottle Addition of the 5 grams of support in the spherical bottle
Evaporation of water using a rotary evaporator at 50 mbar and 60 °C
Scraping of the catalyst from the walls of the bottle
Further drying of the catalyst at 100C
Calcination of the catalyst 5C/min up to 500C, 1 hour at 500C and free cooling.
Grinding of the resulting powder and storage

Exposure to 10% H₂ (rest He) at 450 °C for 1h in order to reduce the metal oxides before the experiment.
2.2 Characterisation

Chemisorption

The inherent activity of the catalyst is expressed in converted molecules per second per active site. Thus in order to calculate the inherent activity of the catalyst, it is necessary to have a good estimation of the number of active sites. One usual way to estimate the active sites is through the adsorption isotherm. By plotting the adsorbed volume of a gas for different equilibrium pressures, one can extrapolate to zero pressure and estimate the volume of gas needed to form a monolayer. If this gas is one of the reactants and it is chemically adsorbed, then we assume that it is only adsorbed on the active sites and that the monolayer covers only said sites. By knowing this volume, the number of metal atoms that each gas molecule occupies and the surface that a metal molecule occupies one can trivially calculate the dispersion, the specific surface of the metal and, by assuming spherical particles, the average diameter of the metallic particles. In order to exclude any gas molecules adsorbed on the support, a process was followed to determine the “reversible” volume i.e. volume of gas that has been weakly adsorbed on the support. In order to determine this volume after the first adsorption the pressure is dropped and it is assumed that all the gas molecules that were adsorbed on the support will desorb. Then we repeat the insertion of gas and assume that the volume that will be adsorbed this time will be only due to the support since the metal will be already occupied. This volume was discounted from the total adsorbed volume. In the case of Cobalt catalysts, CO was used instead of Hydrogen because it was not possible to obtain a usable isotherm with Hydrogen.

The physical parameters used in order to calculate the following values, were taken from the SORPTOMATIC 1900 User Manual 1989. The process is also described in said manual.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas</th>
<th>D [%]</th>
<th>V_m [cm³/g_cat]</th>
<th>d_met [nm]</th>
<th>S_sp [m²/g_met]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru 2% / TiO₂</td>
<td>H₂</td>
<td>15</td>
<td>0,337</td>
<td>6,3</td>
<td>78</td>
</tr>
<tr>
<td>Ru 2% / YSZ</td>
<td>H₂</td>
<td>3.8</td>
<td>0,085</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>Ru 2% / Al₂O₃</td>
<td>H₂</td>
<td>6</td>
<td>0,127</td>
<td>17</td>
<td>30</td>
</tr>
<tr>
<td>Co 15% / TiO₂</td>
<td>CO</td>
<td>0.5</td>
<td>0,280</td>
<td>207</td>
<td>3</td>
</tr>
<tr>
<td>Co 15% / YSZ</td>
<td>CO</td>
<td>0.25</td>
<td>0,152</td>
<td>190</td>
<td>3,5</td>
</tr>
</tbody>
</table>

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Table 2.1: specific active surface of catalysts as estimated by chemisorption

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO</th>
<th>SpCO</th>
<th>Vpore</th>
<th>SpVpore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co 15% / Al2O3</td>
<td>0.1</td>
<td>0.069</td>
<td>420</td>
<td>1.6</td>
</tr>
<tr>
<td>Ru 2% / Co 15% / TiO2</td>
<td>1</td>
<td>0.643</td>
<td>96</td>
<td>7</td>
</tr>
<tr>
<td>Ru 2% / Co 2% / TiO2</td>
<td>4.5</td>
<td>0.502</td>
<td>22</td>
<td>25</td>
</tr>
<tr>
<td>Ru 2% / Co 15% / YSZ</td>
<td>2.3</td>
<td>1.375</td>
<td>22</td>
<td>29</td>
</tr>
<tr>
<td>Ru 2% / Co 15% / BZY</td>
<td>1.7</td>
<td>1.001</td>
<td>30</td>
<td>21.4</td>
</tr>
</tbody>
</table>

With a similar line of thinking but using a gas that is not selectively adsorbed on the surface, one can estimate the total surface of the catalyst as well as the pore distribution.

Using the BET method of nitrogen physical adsorption the pore distribution of the supports was determined experimentally.

Figure 2.1: Pore diameter distribution as estimated by BET
Table 2.2  Specific surface of catalysts as estimated by BET

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Specific Surface</th>
<th>BET Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru 2 % / Co 15 % / BZY</td>
<td>0.0186</td>
<td>9.96</td>
</tr>
</tbody>
</table>
2.3 Set-up

The reactor was a stainless steel tube ¼”, with a replaceable plug of glass wool positioned and held in a specified length with the aid of stainless steel spacers. The tube was used in vertical orientation with the catalyst sitting on top of the glass wool and the reactants were fed from above. The reactor was placed inside an open-ended cylindrical furnace and positioned to match the axis of the furnace with the aid of spacers made of insulator. The heated part of the furnace extended approximately 10 cm above and below the position of the catalytic powder. The position was such to minimise the temperature gradients inside the reactor. The part of the tube that was filed with powder was around 5mm long. In the cases where the quantity of the catalyst was not adequate to fill a full layer, ground quartz glass was mixed with the powder so as to keep the total weight always at 200mg.

Inside the reactor was placed a thermocouple, sealed with a green septum, with its edge touching the catalyst. This was used as an input to the PID thermocontroller which regulates the flow of current from a variac to the furnace through an on-off switch. The reactants were fed from high pressure cylinders. The working pressure was usually 5 bar and the flow-rates were set using Brooks model 5878 controller and brooks flowmeters. The 3 gases (CO₂, H₂ and He) were subsequently mixed in a cross union with 3 inlets and one outlet. The pressure gauge was mounted on a cross union on the top of the reactor the other 2 inlets for the union were used for the thermocouple and the reactants. The pressure was controlled manually when necessary with a throttle valve mounted at the exit of the reactor. A blind piece of tubing was also mounted at the exit of the reactant in order to contain any condensed water from the reaction.

The analytic system consisted of an IR analyser with channels for CO and CO₂ (Fuji) and a GC chromatograph (Shimadju) with a Valco plot Alumina capillary column, coupled with an FID detector which was used to measure hydrocarbons. The output of the FID was calibrated using a standard sample of a mixture of hydrocarbons (Scott).

The composition of the reactants in all experiments was 1% H₂, 7% CO₂, 92% He and unless otherwise mentioned the pressure was 1 bar.
2.4 Results and discussion

2.4.1: 200mg tests with single-metal catalysts

Cobalt 15% and Ruthenium 2% were tested over TiO$_2$, Al$_2$O$_3$, YSZ. Those experiments were carried out with excessive quantity of catalyst (200mg) in order to be able to trace higher H/C.

![Figure 2.1: Activity of catalysts](image)

Although the results were mass-transfer controlled we can see as a general trend that, per gram of catalyst, Ruthenium had higher activity, producing mainly methane but Cobalt produced higher...
hydrocarbons. In the figure below we can compare the selectivities of the above catalysts

![Figure 2.2: Selectivity of catalysts](image)

We can see that the main product in all Ruthenium catalysts was methane and TiO2 had by far the highest selectivity in CH4, while in the Cobalt catalyst methane and CO were equally produced and higher HC's had a stronger presence. Results of other researchers showed that when CO is present, CO2 hydrogenation is hindered [1].

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2.4.2 200mg tests with bimetallic catalysts

In an attempt to combine the best of both metals, we tried a bimetallic catalyst with 2% Ru and 15% Co. The idea was that Ru would produce CH₄ and CO and Co would turn that CO into HC’s. This catalyst was tried in TiO₂, in YSZ and in a newly available BZY support.

![Figure 2.3: Activity and selectivity of bimetallic catalysts](image)

The above experiments were successful as they indeed produced higher hydrocarbons, up to hexane. This could be explained by the fact that cobalt adsorbs the CO that is produced from Ru in
order to initiate a Fisher-Tropsch reaction. An interesting observation is that although Ru and Co in single metal catalysts on YSZ produced a significant amount of CO, in the bimetallic version CO was much less prominent, implying a synergistic effect in CO reduction. As far as the support is concerned an interesting result was that the TOF for CO was significantly higher in BZY than in TiO$_2$. Also the selectivity for HC was improved with the BZY support possibly due to the abundant CO that could feed a F-T reaction.
2.4.3 Higher pressure

In an attempt to detect methanol, higher pressures were also used
In figure 2.4 we see the effect of pressure on the RuCo/TiO2 catalyst. In figure 2.5 we see the effect of pressure on the RuCo/BZY catalyst.
Figure 2.5: Effect of pressure on RuCo/BZY catalyst

Alcohols were never detected (although some traces might be hidden under the signal of pentane) but this was somehow expected since it usually takes partial pressures $> 20$bar for such products to appear.
2.4.4 Schultz-Flory distribution

The concentrations of the hydrocarbons follow closely the Schultz-Flory (S-F) distribution when excluding methane from the products. The model assumes that

1) the growth of the carbon chain happens as a non-selective polymerisation of surface species with the addition of one carbon atom at each step and

2) that each surface species has the same reaction probability regardless of the chain size.

According to this model the following relation should hold:

\[
\log \frac{W_n}{n} = n \log p + \log \left(1 - \frac{p}{p}\right)
\]

Where \(W_n\) is the fraction of the mass of chains with \(n\) carbons over the total mass of hydrocarbons and \(p\) is the probability of chain growth and is the arbitrary parameter when fitting the data on this model. The model suggests that the LHS logarithm is a linear function of \(n\). Indeed in the plotted data we can see a linear relation when we exclude methane. Excluding methane makes sense in that it can be produced from both directly from \(CO_2\) and indirectly via \(CO\).
Figure 2.6: S-F plots for RuCo/TiO2 (top) and RuCO/BZY (bottom)
2.4.5 20 mg tests

In order to study the effect of the substrate on the selectivity, a series of experiments was carried out, this time aiming not to be mass transfer controlled, at the expense of not being able to detect higher hydrocarbons.

The large amount of catalyst in the previous experiments meant that those experiments were mass-transfer controlled. The upside of this was that catalysts were less prone to deactivation, as they were not fully exploited. So the first experiments with smaller quantiles were stability experiments. At first quantities of 2-3 mg were used but this was no more than a dozen of grains, a very small volume which was hard to evenly distribute in the bed. The results lacked repeatability so we finally settled for 20mg.

![Figure 2.7: Selectivity to CO for Ru on different supports at 380 C](image)

We see a remarkable range of the selectivities. In the case of BZY, YSZ and γ-Al₂O₃ we can account for the results by using the rules of promotion of catalysis [2]. Here the promoting species are supplied not via electrical potential but thermal diffusion. O²⁻ in the case of YSZ, H⁺ in the case
of BZY. $\alpha$-Al$_2$O$_3$ is considered to be the most stable form of Al$_2$O$_3$ while the complex behaviour of OH$^-$ species on $\gamma$-Al$_2$O$_3$ [3] could explain the high methane selectivity. The thermal migration hypothesis is further bolstered by electrochemical experiments with the same catalysts. [4]

Another notable phenomenon is that although Ru/BZY yielded mainly CO, the addition of Co in RuCo/BZY significantly limited the presence of CO in the products, as shown in the 200mg experiments, perhaps by consuming it in the production of methane and other HC’s via F-T reaction.

Figure 2.8: Correspondence of metal-support interaction (top) and Electrochemical promotion (bottom)
Figure 2.9: Activities of catalysts in 20 mg experiments

Activation energies

The values below have been calculated by averaging several experiments of the 20 mg series. The results are rounded to 0.5 increments and are shown in Kcal/mol.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Sabatier</th>
<th>RWGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru / TiO₂</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Ru / YSZ</td>
<td>17</td>
<td>18.5</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Activation Energy 1</td>
<td>Activation Energy 2</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>13.5</td>
<td>13.5</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>14.5</td>
<td>18.5</td>
</tr>
<tr>
<td>BZY</td>
<td>17</td>
<td>15.5</td>
</tr>
</tbody>
</table>

*Table 2.1: Activation energies of tested catalysts in Kcal/mol.*
Conclusions

The main conclusions from this research can be summarized as follows:

Ru catalysts were the best for CH₄ production. In terms of selectivity Ru/TiO₂ yielded nearly 100% methane in most cases.

RuCo catalysts have been found particularly suitable for the production of heavier Hydrocarbons.

The Fischer-Tropsch mechanism seems to be involved in the process.

Ru catalysts are not suitable for the production of alcohols at low pressures (<6 bar).

The use of BZY as support greatly promotes the RWGS reaction.

The choice of the support can determine the selectivity of the catalyst and the relevant mechanism can be to a good extent explained by the rules of electrochemical promotion [4] applied for thermal diffusion of anionic and cationic species.
References of part B.2


CURICULUM VITÆ

DIMITRIOS GRIGORIOU

Contact : vitrosoft@gmail.com , T:00306972001740
Languages: Greek (native), English (fluent), French (fluent), German (basic).

Highlights:
Committed to the pursuit of innovation and problem-solving. Graduated from U. of Patras in 2006 (Chem.Eng.) with a national top-3 award. Won a scholarship from the highly selective HEC Paris MBA. Inventor of several utility and design patents. Published (under the alias Mesorahis) a critically acclaimed book illustrating key insights of the process of innovation through fictionalized case-studies.

Education:

HEC PARIS Master's in Business Administration. 2011 - 2012
- GMAT 750 (top 2% internationally).
- Focused on Management of Innovation.
- HEC Paris constantly ranks in the top 2 Business Schools in Europe (FT rankings).

University of TEXAS at AUSTIN, Red McCombs School of Business 2012
- Exchange program

University of PATRAS [Greece] - Diploma in CHEMICAL ENGINEERING 2000 - 2006
- Orientation: biotechnology and environmental engineering.
- University of Patras was ranked #9 Worldwide in Chemical Engineering according to the CPP index of the 2012 QS Rankings.

Professional experience

Freelance professional 2012-now
- Lead Instructor in the IATA-HARVARD program.
- Management and leadership classes for aviation professionals.
- **Management of Innovation for “PAPAELIAS Constructions LTD”**.
- Technical consulting for building and insulation products.
- **PhD researcher in catalysis and gravitation at the U. of Patras, Chem. Eng. Dpt.**

EDG design– Product Development engineer [Industrial Design agency, Athens]. 2010 - 2011
- Offered innovative solutions regarding Design-for-Manufacturing and ergonomics.
- Composed the supporting short descriptions and pitches for the presentation of the company’s projects in contests and exhibitions.

HELBIO – Researcher [R&D in hydrogen production, Patra, Greece]. 2009 - 2010
- Prototyped an innovative architecture of reactor with increased efficiency and lower cost.
- Conducted patent searching to benchmark the “prior art” and draft new applications.

CHROTEX – Continuous Improvement engineer [Paint and varnish, Athens]. 2008 - 2009
- Developed procedures that increased the productivity of a department by 20% while maintaining the same high-quality standards.
- Inquired technical and technological issues and developed specific solutions (methods and tools).
- Developed and implemented Quality Control procedures in the calibration sector, achieving both increased accuracy and reduction of the related yearly costs by 40%.
- Planned out the day-to-day production schedule under lean inventory conditions.
Awards

- Technical Chamber of Greece Award: 3rd place among all chemical engineering graduates of 2006 from Greek schools.
- Winner of the HEC Markstrat tournament / class of 2012.
- Winner of the social entrepreneurship idea pitching contest of Dell Computers, Austin TX, 2012.
- National Design Award “Greek design=Good design” for the product «Scissor Bag», 2013.

Selected Publications

- 2 Utility and 5 Design Patents granted: GR1006717, 20130100508, 20140600036, 20130200093, 20130200092, 20130200091, 20130200090.
- Academic integrity guide of U. of Patras, (adaptation in Greek from MIT Acad. Integrity Guide) in press.

Selected Presentations:

- 10th National conference of scientific chemical engineering, Patras 2015 “Relativistic dependence of gravitational mass form velocity”.
- Series of 10 lectures on “introduction to Chemical Engineering” now embedded in the OCW of University of Patras, with 1500+ views.

Miscellaneous

- Military training and service completed.
- Driving license class: B.
- Excellent MS Office user; Programming with Fortran95; Autocad 2008 Certified user.
- Skilled photographer.
- Member of the technical chamber of Greece.
- Member of the Triple Nine Society (Society for persons certified in the top 0.1% of the IQ distribution).