

**PERFORMANCE TARGETS FOR A CHEMICAL PROCESS USING A
GRAPHICAL TECHNIQUE: A CASE STUDY OF THE METHANOL
SYNTHESIS PROCESS**

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DECLARATION

I hereby declare that this dissertation is my own unaided work. It is being submitted for the degree of Master of Science in Engineering to the University of Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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.....day of.....year.....

ABSTRACT

Chemical processes impose a heavy burden on the world's natural resources, because they use raw materials to manufacture various products and require energy to drive them. Because these processes are also inefficient, much benefit to both industry and energy conservation can be derived from improvements in their design.

This dissertation presents a technique that can be used to analyze the reactions that take place (often more than one, and in competition) in a reactor. This is done via the graphical representation of what occurs during a chemical process in terms of mass balance calculations used together with basic thermodynamic principles. This technique allows the researcher to identify which of the many possible reactions taking place in a reactor is/are likely to dominate in that particular chemical process, and the degree of transformation that is achievable.

The graphical technique postulates that the chemical species involved create lines that define the reaction's attainable boundaries in a $G-H$ space. This makes it possible to evaluate the operating process; identify sources of inefficiency within it; establish systematic performance targets; and improve process performance. A collateral benefit is the contribution these improvements can make not only to the sustainability of the chemical processing industry but to conserving raw material sources and reducing negative environmental impacts.

The most crucial element of the graphical technique is its use to locate the attainable region (AR) for chemical processes in a reactor. In this case it is a thermodynamically achievable region in the state space within which the reactor can function without violating thermodynamic boundaries, using only the process of reactions and mixing.

After finding the AR, we can interpret its boundary in terms of the likely limiting extents of reaction through mass balance calculations. By these means we can deduce the process reaction pathways. The technique is two-dimensional, allowing for easy and rapid interpretation of the results, such as the effects of changing the process feed and operating conditions. It also provides insight into the likely reactions achievable in the reactor under different process conditions.

This approach was applied to the simultaneous methanol synthesis from syngas and water gas shift (WGS) reactions. The graphical plots show that the introduction of either water or CO₂ or both to the feed opens up the mass balance region, resulting in WGS activity, which generates more reaction path alternatives, as does the reverse (RWGS) reaction. They also demonstrate that the change in Gibbs free energy across the reactor and the reaction pathways leading to the product are interlinked. The quantities involved y can be useful to the engineer in setting performance targets for chemical processes.

The examples of graphical analysis supplied in this dissertation show that reaction path analysis could become an important tool in the preliminary stages of process design, because it can identify the most desirable reaction routes.

DEDICATION

This dissertation is entirely dedicated to the Lord Almighty, for His infinite mercy, compassion and guidance throughout this work.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

Energy is a fundamental need of a modern economy, because it is an essential constituent of nearly all goods and services. However, its use entails heavy environmental, financial, and security costs that cannot be quantified in economic terms alone. A strategic method for reducing the cost of energy while retaining its benefits is to use it more efficiently. (OTA, 1993)

Chemical processes consume a high proportion of the world's natural resources, both as a source of the energy required to drive the processes, and as providing the raw materials on which the processes work to form various products. The chemical and petrochemical industries are responsible for 30% of global industrial energy use, and 16% of direct CO₂ emissions to the environment. More than half of this energy demand is dedicated to feedstock, which cannot be trimmed down through energy efficiency measures. (IEA, 2007) It follows that the responsibility for cutting back on the amount of energy needed for chemical processes rests on improving the efficiency of the processes used. This approach offers a number of benefits, particularly in the context of averting climate change. In other words, a reduction in fossil fuel consumption/utilization, as well as the recycling or sequestration of CO₂, could contribute to a fall in the greenhouse gas emissions, especially carbon dioxide (CO₂), which are regarded as the major contributor to global warming. Any reduction in fossil fuel consumption and improvement in the recycling of CO₂ will contribute to a

drop in carbon emissions. This objective, and a global recognition of the need to reduce emissions and counter the depletion of non-renewable resources, has prompted the international community to endorse schemes such as the Kyoto Protocols to address the greenhouse effect and the consequent threat it is believed to pose to the world's environment in terms of climate change. (EIA, 1999; McMillen *et al.*, 1993)

In order to develop energy-efficient chemical processes that focus on reduced raw material and energy requirements and the alleviation of adverse environmental effects, engineers are directing their design skills towards innovative operational systems that take into account such precepts as: The more reversible a process is, the less energy it will consume. Although a reversible system is not practical; it is purely hypothetical, as it would take an infinite amount of time to bring a reversible process to completion. However, it is essential for the thermodynamic analysis and understanding of processes. More effective systems will not only achieve the aims outlined above, but contribute to the industrial sustainability of the chemical processes. (Moran and Shapiro, 2006; OECD, 1998, 2001; IEA, 2008)

Sustainability, simply put, 'implies meeting present needs without conceding the capability of upcoming generations to meet their own needs'. (WCED, 1987; Song, 2002) In other words, when an engineer designs a system, an important consideration is whether it will be viable in the future. For this reason, there is a need for designers to develop technology and equipment that generates energy in cleaner (more environmentally-friendly) ways.

The production of methanol is yet another means of securing sustainable energy. The greatest challenge to its viability lies in the CO₂ that is produced during the course of the synthesis reaction that forms methanol. However, the Carnol process utilizes CO₂

to produce methanol as a promising liquid alternative to fossil fuel consumption, and it has the advantage of lower emissions. Thus the use of renewable methanol can contribute to a substantial reduction of CO₂ emissions when renewable sources of energy are used as energy input and as such can be considered as a bridge to sustainability in the long term. (Choi *et al.*, 2008; McMillen *et al.*, 1993; Song, 2006; Specht *et al.*, 1998; Steinberg, 1996)

1.2 RESEARCH AIMS AND METHODOLOGY

The subject of the research described in this dissertation is to consider what measures could render the production of methanol more efficient. The main objective of this project was to evaluate a chemical process, in this case the synthesis of methanol from syngas, using a simple graphical technique which could be useful to gain insight into the inner workings of a chemical system. This technique could be an important tool for chemical process designers, wishing to achieve not only optimal efficiency but a reduction in materials, energy consumption and carbon dioxide emissions, in this way fostering environmental and industrial sustainability.

The more efficient a process is, the greater the proportion of the feed material is transformed into desired products using only a minimum amount of energy, which in turn reduces the amount of undesirable by-products (such as carbon dioxide). Many researchers have worked in the area of methanol synthesis. A number of them measured methanol synthesis rates, using only CO and H₂, CO₂ and H₂, or CO, CO₂ and H₂ feeds as the starting mixture, with the aim of gaining insight into what happens during the course of the reaction. However unlike other researchers, this work tends to look at what is the best possible pathway for methanol synthesis in order to minimize emissions (CO₂) and energy or work input given a particular feed.

The approach chosen to fulfil the aims of this research involves the use of performance targets for a chemical process that are based on mass, energy and entropy (the second law of thermodynamics). The project presents a case study where methanol synthesis occurs simultaneously with the WGS reaction, and applies the thermodynamic properties and phase behaviour of the chemical systems to evaluate the process work targets. Previous work by Patel et al (2005) has shown that thermodynamic analysis is a very influential tool for the setting and evaluation of process targets. We use analysis of the mass, energy and Gibbs Free Energy of the process to quantify inefficiencies.

Because material, energy and work balances can be formulated to give greater clarity on the inner workings of the process, it can proffer interesting insight into the design of new processes as well as ideas for enhancing the performance of older ones if properly used. Thus, it can serve as guide during the conceptual design of processes/reactors. (Shinnar, 1988; Smith, 2005) It is important that the new process design is capable of answering questions such as: What is the lowest amount of undesirable by-products a process can produce? and What is the relationship between the change in Gibbs Free Energy across the reaction and the reaction pathways and products? This is equivalent to asking how much of the feedstock can be turned into desirable products by the process, (in other words, whether its objective function is maximising or minimising). It is important to be able to define targets (that is, predict achievable quantities) for chemical processes. For example, assessing whether a process is efficient or not can only be done by comparing the results (for example, the process yields Y tons of CO₂ per ton of product) with the target for that process.

The purpose of this research is to extend the approach described above, and in particular to look at how it can be used to compare the reactions of a combined simultaneous process with regard to their kinetic models. This allows us to synthesize flow-sheets that are reversible and which meet the process targets by implementing mass and energy integration. It also provides guidance on what design decisions would be best suited to developing new processes that are more effective and make lower demands on raw material and energy usage.

Through the unique methods developed at Centre of Material and Process Synthesis (COMPS), these concepts can be used to provide practical insights into processes, establish rigorous performance targets, improve the performance of processes, conserve natural resources and reduce negative effects on the environment. The different methanol synthesis processes are evaluated to ascertain which is most feasible and has the lowest work requirement, and the information gained could lead to the design of an optimal process using the Attainable Region (AR) method developed by Hildebrandt, Glasser and Feinberg (Glasser *et al.*, 1987; Hildebrandt and Glasser, 1990; Hildebrandt *et al.*, 1990; Feinberg and Hildebrandt, 1997; Glasser and Hildebrandt, 1997). The approach also provides useful information for evaluating processes through likely limiting extents with respect to the reaction pathways, and comparison between the research findings and their theoretical targets in order to identify any possible energy savings that can be made.

1.3 SIGNIFICANCE AND IMPACT OF THIS RESEARCH

For the reasons already given, the research described in this dissertation aims to contribute to the current debate on how to improve the efficiency of chemical processes and recycle CO₂ emissions. Ideally, the process described will contribute to:

- the reduction of CO₂ emissions, which degrade the environment and accelerate the threat of climate change;
- the use of smaller amounts of raw materials and energy, to increase process efficiency and lower costs, thus ensuring industrial sustainability;
- the substitution of alternate sources of fuel from biomass, coal, or gases; and
- the adoption of methanol fuel as an efficient source of energy that is renewable, economically competitive and has a low environmental impact.

The importance of this research cannot be over-emphasized. Not only was the work supervised by experienced scientists in the field of process engineering, but it formed part of a much larger programme geared toward sustainability in the chemical industry. The results described in this document will be industrially relevant.

1.4 THESIS OUTLINE

The outline of the entire thesis is as follows.

Chapter One contains a discussion of the background and motivation of the study; the challenges posed by threats to environmental sustainability; the objectives of the research; the research problem; the research methodology used; the contribution to knowledge this work is expected to make; and the potential impact of the research findings.

Chapter Two comprises the literature review, which is presented in three parts. The first gives an overview of process design; and the second focuses mainly on thermodynamic analysis. The third discusses the methanol synthesis process, and covers an overview of the process description; the mechanism of CO and CO₂

synthesis; and the role of water and the WGS reaction in the methanol synthesis process.

Chapter Three explains in detail the methodology/approach used, the theory involved, the use of mass balances and extent calculations to map the extent plot, and its subsequent conversion to a G–H plot. In a bid to achieve the AR for the reactor, we consider the energy and work balances in the GH space, and the effect of operational parameters and the feed composition on the GH plot.

Chapter Four discusses the estimated results of the methanol synthesis process under different process conditions. The analysis is made in terms of the reactor's AR, the likely reaction pathway, and the reactions taking place within the reactor. This is succeeded by a second analysis of current industrial practice for methanol synthesis.

Chapter Five gives a summary of the research undertaken, and makes recommendations for further development of the process used in the study, and its applicability to other chemical industrial processes.

CHAPTER 2

LITERATURE REVIEW

2.1 PROCESS DESIGN

In the chemical industry advances are made through innovative developments, like the introduction of new processes, and via the upgrading of existing processes by generating engineering alternatives and choosing the most favourable option. (Cisternas, 1999) As changes occur in the availability and cost of raw materials and in product demand, engineers continually search for alternative technologies that offer better optimizing processes and satisfy the demands of the ever more stringent environmental regulations. (Sachmidt, 1998)

Chemical engineers, who are responsible for the economical operation of chemical plants, have dedicated substantial time to the study and assessment of engineering systems that affect the economics of processes. (Hlavacek, 1978; McMillen *et al.*, 1993) Hence, over the years process design, which creates structures for systems to convert raw materials into useful products through synthesis and analysis, has become an increasingly important area of chemical engineering. (Cisternas, 1999) With the aid of process simulation software (such as Aspen Plus), operational models and simulation algorithms, engineers are able to calculate and simulate results that generate accurate data concerning a particular process plant. (Costal *et al.*, 2005)

Synthesis and analysis are the two key steps in the designing of a chemical process. Whereas synthesis comprises establishing and clarifying the structure of the process from the inputs and outputs, analysis involves ascertaining the outputs resulting from

the process structure and the inputs, and is typically related to modelling or simulating a particular process. (Patel *et al.*, 2007) Simply put, analysis entails studying the process alternatives to assess their behavior, and then selecting the process that serves the design objective best. Hence, synthesis and analysis can be seen as complementary activities in the design of processes.

However, a significant component of synthesizing processes from the available equipment is the ‘high dimensionality’ of achievable designs. (Hlavacek, 1978) As it is impracticable to consider all the physical characteristics of any engineering problem, the designer of a process has to simplify. This means that the size of the problem is broken down into manageable parts or sub-systems that can be dealt with more easily. (Peng *et al.*, 1997)

Process synthesis is the most innovative stage of process design because during the hypothetical phase it entails developing possible process solutions or ways of modifying existing ones. The decisions made by the process engineer can substantially affect the performance and operating cost of a process, the capital needed to launch it commercially, the quality of the products, its operational safety, and its environmental impact. (Hlavacek, 1978; Cisternas, 1999; Patel *et al.*, 2007)

In recent years, reaction path synthesis has become an essential tool of process synthesis, because of its effectiveness in recognizing the most desirable reaction route when several are being assessed. (Cisternas, 1999) In 1968, Rudd was the first to propose a method for the synthesis of processes. Since then several works have been published on the subject, among them research on the systematic development of new reaction paths via different techniques by Rotstein *et al.*, (1982), Stephanopoulos *et al.*, (1982), and Stephanopoulos and Townsend (1986). The synthesis approach they

presented, which falls within the scope of orderly evaluation, was based on using algebraic and thermodynamic tests to screen out alternative reaction schemes that were unacceptable on the grounds of low equilibrium conversion. Stephanopoulos and associates posited the thermodynamic properties of reactions as the basis of path synthesis. (Brown *et al.*, 1991; Peng *et al.*, 1997) In addition, Rotstein *et al.* (1982) made a technical advance in identifying some ‘topological or algebraic properties’ that chemical reactions share within the Gibbs free energy change and temperature ($\Delta G, T$) sphere of influence, and used them to assess the thermodynamic achievability of a number of reactions and to identify different reaction paths concurrently. Fornari *et al.*, (1989) extended this tool to systems having two degrees of freedom. (Peng *et al.*, 1997)

While the overall objective of process designers is to optimize the effectiveness of new or existing processes, they tend to encounter a number of obstacles, among them economic constraints, design complexity, safety and environmental considerations, and inadequacy in the efficiency of equipment. They also face changing demands, as those working in the field of process synthesis are expected to find new chemical reaction pathways/routes that can better serve the demands created by alterations in economic and environmental conditions, and the need both to conserve the rapidly-depleting supply of raw materials and to save energy.

2.2 THERMODYNAMIC ANALYSIS

The performance of chemical reactors is of paramount interest to chemical engineers, because it is the heart of any chemical process through which raw materials are converted into the desired products. The objective function of chemical engineers is to analyze systems in which chemical reactions are taking place (chemical reactors) and

apply the outcome of the analysis to the development of cost- and energy-efficient processes. This is achieved by studying the behaviour of the chemical species reacting in the system so as to evaluate operating parameters, such as temperature and pressure, which affect the overall process. (Hill, 1977; Patel *et al.*, 2005)

Given a reactive system with known reactants and products, the number of possible reactions that could be employed to form desired products might be infinite, but only a few of them are realizable physically. (Lien and Perris, 1996) Thermodynamics is essential to the determination of reaction yield, since chemical reactions occur as a result of changes in the enthalpy and Gibbs free energy of the system, brought about by the formation, destruction, or rearrangement of chemical bonds. Thus thermodynamic analysis can be added to the mechanism of reaction and the economic potential of the product as criteria to evaluate an overall reaction. This enables process engineers to categorize them into feasible (that is, achievable) and infeasible (impracticable) overall reactions. The latter can be achievable only through a number of feasible division reactions. (Peng *et al.*, 1997) Hence, what makes thermodynamics an essential tool for the determination of reaction yield is that it sets boundaries on a reaction's achievable yield. A reaction is said to be *thermodynamically feasible* if a process yield, as specified by thermodynamics, ensures economic feasibility. (Holiastos and Manousiouthakis, 1998)

The advantage of using thermodynamic relations to analyze chemical reactions is that they do not require precise kinetic data. The relative magnitudes of the reaction rates and the range of temperatures over which these relations apply can be estimated, (Shinnar and Feng, 1985) which makes thermodynamic analysis a powerful tool for process improvements and development, both for chemists as well as process and

chemical reactor designers. (Shinnar, 1988) However, its greatest flaw lies in the fact that though it is exceptionally general in its applicability for solving many significant problems, it is unable to answer explicitly questions arising from the problems. For example it can tell that a process will occur, but not how fast it will occur and as such it cannot be used alone, in the determination of transport process or for the design of a reactor/process. Furthermore, thermodynamics does not provide the deep insight into chemical and physical phenomena that is afforded by micro-scopic models and theories. (Annamalai and Puri, 2002)

Previous research has shown that thermodynamic analysis can be of particular service in setting and evaluating process targets, because it provides extremely accurate information on a reaction's path synthesis and attainable yield, which can be applied to identifying the optimal process. This is generally done via the mass and energy balances and Gibbs Free Energy analysis of the process, which quantify process inefficiencies. Various scientific studies have shown that addressing these shortcomings is essential to process optimization (May and Rudd, 1976; Glasser and Hildebrandt, 1997; Patel *et al.*, 2007).

The methodical examination of chemical reactions started with Damkohler's work on reactions and mass transfer in Germany in the 1930s and 1940s. Van Heerden in Holland studied temperature variations in reactors, while Danckwerts and Denbigh in England focused on mixing, flow patterns and multiple steady states. (Sachmidt, 1998) Denbigh (1956) first drew attention to the use of the second law of thermodynamics as important to chemical reactor and process design. Since then, many other researchers have published reports on the same subject. (Aris and Mah, 1963; Hendry *et al.*, 1973; Rieker, 1974; Umeda *et al.*, 1979; Berg, 1980; Nishida *et*

al., 1981; Shinnar *et al.*, 1981; Rotstein *et al.*, 1982; Shinnar *et al.*, 1982; Shinnar and Feng, 1985; Stephanopoulos and Townsend, 1986; Shinnar, 1998). In 1976 May and Rudd proposed a method to synthesize thermodynamically feasible Solvay clusters using the principle of mass conservation, and the conditions imposed on the free energy change of reaction. This led to the testing of the thermodynamic feasibility of a reaction on a single free energy reaction diagram, as long as the reaction can form a nested polygon that exhibits the appropriate model of free energy differences intersections. (May and Rudd, 1976)

Horn (1965) was the first to introduce the ‘attainable region’ (AR) approach to analyzing processes, which was taken further by Glasser *et al.*, (1987) who developed a geometric technique to establish the AR for chemical systems. This is used to determine the ‘limits on the distribution of products which one can obtain by *any* combination of reaction and mixing’. Over the years that followed, Glasser and Hildebrandt refined this technique to describe how the AR for two quantities that follow linear mixing laws can be generated. (May and Rudd, 1976; Glasser *et al.*, 1987; Feinberg and Hildebrandt, 1997; Glasser and Hildebrandt, 1997)

As soon as the stoichiometric coefficients of all the chemical species in an overall reaction are established, it is easy to determine the Gibbs free energy change and conversion ratio of raw materials to products at a specified temperature by means of mass balance calculations. (Peng *et al.*, 1997) For an overall reaction to be thermodynamically feasible, the Gibbs free change must be less than zero (that is, negative), while that with the value of ΔG that is always greater than zero in the specified temperature range is regarded as infeasible. (Chen *et al.*, 2009; Li *et al.*, 2000; Hardiman, 2001) Even though negative values of ΔG point toward favourable

reactions, very large negative values might indicate very low stability in the basic reactants/products and as such are not preferred. (Cisternas, 1998) However, an environmentally suitable and thermodynamically viable overall reaction with maximal economic potential can be identified by solving the optimization problem. (Crabtree and El-Hawalgi, 1994; Peng *et al.*, 1997)

The enthalpy change in reaction (ΔH) provides information that is necessary for any engineering analysis of the system in terms of the first law of thermodynamics, and can control any 'reaction selection process'. It decides whether heat is absorbed or liberated for any given extent of reaction (that is, its exothermicity or endothermicity respectively). (Levenspiel, 1999) It can also be used to determine the consequences of a change in temperature on the equilibrium constant/equilibrium conversion and thus on the reaction yield. A reduction in temperature results in raised equilibrium conversion in exothermic reactions, as do an increase in pressure in gas reactions, which increases conversion when the number of moles decrease with reaction. (Cisternas, 1999; Levenspiel, 1999) Other advantages Gibbs free energy change can offer are determining how changes in the process variables can influence the yield of the reaction, quantifying the thermodynamic inefficiencies in chemical processes, and determining whether or not chemical equilibrium exists in the particular system being studied (Equilibrium in any system is reached when $\Delta G = 0$ for a particular reaction). (Hardiman, 2001)

Since enthalpy (H) and Gibbs free energy (G) are state functions, changes in these quantities will not depend on the number of stages by means of which the reaction takes place. The standard enthalpy change of formation of a compound from its elements and the standard free energy of formation (Gibbs free energy), are denoted

by the symbols ΔH_f^0 and ΔG_f^0 respectively. (Hill, 1977; Hlavacek, 1978; Fornari *et al.*, 1989; Holiastos and Manousiouthakis, 1998).

Nevertheless, given the relation between equilibrium constant (K), ΔG^0 and ΔH^0 in addition to the dependence of each on temperature (T) and pressure (P), a methodology based on mass balance calculations can be developed to analyze and understand the thermodynamic feasibility or lack of it for any reaction under consideration. The aim is to find a thermodynamic region in which the reaction becomes feasible under different process conditions based on Gibbs free energy, since the latter is a function of process conditions. (Holiastos and Manousiouthakis, 1998)

2.3 METHANOL SYNTHESIS

Methanol (CH_3OH), which is also known as methyl or ‘wood’ alcohol, can be made from an array of carbonaceous materials. When it first became an item of commercial value in the later part of the nineteenth century it was prepared from biomass. In contrast, almost all the methanol produced today is made from natural gas, but it can also be synthesized from an array of renewable resources such as biomass and carbon dioxide-rich waste. This makes it possible for the production of methanol to act as a bridge between traditional and renewable technology. Currently, most of the methanol manufactured is synthesized in large-scale plants from syngas (H_2 , CO , and CO_2). [Biegler *et al.*, 2002] The process involves the production of syngas by the steam reforming or partial oxidation (Lee and LeBlanc, 1993) of methane, its subsequent conversion to methanol, and further refining of the crude methanol to the desired specification. (McMillen *et al.*, 1993; Grue and Bendtsen, 2003)

Methanol can also be manufactured from hydrogen and carbon dioxide, by first converting the most of the CO₂ to CO using RWGS, which makes it suitable for the conventional methanol synthesis process. However, this requires adjustment of the CO₂ content and stoichiometric number to 2.05 to maximize the methanol yield. (McMillen *et al.*, 1993)

The volume of methanol manufactured industrially is exceptionally large, because it is one of the bulk chemicals most in demand due to its wide range of application. Methanol may be converted to gasoline by the Mobil process (NZIC, 1998) and can also be converted to electrical power (AMI reported in 1998 that its efficiency was above 34%, which is higher than that of the existing gasoline engines). Methanol is also frequently used as an intermediate or raw material in the synthesis of other various chemicals, such as formaldehyde, dimethyl terephthalate, methylamines and methyl halides, methyl methacrylate, acetic acid, gasoline. (NZIC, 1998) It can function as a solvent for domestic and industrial purposes, because it combines readily with an array of organic liquids as well as with water. (Law *et al.*, 2008), and serve as an automotive fuel. From the ecologically-aware and technical points of view, methanol is the preferred replacement for the petroleum currently used for internal combustion engines and in fuel cells.

Engineers believe that methanol can be the vehicle for a transition from resource-depleting energy to renewable sources of power that would drastically reduce the cost and the environmental burden created at present by the need for transportation fuel and electric power generation. It could also herald a shift to more efficient technologies. (AMI, 1998, 2000; Specht *et al.*, 1998) Current estimates are that

methanol could supply up to half of the world's energy demands by the end of the twenty-first century. (OTA, 1993; McMillen *et al.*, 1993; EIA, 1997)

The synthesis of methanol for commercial use began in the 1920s, when BASF chemists (using BASF equipment for ammonia synthesis) in Germany first synthesized it in 1923 as part of the German research drive for high-pressure operations using hydrogen and synthesis gas. The drive led to a number of influential technological advances, among them the Haber–Bosch ammonia synthesis process, the hydro-desulphurization processes, (Bergius, 1920) and the Fischer–Tropsch (Hans Fischer and Franz Tropsch, 1923) and methanol synthesis processes. (Tijm *et al.*, 2001) The early process developed by BASF to produce methanol operated at high temperatures (roughly 320–450°C) and pressures (up to 250–350 bars), using a zinc-oxide/chromium-based catalyst (ZnO/Cr₂O₃). (Satterfield, 1991; Tijm *et al.*, 2001) Known as a ‘high pressure’ process, it remained the dominant technology for over 45 years. However, in the mid-1960s, Imperial Chemical Industries (ICI) in the United Kingdom made a major breakthrough using a copper-based catalyst. They developed catalysts that could operate at relatively low pressures (35–55 bars/35-80), and temperatures (200–300°C). (Tijm *et al.*, 2001) These ‘low pressure’ processes revolutionized the industrial production of methanol from synthesis gas. (Kung, 1980; Klier, 1982)

Since its commercialization in 1923, the technology of methanol synthesis has undergone several changes, prompted by the need to reduce the industrial investment costs that determine the production cost. Today, methanol is commercially produced in industries from CO/CO₂/H₂ using the ICI or Lurgi processes, which operate at lower temperatures and pressures (250°C, 50 bars), using a copper-zinc-based oxide

catalyst CuO/ZnO/Al₂O₃ catalyst. (Nakamura, 1996) These amendments resulted in a significant decrease of the compression and heat exchange duty in the recycle loop, lower capital and energy costs, enhanced operational reliability and allowed greater flexibility to the designers responsible for determining the size of the production plant. The lower reaction temperature also improved the selectivity of the product by suppressing the co-production of light hydrocarbons. (Satterfield, 1991; McMillen, 1993; Kirk, 1998; Larkin, 1999; Hardiman, 2001; Lange, 2001; Tijm *et al.*, 2001; Reubroycharoen *et al.*, 2003).

The efficacy of methanol synthesis is limited by thermodynamics because it is a strongly exothermic reaction that occurs over a catalyst bed and proceeds under volume contraction (that is, it results in volume reduction). This means that better conversion is achieved at low temperatures and high pressures. (Herman *et al.*, 1981; Graaf *et al.*, 1986; McMillen, 1993; Hardiman, 2001; Lange, 2001; Tijm *et al.*, 2001; Banister and Rumbold, 2005) However, although the equilibrium conditions favour low temperatures and high pressures, methanol reactors are operated at temperatures in the range of 200–300°C to guarantee catalyst activity and effective utilization of the heat of reaction. This results in low conversion, usually less than 20%, per pass, (Marchionna *et al.*, 1997 ; Reubroycharoen *et al.*, 2003) owing to the thermodynamic equilibrium limitations of the process. Because the reactor converts a limited quantity of syngas into methanol, a huge amount of unreacted gas needs to be recycled, and a flush with purge gas is required to remove impurities. (Herman *et al.*, 1981; Graaf *et al.*, 1986; Joo *et al.*, 1999; Enick *et al.*, 1999; Grue and Bendtsen, 2003)

It follows that the use of a low-temperature and low-pressure process for methanol synthesis will not only use far less energy than the high-pressure equivalent, but will

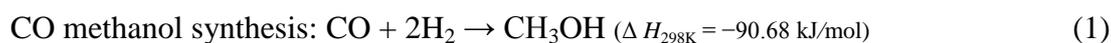
greatly reduce the manufacturing cost by taking advantage of the inherent thermodynamic benefit gained at low temperature. (Tijm *et al.*, 2001; Zeng *et al.*, 2002; Reubroycharoen *et al.*, 2003) However, the reactions involved in the commercial synthesis of methanol are exothermic, and as a result the process requires substantial cooling duty. On the other hand, Le Chatelier's principle or a more explicit equilibrium calculation both show that the RWGS reaction is endothermic, with the WGS reaction proceeding further when the temperatures are relatively low. Hence, there is a predisposition towards the conversion of carbon dioxide to carbon monoxide at higher temperatures, whilst the conversion of steam and CO to CO₂ and hydrogen is favoured by thermodynamic equilibrium at low temperatures. (Benson, 1981; Skrzypek *et al.*, 1990) The equilibrium-limited nature and exothermicity of the methanol synthesis reaction suggest the possibility of driving up productivity and cutting down the size of reactors through clever thermal management. (Banister and Rumbold, 2005) This would also result in vastly reduced costs, because at present most of the investment cost of methanol synthesis plants arises from the recycling of unconverted gas, the large energy demand and the cooling required. (Klier *et al.*, 1982; Joo *et al.*, 1999; Lange, 2001; Tijm *et al.*, 2001; Reubroycharoen *et al.*, 2003; Grue and Bendtsen, 2003; Banister and Rumbold, 2005)

The major improvements in the methanol synthesis process over the decades have concentrated mainly in the area of catalyst formulation to increase productivity and selectivity as well as the design of more efficient reactors to minimize both energy use and adverse environmental effects. (Hardiman, 2001)

2.3.1 Chemistry of Reactions/Process Description

In their published work, Parameswaram (1987) and Lee *et al.* (1988, 1989) have provided authoritative descriptions of the chemistry of the conversion of syngas to methanol based on thermodynamic equilibrium and material balance calculations. They expressed the opinion that the chemistry must be coherent with the direction of the reversible reactions that are influenced by changes in Gibbs free energy and material balance calculations.

In general, the synthesis of methanol from synthesis gas (CO/CO₂/H₂) for commercial purposes occurs over Cu/ZnO catalysts, although CO₂ injection is sometimes considered as an alternative in some schemes. (Chinchen *et al.*, 1987; Liu *et al.*, 1984/85; Lee *et al.* 1993; Muhler *et al.*, 1994; Tijm *et al.*, 2001) It is not only strongly influenced by thermodynamic factors but involves the hydrogenation of carbon oxides (both CO and CO₂) with hydrogen. This is in agreement with the findings of Graaf *et al.*, (1988) as well as Lee *et al.*, (2008). Therefore, the formation of methanol from syngas can be presumed to consist of the following two major reactions:



In addition, the WGS/RWGS reactions occur simultaneously over the copper catalyst in the methanol synthesis reaction because of the hydrogenation of CO₂. (Lange, 2001; Tijm *et al.*, 2001)



The WGS reaction is considered a very rapid reaction at the initial stage of synthesis. it is fairly exothermic to the right, and consequently the gas will become CO₂-rich. CO₂ exhibits the lowest conversion rate. (Choi and Stenger, 2002; Reubroycharoen *et al.*, 2003)

Both the methanol synthesis (Equations 1 and 2), and the WGS (Equation 3) reactions take place simultaneously. However, to simplify the thermodynamics analysis in this dissertation, we take only the independent reactions (1 and 3) into account, since Equation (2) is merely a summation of Equations (1) and (3):



In the presence of CO₂ and/or water (which is usually the case), the synthesis is believed to occur mainly through reaction (2), followed by the WGS reaction (3) to regenerate the CO₂, (Liu *et al.*, 1984/85; Chinchén *et al.*, 1987; Lee *et al.*, 1993; Muhler *et al.*, 1994) which suggests that CO₂ and not CO is the main source of carbon for the synthesis. (Yoshihara *et al.*, 1995) The results of transient experiments with Cu/ZnO/Al₂O₃ catalysts carried out by Chinchén *et al.* (1987) are in agreement with this assumption. Therefore, the WGS reaction can be said to play a significant role in methanol synthesis by increasing the consumption of CO.

However, over the years there has been great controversy among researchers in the field over both the role of CO₂ in the reaction mechanism and the nature of the active site on the surfaces of the catalysts used in the synthesis, since their contribution is not properly reflected in the reaction models. (Lee *et al.*, 1989; Yoshihara *et al.*, 1995;

Nakamura *et al.*, 1998; Lange, 2001; Reubroycharoen *et al.*, 2003; Lee *et al.*, 2008; and others)

Although methanol is the only alcohol that lends itself to very selective synthesis from CO and H₂, (Ebbeson *et al.*, 2000), the selectivity for methanol is so low that sufficient water builds up to cause thermodynamic equilibrium limitations to the methanol synthesis reaction. (Lee *et al.*, 1989) All three of the reactions involved in the methanol synthesis process are limited by chemical equilibrium. (Law *et al.*, 2008). Although most methanol catalysts convert CO rather than CO₂, the rate of conversion from CO/H₂ synthesis gas has been shown to increase considerably with the addition of either CO₂ or H₂O or both. (Herman *et al.*, 1979) An area of particular interest is the conflicting effects on the methanol formation rate of the ratio of CO₂/CO in the feed. (Lee *et al.*, 1993)

Reports from other researchers have shown that the rate of methanol formation is relatively low if there is insufficient CO or CO₂ in the syngas feed (in the case of CO₂ this would usually be between 2.5–3.5%). Dynamic tests conducted by Klier *et al.* (1982) established that for methanol synthesis from CO/CO₂/H₂ feed, an optimal concentration of less than 10% CO₂ is essential to facilitate CO hydrogenation or conversion. (Lee *et al.*, 1989; McMillen, 1993; Wang, 2006) For this reason, carbon dioxide, CO₂ is seen as a promoter of the synthesis at low concentrations, and a retardant at high concentrations. (Klier *et al.*, 1982) Also, Chanchlani *et al.* (1992) observed that below 250°C, methanol synthesis rates demonstrated a slow, almost even rise with increasing CO₂ concentration, while at higher temperatures the rate of synthesis accelerated. This was believed to be a result of the change in the significance of CO and CO₂ as the main source of methanol in the synthesis, with

CO₂ as the dominant source at the above mention condition. Denny and Whan (1978) reported an increase in methanol yield at 250°C and a feed of CO₂/CO/H₂ in the ratio 6:24:70, and concluded that the increase in methanol yield was not attributable to CO₂ hydrogenation. (Klier *et al.*, 1982) However, Kung *et al.* (1984) postulated that the positive influence of CO₂ recorded in their work might indicate that the hydrogenation of CO₂ occurs faster than that of CO, or that the hydrogenation of CO is enhanced by co-adsorption of CO₂.

2.3.2 Mechanism of CO and CO₂ synthesis

Though the mechanism for a given reaction can be described only after laboratory investigation (Li *et al.*, 2000), there has been little agreement on fundamental aspects of the reactions involved in the methanol synthesis and the WGS reactions. Researchers all over the world have conducted series of experiments to ascertain the reaction pathway for methanol synthesis, and have come up with different results and conclusions. (Rozovskii, 1980; Chinchén *et al.*, 1987, among many others) These debatable topics include:

- whether the main source of carbon for methanol synthesis from CO-CO₂-H₂ mixtures is CO or CO₂;
- whether the catalyst surface is where the critical stage of synthesis occurs;
- which of the surface intermediates are involved in both reactions; and
- whether there is a unique synergy between copper and zinc oxide that gives high activity in both reactions. (Chinchén *et al.*, 1987)

While some scientists believe that the synthesis of CO is the pathway, others hold the opposite opinion (that CO₂ synthesis provides the pathway). Boomer and Morris

(1932) were the first to propose a mechanism that identified CO as the main source of carbon in methanol synthesis, and that the function of carbon dioxide was merely to control the activity of the copper in the catalyst, and is hydrogenated to methanol only after it has been transformed to CO by the RWGS reaction. (Herman *et al.*, 1979; Klier *et al.*, 1982; Lee *et al.*, 1993) This is followed by the hydrogenation of carbon monoxide. (Peng *et al.*, 1997) Extensive research by Russian scientists Kagan *et al.*, (1975), Rozovskii *et al.* (1977), Rozovskii (1980) and Rozovskii (1989) resulted in the conclusion that methanol was made mainly from CO₂.

In 1987 Chinchin *et al.* attempted to resolve these uncertainties through extensive experimentation using isotope-labelling experiments under the practical industrial reaction conditions 50 bar and 250°C. (Klier *et al.*, 1982) They reported that carbon in methanol synthesis with a CO/CO₂/H₂ feed, dioxide is the main source of carbon; that hydrogenolysis of adsorbed formate is most likely to be the rate-limiting step; and that the conversion of CO to methanol and the WGS takes place to a lesser degree than the synthesis itself. Even more, they found that different surface intermediates are involved in the methanol synthesis and WGS reactions. Bowker *et al.* (1981) also declared that CO₂ was the predominant reactant in the methanol synthesis mechanism. They also found that at higher CO₂/CO ratios, methanol was formed almost entirely from CO₂. Lee *et al.* (1993) reported that the rate of methanol synthesis tended in most cases to be more rapid with CO₂/H₂ than with CO/H₂, especially at low temperatures. This led to the conclusion that the main source of methanol with CO/CO₂/H₂ feed is CO₂. (Chinchin *et al.*, 1987; Lee *et al.*, 1993) These results agreed entirely with those of Rozovskii (1980) and Rozovskii (1989), obtained under similar operating conditions. (Lee *et al.*, 1993)

Notwithstanding this body of evidence, the subject remains contentious because the three main reactions involved in the methanol synthesis process seem to compete with one another in the course of the hydrogenation process, via various intermediates. (Chanchlani *et al.*, 1992; Joo *et al.*, 1999). Conversely, some of these inconsistencies between various sets of experimental results can be attributed to the choice of, and varieties of, the experimental conditions used. For example, how the catalyst was prepared might affect the results because the nature of the catalyst used (whether bulk or surface) is dictated by the reaction conditions. Another source of disagreement would be differences in individual interpretations of the experimental findings. (Spencer, 1981) It is pertinent to note here that these studies were carried out under different process conditions and using dissimilar catalytic media and parameters, which might account for variations in the CO and CO₂ specificity/selectivity affinity of the catalyst mediums.

Accordingly, the thermodynamic analysis provided in this dissertation will throw more light on the process pathway and reaction sequence of the methanol synthesis reaction as well as that of other industrial-chemical processes.

2.3.3 The Role of Water and the Water Gas shift Reaction

Water plays a very important role in modifying the reaction environment, and consequently affects the rate of methanol synthesis [Parameswaran, 1987] through the WGS and RWGS reactions, which depend on the presence of water in the system. (Lee *et al.*, 1993) An optimal water concentration in the reactor results in the highest achievable methanol synthesis rates. (Klier, 1982) However, an accumulation of water in the catalytic system may cause damage through leaching the catalyst components and promoting crystallite growth. The ideal concentration of water within the reactor

is determined by a balance between the rates of the CO₂ hydrogenation and the WGS reactions. This optimum is largely dependent on the composition of the syngas in the reactor, and, to a lesser extent, on the reaction temperature. (Parameswaran, 1989; McMillen, 1993)

Usually there is a difference between the ratios of carbon oxide to hydrogen in the syngas that is produced by steam reforming and that required for methanol synthesis. The need to adjust this ratio emphasises the importance of the WGS and RWGS reactions (Oudar, 1980) in methanol synthesis. The significance of these reactions in converting carbon monoxide to carbon dioxide was first acknowledged in the latter part of the twentieth century (Wainwright and Trimm, 1995). Ideally, the stoichiometry number (which is the ratio H₂ – CO₂:CO – CO₂ and not the molar ratio H₂:CO) of the synthesis gas required for methanol synthesis should be 2.0. However, a small increment in hydrogen that increases the stoichiometry number to 2.05 has been found to improve catalytic performance, leading to more efficient production of methanol. Generally, the syngas produced from fossil fuels using different gasifiers covers an array of feed gas compositions (CO-free, CO-rich or hydrogen-rich syngas), and consequently the stoichiometric value has to be adjusted. The WGS reaction is an efficient process operation that can be used to achieve the correct syngas feed balance for the efficient production of methanol. (Liebner, 1988; Amor, 1988; Unnasch, 1991; Lee and LeBlanc, 1993; McMillen, 1993; Geissler *et al.*, 2001; Lange, 2001).

CHAPTER 3

METHODOLOGY

Fundamental to the determination of reaction yield are thermodynamics. They provide an appreciative knowledge of the degree and nature of energy transformations, as well as relations between properties such as energy, in terms of temperature and pressure. Hence, thermodynamic analysis if properly utilized can predicts what happen in a chemical reactor, since the properties of substances can be determined using relevant state equations. Taking into account their relationship and dependence on temperature (T) and pressure (P), one can develop a methodology to analyze and consequently understand the performance of chemical systems. The objective was to find a region within which any reaction becomes thermodynamically feasible, even under different process conditions, since free energy is a function of these conditions. (Annamalai, and Puri, 2002; Holiastos and Manousiouthakis, 1998; Sachmidt, 1998) We therefore carried out an analysis of the thermodynamics of the process by calculating the changes in enthalpy, ΔH^0 and ΔG^0 of the reactions, and the mass balances involved in the synthesis of methanol. It is assumed that the synthesis is completely in a gas phase, with pure feed and product streams as shown in Figure 1. The system was considered to be in an ideal gas state, and hence the ideal gas property values were obtained from aspen property for this analysis.

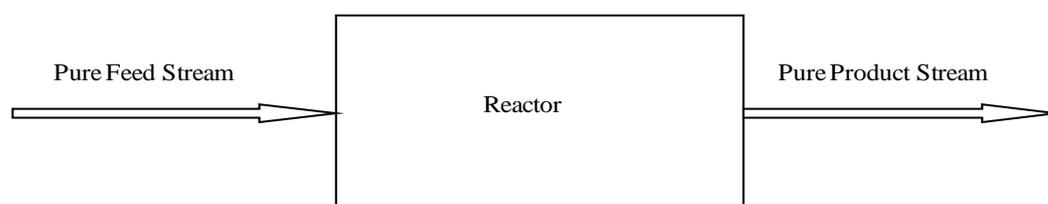


Figure 1: A schematic representation of a process showing feed and process streams.

Although there is a great gap between what the catalyst systems currently used in commercial methanol synthesis allow and what thermodynamic analysis requires, (Peng *et al.*, 1997) we offer an approach to improving the performance of this chemical process that aims to bridge that gap.

Chemical reactors such as gasifiers, reformers, and those used for methanol and Fischer–Tropsch (FT) synthesis are complex pieces of equipment in which many kinds of reaction may take place. The performance of reactors is limited by the mass balance (basically, the composition of each species in the reactor), which must remain positive. Another limiting factor is the energy balance, which is generally related to the value of ΔH , and determines whether heat needs to be added or removed. Entropy/work balance, which is linked to the ΔG of the process, corresponds with the amount of work that needs to be added to ($\Delta G \geq 0$) or removed from ($\Delta G \leq 0$) the reactor. Generally, the requirement is that the ΔG of all the reactions (excluding the mixing) should be less than, or equal to, zero ($\Delta G \leq 0$). The only mechanism we have for adding work in most reactors is via mixing. Although the increment of work is usually very small, the ΔG of mixing, which might cause the limiting line to become convex or concave was excluded in this study.

The issue of selectivity becomes important when more than one reaction occurs in the reactor, because this raises the questions, Which of the reactions is dominant? and How do temperature and pressure affect this favoured status? These need to be investigated and answered before the conceptual design of a chemical process can be put in hand.

This chapter examines the interaction between competing reactions in a reactor in terms of mass balances and thermodynamic analysis. Since there are often many contending reactions, we offer a simple way to assess which of the many possible reactions are likely to dominate by applying a simple graphical technique that uses thermodynamics to locate ARs. In this case, ‘AR’ is a thermodynamically achievable region in the state space within which the reactor can function without violating thermodynamic boundaries. By looking at the reactions taking place in the reactor and determining how G is minimized, we are able to ascertain the reaction pathways (which provide one of the ways in which we explain process chemistry). More so at equilibrium, the Gibbs free energy is expected to achieve a minimum when the state is defined by the various constraints such as temperature and pressure (Chen *et al.*, 2009).

We also investigated the effect on the methanol synthesis process of variations in the operational parameters, such as temperature, pressure, and different proportions of CO , CO_2 , H_2 and H_2O in the feeds, by analyzing the data we obtained. We calculated thermodynamic mass, energy, and entropy balances for the system, and paid particular attention to the effects of the different constraints on the process. (Tsirlin *et al.*, 2006) This enabled us to compare the theoretical targets, reaction pathways and likely limiting extents with those achievable industrially.

3.1 EFFECT OF OPERATING PRESSURE AND TEMPERATURE CHANGES ON A REACTION

Part of our investigation concerned the effect on a reaction of the operating pressure and temperature used for the process. We used Le Chatelier's principle, ‘if any one condition affecting any equilibrium is changed, the equilibrium shifts so as to

minimize the change', to predict how an alteration in the pressure, volume, concentration or temperature would affect the chemical equilibrium.

According to Le Chatelier's principle, the addition of heat to a reacting system increases its temperature, and the stress of the added heat can be relieved only if the equilibrium conditions shift in a direction that absorbs the heat.

However, since the system was considered to be in an ideal gas state, then it should obey the ideal gas equation of state, given as

$$PV = nRT \quad 4$$

The defining equation for enthalpy, applied to an ideal gas model, leads to the conclusion that H, as well as U (the internal energy), is a function of temperature only. From the defining equation,

$$H = U + PV \quad 5$$

The derivation of H with respect to pressure at constant temperature can be formed as

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left[\frac{\partial(PV)}{\partial P}\right]_T \quad 5.1$$

But for an ideal gas, $(\partial U/\partial P)_T = 0$, and from $PV = nRT$, $[\partial(PV)/\partial P]_T = 0$, Therefore this leads to $(\partial H/\partial P)_T = 0$. Similarly, results can be found for $(\partial H/\partial V)_P = 0$.

Assuming that the system is closed and mechanically reversible, then the molar or specific enthalpy can be expressed as a function of temperature and pressure. Hence,

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad 6$$

The constant pressure heat capacity of a substance is defined as; $C_p = (\partial H/\partial T)_P = dH_{(T)}/dT$ hence

$$dH = C_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad 6.1$$

For an ideal gas at constant pressure, $(\partial H/\partial P)_T dP = 0$, therefore we can write the enthalpy of an ideal gas as,

$$dH = C_p dT \quad 6.2$$

On integrating,

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad 6.3$$

Thus the ideal gas heat capacity at constant pressure is a function of temperature only.

C_p value can be calculated from the relation,

$$C_p/R = A + BT + CT^2 + DT^{-2} \quad 7$$

where A, B, C, and D are parameter values given in tables for common compounds.

Substituting C_p as a function of temperature for temperature limits of T_0 and T ;

$$\int_{T_0}^T \frac{C_p}{R} dT = AT_0(\tau - 1) + \frac{B}{2}T_0^2(\tau^2 - 1) + \frac{C}{3}T_0^3(\tau^3 - 1) + \frac{D}{T_0} \left(\frac{\tau-1}{\tau}\right) \quad 8$$

where $\tau = T/T_0$. However, because $\tau - 1 = (T - T_0)/T_0$, the equation may be rewritten as

$$\int_{T_0}^T \frac{C_P}{R} dT = \left[A + \frac{B}{2} T_0 (\tau + 1) + \frac{C}{3} T_0^2 (\tau^2 + \tau + 1) + \frac{D}{\tau T_0^2} \right] (T - T_0) \quad 8.1$$

where the quantity in square bracket is $(C_P)_H/R$, and is defined as the mean capacity.

$$\frac{(C_P)_H}{R} = A + \frac{B}{2} T_0 (\tau + 1) + \frac{C}{3} T_0^2 (\tau^2 + \tau + 1) + \frac{D}{\tau T_0^2} \quad 9$$

Or simply,

$$\Delta H = (C_P)_H (T - T_0) \quad 10$$

Thus taking into account the dependence of the heat capacity themselves on temperature, the heat of reaction, H, over a wide range of temperature can be calculated.

$$\Delta H = H_{(\text{product})} - H_{(\text{reactant})} \quad 11$$

differentiating with respect to temperature at constant pressure,

$$\left(\frac{\partial(\Delta H)}{\partial T} \right)_P = \left(\frac{\partial H_{\text{product}}}{\partial T} \right)_P - \left(\frac{\partial H_{\text{reactant}}}{\partial T} \right)_P \quad 11.1$$

But since $(\partial H / \partial T)_P = C_P$, therefore

$$\left(\frac{\partial(\Delta H)}{\partial T} \right)_P = C_{P(\text{product})} - C_{P(\text{reactant})} = \Delta C_P \quad 11.2$$

Given a general chemical equation,



Recalling equation (6.2), the standard heat of reaction can be expressed mathematically as

$$dH_i^0 = C_{P_i}^0 dT \quad 13$$

where i is the reactant or product, ν_i is the stoichiometric coefficient and A, B, C, D is the chemical formula of the species. We have that

$$d \sum_i (\nu_i H_i^0) = \sum_i \nu_i C_{P_i}^0 dT \quad 13.1$$

The term $\sum_i (\nu_i H_i^0)$ is the standard heat of reaction, defined by equation 9 as ΔH^0 . The standard heat capacity change of reaction is defined similarly as

$$\Delta C_P^0 = \sum_i \nu_i C_{P_i}^0 \quad 13.2$$

As a result of this,

$$d\Delta H^0 = \Delta C_P^0 dT \quad 13.3$$

This is the fundamental equation relating heat of reaction to temperature. Upon integrating,

$$\Delta H^0 = \Delta H_i^0 + R \int_{T_0}^T \frac{\Delta C_P^0}{R} dT \quad 14$$

where ΔH^0 and ΔH_i^0 are heats of reactions at temperature T and a reference temperature T_0 respectively. Given the temperature and the heat capacity of each reactant and product, then the integral is given by the analog equation (8) as;

$$\int_{T_0}^T \frac{\Delta C_P^0}{R} dT = \Delta A T_0 (\tau - 1) + \frac{\Delta B}{2} T_0^2 (\tau^2 - 1) + \frac{\Delta C}{3} T_0^3 (\tau^3 - 1) + \frac{\Delta D}{T_0} \left(\frac{\tau - 1}{\tau} \right) \quad 15$$

where by definition, $\Delta A = \sum_i \nu_i A_i$, with similar definitions for ΔB , ΔC and ΔD .

The mean heat capacity change of reaction is then defined in accordance with equation (9) as;

$$\frac{(\Delta C_p^0)_H}{R} = \Delta A + \frac{\Delta B}{2} T_0 (\tau + 1) + \frac{\Delta C}{3} T_0^2 (\tau^2 + \tau + 1) + \frac{\Delta D}{\tau T_0^2} \quad 16$$

Subsequently, the enthalpy change in a reaction, ΔH with respect to temperature at a constant P, can be determined by the expression:

$$\Delta H^0 = \Delta H_i^0 + (\Delta C_p^0)_H (T - T_0) \quad 17$$

In terms of the heat capacities of the substances involved, equation (17) gives the rate of change of the heat of reaction ΔH in accordance with the temperature.

Likewise, pressure changes in the system will cause a shift in the equilibrium to counteract them. Change in the operating pressure of the system at a constant temperature can have significant effect on the ΔG of the reactions. The WGS reaction, however, has been known to continue for longer at a relatively low temperature that favours high conversion of CO and steam to hydrogen and carbon dioxide. (Chen *et al.*, 2009) The effect of increasing or decreasing the operating pressure at a constant temperature on the WGS equilibrium is negligible (± 0.0001), which indicates that the process is insensitive to pressure changes, as predicted by Le Chatelier's principle. Therefore, increasing the operating pressure of the process will affect the ΔG of the methanol reaction only.

The standard free energy G, is a state function, and can be shown how it varies with temperature and pressure by writing the total differential

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \quad 18$$

However,

$$dG = dU + PdV + VdP - TdS - SdT \quad 18.2$$

Assuming a reversible process, $TdS = \delta q$, and reversible work, $PdV = -\delta w$. From first law of thermodynamics ($dU = \delta q + \delta w$), we have that $dU = TdS - PdV$, or $dU - TdS + PdV = 0$. Therefore,

$$dG = VdP - SdT \quad 18.3$$

Thus, for a reversible process, with only PV work,

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad 19$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad 20$$

For an ideal gas, integration of (20) can be performed to give the free energy change when pressure is changed from P_1 to P_2 at constant temperature. Thus for n moles of a gas,

$$G_2 - G_1 = \int V dP = nRT \int_{P_1}^{P_2} \frac{dP}{P} = nRT \ln \frac{P_2}{P_1} \quad 21$$

For standard states therefore,

$$G - G^0 = nRT \ln \frac{P}{P^0} \quad 21.1$$

Therefore, the molar Gibbs energy of an ideal gas is dependent on its partial pressures, according to the relation

$$G = G^0 + nRT \ln (P/P^0) \quad 21.2$$

where G is the free energy at some pressure, P ; G^0 is the free energy in the standard state; R is the universal gas constant ($R = 8.3145 \text{ J/mol-K}$ or $0.0083145 \text{ kJ/mol-K}$); T is absolute temperature; and P^0 is the ambient pressure (1 standard atm/bar).

The change in free energy of a compound in a reaction is dependent on temperature according to the relation of equation (19)

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = -\Delta S \quad 22$$

But at constant temperature, the change of free energy, enthalpy and entropy for any reaction is related by $\Delta G = \Delta H - T\Delta S$ or $\Delta S = (\Delta H - \Delta G)/T$

Substituting for ΔS in equation (22),

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = \frac{-\Delta H + \Delta G}{T} = -\frac{\Delta H}{T} + \frac{\Delta G}{T} \quad 22.1$$

$$T \left[\frac{\partial(\Delta G/T)}{\partial T}\right]_P = -\frac{\Delta H}{T} \quad 22.2$$

At constant pressure therefore, the free energy change of a chemical reaction,

$$\frac{d(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2} \quad (\text{Gibbs-Helmholtz equation}) \quad 22.3$$

where T is the absolute temperature; ΔG is the change in Gibbs free energy at constant pressure, P ; and with ΔH as the enthalpy change (which is considered to be independent of temperature).

The Gibbs-Helmholtz equation is thus a useful thermodynamic expression for calculating changes in the Gibbs energy of a system as a function of temperature, T .

The equation states that 'the change in the G/T ratio at constant pressure as a result of

an infinitesimally small change in temperature is a factor (H/T^2) '. This, when rearranged, gives:

$$\frac{\Delta G, T_2}{T_2} - \frac{\Delta G^0, T_1}{T_1} = \Delta H^0(P) * \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad 24$$

This can also be expressed as:

$$\frac{\Delta G, T_2}{T_2} = \frac{\Delta G^0}{T_1} + \Delta H^0 * \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad 25$$

This equation makes it possible to calculate the Gibbs free energy change for a chemical reaction at any temperature T_2 when the standard Gibbs free energy change of formation and the standard enthalpy change of formation for the individual components at 25°C and 1 bar are all that is known. The results obtained from pressure variations at constant temperature of the different G values were analyzed and discussed by means of Equation 25 above.

3.2 INTRODUCTION TO THE THEORETICAL CONTEXT

3.2.1 Stoichiometric Subspace

In thermodynamics, the values of ΔH and ΔG of a reaction can be calculated from the ΔH_f^0 and ΔG_f^0 of different species in the reaction mixture. If reactions are denoted as j , this statement can be generalized for species (i) in reactions j ($j = 1, 2, \dots, J$) as:

$$\Delta H_{\text{(reaction } j)} = (\sum v_j \Delta H_{ij})_{\text{products}} - (\sum v_j \Delta H_{ij})_{\text{reactants}} \quad 26$$

$$\Delta G_{\text{(reaction } j)} = (\sum v_j \Delta G_{ij})_{\text{products}} - (\sum v_j \Delta G_{ij})_{\text{reactants}} \quad 27$$

where, v_j represents the respective stoichiometric coefficients.

Thus, when we are considering a chemical process involving a single reaction, such that we have the chemical reaction in equation (12) rewritten as

$$v_a A + v_b B + \dots - v_c C - v_d D + \dots = 0 \quad 28$$

the stoichiometric relation can be expressed on the basis of the number of moles for each atomic/chemical species present as: (Shinnar,1988)

$$\sum v_i N_i = 0 \quad 29$$

If \mathcal{E} is considered to be the extent of the reaction, which is a measure of the degree of conversion of the reactants, it implies that at any given point in time, the molar extent of the reaction (\mathcal{E}) can be determined by the amount of reactant and product present in the reactor. Hence, when the extent tends towards the reactants we can have a negative, or, when the reaction tends towards the products, a positive steady state for the reaction, depending on how one expresses the stoichiometry. In this examination of reactant performance, -2 to $+2$ were chosen as the extent of reaction in order to ascertain the reactant performance.

The molar extent (\mathcal{E}) is a useful measure of the progress of a reaction or the degree of transformation achievable in a chemical reactor. It is a time-dependent extensive variable that is proportional to the mass of the system being investigated. This information can also be written as a mass balance for each of the chemical species. Given that there are I chemical species, for each specie I a mass balance for the reaction can be written as given in the equation below:

$$N_i = N_i^0 + \sum v_{ij} \mathcal{E} \quad (i = 1, \dots, I) \quad 30$$

where \mathcal{E} is the extent of reaction.

Since we require a positive molar flow rate of the reactants, then

$$N_i = N_i^0 + \sum v_{ij} \mathcal{E} \geq 0 \quad (\text{for all } i) \quad 31$$

where N_i^0 is the molar flow rate of specie input to the reactor; N_i is the molar flow rate of specie at some point in the reactor or the output; and v_{ij} is the stoichiometric coefficients of species I in the reaction.

The inequality of all species thus ‘determines the achievable area in the space of constraints’ described by the vector N , within which the system can operate thermodynamically without violating the laws governing mass balance. (Tsirlin *et al.*, 2006) Because the extent is not tied to any particular species, changes in the mole numbers of two species can be related to one another by eliminating \mathcal{E} between two expressions that may be derived from Equation 30. This can be expressed as an extent plot, which will subsequently be transformed into a GH plot.

CHAPTER 4

RESULTS, ANALYSIS AND DISCUSSION

4.1 STOICHIOMETRIC SUBSPACE FOR A SINGLE REACTION

We start our application of the extent plot described in the previous chapter by taking the methanol synthesis reaction and using stoichiometric feed as an example.



Mass Balance for Species (stoichiometric feed)

For carbon monoxide (CO) species;

$$N_{\text{CO}} = N_{\text{CO}}^0 - \mathcal{E} \geq 0 \quad 32$$

where N_{CO} is CO output or product in moles, N_{CO}^0 is CO fed into the process in moles, and \mathcal{E} is the extent of reaction.

$$1 - \mathcal{E} \geq 0, \text{ since } N_{\text{CO}}^0 = 1, \text{ therefore } \mathcal{E} \leq 1.$$

For hydrogen (H_2) species:

$$N_{\text{H}_2} = N_{\text{H}_2}^0 - 2\mathcal{E} \geq 0 \quad 33$$

where N_{H_2} is H_2 output or product in moles, $N_{\text{H}_2}^0$ is H_2 fed into the process in moles.

$$2 - 2\mathcal{E} \geq 0, \text{ since } N_{\text{H}_2}^0 = 2, \text{ therefore } \mathcal{E} \leq 1.$$

For methanol (CH_3OH) species:

$$N_{\text{CH}_3\text{OH}} = N_{\text{CH}_3\text{OH}}^0 + \varepsilon \geq 0$$

34

where $N_{\text{CH}_3\text{OH}}$ is methanol output or product in moles, and $N_{\text{CH}_3\text{OH}}^0$ is methanol fed into the process in moles. Since $N_{\text{CH}_3\text{OH}}^0 = 0$, therefore $\varepsilon \geq 0$.

The above mass balance result can be expressed as an extent plot, as shown in Figure 2 below.

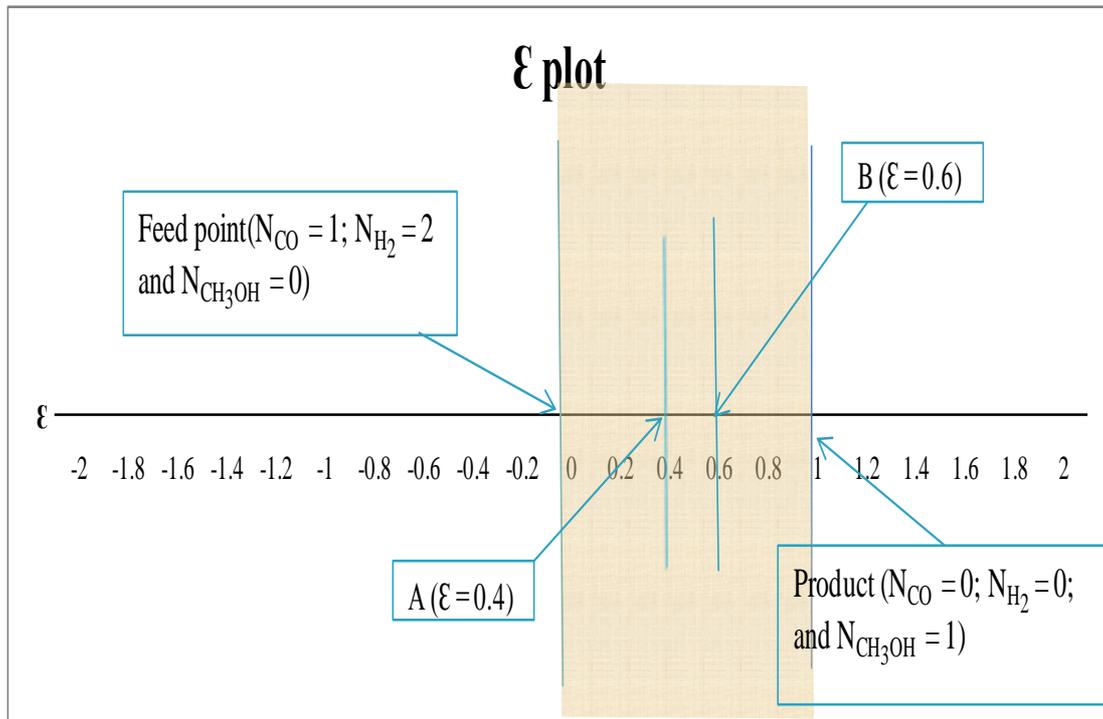


Figure 2: A single reaction represented by an extent plot.

In the above Figure, the feed is located at the origin (0), where the extent of reaction is zero, and any point along the line between the feed and the products. For example, points A ($\varepsilon = 0.4$) and B ($\varepsilon = 0.6$), which represent 40% and 60% conversion of the feed respectively, show a process output for the given feed whose overall mass balance is an incomplete reaction. The reactants are completely converted to the product at extent ε , equalling 1 for the given feed.

4.1.1 Transforming Stoichiometric Subspace to G – H Space

Since the molar extent of the reaction (\mathcal{E}) can be determined by the amount of reactants and products in the reactor, the ΔH and ΔG of the reaction at any time can be expressed as:

$$\Delta H = \mathcal{E}\Delta H_f \quad 35$$

$$\Delta G = \mathcal{E}\Delta G_f \quad 36$$

where, ΔH_f and ΔG_f are the enthalpy change of formation of a compound from its elements (i.e. the enthalpy or heat of formation of the compound), and the standard free energy of formation (Gibbs free energy), respectively.

From the above relations, a linear relationship will be obtained for each of the chemical species (CO, CO₂, H₂, H₂O and CH₃OH) present if \mathcal{E} is eliminated and N_i for each species in terms of ΔH and ΔG is evaluated. Therefore, the limits of each species ($N_i=0 \ i=1, \dots, I$) taking part in the reaction can be represented in a G–H space (ΔG – ΔH plot, hereafter referred to as the GH domain), because it is an area of activity influenced by ΔG and ΔH . A linear relationship can be obtained between ΔH and ΔG by varying the extent of reaction for the process, and this can then be represented in a G–H plot as shown in Figure 3.

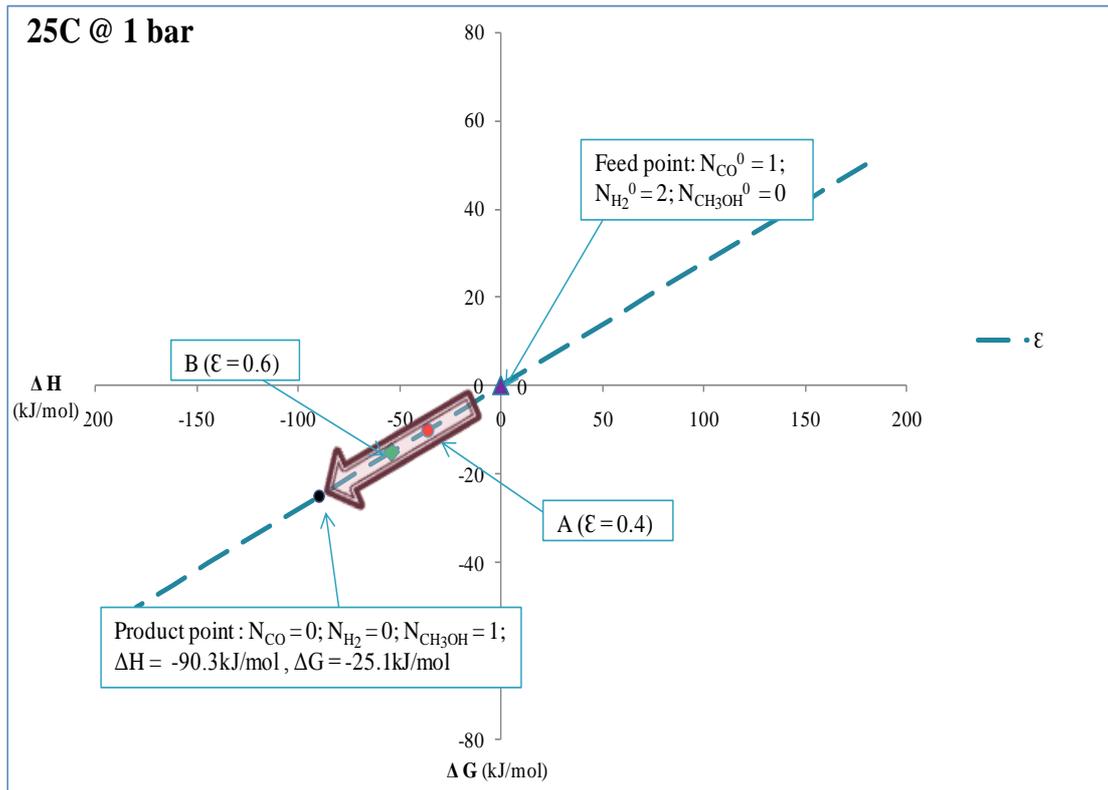


Figure 3: Representation of a chemical process using the G–H plot for one reaction, at 25°C and 1 bar.

In Figure 3, the feed is located at the origin (0) where the extent of reaction is zero. ΔG and ΔH are also zero, because at this point there is no net reaction taking place in the system, and the location of the products corresponds with the net ΔG and ΔH values of the reacting system. As in the extent plots, we can see in the Figure that the points along the line between the feed and the products, for example points A ($\epsilon = 0.4$) and B ($\epsilon = 0.6$), represent a process output whose overall mass balance is an incomplete reaction (40% and 60% conversion respectively) for the given feed. The reaction is expected to follow the path of the arrow from the feed within the mass balance region (which in this case is along the line) and to terminate at the product with an extent of 1, with the net ΔG and ΔH values for the reaction.

4.2 ENERGY BALANCE AND WORK BALANCE IN THE G–H SPACE

Since the value of ΔH determines whether heat needs to be added or removed from the reacting system, and ΔG corresponds to the amount of work that needs to be added ($\Delta G \geq 0$) or removed ($\Delta G \leq 0$), a simple energy and work balance analysis can be plotted. (See Figures 4 and 5 below.)

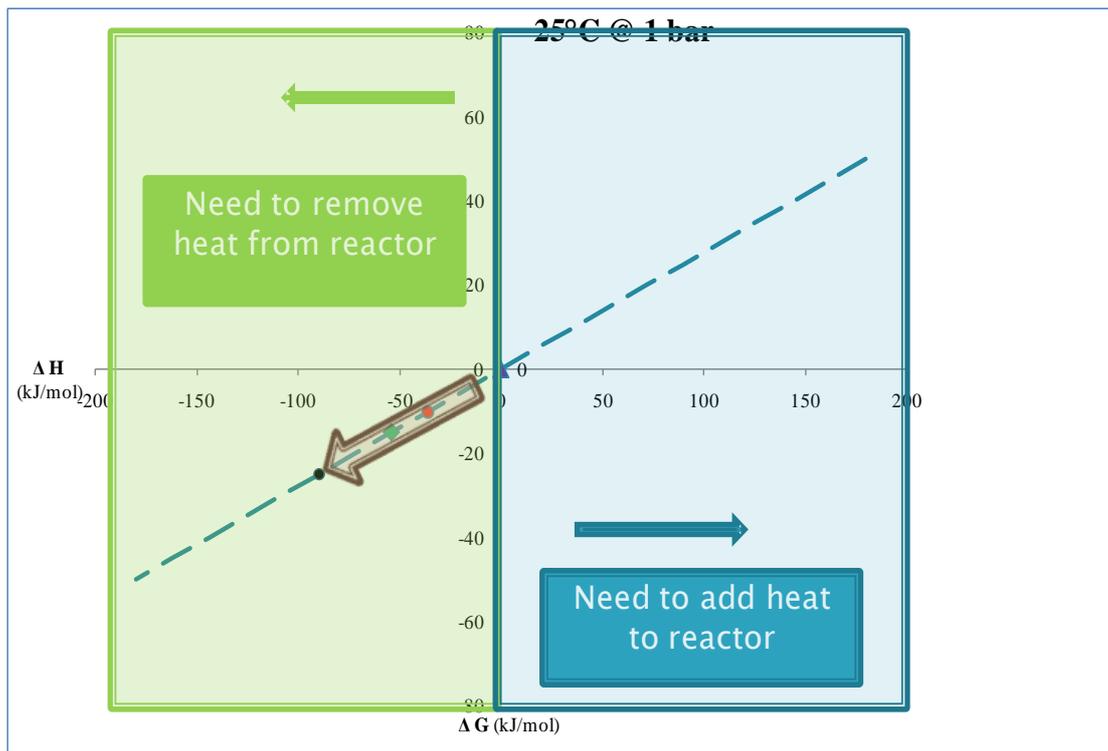


Figure 4: Energy balance analysis using the G–H plot.

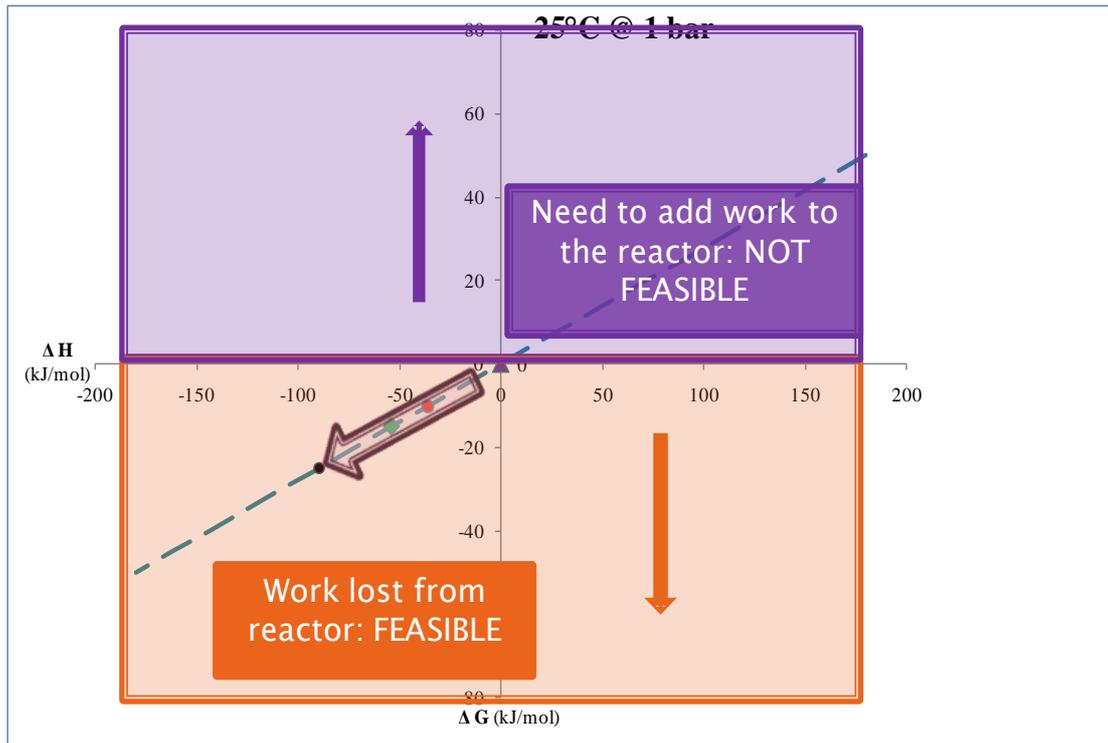


Figure 5: Work balance analysis using the G–H plot.

The conclusion we can derive from both analyses is that for a complete conversion of the feed materials (with an extent of reaction, 1), the methanol synthesis reaction at 25C and 1 bar is feasible and requires the rejection of heat.

4.3 EFFECT OF CHANGES IN OPERATING CONDITIONS ON G–H SPACE FOR A SINGLE REACTION

The effect of the operating parameters such as temperature and pressure on a reaction can also be illustrated on a G–H plot. This makes it possible for us to analyze the effects of the different H and G values on temperature variation at constant pressure. Temperature range of 250 – 350C was chosen to show the performance at the industrial temperature of methanol synthesis reaction as compared to ambient condition.

As can be seen in Figure 6 below, variations in the temperature of the operating system had an effect on both the ΔH and the ΔG of the reaction, making the reaction less successful at higher temperatures. With the value of ΔH slightly decreasing with temperature increase, while that of G increases tremendously.

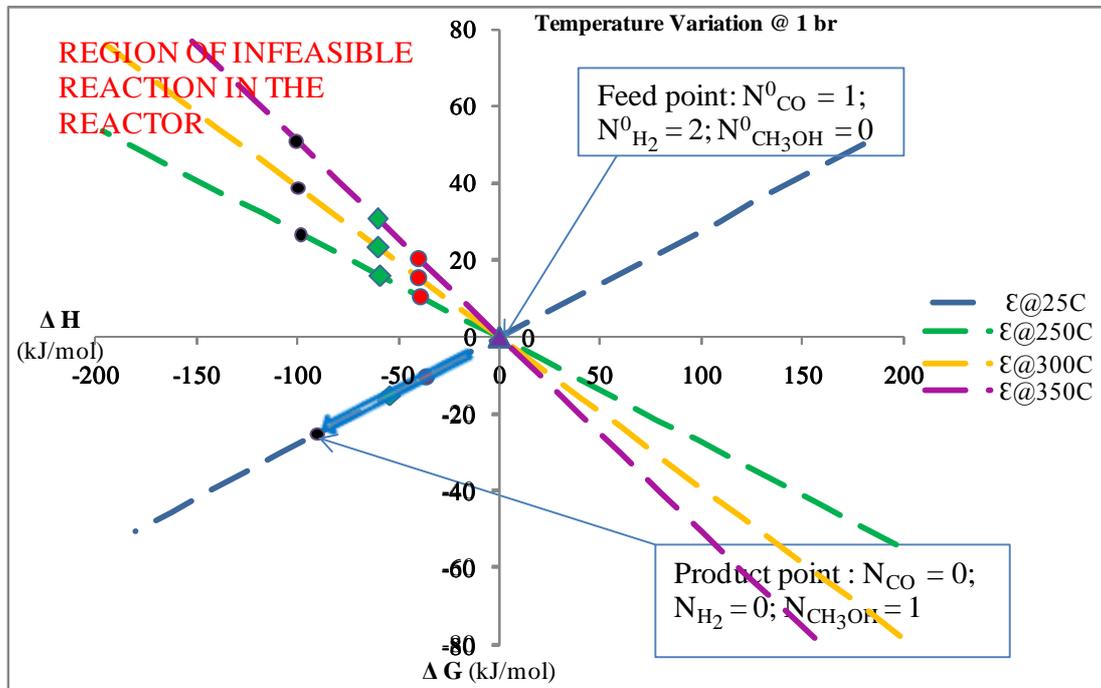


Figure 6: Representation of a chemical process using the G–H plot to show the effects of temperature variations on a single reaction at 1 bar, using a feed consisting of 1 mol CO and 2 mols H₂.

From the Figure we observe that when the temperature increases, so does the positive slope of the reaction, making G more positive and moving the mass balance region into positive ΔG space. Therefore the higher temperatures are not conducive to forward reaction, because thermodynamically it will choose to remain at the feed point due to its lower ΔG . To make the reaction feasible at higher temperatures, we need to put some work into the system in the form of pressure.

At higher pressures however, the results of pressure variations while the temperature of the system remains constant can be found to have a significant effect, but only on

the G of the reaction. Increasing the pressure to 20, 50 and 90 bars, we obtained the plots shown in Figures 7 and 8 for 25°C and 250°C respectively.

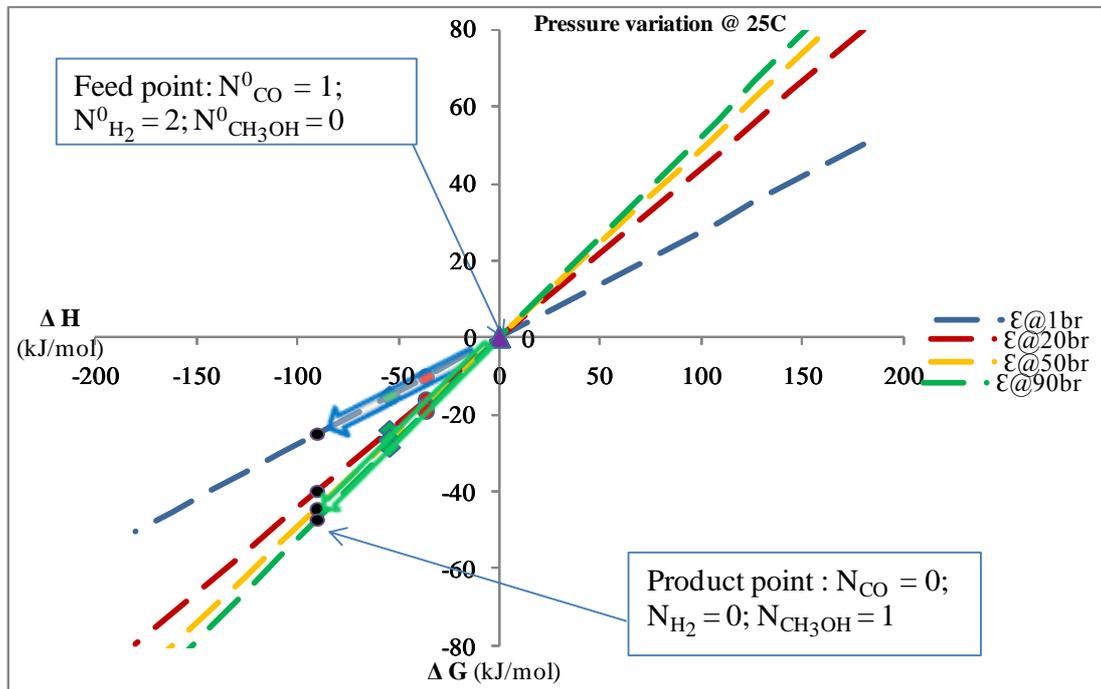


Figure 7: Representation of a chemical process using the G–H plot to show the effects of pressure variations on a single reaction at 25°C, using a feed consisting of 1 mol CO and 2 mols H₂.

As we can see in this Figure 7, while ΔH remains constant with the increase in pressure, the ΔG of the reaction increased considerably becoming more negative, thereby deepening the slope of the line, and resulting in a more spontaneous forward reaction. In other words, when the pressure increases, so does the negative slope of the reaction. Therefore the higher pressure appears to favour the forward reaction, because thermodynamically it will choose the path with a maximum change in G, due to its lower ΔG . And the reaction at 90 bars would be expected to be more thermodynamically stable.

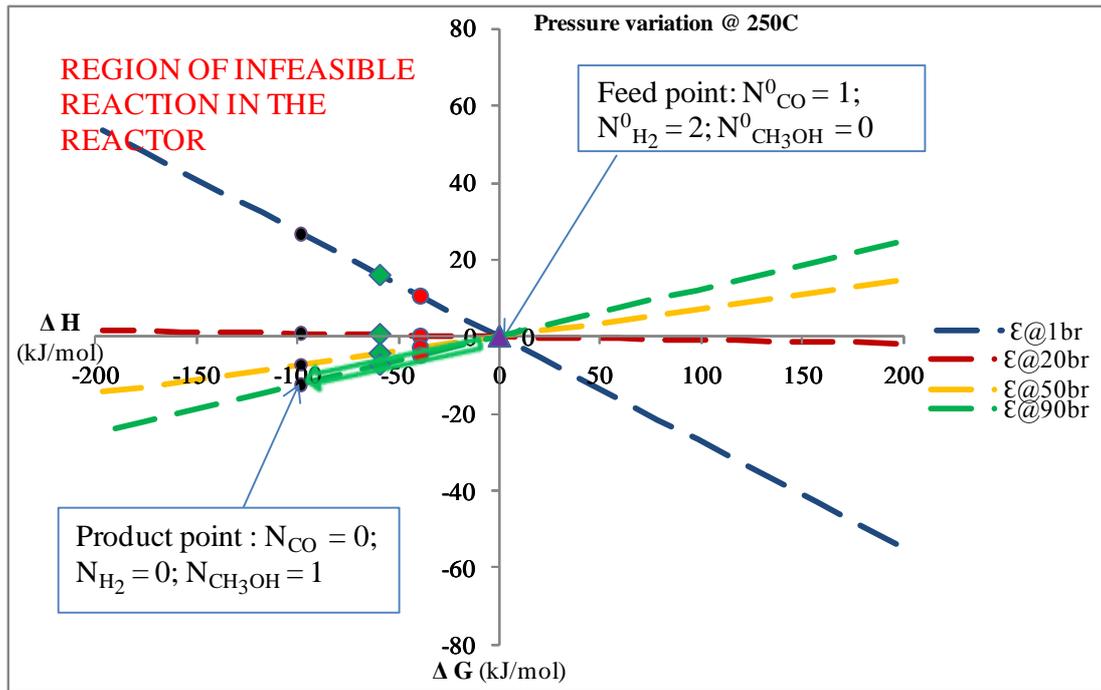


Figure 8: Representation of a chemical process using the G–H plot to show the effects of pressure variations on a single reaction at 250°C, using a feed consisting of 1 mol CO and 2 mols H₂.

The plot above shows that although at higher temperatures the reaction is not feasible thermodynamically at 1 bar, the situation can be reversed (that is, made thermodynamically feasible). This is achieved by increasing the pressure at a high temperature. The slope changes from positive through zero to negative, allowing the reaction to proceed from the feed to the product in the direction of the arrow.

Variation of temperature and pressure has caused the mass balance line to rotate, with the length in the H direction remaining more constant than that of the G, causing this rotation. It can be seen that at much higher temperatures, the system will require much more work input in form of pressure to make the reaction feasible. For example at 350°C the reaction is not feasible even at 90 bars, as is illustrated in Figure 9, with the value of ΔH changing to -100.6kJ/mol as a result of the change in temperature.

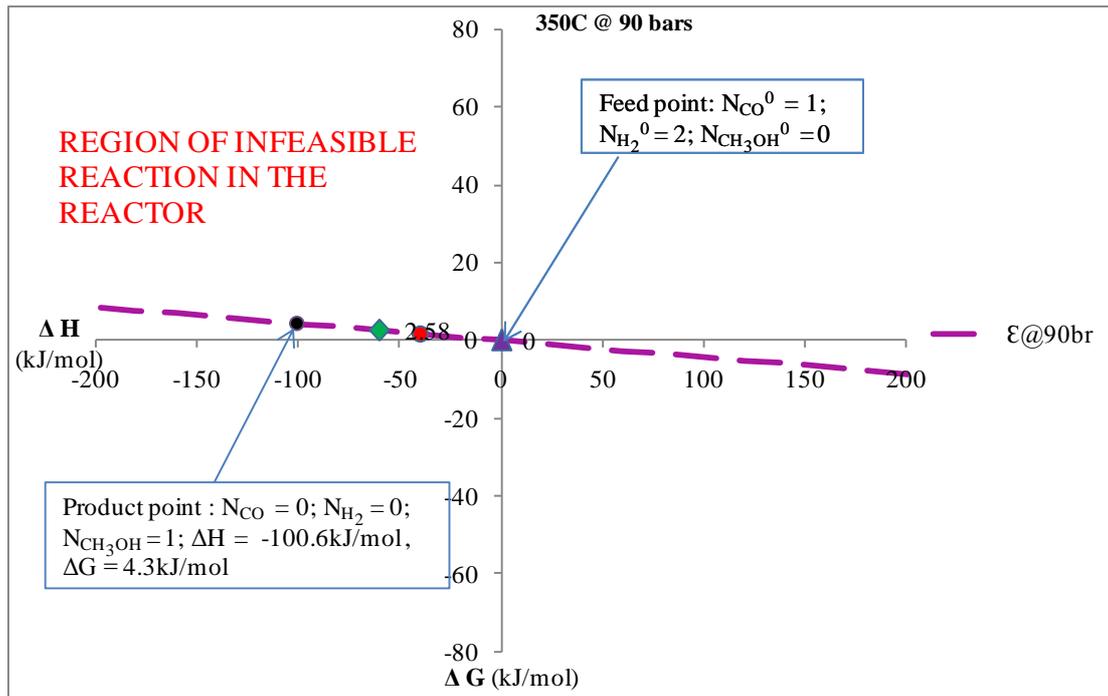


Figure 9: Representation of a chemical process using the G–H plot to show the effects of pressure variations on a single reaction at 350°C and 90 bars, using a feed consisting of 1 mol CO and 2 mols H₂ only.

4.4 STOICHIOMETRIC SUBSPACE AND GH SPACE INVOLVING TWO REACTIONS

At this point we can consider a more complex case in which:

- more than one chemical reaction takes place in the reactor (because many reactions can be combined in a single unit),
- one or two chemical species is/are present in both reactions, and
- the extent of reactions is ϵ_j for reactions j (in this case, $j = 1, 2$).

The extents of these reactions can be used to calculate values for ΔH and ΔG of the combined process while obtaining those for ΔH_j and ΔG_j from the published literature.

In agreement with Hess's law;

$$\Delta H = \epsilon_1 \Delta H_1 + \epsilon_2 \Delta H_2$$

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$$\Delta G = \varepsilon_1 \Delta G_1 + \varepsilon_2 \Delta G_2 \quad 38$$

In a more general form, this equation can be expressed as:

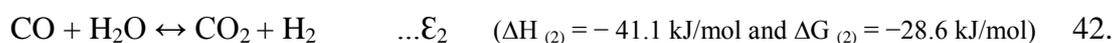
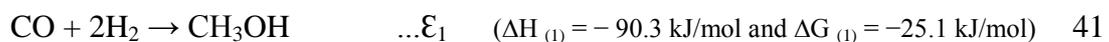
$$\Delta H = \sum v_{ij} \varepsilon_j \Delta H_j \quad 39$$

$$\Delta G = \sum v_{ij} \varepsilon_j \Delta G_j \quad 40$$

where, ε_1 and ε_2 are the extents of reactions 1 and 2; ΔH_1 , ΔG_1 and ΔH_2 , ΔG_2 are the enthalpy (ΔH) and Gibbs free energies of reactions 1 and 2 respectively; and ΔH and ΔG stand for the enthalpy and Gibbs free energy of the combined process.

As an example of the use of the graphical technique, we now consider the simultaneous reactions that occur in the synthesis of methanol from syngas, in an attempt to ascertain the performance of both reactants and species during methanol synthesis. One is an exothermic reaction that is subject to thermodynamic limitations, while the other is the WGS reaction, which appears to be the rate-limiting step of the methanol synthesis reaction. These are represented by the chemical equations 41 and 42 below, which presuppose the use of a stoichiometric feed of carbon monoxide and hydrogen only, in the ratio of 1:2 (a two-component feed). The two reactions involve five chemical species and values of ΔH_j and ΔG_j that are theoretically obtained from Equations 37 and 38. We chose -2 to $+2$ as the extent of reaction.

The equations for the reactions involved in methanol synthesis and WGS are as follows.



4.4.1 Mass Balance Calculations for Chemical Species

The mass balance for carbon monoxide (CO) species when both reactions are considered can be expressed as:

$$N_{\text{CO}} = N_{\text{CO}}^0 - \varepsilon_1 - \varepsilon_2 \geq 0 \quad 43$$

$$N_{\text{CO}}^0 - \varepsilon_1 \geq \varepsilon_2 \quad 43.1$$

where N_{CO} = CO output or product in moles; N_{CO}^0 = CO fed into the process in moles; and ε_1 and ε_2 are the extent of reactions 1 and 2 respectively. Since the concentration of CO fed into the process in moles equals 1 ($N_{\text{CO}}^0 = 1$), it follows that:

$$\varepsilon_2 \leq 1 - \varepsilon_1 \quad 43.2$$

The mass balance for hydrogen (H_2) species when both reactions are considered can be expressed as:

$$N_{\text{H}_2} = N_{\text{H}_2}^0 - 2\varepsilon_1 + \varepsilon_2 \geq 0 \quad 44$$

$$N_{\text{H}_2}^0 + \varepsilon_2 \geq 2\varepsilon_1 \quad 44.1$$

where N_{H_2} = H_2 output or product in moles; $N_{\text{H}_2}^0$ = H_2 fed into the process in moles; and ε_1 and ε_2 are the extent of reactions 1 and 2 respectively. Since the moles of H_2 feed into the process equal 2 ($N_{\text{H}_2}^0 = 2$), it follows that:

$$\varepsilon_2 \geq 2\varepsilon_1 - 2 \quad 44.2$$

The mass balance for water (H_2O) species, when both reactions are considered, can be expressed as:

$$N_{\text{H}_2\text{O}} = N_{\text{H}_2\text{O}}^0 - \varepsilon_2 \geq 0 \quad 45$$

$$N_{\text{H}_2\text{O}}^0 \geq \varepsilon_2 \quad 45.1$$

where $N_{\text{H}_2\text{O}} = \text{H}_2\text{O}$ output or product in moles; $N_{\text{H}_2\text{O}}^0 = \text{H}_2\text{O}$ fed into the process in moles; and ε_2 is the extent of reactions 2. Since the moles of H_2O fed into the process equal 0 ($N_{\text{H}_2\text{O}}^0 = 0$), it follows that:

$$\varepsilon_2 \leq 0 \quad 45.2$$

The mass balance for carbon dioxide (CO_2) species, when both reactions are considered, can be expressed as:

$$N_{\text{CO}_2} = N_{\text{CO}_2}^0 + \varepsilon_2 \geq 0 \quad 46$$

$$\varepsilon_2 \geq -N_{\text{CO}_2}^0 \quad 46.1$$

where $N_{\text{CO}_2} = \text{CO}_2$ output or product in moles; $N_{\text{CO}_2}^0 = \text{CO}_2$ fed into the process in moles; and ε_2 is the extent of reactions 2. Since the moles of CO_2 fed into the process equal zero ($N_{\text{CO}_2}^0 = 0$), it follows that:

$$\varepsilon_2 \leq 0 \quad 46.2$$

The mass balance for methanol (CH_3OH) species, when both reactions are considered, can be expressed as:

$$N_{\text{CH}_3\text{OH}} = N_{\text{CH}_3\text{OH}}^0 + \varepsilon_1 \geq 0 \quad 47$$

$$\varepsilon_1 \geq -N_{\text{CH}_3\text{OH}}^0 \quad 47.1$$

where $N_{\text{CH}_3\text{OH}} = \text{CH}_3\text{OH}$ output or product in moles; $N_{\text{CH}_3\text{OH}}^0 = \text{CH}_3\text{OH}$ fed into the process in moles; and ϵ_1 is the extent of reactions 1. Since the moles of CH_3OH fed into the process equal 0 ($N_{\text{CH}_3\text{OH}}^0 = 0$), it follows that:

$$\epsilon_1 \geq 0 \quad 47.2$$

We obtain Figure 10 when the mass balance result for the different chemical species (N_i) is shown on the extent plot.

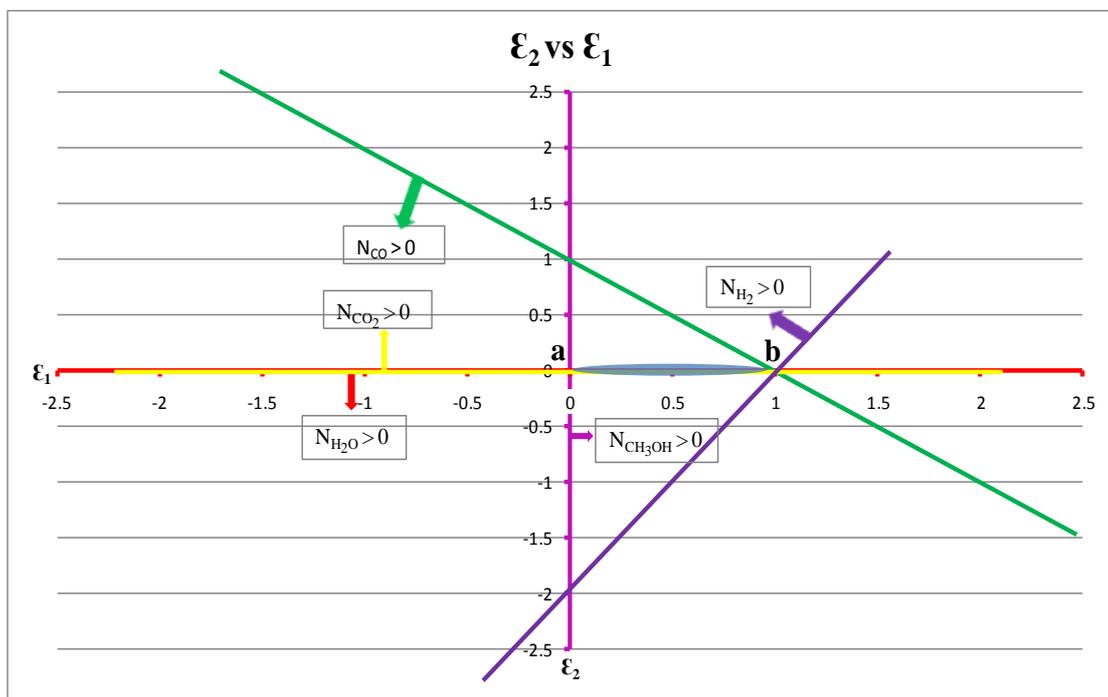


Figure 10: Extent plot for two reactions using a feed of 1 mol CO and 2 mol H₂ only.

Evaluating ϵ_1 and ϵ_2 gives a linear relationship for each of the chemical species (CO, CO₂, H₂, H₂O and CH₃OH) in the combined process. The limits of each species ($N_i = 0$, $i=1, \dots, I$), when represented in the extent plot, are expected to give rise to a polygon, with a number of sides equal to the number of chemical species present. But this is not always the case, because there can be a relationship between the mass balance limiting lines, the quantity fed and the feed component that causes some of

the lines to collapse into each other, as can be seen in this Figure. In this instance, the mass balance region collapses into a straight line from point a to point b of Figure 10 as a result of the mass balance calculations on the two species (CO and H₂) fed into the process. This straight line represents all the possible extents of the given feed, as shown in Figure 10.

4.4.2 Transforming the Extent Plot to G–H Space

When performing a mass balance for the chemical species, one can calculate the point at which the molar flow rate in the reactor is greater than, or equal to, zero ($N_i \geq 0$), which enables one to obtain a linear relationship for the respective species for different feeds. If we eliminate ϵ_1 , ϵ_2 , and N_i for each species (CO, CO₂, H₂, H₂O and CH₃OH) in terms of the ΔH and ΔG evaluated for the combined process, we can plot a linear relationship that would meet the requirements of the ARs for each of them. The resultant ΔH and ΔG limits of each species ($N_i = 0$, $i=1, \dots, I$) in the combined process can then be represented in a G–H space, as in Figure 11. The plot in Figure 11, compared with that of the single reaction involving the methanol synthesis shown in Figure 3, gives the same result, with the reaction proceeding from point a (the feed) to b (the product), where there is complete conversion of the reactants. What this means is that only the methanol synthesis reaction could be carried out in the absence of either the water or the CO₂ that facilitates the WGS shift reaction, and that if neither is present the AR will always be a straight line that does not give the system room for reaction path alternatives.

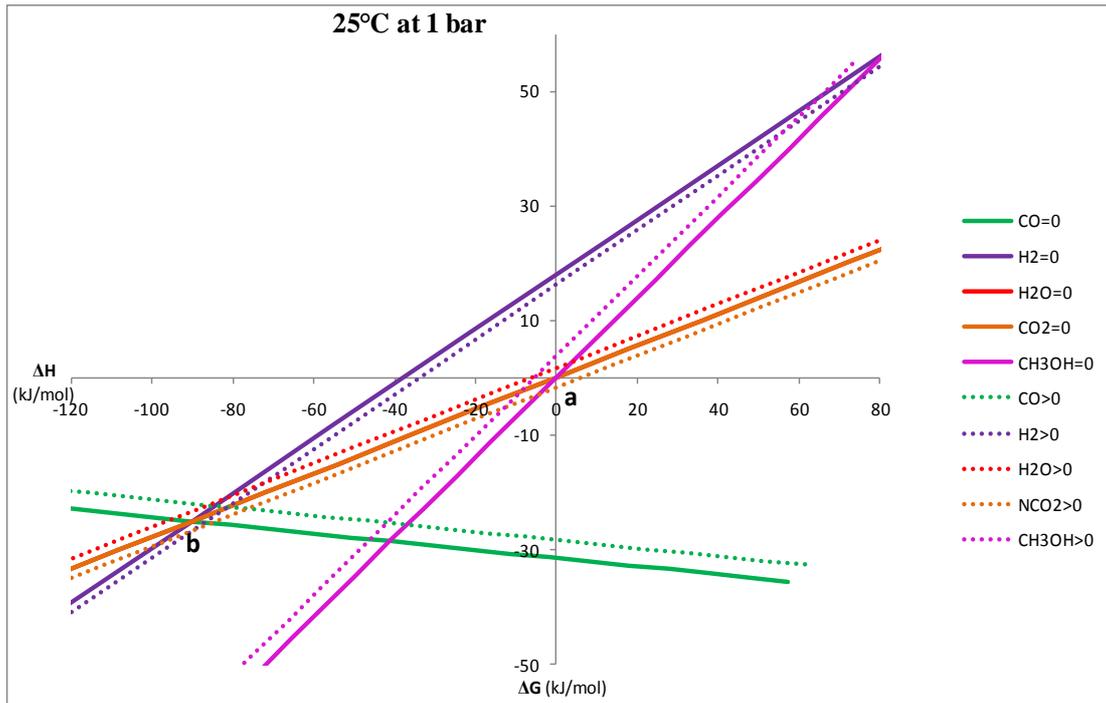


Figure 11: Representation of a chemical process using the G–H plot to show two reactions, methanol synthesis and WGS, at 25°C and 1 bar, using a feed of 1mol CO and 2 mol H₂ only.

4.5 FEED ANALYSIS ON THE G–H SPACE

Using a three-component feed consisting of CO (1 mol), H₂ (2 mols) and 0.5 mols of H₂O, we performed a mass balance for the different chemical species, eliminating ϵ_1 , ϵ_2 , and the resulting N_i for each species in terms of the ΔH and ΔG of the combined process evaluated for the given feed. Our objective was to ascertain the performance of the reactant and species. The result, represented in a G–H domain, is shown in Figure 12.

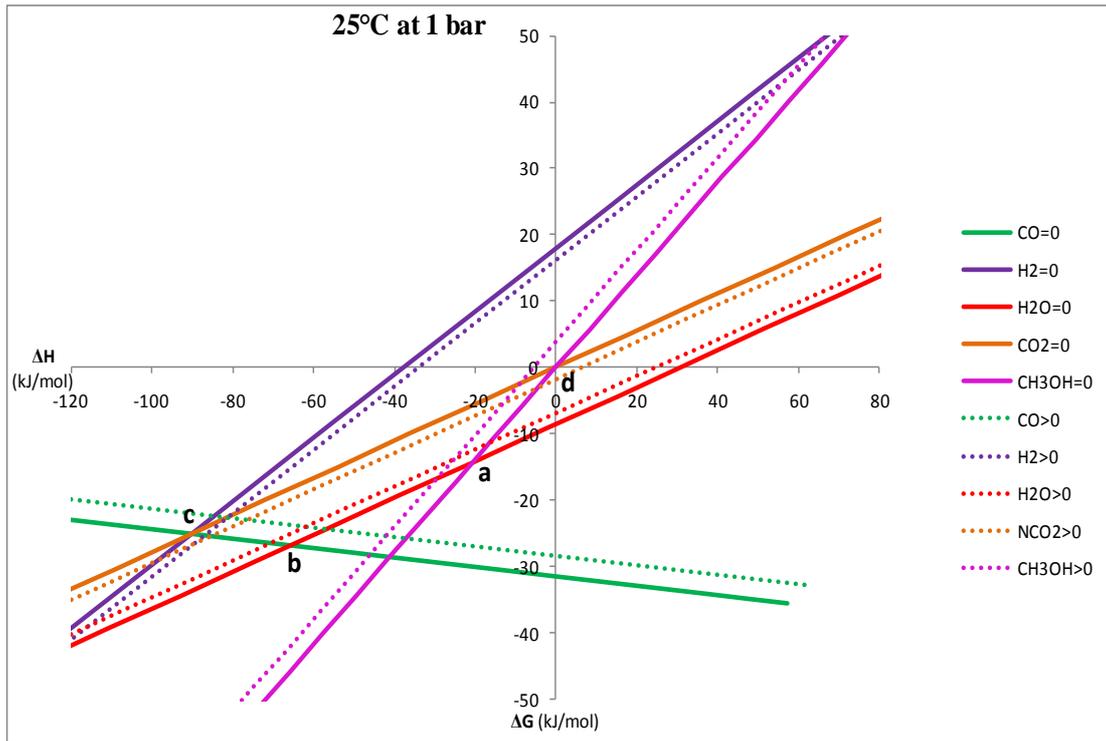


Figure 12: Representation of a chemical process using the G–H plot for two reactions, methanol synthesis and WGS, at 25°C and 1 bar, using a feed consisting of CO (1 mol), H₂ (2 mols) and H₂O (0.5 mol).

The G–H plot shown in Figure 13 below records the results of using a four-component feed consisting of CO (1 mol), H₂ (2 mols), H₂O (0.5 mols) and 1 mol CO₂, and performing a mass balance for each of the chemical species. We eliminated ϵ_1 , ϵ_2 and the resulting N_i for each species in terms of the ΔH and ΔG of the combined process evaluated for the given feed. This experiment was also carried out to chart the behaviour of the reactants and species.

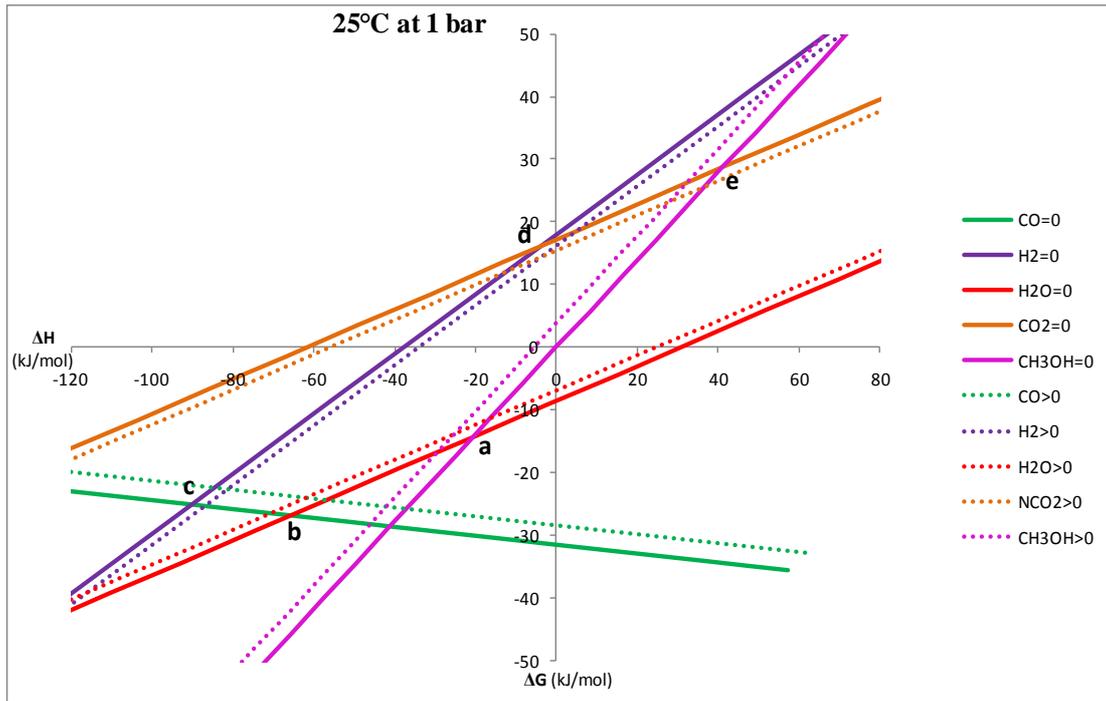


Figure 13: Representation of a chemical process using the G–H plot for two reactions, methanol synthesis and WGS, at 25°C and 1 bar, using a feed consisting of CO (1 mol), H₂ (2 mols), H₂O (0.5 mols) and CO₂ (1 mol).

It is clearly shown in Figures 12 and 13 that the introduction of either water or CO₂, or both in the feed increases the mass balance region. This results in WGS activity, and therefore generates more reaction pathways. Put another way, the introduction of extra feed components (and the amount fed) will not only change the shape and size of the mass balance region, but will also result in a greater number of reaction path options.

Building on these results, we can use a feed consisting of CO (1 mol), CO₂ (1 mol), H₂ (3 mols) and H₂O (0.5 mol) to explain the reactor’s AR, and to identify how G is minimized within the reactor. The mass balance calculations as well as the resulting ΔH and ΔG values can be calculated to evaluate the ARs for the given feed, and in this way to plot the activities of the reactant and species.

4.5.1 Mass Balance for Chemical Species

For carbon monoxide (CO) species, derived from Equation 43,

$$N_{\text{CO}} = N_{\text{CO}}^0 - \varepsilon_1 - \varepsilon_2 \geq 0$$

$$N_{\text{CO}}^0 - \varepsilon_1 \geq \varepsilon_2$$

where N_{CO} = CO output or product in moles; N_{CO}^0 = CO fed into the process in moles; and ε_1 and ε_2 are the extent of reactions 1 and 2 respectively. The concentration of CO fed into the process in moles equals 1 ($N_{\text{CO}}^0 = 1$), therefore:

$$\varepsilon_2 \leq 1 - \varepsilon_1$$

For hydrogen (H₂) species, derived from Equation 44,

$$N_{\text{H}_2} = N_{\text{H}_2}^0 - 2\varepsilon_1 + \varepsilon_2 \geq 0$$

$$N_{\text{H}_2}^0 + \varepsilon_2 \geq 2\varepsilon_1$$

where, N_{H_2} = H₂ output or product in moles; $N_{\text{H}_2}^0$ = H₂ fed into the process in moles; and ε_1 and ε_2 are the extent of reactions 1 and 2 respectively. As the moles of H₂ fed into the process equal 3 ($N_{\text{H}_2}^0 = 3$), it follows that:

$$\varepsilon_2 \geq 2\varepsilon_1 - 3$$

For water (H₂O) species, derived from Equation 45,

$$N_{\text{H}_2\text{O}} = N_{\text{H}_2\text{O}}^0 - \varepsilon_2 \geq 0$$

$$N_{\text{H}_2\text{O}}^0 \geq \varepsilon_2$$

where, $N_{\text{H}_2\text{O}} = \text{H}_2\text{O}$ output or product in moles; $N_{\text{H}_2\text{O}}^0 = \text{H}_2\text{O}$ fed into the process in moles; and ε_2 is the extent of reaction 2. The moles of H_2O fed into the process equal 0.5 ($N_{\text{H}_2}^0 = 0.5$), so:

$$\varepsilon_2 \leq 0.5$$

For carbon dioxide (CO_2) species, derived from Equation 46,

$$N_{\text{CO}_2} = N_{\text{CO}_2}^0 + \varepsilon_2 \geq 0$$

$$\varepsilon_2 \geq -N_{\text{CO}_2}^0$$

where $N_{\text{CO}_2} = \text{CO}_2$ output or product in moles; $N_{\text{CO}_2}^0 = \text{CO}_2$ fed into the process in moles; and ε_2 is the extent of reaction 2. Since the moles of CO_2 fed into the process equal 1 ($N_{\text{CO}_2}^0 = 1$), it follows that:

$$\varepsilon_2 \leq -1$$

For methanol (CH_3OH) species, derived from Equation 47,

$$N_{\text{CH}_3\text{OH}} = N_{\text{CH}_3\text{OH}}^0 + \varepsilon_1 \geq 0$$

$$\varepsilon_1 \geq -N_{\text{CH}_3\text{OH}}^0$$

where $N_{\text{CH}_3\text{OH}} = \text{CH}_3\text{OH}$ output or product in moles; $N_{\text{CH}_3\text{OH}}^0 = \text{CH}_3\text{OH}$ fed into the process in moles; and ε_1 is the extent of reaction 1. Since the moles of CO_2 fed into the process equal 1 ($N_{\text{CO}_2}^0 = 1$), we can reason that:

$$\varepsilon_1 \geq 0$$

However, when the above mass balance result for the different chemical species (N_i) was represented on an extent plot, a polygon with a number of sides equal to the number of chemical species present was generated. See Figure 14 below.

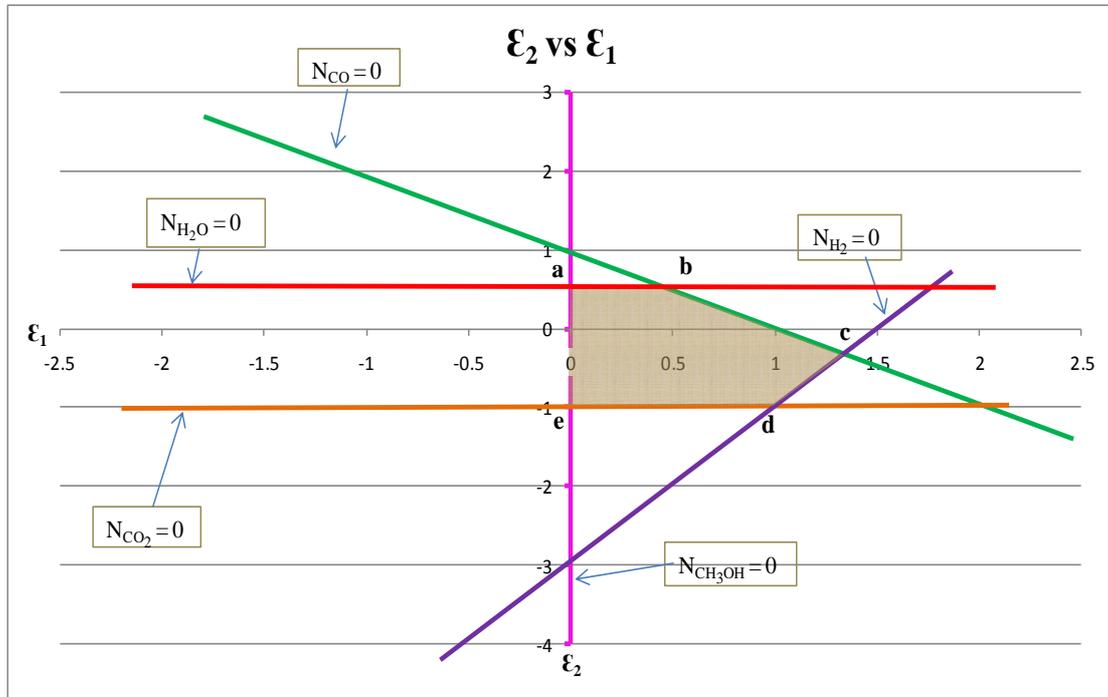


Figure 14: Extent plot for two reactions, methanol synthesis and WGS, using a feed of 1 mol CO, 3 mols H₂, 1 mol CO₂ and 0.5 mol H₂O.

In the Figure we can see that the pentagonal region marked by **a**, **b**, **c**, **d**, and **e** is the mass balance AR, which represents all the possible extents for the given feed. As such it is the region of feasible methanol synthesis reaction.

4.5.2 Transforming To G–H Space

When performing a mass balance for the respective chemical species, we use the following equations.

For carbon monoxide (CO) species,

$$N_{CO} = 1 - \epsilon_1 - \epsilon_2 \geq 0$$

For hydrogen (H₂) species,

$$N_{\text{H}_2} = 3 - 2\varepsilon_1 + \varepsilon_2 \geq 0$$

For water (H₂O) species,

$$N_{\text{H}_2\text{O}} = 0.5 - \varepsilon_2 \geq 0$$

For carbon dioxide (CO₂) species,

$$N_{\text{CO}_2} = 1 + \varepsilon_2 \geq 0$$

For methanol (CH₃OH) species,

$$N_{\text{CH}_3\text{OH}} = 0 + \varepsilon_1 \geq 0$$

The limits for each species ($N_i = 0$, $i=1, \dots, I$) can therefore be represented in a G–H space.

If the ΔH and ΔG results for the combined processes of the different chemical species (N_i) is plotted on the G–H space, as in Figure 11, a polygon with the same number of sides as in the extent plot is generated, as a result of the mass balance calculations on the species. However, since the region bounded by the lines will represent all the possible combinations of the species participating in the reactions, these lines define the attainable boundaries in a G–H plot. Within them is the region of feasible methanol synthesis that will not violate thermodynamic relations, and can then be referred to as the mass balance (AR).

As already noted, in the context of this dissertation the AR refers to the thermodynamically achievable region in the state space within which the reactor can

function without violating thermodynamic boundaries, using only the process of reactions. The AR should contain the feed point, it should be equal to zero at the intersection of the species, and it should represent all the possible combinations of the species taking part in the reactions.

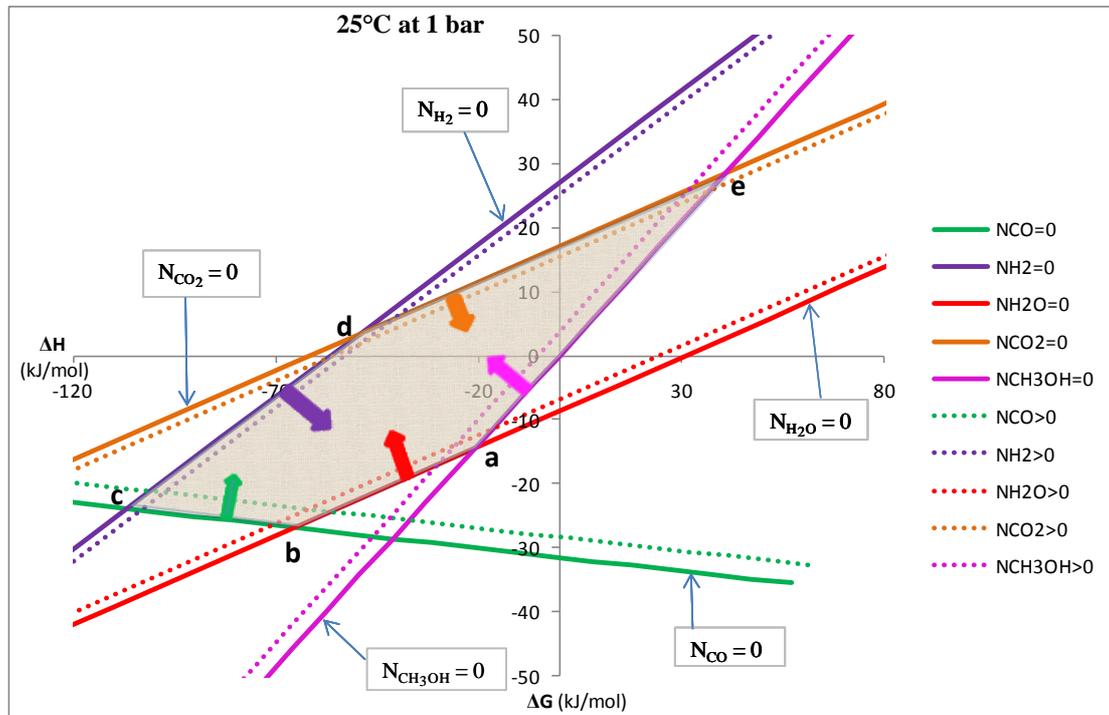


Figure 15: Representation of a chemical process using the G–H plot for two reactions, methanol synthesis and WGS, at 25°C and 1 bar, using a feed consisting of CO (1 mol), CO₂ (1 mol), H₂ (3 mols) and H₂O (0.5 mol).

In Figure 15, we can see that the mass balance region (the area in which a positive number of moles of respective species is indicated by arrows, and marked by the vertices a, b, c, d and e) corresponds with the sides of the extent plot in Figure 14. This is the area where there are feasible reactions, because the conditions required to optimize the process in a steady state system are satisfied and all the species are positive. (In other words, this region contains the feed point, it is zero on the boundaries, and it represents all the possible combinations of the species involved in the reactions.) It can therefore be referred to as the mass balance AR.

Looking at the edges of the region, from Figure 15, we can observe that:

At point a, where $N_{\text{CH}_3\text{OH}} = 0$, $N_{\text{H}_2\text{O}} = 0$ and $\varepsilon_1 = 0$, and recalling Equations 45 and 47,

$$N_{\text{CH}_3\text{OH}}^0 + \varepsilon_1 = N_{\text{H}_2\text{O}}^0 - \varepsilon_2 = 0 \quad 48;$$

but, since $N_{\text{CH}_3\text{OH}}^0 = 0$, $\varepsilon_1 = 0$ and $N_{\text{H}_2\text{O}}^0 = 1/2$, therefore, $\varepsilon_2 = 1/2$

we have $\varepsilon_1 = 0$ and $\varepsilon_2 = 1/2$ at point a.

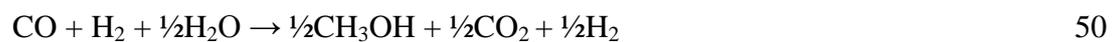
At point b of Figure 15, $N_{\text{CO}} = 0$ and $N_{\text{H}_2\text{O}} = 0$, and recalling Equations 43 and 45,

$$N_{\text{CO}}^0 - \varepsilon_1 - \varepsilon_2 = N_{\text{H}_2\text{O}}^0 - \varepsilon_2 \quad 49$$

Since $N_{\text{CO}}^0 = 1$, and $N_{\text{H}_2\text{O}}^0 = 1/2$

$\varepsilon_1 = 1 - 1/2 = 1/2$, hence we have that $\varepsilon_1 = 1/2$

Substituting ε_1 value into equations 43.1, gives $\varepsilon_2 = 1/2$. Thus, we have $\varepsilon_1 = 1/2$ and $\varepsilon_2 = 1/2$, and the overall equation will be;



At point c of Figure 15, $N_{\text{CO}} = 0$ and $N_{\text{H}_2} = 0$, and from Equations 31 and 32,

$$N_{\text{CO}}^0 - \varepsilon_1 - \varepsilon_2 = N_{\text{H}_2}^0 - 2\varepsilon_1 + \varepsilon_2 = 0 \quad 51$$

Since $N_{\text{CO}}^0 = 1$ and $N_{\text{H}_2}^0 = 3$,

Therefore, from Equation 43.2,

$$\varepsilon_2 = 1 - \varepsilon_1 \quad 51.1$$

Substituting Equation 51.1 for the value of ϵ_2 into equation 51, then

$$3 - 1 - 2\epsilon_1 + \epsilon_1 + 2(1 - \epsilon_1) = 0$$

$$4 - 3\epsilon_1 = 0$$

therefore $\epsilon_1 = 1\frac{1}{3}$. And from equation 51.1, $\epsilon_2 = 1 - 4/3 = -\frac{1}{3}$

thus, $\epsilon_1 = 1\frac{1}{3}$ (4/3) and $\epsilon_2 = -\frac{1}{3}$, and the overall equation will be:



At point d of Figure 15, $N_{\text{CO}_2} = 0$ and $N_{\text{H}_2} = 0$, and from Equations 44 and 46,

$$N_{\text{H}_2}^0 - 2\epsilon_1 + \epsilon_2 = N_{\text{CO}_2}^0 + \epsilon_2 = 0 \quad 53.$$

Since $N_{\text{CO}_2}^0 = 1$ and $N_{\text{H}_2}^0 = 3$, then $3 - 2\epsilon_1 = 1$

$$2\epsilon_1 = 3 - 1, \text{ therefore } \epsilon_1 = 2/2 = 1$$

Substituting the value of ϵ_1 into Equation 44 or from Equation 46, it follows that:

$$\epsilon_2 = -1$$

thus, $\epsilon_1 = 1$ and $\epsilon_2 = -1$.

At point e of Figure 15, $N_{\text{CO}_2} = 0$, $N_{\text{CH}_3\text{OH}} = 0$ and $\epsilon_1 = 0$, and from Equations 46 and

47,

$$N_{\text{CO}_2}^0 + \epsilon_2 = N_{\text{CH}_3\text{OH}}^0 + \epsilon_1 = 0 \quad 54$$

Since $N_{\text{CH}_3\text{OH}}^0 = 0$, $N_{\text{CO}_2}^0 = 1$ and $\epsilon_1 = 0$, from Equation 54, $\epsilon_2 = -1$

therefore $\epsilon_1 = 0$ and $\epsilon_2 = -1$.

One can deduce from this that between points e and a (the $N_{\text{CH}_3\text{OH}} = 0$ line), we have only the WGS reaction taking place until all the water is used up, because $\epsilon_1 = 0$ and $\epsilon_2 = 1/2$. Between points a and b (the water-limiting line), some methanol production takes place. At b where $\epsilon_1 = 1/2$ and $\epsilon_2 = 1/2$, the water and the carbon monoxide (CO) appear to have been completely consumed in the synthesis reaction process, because at this point, $N_{\text{H}_2\text{O}} = 0$ and $N_{\text{CO}} = 0$. And there seems to be a characteristic change in the behaviour of the reactants after this point, making the ΔG more positive. Between points b and c (the CO limiting line), there is further methanol synthesis through CO_2 hydrogenation, and the system starts producing CH_3OH and H_2O under the process conditions mentioned above, as is seen from the result at point c. At point c, where $\epsilon_1 = 1/3$ and $\epsilon_2 = -1/3$, maximum production of methanol is expected, and the equilibrium system starts to operate in the reverse direction (the RWGS), under the process conditions mentioned producing water and CO, as indicated by the negative sign ϵ_2 . At point d, where $\epsilon_1 = 1$ and $\epsilon_2 = -1$, the production of methanol runs along side the RWGS reaction producing water and CO. At point e, where $\epsilon_1 = 0$ and $\epsilon_2 = -1$, there is no production of methanol as only the RWGS reaction occurs.

Looking at Figure 16 below, we can deduce that if one started the process at the feed and ended at point a, the apparent overall reaction would be, $1/2\text{CO} + 1/2\text{H}_2\text{O} \leftrightarrow 1/2\text{CO}_2 + 1/2\text{H}_2$. If the reaction were to end at point b following the path of the arrow, then the overall reaction would be $1\text{CO} + 1/2\text{H}_2 + 1/2\text{H}_2\text{O} \rightarrow 1/2\text{CO}_2 + 1/2\text{CH}_3\text{OH}$. However, if the reaction proceeded to point c, then the overall reaction would be $1\text{CO} + 3\text{H}_2 + 1/3\text{CO}_2 \rightarrow 1/3\text{CH}_3\text{OH} + 1/3\text{H}_2\text{O}$. This can be done under the process conditions described

above only if some work in the form of pressure has been added to the system to counteract the increase in G.

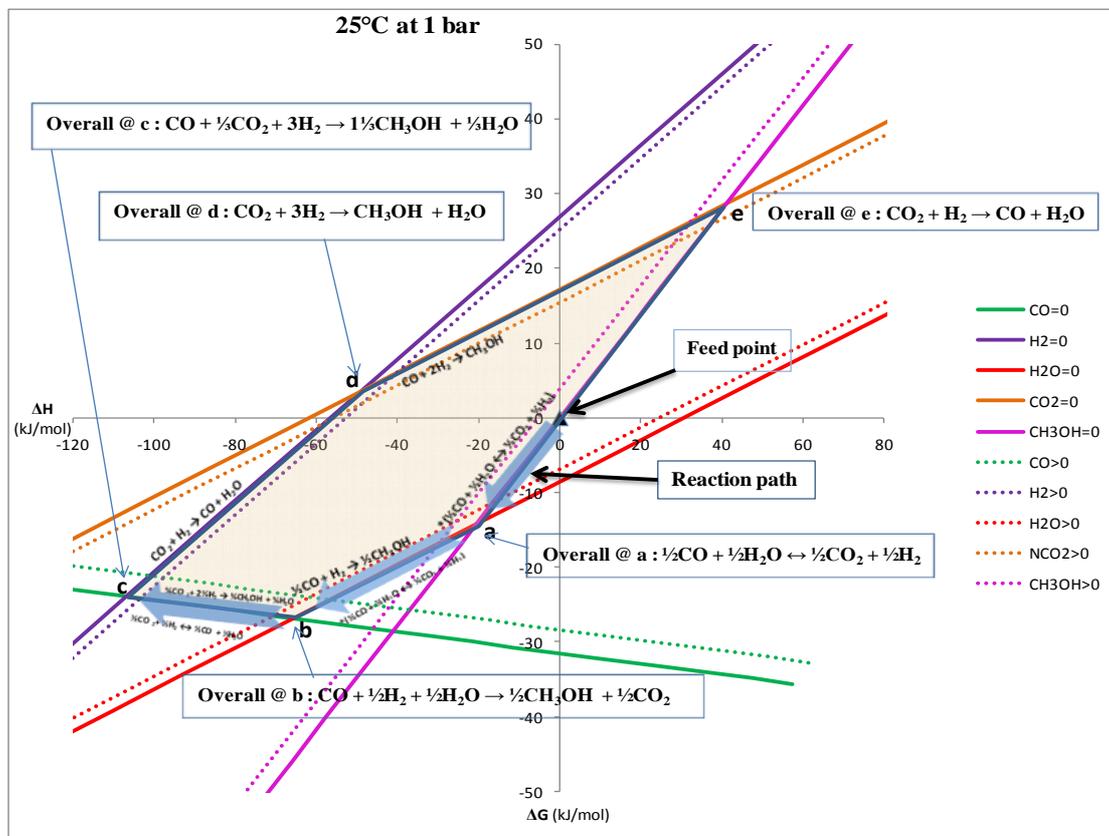


Figure 16: Representation of a chemical process using the G–H plot for two reactions, methanol synthesis and WGS, at 25°C and 1 bar, using a feed consisting of CO (1 mol), CO₂ (1 mol), H₂ (3 mols) and H₂O (0.5 mol), showing the pathways and expected reactions.

4.6 THE REACTOR'S ATTAINABLE REGION

However, since it is a general requirement that the ΔG of all the reactions (excluding the mixing) occurring across the reactor should be less than, or equal to, zero ($\Delta G \leq 0$), then its AR for the given feed can be represented as shown in Figure 17.

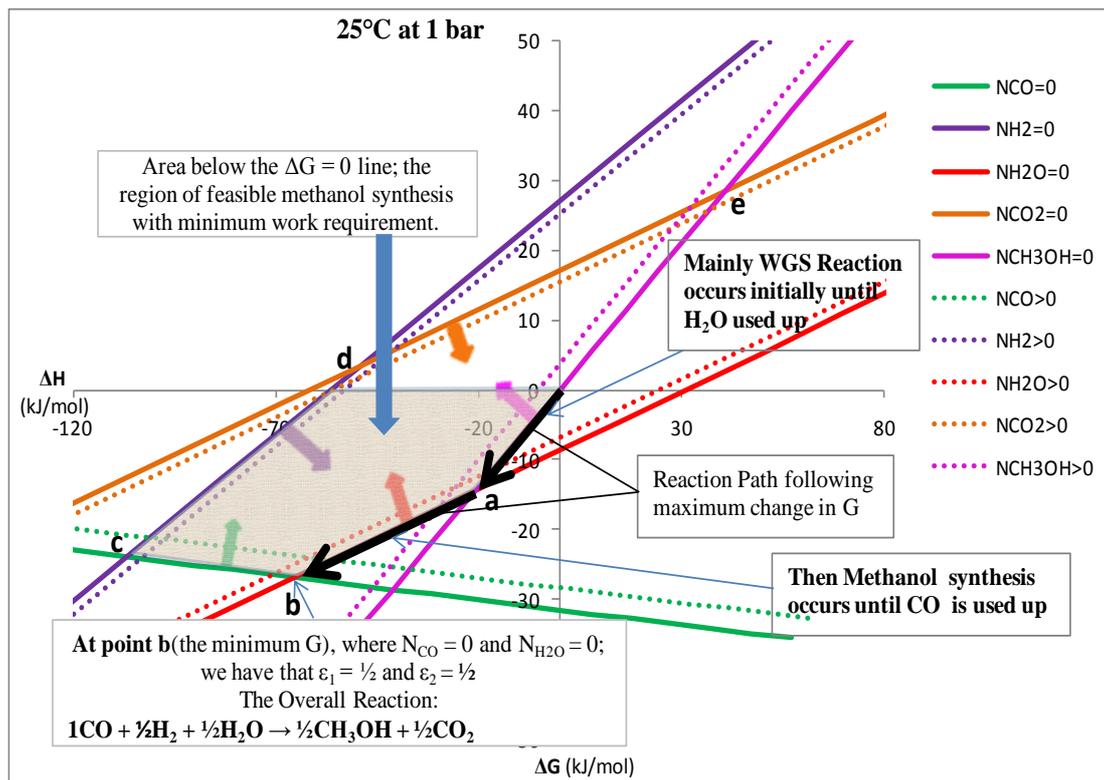


Figure 17: Plot of a reactor's AR for methanol synthesis in G–H space at 25 C and 1 bar, using a feed consisting of CO (1 mol), CO₂ (1 mol), H₂ (3 mols) and H₂O (0.5 mol).

The assumption is that the reaction path will follow the maximum change in G, since a large area of negative Gibbs free energy will point to the relative stability of intermediates, as discussed in the case of Solvay clusters, (May and Rudd, 1976). The overall reaction at point b (with a value of -26.7114 kJ/mol as read from Figure 17) will be more thermodynamically stable, and yield the maximum possible conversion under the given process conditions. It can also be seen from Figure 17 that the reactor's AR is part of the mass balance region. The synthesis reaction starting from the feed point at origin 0, would be expected to go through point a and stop at point b, with an overall reaction of $1CO + \frac{1}{2}H_2 + \frac{1}{2}H_2O \rightarrow \frac{1}{2}CO_2 + \frac{1}{2}CH_3OH$, at the mentioned process condition. The gas composition at this stage would be $1\frac{1}{2}$ moles

CO₂, ½ moles CH₃OH and 3 moles H₂. Hence, this reaction would be the most likely to occur of all the possibilities obtained in the reactor under the process conditions.

From the above, one can deduce what the reaction pathway will be, and predict its boundary in terms of the likely limiting extents of reaction. This in turn helps us to find the reactor's AR, and to see the results of changes in the process feed and operating conditions.

4.7 EFFECT OF CHANGE IN OPERATING CONDITIONS AS SHOWN ON THE G–H SPACE FOR TWO REACTIONS

A G–H plot for the combined methanol synthesis and WGS reactions, can be drawn up for any given temperature and pressure. The range of computed ΔH and ΔG values that result from the use of different pressure values for the ranges of ΔH and ΔG at 25°C, 250°C and 300°C respectively are shown in Tables 3, 4 and 5 (Appendix C, D and E respectively), and their effect on the extent of reactions ϵ_1 and ϵ_2 with respect to the chemical species under consideration.

4.7.1 Effect of Change in Operating Pressure for Two Reactions

From the Gibbs energy–pressure relationship, equilibrium calculations and the results presented in Table 3, we can confirm that the WGS/equilibrium is insensitive to the effect of operating pressure at a constant temperature, as predicted by Le Chatelier's principle. This deviation is revealed in the different values of ΔH and ΔG for the disparate species involved in the reaction. However, the operating pressure of the system can be found to have a significant effect on the ΔG of reaction 1, for the methanol synthesis. It is not surprising, therefore, that different ΔG values were obtained when we were taking the mass balance for each of the chemical species (as

shown in Table 3). Each of the results for pressure variation at constant temperature (25°C) is discussed below.

Figure 18 was obtained when we increased the pressure to about 20 bars.

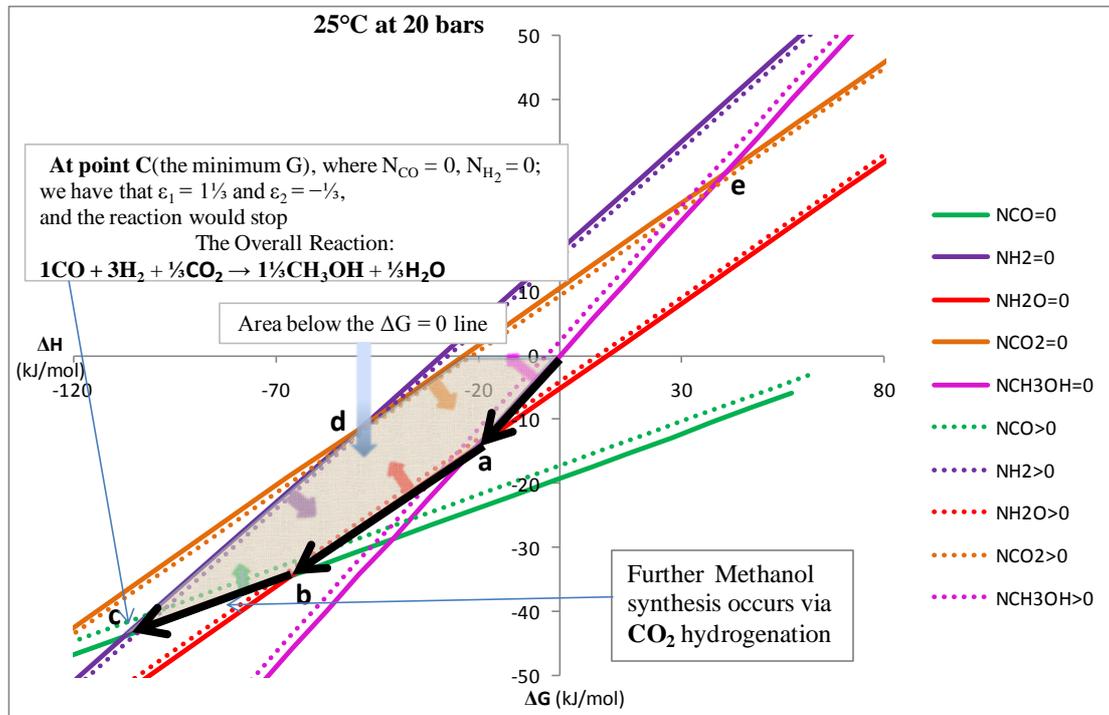


Figure 18: G–H plot for methanol synthesis and WGS reactions at 25°C and 20 bars, using a feed consisting of CO (1 mol), CO₂ (1 mol), H₂ (3 mols) and H₂O (0.5 mol).

From the above Figure, one can see the pentagon/region marked by a, b, c, d and e. (This area represents the mass balance as well as the AR, where there is a feasible reaction.) The most notable feature of the pentagon is that it seems to have been reduced in size, but the area below the $\Delta G = 0$ line (the reactor's AR) has increased in ratio as compared with a corresponding decrease in the mass balance region. However, the minimum Gibbs free energy is at point c (– 43.3557 kJ/mol, as read from Figure 18), with an overall reaction of $1CO + 3H_2 + \frac{1}{3}CO_2 \rightarrow 1\frac{1}{3}CH_3OH + \frac{1}{3}H_2O$. The gas composition at point c would be $\frac{2}{3}$ moles CO₂, $\frac{1}{3}$ moles CH₃OH and $\frac{1}{3}$ moles H₂O. This gives maximum methanol production, because further methanol synthesis occurs as a result of CO₂ hydrogenation. This is in marked contrast to the

case at 1 bar, where the synthesis reaction would be expected to stop at point b, with a large quantity of the feed having been converted to CO_2 rather than the desired product, methanol (CH_3OH), and leaving a considerable amount of unreacted hydrogen to recycle.

When the pressure was increased to about 50 bars, the results shown in Figure 19 were obtained.

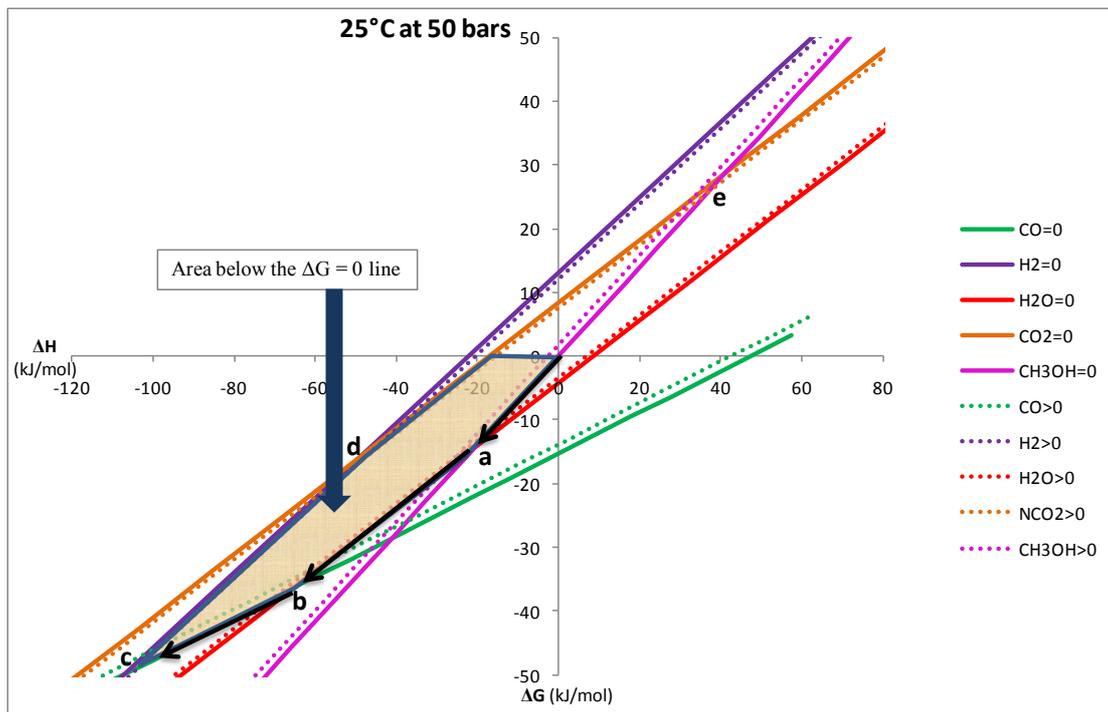


Figure 19: G–H plot for methanol synthesis and WGS reactions at 25°C and 50 bars, using a feed consisting of CO (1 mol), CO_2 (1 mol), H_2 (3 mols) and H_2O (0.5 mol).

From this Figure, we can observe that although the minimum Gibbs free energy is still at point c (giving maximum methanol production), the value at c has changed to -49.7315 kJ/mol. Here, despite the narrowing of the pentagon/region marked by a, b, c, d and e, the ratio of the area below the $\Delta G = 0$ line has grown. This implies that the reactor's AR (the area where there is a minimum work requirement) has increased correspondingly.

Raising the pressure even further, to about 90 bars, creates the plot represented in Figure 20.

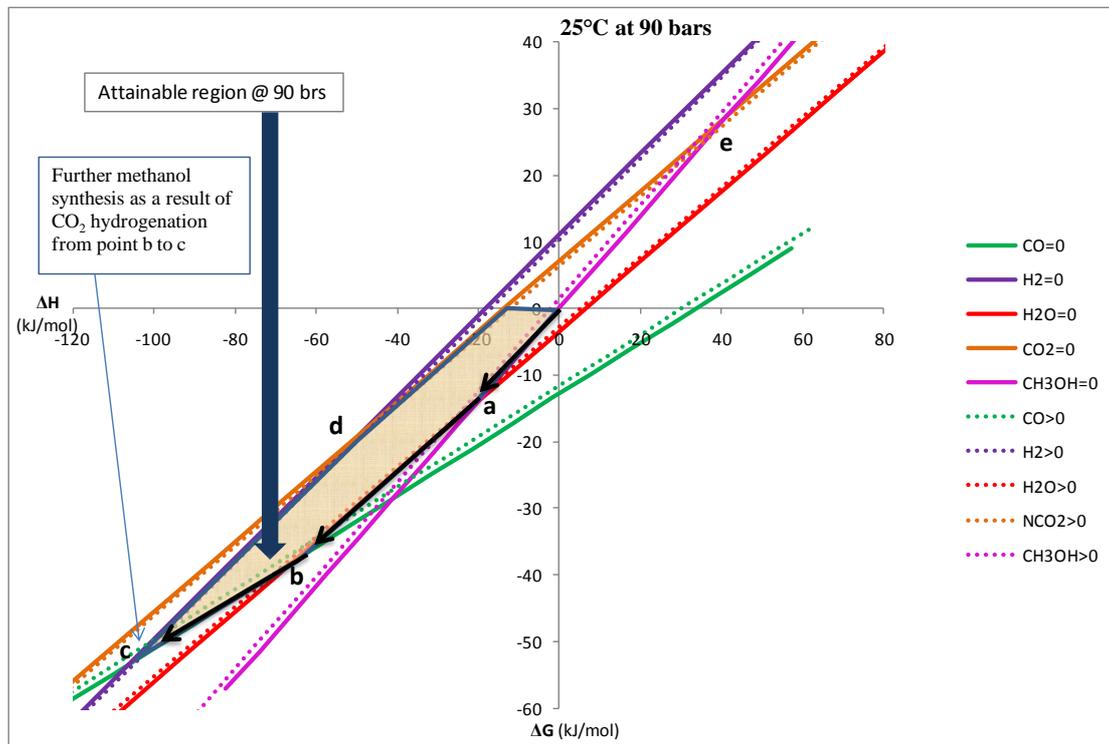


Figure 20: G–H plot for methanol synthesis and WGS reactions at 25°C and 90 bars, using a feed consisting of CO (1 mol), CO₂ (1 mol), H₂ (3 mols) and H₂O (0.5 mol).

The plot shown above demonstrates that although the minimum Gibbs free energy is still at point c, the value at c has now changed to – 53.3557 kJ/mol, with the ratio of the area below the $\Delta G = 0$ line enlarging in parallel with the increase in pressure.

Figures 18, 19 and 20 also make it clear that increasing the pressure adds to the lost work in the reactor for the reaction to be feasible, as deduced from the rising value of the minimum G.

It can be seen in Figure 21 that even though the pentagon a, b, c, d and e has shrunk in size, the ratio of the area below the $\Delta G = 0$ line continually expands with the rise in pressure, leading to a further methanol synthesis as a result of CO₂ hydrogenation at

higher pressures. This is in agreement with Le Chatelier's principle that higher pressure will push systems towards making products.

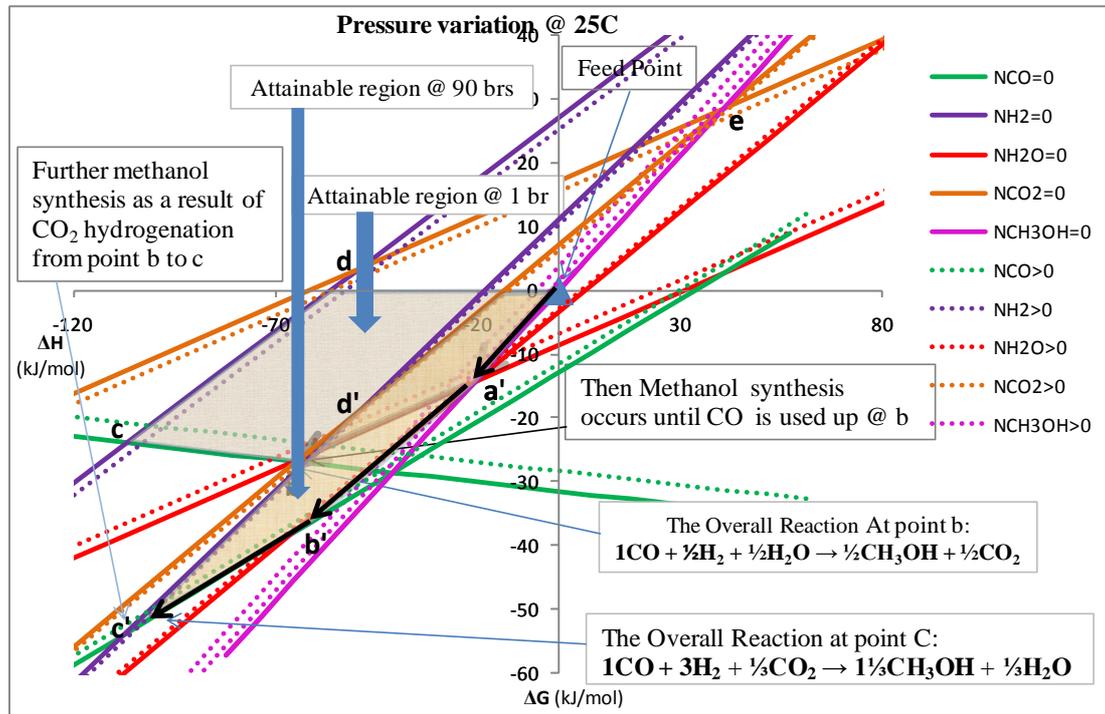


Figure 21: Effect of pressure variations at 25°C on the G–H plot for methanol synthesis and WGS reactions, using a feed consisting of CO (1 mol), CO₂ (1 mol), H₂ (3 mols) and H₂O (0.5 mol).

As seen on Figure 20, the minimum Gibbs free energy changes from -26.7114 kJ/mol at point b to -53.3557 kJ/mol at point c'. At point b we have $\epsilon_1 = \frac{1}{2}$ and $\epsilon_2 = \frac{1}{2}$, and the overall equation will be; $\text{CO} + \text{H}_2 + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{CH}_3\text{OH} + \frac{1}{2}\text{CO}_2 + \frac{1}{2}\text{H}_2$, while at point c' we have $\epsilon_1 = \frac{1}{3}$ ($\frac{4}{3}$) and $\epsilon_2 = -\frac{1}{3}$, and the overall equation will be: $1\text{CO} + 3\text{H}_2 + \frac{1}{3}\text{CO}_2 \rightarrow 1\frac{1}{3}\text{CH}_3\text{OH} + \frac{1}{3}\text{H}_2\text{O}$. The Figure above shows that for a pressure to 90 bars, the methanol synthesis in the reactor follows the same path until the water in the system is used up. This is followed by a shift in pathway as the reaction goes through b' to C' with a further methanol synthesis from CO₂ hydrogenation occurring as a result of the increase in pressure and a corresponding expansion of the reactor's AR region.

4.7.2 Effect of Change in Operating Temperature for Two Reactions

4.7.2.1 GH domain at 250°C

Figure 22 illustrates the effect of increasing the operating temperature to 250°C at 1 bar. The ΔH and ΔG of reactions 1 and 2, as calculated from the Aspen property values given in Table 1, and using Equations 26 and 27 respectively, become:

$$\Delta H_{(1)} = \Delta H_f^0(\text{CH}_3\text{OH}) - [\Delta H_f^0(\text{CO}) + 2\Delta H_f^0(\text{H}_2)]$$

$$\Delta G_{(1)} = \Delta G_f^0(\text{CH}_3\text{OH}) - [\Delta G_f^0(\text{CO}) + 2\Delta G_f^0(\text{H}_2)]$$

thus $\Delta H_{\text{reaction (1)}} = -98.2 \text{ kJ/mol}$ and $\Delta G_{\text{reaction (1)}} = 26.8 \text{ kJ/mol}$

Similarly,

$$\Delta H_{(2)} = [\Delta H_f^0(\text{CO}_2) + \Delta H_f^0(\text{H}_2)] - [\Delta H_f^0(\text{CO}) + \Delta H_f^0(\text{H}_2)]$$

$$\Delta G_{(2)} = [\Delta G_f^0(\text{CO}_2) + \Delta G_f^0(\text{H}_2)] - [\Delta G_f^0(\text{CO}) + \Delta G_f^0(\text{H}_2)]$$

therefore $\Delta H_{\text{reaction (2)}} = -39.5 \text{ kJ/mol}$ and $\Delta G_{\text{reaction (2)}} = -19.6 \text{ kJ/mol}$

From the computed range of ΔH and ΔG values, one can plot the graph of ΔG against ΔH for the process conditions detailed below.

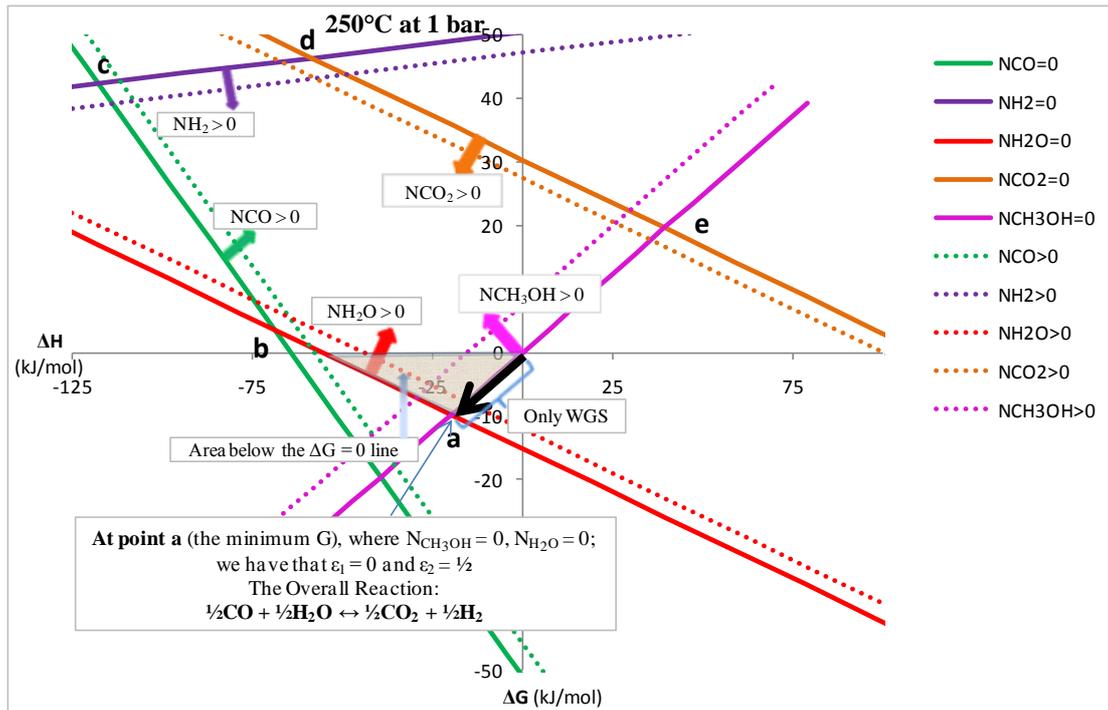


Figure 22: G–H plot for methanol synthesis and WGS reactions at 250°C and 1 bar, using a feed consisting of CO (1 mol), CO₂ (1 mol), H₂ (3 mols) and H₂O (0.5 mol).

As can be seen in the Figure, with an increase in the temperature, the region marked by points a, b, c, d, and e grows larger and becomes more positive. This is the AR mass balance region, which satisfies the conditions required to optimize the process in a steady state. However, there will not be any production of methanol under the above process conditions because the minimum Gibbs free energy, ΔG , is at point a (–10 kJ/mol as read from Figure 22), where $N_{\text{CH}_3\text{OH}} = 0$ and $N_{\text{H}_2\text{O}} = 0$. Because the extent of reaction 1, ϵ_1 , as deduced from Equation 48, equals zero ($\epsilon_1 = 0$), only the WGS reaction will be feasible within the AR. Also, we can note that although the attainable mass balance region increased with the rise in temperature, the reactor’s AR reduced considerably at the higher temperature because more of the mass balance attainable region had moved into positive ΔG space.

4.7.2.1.1 Effect of Increasing Operating Pressure on the System at 250°C

Since the effect of increasing or decreasing the operating pressure at a constant temperature on the WGS equilibrium is negligible, a rise in pressure will affect only the ΔG of reaction 1. Thus, taking the mass balance for each of the chemical species will give us different ΔG values for a given pressure. The results obtained are presented in Table 4 (Appendix D). Each of the results of pressure variation at constant temperature (250°C) is discussed below.

If the pressure is increased to about 50 bars, we obtain the plot shown in Figure 23.

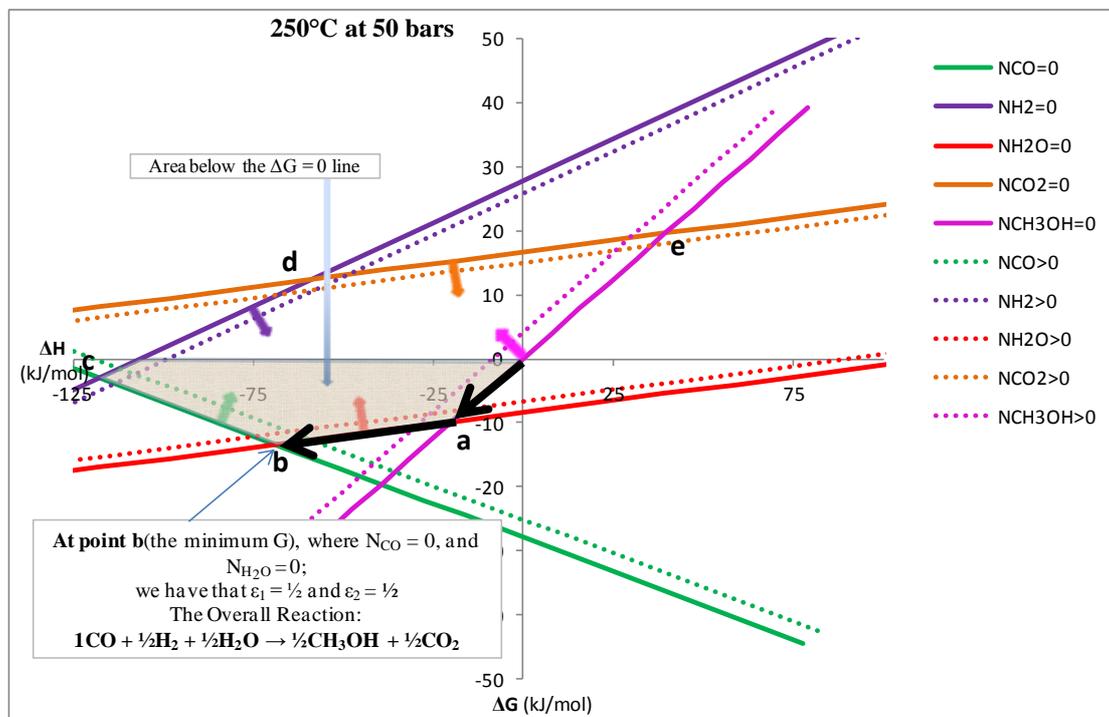


Figure 23: G–H plot for methanol synthesis and WGS reactions at 250°C and 50 bars, using a feed consisting of CO (1 mol), CO₂ (1 mol), H₂ (3 mols) and H₂O (0.5 mol).

From the above, we can see that the minimum Gibbs free energy has shifted to point b (– 13.37 kJ/mol), and methanol production is expected. This leads to the inference

that raising the pressure at higher temperatures is another way to make the reaction feasible. Also, the area below the $\Delta G = 0$ line has become larger.

Increasing the pressure further still, to 90 bars, results in the plot shown below.

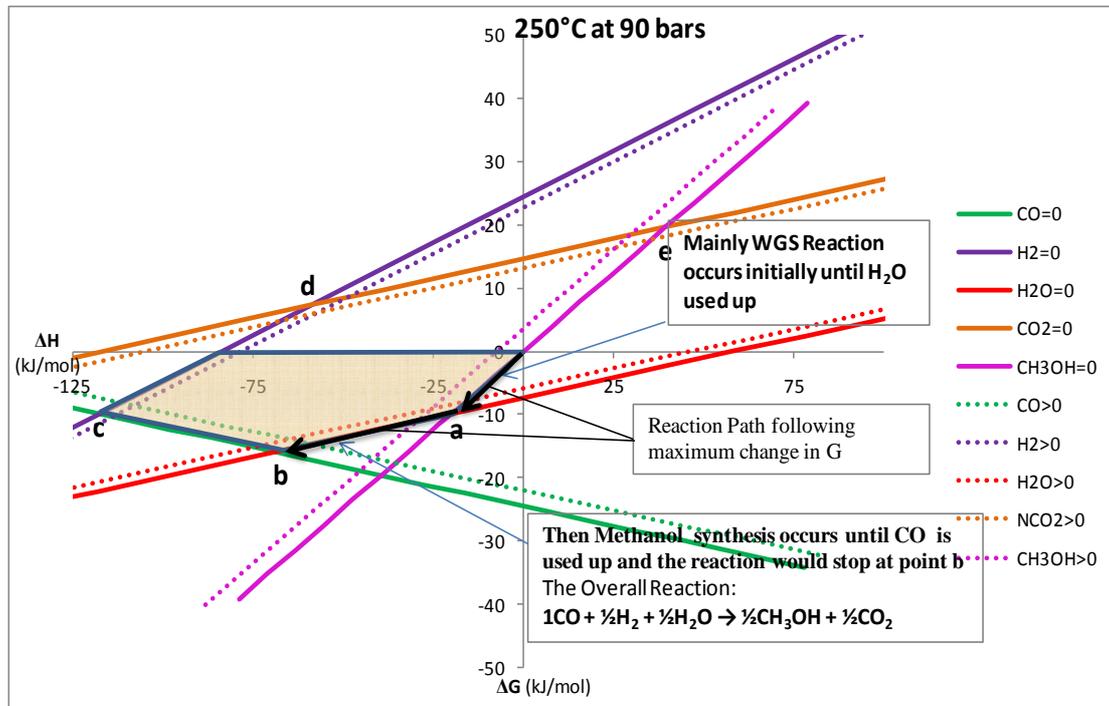


Figure 24: G–H plot for methanol synthesis and WGS reactions at 250°C and 90 bars, using a feed consisting of CO (1 mol), CO₂ (1 mol), H₂ (3 mols) and H₂O (0.5 mol).

From Figure 24, it can be seen that the minimum Gibbs free energy is still at point b. The value at b has changed to –15.62 kJ/mol, but there is no indication that it will shift to point c, because the free energy G becomes more positive.

4.7.2.2 GH domain at 300°C

Figure 25 charts the effect of raising the operating temperature to 300°C at 1 bar. The ΔH and ΔG of reactions 1 and 2, as calculated from the Aspen property values in Table 1, and using Equations 26 and 27 respectively, become:

$$\Delta H_{(1)} = \Delta H_f^0(\text{CH}_3\text{OH}) - [\Delta H_f^0(\text{CO}) + 2\Delta H_f^0(\text{H}_2)]$$

$$\Delta G_{(1)} = \Delta G_f^0(\text{CH}_3\text{OH}) - [\Delta G_f^0(\text{CO}) + 2\Delta G_f^0(\text{H}_2)]$$

thus $\Delta H_{\text{reaction}(1)} = -99.5 \text{ kJ/mol}$ and $\Delta G_{\text{reaction}(1)} = 38.8 \text{ kJ/mol}$.

Similarly,

$$\Delta H_{(2)} = [\Delta H_f^0(\text{CO}_2) + \Delta H_f^0(\text{H}_2)] - [\Delta H_f^0(\text{CO}) + \Delta H_f^0(\text{H}_2)]$$

$$\Delta G_{(2)} = [\Delta G_f^0(\text{CO}_2) + \Delta G_f^0(\text{H}_2)] - [\Delta G_f^0(\text{CO}) + \Delta G_f^0(\text{H}_2)]$$

therefore; $\Delta H_{\text{reaction}(2)} = -39.1 \text{ kJ/mol}$ and $\Delta G_{\text{reaction}(2)} = -17.7 \text{ kJ/mol}$.

From the computed range of ΔH and ΔG values, one can plot the graph of ΔG against ΔH for 300°C and 1 bar. As shown in Figure 25, the region marked by a, b, c, d and e is the mass balance AR, where a feasible reaction can take place.

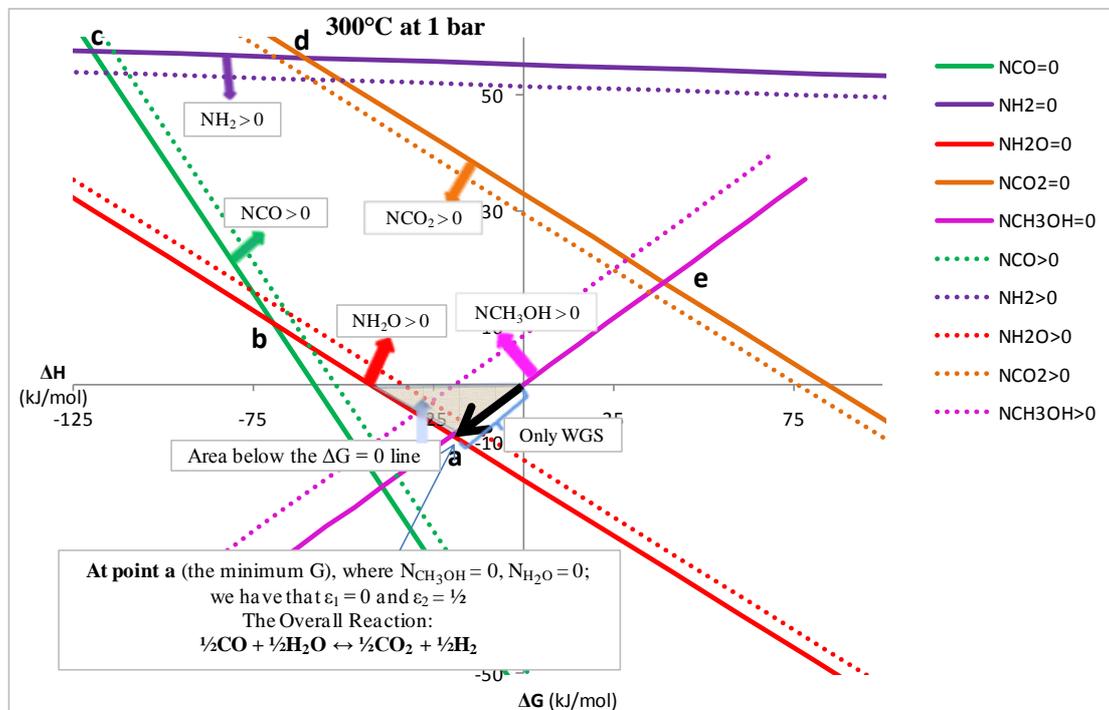


Figure 25: G–H plot for methanol synthesis and WGS reactions at 300°C and 1 bar, using a feed consisting of CO (1 mol), CO_2 (1 mol), H_2 (3 mols) and H_2O (0.5 mol).

The plot in Figure 25 shows that elevating the temperature of the system to 300°C at 1 bar pushes the pentagon marked by a, b, c, d, and e closer to the positive axis of the Gibbs free energy. Although the region marked by points a, b, c, d, and e increased, no methanol will be produced, because of the minimum Gibbs free energy. The ΔG (-8.99 kJ/mol) is at point a, where $N_{\text{CH}_3\text{OH}} = 0$ and $N_{\text{H}_2\text{O}} = 0$, and the extent of reaction one, ϵ_1 , as deduced from Equation 48, equals zero.

4.7.2.2.1 *Effect of Increasing Operating Pressure of the System at 300C*

Since raising or lowering the operating pressure at a constant temperature does not affect the WGS/equilibrium (as predicted by Le Chatelier's principle), we expect that increasing the operating pressure of the process will affect only the ΔG of reaction 1. Thus, taking the mass balance for each of the chemical species will give us different ΔG values for each pressure as presented in Table 5, where each of the results of pressure variation at constant temperature (300°C) is represented.

However, when the pressure was increased to about 50 bars, the G-H plot given in Figure 26 was obtained.

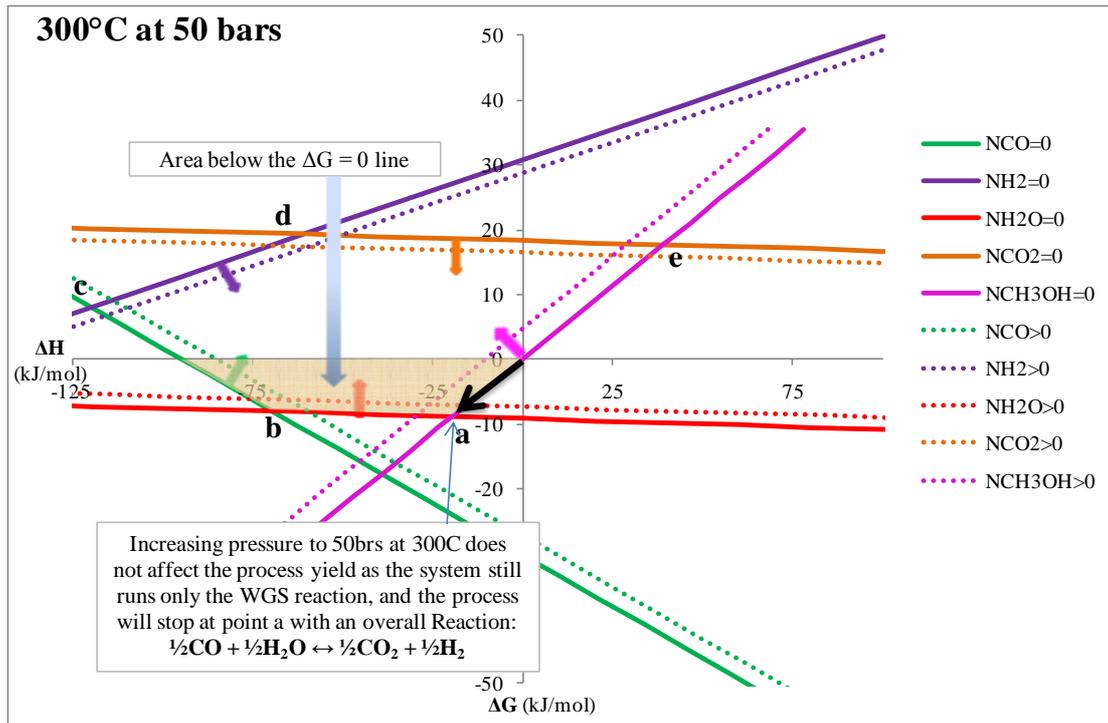


Figure 26: G–H plot for methanol synthesis and WGS reactions at 300°C and 50 bars, using a feed consisting of CO (1 mol), CO₂ (1 mol), H₂ (3 mols) and H₂O (0.5 mol).

We can see in Figure 26 that while the minimum Gibbs free energy remains at point a (– 8.99 kJ/mol), which appears to lie almost on the H₂O limiting line (N_{H₂O} = 0), it has the tendency to shift to point b with the increase in pressure. Although the area below the ΔG = 0 line has become larger, the escalation in pressure to 50 bars at 300°C does not affect the process yield, as the system continues to run only the WGS reaction. The process will stop at point a, in contrast to its response at 250°C, where the process proceeds to point b at 50 bars.

When we raise the pressure further still, to 90 bars, the results are as shown in Figure 27.

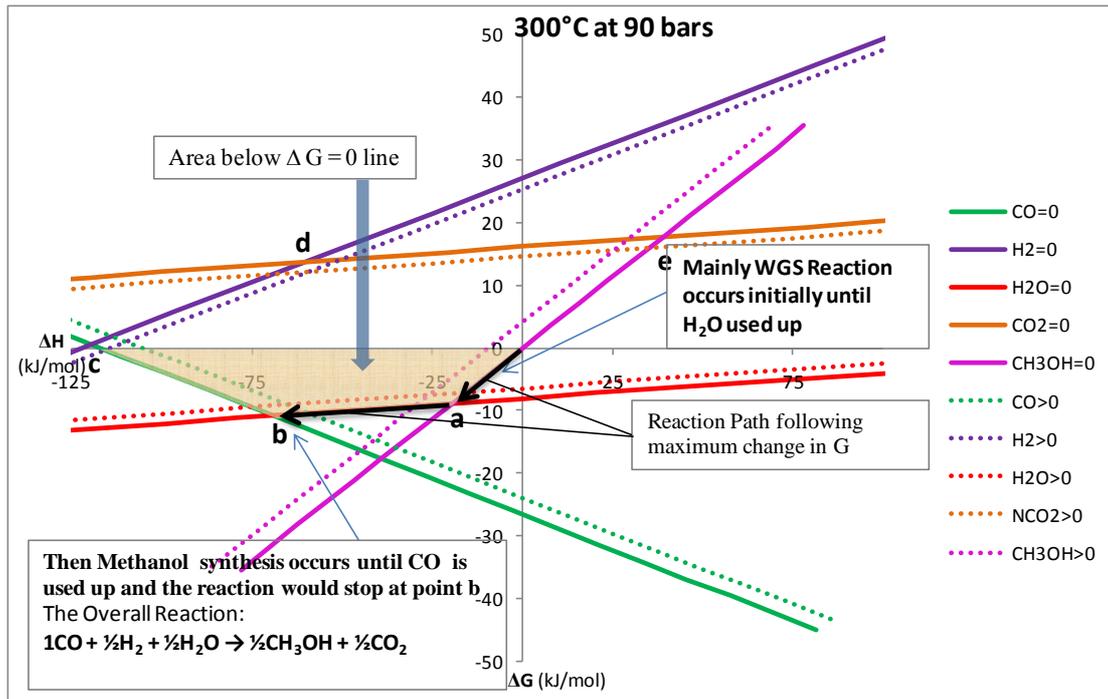


Figure 27: G–H plot for methanol synthesis and WGS reactions at 300°C and 90 bars, using a feed consisting of CO (1 mol), CO₂ (1 mol), H₂ (3 mols) and H₂O (0.5 mol).

What we can elicit from this Figure is that the minimum Gibbs free energy is now at point b, as expected, the value has changed to –11.12 kJ/mol, and methanol production can be expected. There is no indication of a shift from point b to c, because the pressure has not been increased sufficiently to cause one.

4.8 ANALYSIS OF CURRENT INDUSTRIAL PROCESSES FOR THE SYNTHESIS OF METHANOL

In the mid-1960s, ICI developed a low-pressure process that could operate at 35–55 bars, at a temperature range of 200–300°C. (Tijm *et al.*, 2001) This revolutionized the industrial production of methanol from synthesis gas. (Kung, 1980; Klier, 1982) Today, methanol is commercially produced in industries from CO/CO₂/H₂ feed (which consists of 30% CO, 60% H₂ and roughly 8% CO₂), using the ICI or Lurgi

processes that operate at lower temperatures and pressures (250°C, 50 bars), over a copper-zinc-based oxide catalyst CuO/ZnO/Al₂O₃ catalyst. (Nakamura 1996)

Using this feed (represented by 1 mol CO, 2 mols H₂ and 0.267 mols CO₂), and performing a mass balance for each of the different chemical species at 250°C and 50 bars, an analysis of the current industrial process was carried out. The GH plot was developed to represent what occurs when ϵ_1 and ϵ_2 are eliminated and the resulting N_i for each chemical species represented in the combined process is evaluated in terms of the ΔH and ΔG for the given feed, to ascertain the reactant/species performance. The extent plot resulting from the mass balance calculations for the different chemical species (N_i) for the given feed is shown in Figure 28, and the resulting G–H plot, is shown in Figure 29 below. This is a theoretical depiction of the process conditions actually in use in the industry for the methanol synthesis and WGS reactions. (The ΔG of mixing, which might cause the limiting line to become convex or concave has been excluded in this study.)

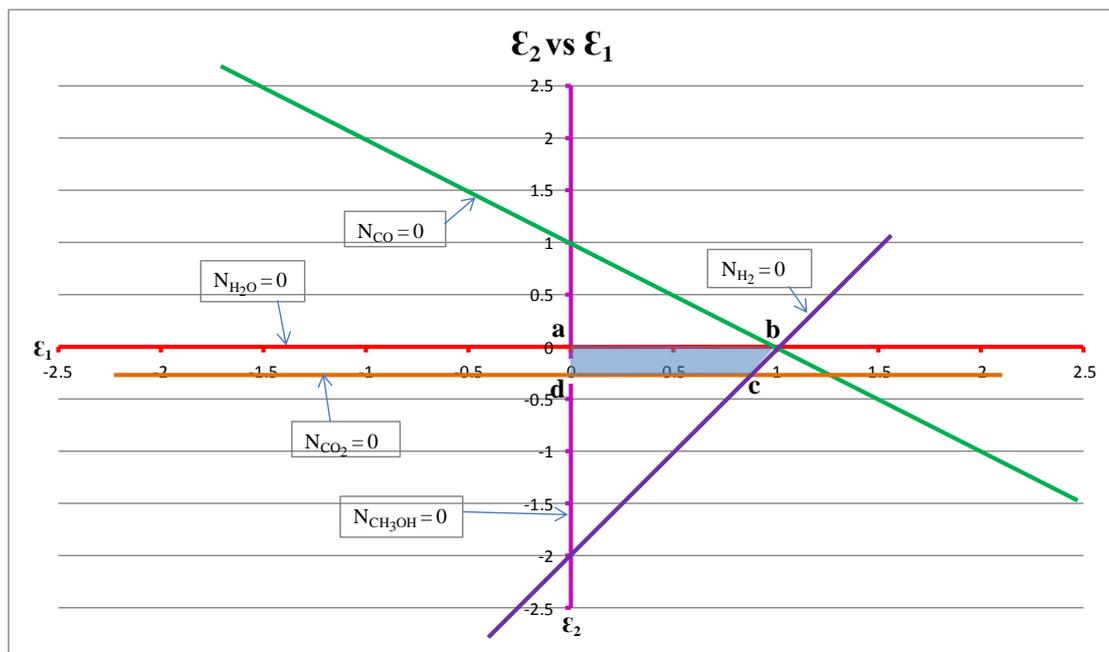


Figure 28: Extent plot for two reactions using a feed consisting of CO (1 mol), H₂ (2 mols) and CO₂ (0.267 mol).

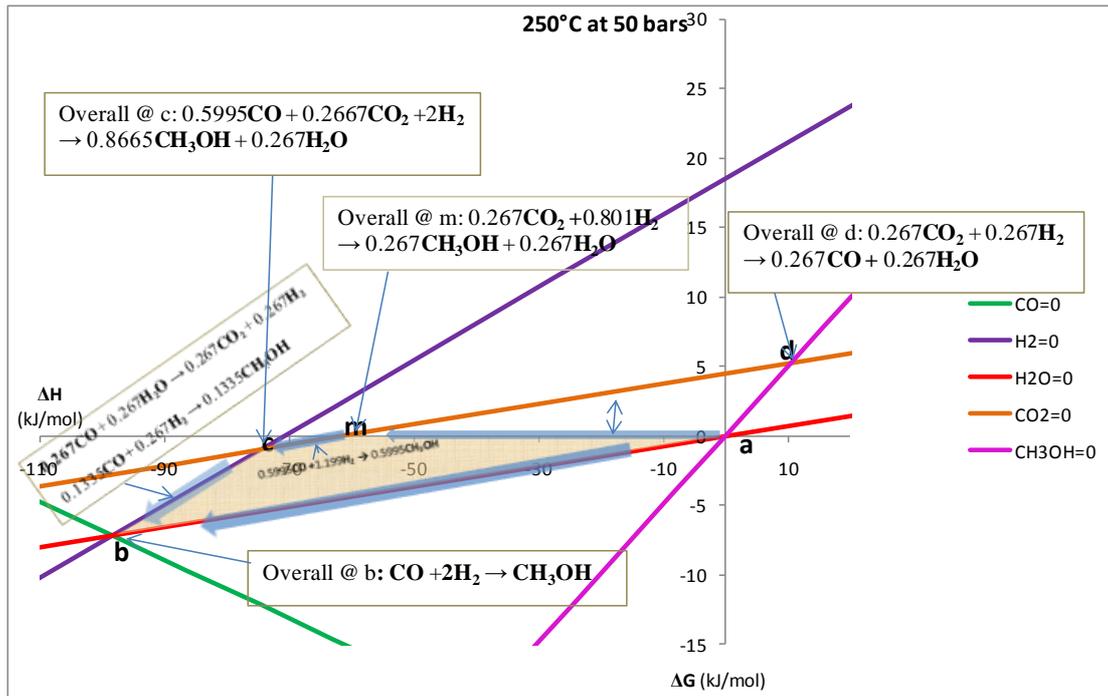


Figure 29: Representation of a chemical process using the G–H plot for two reactions, methanol synthesis and WGS, at 250°C and 50 bars, using a feed consisting of CO (1 mol), H₂ (2 mols) and CO₂ (0.267 mol).

As indicated in Figure 29, though there are other pathways within the region, only two likely paths at the mentioned process condition can be accessed and explained thermodynamically for the synthesis of methanol. Thus depending on the activity of the catalyst that is used, a desired pathway can be chosen. The **first** is the path going through points m, c to b. Hence, if one started at the feed point and followed this path, then the reactions likely to occur in the reactor during the synthesis would follow the following sequence.

- I. Between points a and m, there would be methanol synthesis via CO₂ hydrogenation, giving an overall reaction of $0.267\text{CO}_2 + 0.801\text{H}_2 \rightarrow 0.267\text{CH}_3\text{OH} + 0.267\text{H}_2\text{O}$ at point m. The gas composition would be 30% CO (1 mol); 8% CH₃OH (0.267); 8% H₂O (0.267 mol); and 35.97% H₂ (1.199 mol).

II. Between points m and c, the reaction would be $0.5995\text{CO} + 1.199\text{H}_2 \rightarrow 0.5995\text{CH}_3\text{OH}$, and the overall reaction at point c would be an exothermic equilibrium synthesis of methanol from synthesis via the hydrogenation of carbon oxides $0.5995\text{CO} + 0.2667\text{CO}_2 + 2\text{H}_2 \rightarrow 0.8665\text{CH}_3\text{OH} + 0.267\text{H}_2\text{O}$. The gas composition would be 12.015% CO (0.4005 mol); 8% H₂O (0.267 mol); and 25.995% CH₃OH (0.8665 mol).

III. Finally, the stage between points c and b is characterised by two reactions:

a. Some CO is converted by the WGS reaction to CO₂ and hydrogen, to obtain the correct ratio of H₂/CO, with the CO₂ being rejected from the system. $0.267\text{CO} + 0.267\text{H}_2\text{O} \rightarrow 0.267\text{CO}_2 + 0.267\text{H}_2$

b. After the water gas shift reaction, the ratio of H₂ to CO achieved is 2:1, and the remaining syngas composition is then converted into the desired methanol product in the methanol synthesis reactor;



Hence, there will be some significant level of CO₂ hydrogenation through path a – m – c – b depending on the activity of the catalyst that is used, but not on the direct path from a – b.

The **second** path is the direct methanol synthesis route following CO hydrogenation from the feed point a to the product point b. It is generally believed that this would be the major reaction that takes place in the methanol synthesis reactor, since the reaction would tend to follow the path of minimal change in G.

The overall gas composition at b would then be 1mol CH₃OH (which would represent 100% conversion of the CO feed) and 0.267mol of CO₂, which is also obtained from the direct route from point a to point b. Thus the amount of CO₂ rejected from the

system is low compared with that of the methanol recovered, (Holiastos and Manousiouthakis, 1998) and since this is the same amount as was originally introduced, it can be recycled as feed. (Grue and Bendtsen, 2003) As a result, there will be a net zero CO₂ effluent from the system. As can be seen in Figure 29, although the system will need to expel a great deal of heat, the work lost which corresponds to the G of the reacting system will be minimal.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

Chemical processes use up a large proportion of the world's natural resources, because they consume raw materials in manufacturing various products and require energy to drive the processes. This burden on the environment can be ameliorated if chemical processes are made more efficient.

The research described in this dissertation aimed at developing a technique to assess the achievable regions of processes taking place within chemical reactors. Since there are often many competing reactions occurring in the reactor during the same product run, we developed a simple graphical technique to show the interaction between these reactions in terms of mass balances and thermodynamic analysis. This made it possible to identify which of a wide range of reactions that could be taking place in the reactor are likely to dominate in a particular chemical process. The technique does this by using the thermodynamic properties of the reactants and products to assess the degree of transformation achievable in the separate co-existing reactions, and to ascertain the attainable regions in a particular chemical process.

The main objective of this project was to find a theoretical means to develop energy-efficient processes. This was done in two stages. The first was the evaluation of a chemical process, in this case the synthesis of methanol from syngas. The second was the use of the information obtained to outline a specification for the design of a better process that achieves optimal product yield while emphasizing the reduction of materials, energy consumption and carbon dioxide emissions to the environment.

Although a number of scientists have worked in the area of methanol synthesis, most have focused on measuring synthesis rates when different feed compositions are used. The work described here contributes to the body of research by providing insight into the reactions likely to be achievable in the reactor during the course of the synthesis under different process conditions. The approach also provides useful information for evaluating an operating process because it can help the engineer or designer to identify sources of inefficiency within a process, which will affect the performance target. Design decisions that aim to develop new, more environmentally friendly and cost-effective processes can then be incorporated at an early stage. Most important is that this unique method allows engineers to gain greater insight into processes, establish systematic and realistic performance targets and improve process yields. This can be achieved while also meeting the requirement to conserve raw material sources and reduce the negative environmental impact caused by the chemical industry.

This work introduces a graphical technique used to identify the Attainable Region (AR) for chemical processes in a reactor. In this case it refers to a thermodynamically achievable region in which the reactor can function without violating thermodynamic boundaries. The approach is to find the AR and interpret its boundary in terms of the likely limiting extents of reaction through mass balance calculations. The technique is always two-dimensional, allowing for easy and rapid interpretation of the results, and one can readily see the result of changing the process feed and operating conditions. Thus one can readily see how reaction path analysis can become a crucial preliminary tool in identifying the most desirable reaction routes when designing a process. The AR should contain the feed point, it should be zero at the intersection of the chemical

species and it should represent all possible combinations of the species taking part in the reactions being considered.

5.1 SUMMARY OF RESULTS

We found that variation of the temperature of the operating system affected both the ΔH and the ΔG of the reaction. In the case of single reaction considered in this study, the most favourable conditions were obtained at lower temperatures. When the results were plotted in the GH domain, the positive slope of the reaction rose with the temperature increase, making G more positive. This indicated that the higher temperatures caused an unfavourable forward reaction. The reason is that the thermodynamics of the reaction remain at the feed point because its ΔG is too low unless work is added to the system to make the reaction feasible. (This is achieved through mixing, which generally adds a very small quantity of work.)

At constant temperature, variations in the form of increases in pressure were found to have a significant effect on the G of the reaction only while the ΔH remained unchanged assuming ideal conditions. Raising the pressure increased the negative slope of the line representing the ΔG of the reaction, indicating that the reaction had become more spontaneous and forward (that is, tending towards product-forming). At higher temperatures the reaction was not feasible thermodynamically at 1 bar, but at increased pressure the reaction could again become favourable and thermodynamically feasible. This was shown on the GH plot by a change in the slope from positive through zero to negative. The variation in temperature and pressure rotated the mass balance line because the length in the H direction remained more constant than the G length. As already noted, at very high temperatures the system requires much greater work input to make the reaction feasible.

However, if the GH space for the combined methanol synthesis process is plotted, a polygon with the same number of sides as in the extent plot is generated as a result of the mass balance calculations on the different chemical species (N_i). The region bounded by the lines will represent all possible combinations of the species taking part in the reactions, in this way defining the mass balance attainable boundaries (referred to as the mass balance Attainable Region—AR) that establish the conditions for a feasible synthesis process that will not violate thermodynamic relations. Although the reactors attainable region is part of the mass balance region; the mass balance attainable region increases with temperature becoming more positive because ΔG is positive hence the reaction is less favourable, while increase in pressure at constant temperature decreases the region and makes ΔG less negative, thereby making the reaction more favourable and increasing the yield of methanol, for the methanol synthesis process. However, the reactors attainable region increases correspondingly with increase in pressure i.e., increasing pressure will push systems further to the products for maximum production in agreement with LeChatelier's Principle, otherwise the designer has to think of some means of adding work into the system to achieve the desired objective.

This dissertation also shows that the introduction of either water or CO_2 , or both, to the feed opens up the mass balance region, resulting in WGS activity and generating more reaction path alternatives. Therefore, the RWGS/WGS reactions also determine the routes reactions can take. Again, the change in Gibbs free energy across the reactor and the reaction pathways leading to product are interlinked.

All of these factors are useful to the engineer who is setting performance targets for chemical processes. They enable designers to find the reactor's AR, deduce the

process reaction pathways, and interpret their boundaries in terms of the likely limiting extents of reaction. The GH model makes the results of changing the process feed and operating conditions of reactions clear in an easily accessible manner that makes it an indispensable tool in the conceptual design phase of a chemical process.

5.2 RECOMMENDATIONS AND FURTHER WORK

This thermodynamic analysis has shed light on the reaction pathway of synthesizing methanol from syngas. It can be applied to evaluate other chemical processes in the industry, where designers are aiming to develop energy-efficient processes with reduced raw material and energy requirements that are also mindful of environmental issues. In this way, the sustainability of both industry and the biosphere can be supported.

The graphical technique demonstrated by the use of the GH plot was expanded to chart the characteristics of more than two reactions occurring in a reactor, in an effort to explain in thermodynamic terms why some reactions dominate (or are favoured) in the reactor under some process conditions. This too will aid a process designer during the conceptual design phase of a system.

Another benefit offered by this approach is that it provides a useful means of evaluating the efficiency of an actual operating process as compared with its theoretical target, because it will help to identify the major sources of inefficiency within a process. The method can be applied to the Fischer-Tropsch synthesis and other industrial processes to obtain optimal results, to identify possible means of saving energy, and devise methods of supplying or recovering energy from the processes so as to improve process reversibility and efficiency.

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APPENDIX A: Thermodynamic Data

The thermodynamic data used in this research to analyze the performance of the methanol synthesis process, was obtained/estimated from Aspen properties for each of the chemical species, at different temperatures and pressure, as shown in Table 1. The temperature ranges of 200°C - 300°C and pressure range of 1bar – 90bars were used in this study, to evaluate the performance of the methanol synthesis process at today's current process conditions.

From thermodynamics, the values of ΔH and ΔG of a reactions can be calculated from the ΔH_f^0 and ΔG_f^0 of the different species in the reaction mixture. Hence for the methanol synthesis reaction;

$$\Delta H_{(1)} = \Delta H_f^0(\text{CH}_3\text{OH}) - [\Delta H_f^0(\text{CO}) + 2\Delta H_f^0(\text{H}_2)]$$

$$\Delta G_{(1)} = \Delta G_f^0(\text{CH}_3\text{OH}) - [\Delta G_f^0(\text{CO}) + 2\Delta G_f^0(\text{H}_2)]$$

Therefore; $\Delta H_{(1)} = -90.3$ kJ/mol and $\Delta G_{(1)} = -25.1$ kJ/mol

Similarly, for the water gas shift reaction;

$$\Delta H_{(2)} = [\Delta H_f^0(\text{CO}_2) + \Delta H_f^0(\text{H}_2)] - [(\Delta H_f^0(\text{CO}) + \Delta H_f^0(\text{H}_2))]$$

$$\Delta G_{(2)} = [\Delta G_f^0(\text{CO}_2) + \Delta G_f^0(\text{H}_2)] - [(\Delta G_f^0(\text{CO}) + \Delta G_f^0(\text{H}_2))]$$

Therefore; $\Delta H_{(2)} = -41.1$ kJ/mol and $\Delta G_{(2)} = -28.6$ kJ/mol

Table 1: Thermodynamic data obtained from Aspen properties for the chemical species, at different temperatures and pressures.

TEMP (°C)	PRESS.	CO ₂ Vapor	CO Vapor	H ₂ Vapor	H ₂ O Vapor	CH ₃ OH Vapor
$\Delta H @$	(bar)	kcal/mol	kcal/mol	kcal/mol	kcal/mol	kcal/mol
25°C	1	-93.98825	-26.39964	0	-57.75628	-47.99369
200°C	1	-92.27656	-25.17385	1.217377	-56.32795	-45.87716
230°C	1	-91.95852	-24.96085	1.427364	-56.07642	-45.45556
250°C	1	-91.74329	-24.81817	1.567387	-55.90747	-45.16518
300°C	1	-91.19468	-24.45883	1.917488	-55.48051	-44.40773
350°C	1	-90.63196	-24.09542	2.267678	-55.04682	-43.60716
$\Delta G @ 1\text{bar}$						
25°C	1	-94.20145	-32.76551	-0.0077935	-54.60558	-38.77726
200°C	1	-94.73868	-36.80574	-0.3139836	-53.10863	-33.8662
230°C	1	-94.90464	-37.54987	-0.4175995	-52.9123	-33.11765
250°C	1	-95.02596	-38.05307	-0.4936828	-52.78984	-32.63289
300°C	1	-95.365	-39.33461	-0.7068904	-52.51161	-31.46987
350°C	1	-95.75257	-40.64772	-0.9506817	-52.27095	-30.37484
$\Delta G @ 20\text{bars}$						
25°C	20	-92.42774	-30.9918	1.765917	-52.83187	-37.00355
200°C	20	-91.92389	-33.99094	2.500812	-50.29383	-31.0514
230°C	20	-91.91137	-34.5566	2.575668	-49.91904	-30.12438
250°C	20	-91.91371	-34.94082	2.618566	-49.67759	-29.52065
300°C	20	-91.9553	-35.92491	2.702811	-49.10191	-28.06016
350°C	20	-92.04542	-36.94056	2.756472	-48.56379	-26.66769
$\Delta G @ 50\text{bars}$						
25°C	50	-91.88522	-30.44928	2.308434	-52.28935	-36.46103
200°C	50	-91.06294	-33.13	3.361761	-49.43288	-30.19046
230°C	50	-90.99584	-33.64106	3.491205	-49.0035	-29.20885
250°C	50	-90.96178	-33.98889	3.570495	-48.72567	-28.56872
300°C	50	-90.91239	-34.882	3.74572	-48.059	-27.01725
350°C	50	-90.91153	-35.80667	3.890362	-47.4299	-25.5338
$\Delta G @ 70\text{bars}$						
25°C	70	-91.686	-30.25006	2.507652	-52.09013	-36.26181
200°C	70	-90.74679	-32.81385	3.677911	-49.11673	-29.87431
230°C	70	-90.65964	-33.30487	3.8274	-48.66731	-28.87265
250°C	70	-90.61222	-33.63934	3.920054	-48.37611	-28.21916
300°C	70	-90.52943	-34.49904	4.128689	-47.67603	-26.63429
350°C	70	-90.49515	-35.39029	4.30674	-47.01353	-25.11742
$\Delta G @ 90\text{bars}$						
25°C	90	-91.53721	-30.10126	2.656451	-51.94133	-36.11302
200°C	90	-90.51065	-32.57771	3.914046	-48.8806	-29.63817
230°C	90	-90.40853	-33.05376	4.078508	-48.4162	-28.62154
250°C	90	-90.35114	-33.37825	4.181143	-48.11502	-27.95807
300°C	90	-90.24338	-34.21299	4.414731	-47.38998	-26.34824
350°C	90	-90.18416	-35.0793	4.617736	-46.70253	-24.80643

APPENDIX B: Mass balance calculations for the respective chemical species in two reactions using a feed of 1mol CO and 2 mol H₂ only.

The mass balance for carbon monoxide (CO) specie when both reactions are considered can be expressed from equation 31 as;

$$N_{\text{CO}} = N_{\text{CO}}^0 - \varepsilon_1 - \varepsilon_2 \geq 0$$

When $N_{\text{CO}} = 0$

$$N_{\text{CO}}^0 - \varepsilon_1 = \varepsilon_2$$

For the case where the number of moles of CO fed into the process equals 1 ($N_{\text{CO}}^0 = 1$), it follows that ε_2 will thus, compute a range of values for each ε_1 value (-2 to +2) to be from 3 to -1. Therefore, ΔH and ΔG values for the combined process, from equations 25 and 26 are then computed as;

$$\Delta H = [(-2)*(-90.3) + 3*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + (-1)*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + 3*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + (-1)*(-28.6)] \text{ kJ/mol}$$

Thus, ΔH and ΔG values for the combined process will range as, $\Delta H = 57.3 \text{ kJ/mol}$ to -139.5 kJ/mol and $\Delta G = -35.6 \text{ kJ/mol}$ to -21.86 kJ/mol .

When $N_{\text{CO}} > 0$

$$N_{\text{CO}}^0 - \varepsilon_1 > \varepsilon_2$$

Then, decreasing $\varepsilon_2 = 0$ values by 0.1 (i.e. $\varepsilon_2 = N_{\text{CO}}^0 - \varepsilon_1 - 0.1$), the ε_2 range of values for each ε_1 value can be from 2.9 to -1.1. Therefore, from equations 25 and 26 one can have that;

$$\Delta H = [(-2)*(-90.3) + 2.9*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + (-1.1)*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + 2.9*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + (-1.1)*(-28.6)] \text{ kJ/mol}$$

Hence, ΔH and ΔG for the combined process will have the range of values to be, $\Delta H = 61.41 \text{ kJ/mol to } -135.39 \text{ kJ/mol}$ and $\Delta G = -32.74 \text{ kJ/mol to } -18.74 \text{ kJ/mol}$.

The mass balance for hydrogen (H_2) specie when both reactions are considered can be expressed from equation 32 as;

$$N_{H_2} = N_{H_2}^0 - 2\varepsilon_1 + \varepsilon_2 \geq 0$$

When $N_{H_2} = 0$

$$\varepsilon_2 = 2\varepsilon_1 - N_{H_2}^0$$

Since, the moles of H_2 feed, into the process equals 2 ($N_{H_2}^0 = 2$), it follows that ε_2 values will compute a range of values for each ε_1 value (-2 to $+2$) to be from -6 to 2 .

Computing these values into equations 25 and 26, then one will have that;

$$\Delta H = [(-2)*(-90.3) + (-6)*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + 2*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + (-6)*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + 2*(-28.6)] \text{ kJ/mol}$$

Therefore, ΔH and ΔG for the combined process will have the range of values to be, $\Delta H = 427.2 \text{ kJ/mol to } -262.8 \text{ kJ/mol}$ and $\Delta G = 221.8 \text{ kJ/mol to } -107.4 \text{ kJ/mol}$.

When $N_{H_2} > 0$; then

$$\varepsilon_2 > 2\varepsilon_1 - N_{H_2}^0$$

Since, the moles of H₂ feed equals 2 (N⁰_{H₂} = 2), increasing $\epsilon_2 = 0$ values by 0.2 (i.e. $\epsilon_2 = 2\epsilon_1 - N^0_{H_2} + 0.2$), the range of values for each ϵ_1 value can be -5.8 to 2.2.

Therefore, ΔH and ΔG values as computed from equations 25 and 26 will be;

$$\Delta H = [(-2)*(-90.3) + (-5.8)*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + 2.2*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + (-5.8)*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + 2.2*(-28.6)] \text{ kJ/mol}$$

Hence, ΔH and ΔG for the combined process will have the range of values to be, $\Delta H = 418.98 \text{ kJ/mol to } -271.02 \text{ kJ/mol}$ and $\Delta G = 216.08 \text{ kJ/mol to } -113.12 \text{ kJ/mol}$.

The mass balance for water (H₂O) specie when both reactions are considered can be expressed from equation 33 as;

$$N_{H_2O} = N^0_{H_2O} - \epsilon_2 \geq 0$$

When $N_{H_2O} = 0$; then

$$\epsilon_2 = N^0_{H_2O} = 0$$

Since, the moles of H₂O feed equals 0 (N⁰_{H₂O} = 0), ϵ_2 values will be 0 for all ϵ_1 values,

ΔH and ΔG values as computed from equations 25 and 26 will then be;

$$\Delta H = [(-2)*(-90.3) + 0*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + 0*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + 0*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + 0*(-28.6)] \text{ kJ/mol}$$

Therefore, ΔH and ΔG for the combined process will have the range of values as computed to be, $\Delta H = 180.6 \text{ kJ/mol to } -180.6 \text{ kJ/mol}$ and $\Delta G = 50.2 \text{ kJ/mol to } -50.2 \text{ kJ/mol}$

When $N_{\text{H}_2\text{O}} > 0$; then

$$N_{\text{H}_2\text{O}}^0 > \varepsilon_2$$

rearranging

$$\varepsilon_2 < N_{\text{H}_2\text{O}}^0$$

Since, $N_{\text{H}_2\text{O}}^0 = 0$, decreasing $\varepsilon_2 = 0$ value by 0.1 (i.e. $\varepsilon_2 = N_{\text{H}_2\text{O}}^0 - 0.1$), then $\varepsilon_2 = -0.1$ value for all ε_1 values. Computing for ΔH and ΔG range of values from equations 25 and 26, then;

$$\Delta H = [(-2)*(-90.3) + (-0.1)*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + (-0.1)*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + (-0.1)*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + (-0.1)*(-28.6)] \text{ kJ/mol}$$

Therefore, ΔH and ΔG for the combined process will have the range of values as computed to be, $\Delta H = 184.71 \text{ kJ/mol to } -176.49 \text{ kJ/mol}$ and $\Delta G = 53.06 \text{ kJ/mol to } -47.34 \text{ kJ/mol}$.

The mass balance for carbon dioxide (CO_2) specie when both reactions are considered can be expressed from equation 34 as;

$$N_{\text{CO}_2} = N_{\text{CO}_2}^0 + \varepsilon_2 \geq 0$$

When $N_{\text{CO}_2} = 0$; then

$$\varepsilon_2 = -N_{\text{CO}_2}^0 = 0$$

Thus, ϵ_2 values will be equal to 0 for all ϵ_1 values ($\epsilon_2 = 0$), because the CO_2 feed equals 0 ($N_{\text{CO}_2}^0 = 0$). Therefore, ΔH and ΔG values from equations 25 and 26 will be,

$$\Delta H = [(-2)*(-90.3) + 0*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + 0*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + 0*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + 0*(-28.6)] \text{ kJ/mol}$$

Hence, ΔH and ΔG for the combined process will have the range of values as computed to be, $\Delta H = 180.6 \text{ kJ/mol to } -180.6 \text{ kJ/mol}$ and $\Delta G = 50.2 \text{ kJ/mol to } -50.2 \text{ kJ/mol}$.

When $N_{\text{CO}_2} > 0$; then

$$\epsilon_2 > -N_{\text{CO}_2}^0$$

Thus, increasing $\epsilon_2 = 0$ value by 0.1 (i.e. $\epsilon_2 = -N_{\text{CO}_2}^0 + 0.1$), then $\epsilon_2 = 0.1$ for all ϵ_1 values. Therefore, ΔH and ΔG values from equations 25 and 26 will be;

$$\Delta H = [(-2)*(-90.3) + (0.1)*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + (0.1)*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + (0.1)*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + (0.1)*(-28.6)] \text{ kJ/mol}$$

Hence, ΔH and ΔG for the combined process will have the range of values as computed to be, $\Delta H = 176.49 \text{ kJ/mol to } -184.71 \text{ kJ/mol}$ and $\Delta G = 47.34 \text{ kJ/mol to } -53.06 \text{ kJ/mol}$.

The mass balance for methanol (CH_3OH) specie when both reactions are considered can be expressed from equation 35 as;

$$N_{\text{CH}_3\text{OH}} = N_{\text{CH}_3\text{OH}}^0 + \epsilon_1 \geq 0$$

When $N_{\text{CH}_3\text{OH}} = 0$, then

$$\varepsilon_1 = -N_{\text{CH}_3\text{OH}}^0$$

If, ε_2 values can be taken to be from -2 to $+2$, considering that there is no methanol feed (i.e., $N_{\text{CH}_3\text{OH}}^0 = 0$), therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [0*(-90.3) + (-2)*(-41.1)] \text{ kJ/mol to } [0*(-90.3) + (+2)*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [0*(-25.1) + (-2)*(-28.6)] \text{ kJ/mol to } [0*(-25.1) + (+2)*(-28.6)] \text{ kJ/mol}$$

Hence, ΔH and ΔG for the combined process will have the range of values as computed to be, $\Delta H = 82.2 \text{ kJ/mol to } -82.2 \text{ kJ/mol}$ and $\Delta G = 57.2 \text{ kJ/mol to } -57.2 \text{ kJ/mol}$.

When $N_{\text{CH}_3\text{OH}} > 0$; then

$$\varepsilon_1 > -N_{\text{CH}_3\text{OH}}^0$$

Since, ε_2 values can be taken to be from -2 to $+2$, considering that there is no methanol feed (i.e., $N_{\text{CH}_3\text{OH}}^0 = 0$), and increasing $\varepsilon_1 = 0$ value by 0.1 (i.e. $\varepsilon_2 = -N_{\text{CH}_3\text{OH}}^0 + 0.1$). Thus, $\varepsilon_1 = 0.1$ for all ε_2 values and the ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [0.1*(-90.3) + (-2)*(-41.1)] \text{ kJ/mol to } [0.1*(-90.3) + (+2)*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [0.1*(-25.1) + (-2)*(-28.6)] \text{ kJ/mol to } [0.1*(-25.1) + (+2)*(-28.6)] \text{ kJ/mol}$$

Therefore, ΔH and ΔG for the combined process will have the range of values as computed to be, $\Delta H = 73.17$ kJ/mol to -91.23 kJ/mol and $\Delta G = 54.69$ kJ/mol to -59.71 kJ/mol.

The above computed values are hereby shown in table 2.

Table 2: Range of ΔH and ΔG values at 25°C and different pressures for the extent of reaction ϵ with respect to the given feed of 1 mol CO and 2 mol H_2 .

Feed				
CO	1 mols			
H_2	2 mols			
H_2O	0 mols	25°C	H (kJ/mol)	G (kJ/mol)
CO_2	0 mols	Rxn 1	-90.3	-25.1
CH_3OH	0 mols	Rxn 2	-41.1	-28.6
Species	ϵ_1 (Species = 0)	ϵ_2 (Species = 0)	ϵ_1 (Species > 0)	ϵ_2 (Species > 0)
$\epsilon_1 = 0$	0	-2 to +2	0.1	-2 to +2
$\epsilon_2 = 0$	-2 to +2	0	0	0.1
CO	-2 to +2	3 to -1	-2 to +2	2.9 to -1.1
H_2	-2 to +2	-6 to 2	-2 to +2	-5.8 to 2.2
H_2O	-2 to +2	0.5	-2 to +2	0.4
CO_2	-2 to +2	-1	-2 to +2	-0.9
CH_3OH	0	-2 to +2	0.1	-2 to +2
	ΔH values (kJ/mol)		ΔG values (kJ/mol)	
Species	ΔH (Species = 0)	ΔH (Species > 0)	ΔG (Species = 0)	ΔG (Species > 0)
$\epsilon_1 = 0$	82.2 to -82.2	73.17 to -91.23	57.2 to -57.2	54.69 to -59.71
$\epsilon_2 = 0$	180.6 to -180.6	176.49 to -184.71	50.2 to -50.2	47.34 to -53.06
CO	57.3 to -139.5	61.41 to -135.39	-35.6 to -21.6	-32.74 to -18.74
H_2	427.2 to -262.8	418.98 to -271.02	221.8 to -107.4	216.08 to -113.12
H_2O	180.6 to -180.6	184.71 to -176.49	50.2 to -50.2	53.06 to -47.34
CO_2	180.6 to -180.6	176.49 to -184.71	50.2 to -50.2	47.34 to -53.06
CH_3OH	82.2 to -82.2	73.17 to -91.23	57.2 to -57.2	54.69 to -59.71

ΔH is the enthalpy of the reaction in kJ/mol, ΔG is the free energy of reaction in kJ/mol, and $G_{(p)}$ is the free energy (ΔG , in kJ/mol) of the reaction at a pressure, P, in bars (br). ϵ_1 and ϵ_2 are extents of reaction 1 and 2, respectively.

APPENDIX C: Mass balance calculations for the chemical species in two reactions using a feed of 1mol CO, 1mol CO₂, 3mol H₂ and 0.5mol H₂O @ 25C.

For carbon monoxide (CO) specie; from equation 31,

$$N_{CO} = N_{CO}^0 - \epsilon_1 - \epsilon_2 \geq 0$$

When $N_{CO} = 0$

$$N_{CO}^0 - \epsilon_1 = \epsilon_2$$

Since the number of moles of CO fed into the process equals 1 ($N_{CO}^0 = 1$), it follows that ϵ_2 will thus, compute a range of values for each ϵ_1 value (-2 to +2) to be from 3 to -1. Therefore, ΔH and ΔG values for the combined process, from equations 25 and 26 are then computed as;

$$\Delta H = [(-2)*(-90.3) + 3*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + (-1)*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + 3*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + (-1)*(-28.6)] \text{ kJ/mol}$$

Thus, ΔH and ΔG values for the combined process will range as, $\Delta H = 57.3 \text{ kJ/mol}$ to -139.5 kJ/mol and $\Delta G = -35.6 \text{ kJ/mol}$ to -21.86 kJ/mol .

When $N_{CO} > 0$

$$N_{CO}^0 - \epsilon_1 > \epsilon_2$$

Then, decreasing $\epsilon_2 = 0$ values by 0.1 (i.e. $\epsilon_2 = N_{CO}^0 - \epsilon_1 - 0.1$), the ϵ_2 range of values for each ϵ_1 value can be from 2.9 to -1.1. Therefore, from equations 25 and 26, it the values can be computed as;

$$\Delta H = [(-2)*(-90.3) + 2.9*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + (-1.1)*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + 2.9*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + (-1.1)*(-28.6)] \text{ kJ/mol}$$

Hence, ΔH and ΔG for the combined process will have the range of values to be, $\Delta H = 61.41 \text{ kJ/mol to } -135.39 \text{ kJ/mol}$ and $\Delta G = -32.74 \text{ kJ/mol to } -18.74 \text{ kJ/mol}$.

For hydrogen (H_2) specie; from equation 32,

$$N_{\text{H}_2} = N_{\text{H}_2}^0 - 2\varepsilon_1 + \varepsilon_2 \geq 0$$

When $N_{\text{H}_2} = 0$

$$N_{\text{H}_2}^0 - 2\varepsilon_1 = -\varepsilon_2$$

Since, the moles of H_2 feed, into the process equals 3 ($N_{\text{H}_2}^0 = 3$), it follows that ε_2 values will compute a range of values for each ε_1 value (-2 to $+2$) to be from -7 to 1 .

Computing these values into equations 25 and 26, we have that;

$$\Delta H = [(-2)*(-90.3) + (-7)*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + 1*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + (-7)*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + 1*(-28.6)] \text{ kJ/mol}$$

Therefore, ΔH and ΔG for the combined process will have the range of values to be, $\Delta H = 468.3 \text{ kJ/mol to } -221.7 \text{ kJ/mol}$ and $\Delta G = 250.4 \text{ kJ/mol to } -78.8 \text{ kJ/mol}$.

When $N_{\text{H}_2} > 0$; then

$$\varepsilon_2 > 2\varepsilon_1 - N_{\text{H}_2}^0$$

Since, the moles of H₂ feed equals 3 ($N_{H_2}^0 = 3$), increasing $\epsilon_2 = 0$ values by 0.2 (i.e. $\epsilon_2 = 2 \epsilon_1 - N_{H_2}^0 + 0.2$), the range of values for each ϵ_1 value can be -6.8 to 1.2 .

Therefore, ΔH and ΔG values as computed from equations 25 and 26 will be,

$$\Delta H = [(-2)*(-90.3) + (-6.8)*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + 1.2*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + (-6.8)*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + 1.2*(-28.6)] \text{ kJ/mol}$$

Hence, ΔH and ΔG for the combined process will have the range of values to be, $\Delta H = 460.08 \text{ kJ/mol}$ to -229.92 kJ/mol and $\Delta G = 224.68 \text{ kJ/mol}$ to -84.52 kJ/mol .

For water (H₂O) specie; from equation 33,

$$N_{H_2O} = N_{H_2O}^0 - \epsilon_2 \geq 0$$

When $N_{H_2O} = 0$; then

$$\epsilon_2 = N_{H_2O}^0 = 0.5$$

Since, the moles of H₂O feed equals 0.5 ($N_{H_2O}^0 = 0.5$), ϵ_2 values will be 0.5 for all ϵ_1 values, ΔH and ΔG values as computed from equations 25 and 26 will then be,

$$\Delta H = [(-2)*(-90.3) + 0.5*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + 0.5*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + 0.5*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + 0.5*(-28.6)] \text{ kJ/mol}$$

Therefore, ΔH and ΔG for the combined process will have the range of values as computed to be, $\Delta H = 160.05 \text{ kJ/mol}$ to -201.15 kJ/mol and $\Delta G = 35.9 \text{ kJ/mol}$ to -64.5 kJ/mol

When $N_{\text{H}_2\text{O}} > 0$; then

$$N_{\text{H}_2\text{O}}^0 > \varepsilon_2$$

rearranging

$$\varepsilon_2 < N_{\text{H}_2\text{O}}^0$$

Since, $N_{\text{H}_2\text{O}}^0 = 0.5$, decreasing $\varepsilon_2 = 0$ value by 0.1 (i.e. $\varepsilon_2 = N_{\text{H}_2\text{O}}^0 - 0.1$), then $\varepsilon_2 = 0.4$ value for all ε_1 values. Computing for ΔH and ΔG range of values from equations 25 and 26,

$$\Delta H = [(-2)*(-90.3) + 0.4*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + 0.4*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + 0.4*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + 0.4*(-28.6)] \text{ kJ/mol}$$

Therefore, ΔH and ΔG for the combined process will have the range of values as computed to be, $\Delta H = 164.16 \text{ kJ/mol to } -197.04 \text{ kJ/mol}$ and $\Delta G = 38.76 \text{ kJ/mol to } -61.64 \text{ kJ/mol}$.

For carbon dioxide (CO_2) specie; from equation 34,

$$N_{\text{CO}_2} = N_{\text{CO}_2}^0 + \varepsilon_2 \geq 0$$

When $N_{\text{CO}_2} = 0$; then

$$\varepsilon_2 = -N_{\text{CO}_2} = -1$$

Thus, ε_2 values will be equal to -1 for all ε_1 values ($\varepsilon_2 = -1$), because the CO_2 feed equals 1 ($N_{\text{CO}_2}^0 = 1$). Therefore, ΔH and ΔG values from equations 25 and 26 will be,

$$\Delta H = [(-2)*(-90.3) + (-1)*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + (-1)*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + (-1)*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + (-1)*(-28.6)] \text{ kJ/mol}$$

Hence, ΔH and ΔG for the combined process will have the range of values as computed to be, $\Delta H = 221.7 \text{ kJ/mol to } -139.5 \text{ kJ/mol}$ and $\Delta G = 78.8 \text{ kJ/mol to } -21.6 \text{ kJ/mol}$.

When $N_{\text{CO}_2} > 0$; then

$$\varepsilon_2 > -N^0_{\text{CO}_2}$$

Thus, increasing $\varepsilon_2 = 0$ value by 0.1 (i.e. $\varepsilon_2 = -N^0_{\text{CO}_2} + 0.1$), then $\varepsilon_2 = -0.9$ for all ε_1 values. Therefore, ΔH and ΔG values from equations 25 and 26 will be,

$$\Delta H = [(-2)*(-90.3) + (-0.9)*(-41.1)] \text{ kJ/mol to } [+2*(-90.3) + (-0.9)*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(-25.1) + (-0.9)*(-28.6)] \text{ kJ/mol to } [+2*(-25.1) + (-0.9)*(-28.6)] \text{ kJ/mol}$$

Hence, ΔH and ΔG for the combined process will have the range of values as computed to be, $\Delta H = 217.59 \text{ kJ/mol to } -143.61 \text{ kJ/mol}$ and $\Delta G = 75.94 \text{ kJ/mol to } -24.46 \text{ kJ/mol}$.

For Methanol (CH_3OH) specie; from equation 35,

$$N_{\text{CH}_3\text{OH}} = N^0_{\text{CH}_3\text{OH}} + \varepsilon_1 \geq 0$$

When $N_{\text{CH}_3\text{OH}} = 0$, then

$$\varepsilon_1 = -N_{\text{CH}_3\text{OH}}^0$$

If, ε_2 values can be taken to be from -2 to $+2$, considering that there is no methanol feed (i.e., $N_{\text{CH}_3\text{OH}}^0 = 0$), therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [0*(-90.3) + (-2)*(-41.1)] \text{ kJ/mol to } [0*(-90.3) + (+2)*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [0*(-25.1) + (-2)*(-28.6)] \text{ kJ/mol to } [0*(-25.1) + (+2)*(-28.6)] \text{ kJ/mol}$$

Hence, ΔH and ΔG for the combined process will have the range of values as computed to be, $\Delta H = 82.2 \text{ kJ/mol to } -82.2 \text{ kJ/mol}$ and $\Delta G = 57.2 \text{ kJ/mol to } -57.2 \text{ kJ/mol}$.

When $N_{\text{CH}_3\text{OH}} > 0$; then

$$\varepsilon_1 > -N_{\text{CH}_3\text{OH}}^0$$

Since, ε_2 values can be taken to be from -2 to $+2$, considering that there is no methanol feed (i.e., $N_{\text{CH}_3\text{OH}}^0 = 0$), and increasing $\varepsilon_1 = 0$ value by 0.1 (i.e. $\varepsilon_2 = -N_{\text{CH}_3\text{OH}}^0 + 0.1$). Thus, $\varepsilon_1 = 0.1$ for all ε_2 values and the ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [0.1*(-90.3) + (-2)*(-41.1)] \text{ kJ/mol to } [0.1*(-90.3) + (+2)*(-41.1)] \text{ kJ/mol}$$

$$\Delta G = [0.1*(-25.1) + (-2)*(-28.6)] \text{ kJ/mol to } [0.1*(-25.1) + (+2)*(-28.6)] \text{ kJ/mol}$$

Therefore, ΔH and ΔG for the combined process will have the range of values as computed to be, $\Delta H = 73.17 \text{ kJ/mol to } -91.23 \text{ kJ/mol}$ and $\Delta G = 54.69 \text{ kJ/mol to } -59.71 \text{ kJ/mol}$.

The above computed values are hereby shown in table 3.

Table 3: Range of ΔH and ΔG values at 25°C and different pressures for the extent of reaction ϵ with respect to the chemical species under consideration using a feed of 1mol CO, 3mols H₂, 1mol CO₂ and 0.5mol H₂O.

Feed					H (kJ/mol)	G (kJ/mol)
CO	1 mols					
H ₂	3 mols					
H ₂ O	0.5 mols					
CO ₂	1 mols		Rxn 1	-90.3	-25.1	
CH ₃ OH	0 mols	25°C	Rxn 2	-41.1	-28.6	
						ΔH values (kJ/mol)
Species	ϵ_1 (Species = 0)	ϵ_2 (Species = 0)	ϵ_1 (Species > 0)	ϵ_2 (Species > 0)	ΔH (Species = 0)	ΔH (Species > 0)
$\epsilon_1 = 0$	0	-2 to +2	0.1	-2 to +2	82.2 to -82.2	73.17 to -91.23
$\epsilon_2 = 0$	-2 to +2	0	0	0.1	180.6 to -180.6	176.49 to -184.71
CO	-2 to +2	3 to -1	-2 to +2	2.9 to -1.1	57.3 to -139.5	61.41 to -135.39
H ₂	-2 to +2	-7 to 1	-2 to +2	-6.8 to 1.2	468.3 to -221.7	460.08 to -229.92
H ₂ O	-2 to +2	0.5	-2 to +2	0.4	160.05 to -201.15	164.16 to -197.04
CO ₂	-2 to +2	-1	-2 to +2	-0.9	221.7 to -139.5	217.59 to -143.61
CH ₃ OH	0	-2 to +2	0.1	-2 to +2	82.2 to -82.2	73.17 to -91.23
ΔG values (kJ/mol)						
	G _p at 25°C, 1 br	-25.1	G _p at 25°C, 20 br	-39.9	G _p at 25°C, 50 br	-44.5
Species	ΔG (Species = 0)	ΔG (Species > 0)	ΔG (Species = 0)	ΔG (Species > 0)	ΔG (Species = 0)	ΔG (Species > 0)
$\epsilon_1 = 0$	57.2 to -57.2	54.69 to -59.71	57.2 to -57.2	53.21 to -61.19	57.2 to -57.2	52.75 to -61.65
$\epsilon_2 = 0$	50.2 to -50.2	47.34 to -53.06	79.8 to -79.8	76.94 to -82.66	89 to -89	86.14 to -91.86
CO	-35.6 to -21.6	-32.74 to -18.74	-6 to -51.2	-3.14 to -48.34	3.2 to -60.4	6.06 to -57.54
H ₂	250.4 to -78.8	224.68 to -84.52	280 to -108.4	274.28 to -114.12	289.2 to -117.6	283.48 to -123.32
H ₂ O	35.9 to -64.5	38.76 to -61.64	65.5 to -94.1	68.36 to -91.24	74.7 to -103.3	77.56 to -100.44
CO ₂	78.8 to -21.6	75.94 to -24.46	108.4 to -51.2	105.54 to -54.06	117.6 to -60.4	114.74 to -63.26
CH ₃ OH	57.2 to -57.2	54.69 to -59.71	57.2 to -57.2	53.21 to -61.19	57.2 to -57.2	52.75 to -61.65
ΔG values (kJ/mol)						
	G _p at 25°C, 70 br	-46.1	G _p at 25°C, 90 br	-47.4		
Species	ΔG (Species = 0)	ΔG (Species > 0)	ΔG (Species = 0)	ΔG (Species > 0)		
$\epsilon_1 = 0$	57.2 to -57.2	52.59 to -61.81	57.2 to -57.2	52.46 to -61.94		
$\epsilon_2 = 0$	92.2 to -92.2	89.34 to -95.06	94.8 to -94.8	91.94 to -97.66		
CO	6.4 to -63.6	9.26 to -60.74	9 to -66.2	11.86 to -63.34		
H ₂	292.4 to -120.8	286.68 to -126.52	295 to -123.4	289.28 to -129.12		
H ₂ O	77.9 to -106.5	80.76 to -103.64	80.5 to -109.1	83.36 to -106.24		
CO ₂	120.8 to -63.6	117.94 to -66.46	123.4 to -66.2	75.94 to -24.64		
CH ₃ OH	57.2 to -57.2	52.59 to -61.81	57.2 to -57.2	54.69 to -59.71		

ΔH is the enthalpy of the reaction in kJ/mol, ΔG is the free energy of reaction in kJ/mol, and $G_{(p)}$ is the free energy (ΔG , in kJ/mol) of the reaction at a pressure, P, in bars (br). ϵ_1 and ϵ_2 are extents of reaction 1 and 2, respectively.

APPENDIX D: Mass balance calculations for the chemical species in two reactions using a feed of 1mol CO, 1mol CO₂, 3mol H₂ and 0.5mol H₂O @ 250C

Substituting the values for ΔH_j and ΔG_j into equations 25 and 26, and taking the mass balance around the chemical species at 250°C, 1 bar, then:

When $\epsilon_1 = 0$ (i.e., $\epsilon_1 \Delta H_1 = 0$ and $\epsilon_1 \Delta G_1 = 0$), the ΔH and ΔG will be determined by $\epsilon_2 \Delta H_2$ & $\epsilon_2 \Delta G_2$ respectively. Therefore, ΔH and ΔG values from equations 25 and 26 are then computed as;

$$\Delta H = [0*(-98.2) + (-2)*(-39.5)] \text{ kJ/mol to } [0*(-98.2) + (+2)*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [0*(26.8) + (-2)*(-19.6)] \text{ kJ/mol to } [0*(26.8) + (+2)*(-19.6)] \text{ kJ/mol}$$

Thus, from equations 6.1 and 6.2, ΔH and ΔG range of values become; $\Delta H = 79$ kJ/mol to -79 kJ/mol and $\Delta G = 39.2$ kJ/mol to -39.2 kJ/mol.

And when ϵ_1 should be > 0 ; increasing $\epsilon_1 = 0$ value by 0.1 (i.e. $\epsilon_2 = 0 + 0.1$), then $\epsilon_1 = 0.1$ for all ϵ_2 values of -2 to $+2$. Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [0.1*(-98.2) + (-2)*(-39.5)] \text{ kJ/mol to } [0.1*(-98.2) + (+2)*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [0.1*(26.8) + (-2)*(-19.6)] \text{ kJ/mol to } [0.1*(26.8) + (+2)*(-19.6)] \text{ kJ/mol}$$

Hence, $\Delta H = 69.18$ kJ/mol to -88.82 kJ/mol and $\Delta G = 41.88$ kJ/mol to -36.52 kJ/mol

Similarly, when $\epsilon_2 = 0$ (i.e., $\epsilon_2 \Delta H_2 = 0$ and $\epsilon_2 \Delta G_2 = 0$), it then implies that the ΔH and ΔG is determined by $\epsilon_1 \Delta H_1$ & $\epsilon_1 \Delta G_1$, respectively. Therefore, ΔH and ΔG values will range as:

$$\Delta H = [(-2)*(-98.2) + 0*(-39.5)] \text{ kJ/mol to } [(+2)*(-98.2) + 0*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(26.8) + 0*(-19.6)] \text{ kJ/mol to } [(+2)*(26.8) + 0*(-19.6)] \text{ kJ/mol}$$

Hence, $\Delta H = 196.4 \text{ kJ/mol to } -196.4 \text{ kJ/mol}$ and $\Delta G = -53.6 \text{ kJ/mol to } 53.6 \text{ kJ/mol}$.

And when $\epsilon_2 > 0$, increasing $\epsilon_2 = 0$ value by 0.1 (i.e. $\epsilon_2 = 0 + 0.1$), then $\epsilon_2 = 0.1$ for all ϵ_1 values of -2 to $+2$. Therefore ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-98.2) + 0.1*(-39.5)] \text{ kJ/mol to } [(+2)*(-98.2) + 0.1*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(26.8) + 0.1*(-19.6)] \text{ kJ/mol to } [(+2)*(26.8) + 0.1*(-19.6)] \text{ kJ/mol}$$

Hence, $\Delta H = 192.45 \text{ kJ/mol to } -200.35 \text{ kJ/mol}$ and $\Delta G = -55.56 \text{ kJ/mol to } 51.64 \text{ kJ/mol}$.

For carbon monoxide (CO) specie; from the deductions of equations 31 through 3.2, ϵ_2 will compute a range of values for each ϵ_1 value of -2 to $+2$, to be from 3 to -1 . Therefore ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-98.2) + 3*(-39.5)] \text{ kJ/mol to } [(+2)*(-98.2) + (-1)*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(26.8) + 3*(-19.6)] \text{ kJ/mol to } [(+2)*(26.8) + (-1)*(-19.6)] \text{ kJ/mol}$$

Hence, $\Delta H = 77.9 \text{ kJ/mol to } -156.9 \text{ kJ/mol}$ and $\Delta G = -112.4 \text{ kJ/mol to } 73.2 \text{ kJ/mol}$.

When $N_{CO} > 0$; as deduced from equations 31 through 3.2, decreasing $\epsilon_2 = 0$ values by 0.1 (i.e. $\epsilon_2 = N_{CO}^0 - \epsilon_1 - 0.1$), the range of values for each ϵ_1 value (-2 to $+2$) can be computed to be from 2.9 to -1.1 . Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-98.2) + 2.9*(-39.5)] \text{ kJ/mol to } [(+2)*(-98.2) + (-1.1)*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(26.8) + 2.9*(-19.6)] \text{ kJ/mol to } [(+2)*(26.8) + (-1.1)*(-19.6)] \text{ kJ/mol}$$

Hence, $\Delta H = 81.85 \text{ kJ/mol to } -152.95 \text{ kJ/mol}$ and $\Delta G = -110.44 \text{ kJ/mol to } 75.16 \text{ kJ/mol}$.

For hydrogen (H_2) specie; from equations 32 through 32.1 deductions, \mathcal{E}_2 values will compute a range of values for each \mathcal{E}_1 value (-2 to +2) to be -7 to 1. Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-98.2) + (-7)*(-39.5)] \text{ kJ/mol to } [(+2)*(-98.2) + 1*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(26.8) + (-7)*(-19.6)] \text{ kJ/mol to } [(+2)*(26.8) + 1*(-19.6)] \text{ kJ/mol}$$

Hence, $\Delta H = 472.9 \text{ kJ/mol to } -235.9 \text{ kJ/mol}$ and $\Delta G = 83.6 \text{ kJ/mol to } 34 \text{ kJ/mol}$.

When $N_{\text{H}_2} > 0$; deductions from equation 32 through 32.1, and increasing $\mathcal{E}_2 = 0$ values by 0.2 (i.e. $\mathcal{E}_2 = 2\mathcal{E}_1 - N_{\text{H}_2}^0 + 0.2$), we then have a range of values for each \mathcal{E}_1 value (-2 to +2) to be -6.8 to 1.2. Therefore, ΔH and ΔG values from equations 25 and 26 will then range as;

$$\Delta H = [(-2)*(-98.2) + (-6.8)*(-39.5)] \text{ kJ/mol to } [(+2)*(-98.2) + 1.2*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(26.8) + (-6.8)*(-19.6)] \text{ kJ/mol to } [(+2)*(26.8) + 1.2*(-19.6)] \text{ kJ/mol}$$

Hence, the range of values will be; $\Delta H = 465 \text{ kJ/mol to } -243.8 \text{ kJ/mol}$ and $\Delta G = 79.68 \text{ kJ/mol to } 30.08 \text{ kJ/mol}$.

For water (H₂O) specie; deductions from equations 33 through 33.1 allows one to compute ϵ_2 values to be 0.5 for all ϵ_1 values of -2 to +2. Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-98.2) + 0.5*(-39.5)] \text{ kJ/mol to } [(+2)*(-98.2) + 0.5*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(26.8) + 0.5*(-19.6)] \text{ kJ/mol to } [(+2)*(26.8) + 0.5*(-19.6)] \text{ kJ/mol}$$

Hence, the range of values will be; $\Delta H = 176.65 \text{ kJ/mol to } -216.15 \text{ kJ/mol}$ and $\Delta G = -63.4 \text{ kJ/mol to } 43.8 \text{ kJ/mol}$.

When $N_{\text{H}_2\text{O}} > 0$; from the deductions of equations 33 through 33.1, and computing by decreasing $\epsilon_2 = 0$ value by 0.1 (i.e. $\epsilon_2 = N_{\text{H}_2\text{O}}^0 - 0.1$), then $\epsilon_2 = 0.4$ for all ϵ_1 values of -2 to +2. Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-98.2) + 0.4*(-39.5)] \text{ kJ/mol to } [(+2)*(-98.2) + 0.4*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(26.8) + 0.4*(-19.6)] \text{ kJ/mol to } [(+2)*(26.8) + 0.4*(-19.6)] \text{ kJ/mol}$$

Hence, range of values; $\Delta H = 180.6 \text{ kJ/mol to } -212.2 \text{ kJ/mol}$ and $\Delta G = -61.44 \text{ kJ/mol to } 45.76 \text{ kJ/mol}$.

For carbon dioxide (CO₂) specie; as deduced from equations 34 through 34.1, ϵ_2 value will be equal to -1 for all ϵ_1 values (-2 to +2), since $\epsilon_2 = -1$. Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-98.2) + (-1)*(-39.5)] \text{ kJ/mol to } [(+2)*(-98.2) + (-1)*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(26.8) + (-1)*(-19.6)] \text{ kJ/mol to } [(+2)*(26.8) + (-1)*(-19.6)] \text{ kJ/mol}$$

Hence, range of values; $\Delta H = 235.9 \text{ kJ/mol}$ to -156.9 kJ/mol and $\Delta G = -34 \text{ kJ/mol}$ to -73.2 kJ/mol .

When $N_{\text{CO}_2} > 0$; from equation 34 through 34.1 deduction, and increasing $\epsilon_2 = 0$ value by 0.1 (i.e. $\epsilon_2 = -N_{\text{CO}_2}^0 + 0.1$), then $\epsilon_2 = -0.9$ for all ϵ_1 values (-2 to $+2$). Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-98.2) + (-0.9)*(-39.5)] \text{ kJ/mol to } [(+2)*(-98.2) + (-0.9)*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(26.8) + (-0.9)*(-19.6)] \text{ kJ/mol to } [(+2)*(26.8) + (-0.9)*(-19.6)] \text{ kJ/mol}$$

Hence, the range of values are; $\Delta H = 231.95 \text{ kJ/mol}$ to -160.85 kJ/mol and $\Delta G = -35.96 \text{ kJ/mol}$ to 71.24 kJ/mol .

For Methanol (CH_3OH) specie; and deduction from equations 35 through 35.1, If ϵ_2 values is taken to be from -2 to $+2$ (since, $N_{\text{CH}_3\text{OH}}^0 = 0$), therefore ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(0)*(-98.2) + (-2)*(-39.5)] \text{ kJ/mol to } [(0)*(-98.2) + (+2)*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [(0)*(26.8) + (-2)*(-19.6)] \text{ kJ/mol to } [(0)*(26.8) + (+2)*(-19.6)] \text{ kJ/mol}$$

Hence, the range of values; $\Delta H = 79 \text{ kJ/mol}$ to -79 kJ/mol and $\Delta G = 39.2 \text{ kJ/mol}$ to -39.2 kJ/mol .

When $N_{\text{CH}_3\text{OH}} > 0$; from the deduction of equation 35 through 35.1, and increasing $\epsilon_1 = 0$ value by 0.1 (i.e. $\epsilon_2 = -N_{\text{CH}_3\text{OH}}^0 + 0.1$), then $\epsilon_1 = 0.1$ for all ϵ_2 values of -2 to $+2$. Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(0.1)*(-98.2) + (-2)*(-39.5)] \text{ kJ/mol to } [(0.1)*(-98.2) + (+2)*(-39.5)] \text{ kJ/mol}$$

$$\Delta G = [(0.1)*(26.8) + (-2)*(-19.6)] \text{ kJ/mol to } [(0.1)*(26.8) + (+2)*(-19.6)] \text{ kJ/mol}$$

Hence, $\Delta H = 69.18 \text{ kJ/mol to } -88.82 \text{ kJ/mol}$ and $\Delta G = 41.88 \text{ kJ/mol to } -36.52 \text{ kJ/mol}$.

The above computed values for 250C are hereby shown in table 4.

Table 4: Range of ΔH and ΔG values at 250°C and different pressures for the extent of reaction ϵ with respect to the chemical species under consideration.

Feed					H (kJ/mol)	G (kJ/mol)
CO	1 mols					
H ₂	3 mols					
H ₂ O	0.5 mols					
CO ₂	1 mols		Rxn 1	-98.2	26.8	
CH ₃ OH	0 mols	250°C	Rxn 2	-39.5	-19.6	

						ΔH values (kJ/mol)	
Species	ϵ_1 (Species = 0)	ϵ_2 (Species = 0)	ϵ_1 (Species > 0)	ϵ_2 (Species > 0)	ΔH (Species = 0)	ΔH (Species > 0)	
$\epsilon_1 = 0$	0	-2 to +2	0.1	-2 to +2	79 to -79	69.18 to -88.82	
$\epsilon_2 = 0$	-2 to +2	0	0	0.1	196.4 to -196.4	192.45 to -200.35	
CO	-2 to +2	3 to -1	-2 to +2	2.9 to -1.1	77.9 to -156.9	81.85 to -152.95	
H ₂	-2 to +2	-7 to 1	-2 to +2	-6.8 to 1.2	472.9 to -235.9	465 to -243.8	
H ₂ O	-2 to +2	0.5	-2 to +2	0.4	176.65 to -216.15	180.6 to -212.2	
CO ₂	-2 to +2	-1	-2 to +2	-0.9	235.9 to -156.9	231.95 to -160.85	
CH ₃ OH	0	-2 to +2	0.1	-2 to +2	79 to -79	69.18 to -88.82	

ΔG values (kJ/mol)							
		G_p at 250°C, 1 br	22.8	G_p at 250°C, 20 br	0.8	G_p at 250°C, 50 br	-7.2
Species	ΔG (Species = 0)	ΔG (Species > 0)	ΔG (Species = 0)	ΔG (Species > 0)	ΔG (Species = 0)	ΔG (Species > 0)	
$\epsilon_1 = 0$	39.2 to -39.2	41.88 to -36.52	39.2 to -39.2	39.28 to -39.12	39.2 to -39.2	38.43 to -39.92	
$\epsilon_2 = 0$	-53.6 to 53.6	-55.56 to 51.64	-1.6 to 1.6	-3.56 to -0.36	14.4 to -14.4	12.44 to -16.36	
CO	-112.4 to 73.2	-110.44 to 75.16	-60.4 to 21.2	-58.44 to 23.16	-44.4 to 5.2	-42.44 to 7.16	
H ₂	83.6 to 34	79.68 to 30.08	135.6 to -18	131.68 to -21.92	151.6 to -34	147.68 to -37.92	
H ₂ O	-63.4 to 43.8	-61.44 to 45.76	-11.4 to -8.2	-9.44 to -6.24	4.6 to -24.2	6.56 to -22.24	
CO ₂	-34 to 73.2	-35.96 to 71.24	18 to 21.2	16.04 to 19.24	34 to 5.2	33.04 to 3.24	
CH ₃ OH	39.2 to -39.2	41.88 to -36.52	39.2 to -39.2	39.28 to -39.12	39.2 to -39.2	38.43 to -39.92	

ΔG values (kJ/mol)					
		G_p at 250°C, 70 br	-10.1	G_p at 250°C, 90 br	-12.3
Species	ΔG (Species = 0)	ΔG (Species > 0)	ΔG (Species = 0)	ΔG (Species > 0)	
$\epsilon_1 = 0$	39.2 to -39.2	38.19 to -40.21	39.2 to -39.2	37.97 to -40.43	
$\epsilon_2 = 0$	20.2 to -20.2	18.24 to -22.16	24.6 to -24.6	22.64 to -26.56	
CO	-38.6 to -0.6	-36.64 to 1.36	-34.2 to -5	-32.24 to -3.04	
H ₂	157.4 to -37.8	153.48 to -43.72	161.8 to -44.2	157.88 to -48.12	
H ₂ O	10.4 to -30	12.36 to -28.04	14.8 to -34.4	16.76 to -32.44	
CO ₂	39.8 to -0.6	37.84 to -2.56	44.2 to -5	42.24 to -6.96	
CH ₃ OH	39.2 to -39.2	38.19 to -40.21	39.2 to -39.2	37.97 to -40.43	

H is the enthalpy of the reaction in kJ/mol, ΔG is the free energy of reaction in kJ/mol, and $G_{(p)}$ is the free energy (ΔG , in kJ/mol) of the reaction at a pressure, P, in bars (br). ϵ_1 and ϵ_2 are extents of reaction 1 and 2, respectively.

APPENDIX E: Mass balance calculations for the chemical species in two reactions using a feed of 1mol CO, 1mol CO₂, 3mol H₂ and 0.5mol H₂O @ 300C

Substituting the values for ΔH_j and ΔG_j into equations 25 and 26, and taking the mass balance around the chemical species at 300°C, 1 bar, then:

When $\epsilon_1 = 0$ (i.e., $\epsilon_1 \Delta H_1 = 0$ and $\epsilon_1 \Delta G_1 = 0$), the ΔH and ΔG will be determined by $\epsilon_2 \Delta H_2$ & $\epsilon_2 \Delta G_2$ respectively. Therefore, ΔH and ΔG values from equations 25 and 26 are then computed as;

$$\Delta H = [0*(-99.5) + (-2)*(-39.1)] \text{ kJ/mol to } [0*(-99.5) + (+2)*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [0*(38.8) + (-2)*(-17.7)] \text{ kJ/mol to } [0*(38.8) + (+2)*(-17.7)] \text{ kJ/mol}$$

Thus, from equations 25 and 26, ΔH and ΔG range of values become; $\Delta H = 78.2$ kJ/mol to -78.2 kJ/mol and $\Delta G = 35.4$ kJ/mol to -35.4 kJ/mol.

And when $\epsilon_1 > 0$, increasing $\epsilon_1 = 0$ value by 0.1 (i.e. $\epsilon_2 = 0 + 0.1$), then $\epsilon_1 = 0.1$ for all ϵ_2 values of -2 to $+2$. Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [0.1*(-99.5) + (-2)*(-39.1)] \text{ kJ/mol to } [0.1*(-99.5) + (+2)*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [0.1*(38.8) + (-2)*(-17.7)] \text{ kJ/mol to } [0.1*(38.8) + (+2)*(-17.7)] \text{ kJ/mol}$$

Hence, $\Delta H = 68.25$ kJ/mol to -88.15 kJ/mol and $\Delta G = 39.28$ kJ/mol to -31.52 kJ/mol.

Similarly, when $\epsilon_2 = 0$ (i.e., $\epsilon_2\Delta H_2 = 0$ and $\epsilon_2\Delta G_2 = 0$), it then implies that the ΔH and ΔG is determined by $\epsilon_1\Delta H_1$ & $\epsilon_1\Delta G_1$, respectively. Therefore, ΔH and ΔG values will range as:

$$\Delta H = [(-2)*(-99.5) + 0*(-39.1)] \text{ kJ/mol to } [(+2)*(-99.5) + 0*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(38.8) + 0*(-17.7)] \text{ kJ/mol to } [(+2)*(38.8) + 0*(-17.7)] \text{ kJ/mol}$$

Hence, $\Delta H = 199 \text{ kJ/mol to } -199 \text{ kJ/mol}$ and $\Delta G = -77.6 \text{ kJ/mol to } 77.6 \text{ kJ/mol}$.

And when $\epsilon_2 > 0$, increasing $\epsilon_2 = 0$ value by 0.1 (i.e. $\epsilon_2 = 0 + 0.1$), then $\epsilon_2 = 0.1$ for all ϵ_1 values of -2 to $+2$. Therefore ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-99.5) + 0.1*(-39.1)] \text{ kJ/mol to } [(+2)*(-99.5) + 0.1*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(38.8) + 0.1*(-17.7)] \text{ kJ/mol to } [(+2)*(38.8) + 0.1*(-17.7)] \text{ kJ/mol}$$

Hence, $\Delta H = 195.09 \text{ kJ/mol to } -202.91 \text{ kJ/mol}$ and $\Delta G = -79.37 \text{ kJ/mol to } 75.83 \text{ kJ/mol}$.

For carbon monoxide (CO) specie; from the deductions of equations 31 through 31.1, ϵ_2 will compute a range of values for each ϵ_1 value of -2 to $+2$, to be from 3 to -1 . Therefore ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-99.5) + 3*(-39.1)] \text{ kJ/mol to } [(+2)*(-99.5) + (-1)*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(38.8) + 3*(-17.7)] \text{ kJ/mol to } [(+2)*(38.8) + (-1)*(-17.7)] \text{ kJ/mol}$$

Hence, $\Delta H = 81.7 \text{ kJ/mol to } -159.9 \text{ kJ/mol}$ and $\Delta G = -130.7 \text{ kJ/mol to } 95.3 \text{ kJ/mol}$.

When $N_{CO} > 0$; as deduced from equations 31 through 31.1, decreasing $\varepsilon_2 = 0$ values by 0.1 (i.e. $\varepsilon_2 = N_{CO}^0 - \varepsilon_1 - 0.1$), the range of values for each ε_1 value (-2 to +2) can be computed to be from 2.9 to -1.1. Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-99.5) + 2.9*(-39.1)] \text{ kJ/mol to } [(+2)*(-99.5) + (-1.1)*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(38.8) + 2.9*(-17.7)] \text{ kJ/mol to } [(+2)*(38.8) + (-1.1)*(-17.7)] \text{ kJ/mol}$$

Hence, $\Delta H = 85.61 \text{ kJ/mol}$ to -155.99 kJ/mol and $\Delta G = -128.93 \text{ kJ/mol}$ to 97.07 kJ/mol .

For hydrogen (H_2) specie; from equations 32 through 32.1 deductions, ε_2 values will compute a range of values for each ε_1 value (-2 to +2) to be -7 to 1. Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-99.5) + (-7)*(-39.1)] \text{ kJ/mol to } [(+2)*(-99.5) + 1*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(38.8) + (-7)*(-17.7)] \text{ kJ/mol to } [(+2)*(38.8) + 1*(-17.7)] \text{ kJ/mol}$$

Hence, $\Delta H = 472.7 \text{ kJ/mol}$ to -238.1 kJ/mol and $\Delta G = 46.3 \text{ kJ/mol}$ to 59.9 kJ/mol .

When $N_{H_2} > 0$; deductions from equation 32.1 and increasing $\varepsilon_2 = 0$ values by 0.2 (i.e. $\varepsilon_2 = 2\varepsilon_1 - N_{H_2}^0 + 0.2$), we then have a range of values for each ε_1 value (-2 to +2) to be -6.8 to 1.2. Therefore, ΔH and ΔG values from equations 25 and 26 will then range as;

$$\Delta H = [(-2)*(-99.5) + (-6.8)*(-39.1)] \text{ kJ/mol to } [(+2)*(-99.5) + 1.2*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(38.8) + (-6.8)*(-17.7)] \text{ kJ/mol to } [(+2)*(38.8) + 1.2*(-17.7)] \text{ kJ/mol}$$

Hence, the range of values will be; $\Delta H = 464.88 \text{ kJ/mol}$ to -245.92 kJ/mol and $\Delta G = 42.76 \text{ kJ/mol}$ to 56.36 kJ/mol .

For water (H_2O) specie; deductions from equations 33 through 33.1 allows one to compute ϵ_2 values to be 0.5 for all ϵ_1 values of -2 to $+2$. Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-99.5) + 0.5*(-39.1)] \text{ kJ/mol to } [(+2)*(-99.5) + 0.5*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(38.8) + 0.5*(-17.7)] \text{ kJ/mol to } [(+2)*(38.8) + 0.5*(-17.7)] \text{ kJ/mol}$$

Hence, the range of values will be; $\Delta H = 179.45 \text{ kJ/mol}$ to -218.55 kJ/mol and $\Delta G = -86.45 \text{ kJ/mol}$ to 68.75 kJ/mol .

When $N_{\text{H}_2\text{O}} > 0$; from the deductions of equations 33 through 33.1, and computing by decreasing $\epsilon_2 = 0$ value by 0.1 (i.e. $\epsilon_2 = N_{\text{H}_2\text{O}}^0 - 0.1$), then $\epsilon_2 = 0.4$ for all ϵ_1 values of -2 to $+2$. Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-99.5) + 0.4*(-39.1)] \text{ kJ/mol to } [(+2)*(-99.5) + 0.4*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(38.8) + 0.4*(-17.7)] \text{ kJ/mol to } [(+2)*(38.8) + 0.4*(-17.7)] \text{ kJ/mol}$$

Hence, range of values; $\Delta H = 183.36 \text{ kJ/mol}$ to -214.64 kJ/mol and $\Delta G = -84.68 \text{ kJ/mol}$ to 70.52 kJ/mol .

For carbon dioxide (CO_2) specie; as deduced from equations 34 through 34.1, ϵ_2 value will be equal to -1 for all ϵ_1 values (-2 to $+2$), since $\epsilon_2 = -1$. Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-99.5) + (-1)*(-39.1)] \text{ kJ/mol to } [(+2)*(-99.5) + (-1)*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(38.8) + (-1)*(-17.7)] \text{ kJ/mol to } [(+2)*(38.8) + (-1)*(-17.7)] \text{ kJ/mol}$$

Hence, range of values; $\Delta H = 238.1 \text{ kJ/mol}$ to -159.9 kJ/mol and $\Delta G = -59.9 \text{ kJ/mol}$ to 95.3 kJ/mol .

When $N_{\text{CO}_2} > 0$; from equation 34.1 deduction, and increasing $\epsilon_2 = 0$ value by 0.1 (i.e. $\epsilon_2 = -N^0_{\text{CO}_2} + 0.1$), then $\epsilon_2 = -0.9$ for all ϵ_1 values (-2 to $+2$). Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(-2)*(-99.5) + (-0.9)*(-39.1)] \text{ kJ/mol to } [(+2)*(-99.5) + (-0.9)*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [(-2)*(38.8) + (-0.9)*(-17.7)] \text{ kJ/mol to } [(+2)*(38.8) + (-0.9)*(-17.7)] \text{ kJ/mol}$$

Hence, the range of values are; $\Delta H = 243.19 \text{ kJ/mol}$ to -163.81 kJ/mol and $\Delta G = -61.67 \text{ kJ/mol}$ to 93.53 kJ/mol .

For Methanol (CH_3OH) specie; and deduction from equations 35 through 35.1, If ϵ_2 values is taken to be from -2 to $+2$ (since, $N^0_{\text{CH}_3\text{OH}} = 0$), therefore ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(0)*(-99.5) + (-2)*(-39.1)] \text{ kJ/mol to } [(0)*(-99.5) + (+2)*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [(0)*(38.8) + (-2)*(-17.7)] \text{ kJ/mol to } [(0)*(38.8) + (+2)*(-17.7)] \text{ kJ/mol}$$

Hence, the range of values; $\Delta H = 78.2 \text{ kJ/mol}$ to -78.2 kJ/mol and $\Delta G = 35.4 \text{ kJ/mol}$ to -35.4 kJ/mol .

When $N_{\text{CH}_3\text{OH}} > 0$; from the deduction of equation 35 through 35.1, and increasing $\epsilon_1 = 0$ value by 0.1 (i.e. $\epsilon_2 = -N_{\text{CH}_3\text{OH}}^0 + 0.1$), then $\epsilon_1 = 0.1$ for all ϵ_2 values of -2 to $+2$.

Therefore, ΔH and ΔG values from equations 25 and 26 will range as;

$$\Delta H = [(0.1)*(-99.5) + (-2)*(-39.1)] \text{ kJ/mol to } [(0.1)*(-99.5) + (+2)*(-39.1)] \text{ kJ/mol}$$

$$\Delta G = [(0.1)*(38.8) + (-2)*(-17.7)] \text{ kJ/mol to } [(0.1)*(38.8) + (+2)*(-17.7)] \text{ kJ/mol}$$

Hence, ΔH and ΔG range of values will be; $\Delta H = 68.25 \text{ kJ/mol to } -88.15 \text{ kJ/mol}$ and $\Delta G = 39.28 \text{ kJ/mol to } -31.52 \text{ kJ/mol}$. The above computed values for 300C are hereby shown in table 5.

Table 5: Range of ΔH and ΔG values at 300°C and different pressures for the extent of reaction \mathcal{E} with respect to the chemical species under consideration.

Feed						
CO	1 mols					
H ₂	3 mols					
H ₂ O	0.5 mols				H (kJ/mol)	G (kJ/mol)
CO ₂	1 mols		Rxn 1		-99.5	38.8
CH ₃ OH	0 mols	300°C	Rxn 2		-39.1	-17.7
					ΔH values (kJ/mol)	
Species	\mathcal{E}_1 (Species = 0)	\mathcal{E}_2 (Species = 0)	\mathcal{E}_1 (Species > 0)	\mathcal{E}_2 (Species > 0)	ΔH (Species = 0)	ΔH (Species > 0)
$\mathcal{E}_1 = 0$	0	-2 to +2	0.1	-2 to +2	78.2 to -78.2	68.25 to -88.15
$\mathcal{E}_2 = 0$	-2 to +2	0	0	0.1	199 to -199	195.09 to -202.91
CO	-2 to +2	3 to -1	-2 to +2	2.9 to -1.1	81.7 to -159.9	85.61 to -155.99
H ₂	-2 to +2	-7 to 1	-2 to +2	-6.8 to 1.2	472.7 to -238.1	464.88 to -245.92
H ₂ O	-2 to +2	0.5	-2 to +2	0.4	179.45 to -218.55	183.36 to -214.64
CO ₂	-2 to +2	-1	-2 to +2	-0.9	238.1 to -159.9	243.19 to -163.81
CH ₃ OH	0	-2 to +2	0.1	-2 to +2	78.2 to -78.2	68.25 to -88.15
					ΔG values (kJ/mol)	
	G_p at 300°C, 1 br	38.8	G_p at 300°C, 20 br	10.3	G_p at 300°C, 50 br	1.6
Species	ΔG (Species = 0)	ΔG (Species > 0)	ΔG (Species = 0)	ΔG (Species > 0)	ΔG (Species = 0)	ΔG (Species > 0)
$\mathcal{E}_1 = 0$	35.4 to -35.4	39.28 to -31.52	35.4 to -35.4	36.43 to -34.37	35.4 to -35.4	35.56 to -35.24
$\mathcal{E}_2 = 0$	-77.6 to 77.6	-79.37 to 75.83	-20.6 to 20.6	-22.37 to 18.83	-3.2 to 3.2	-4.97 to 1.43
CO	-130.7 to 95.3	-128.93 to 97.07	-73.7 to 38.3	-71.93 to 40.07	-56.3 to 20.9	-54.53 to 22.67
H ₂	46.3 to 59.9	42.76 to 56.36	103.3 to 2.9	99.76 to -0.64	120.7 to -14.5	117.16 to -18.04
H ₂ O	-86.45 to 68.75	-84.68 to 70.52	-29.45 to 11.75	-27.68 to 13.52	-12.05 to -5.65	-10.28 to -3.88
CO ₂	-59.9 to 95.3	-61.67 to 93.53	-2.9 to 38.3	-4.67 to 36.53	14.5 to 20.9	12.73 to 19.13
CH ₃ OH	35.4 to -35.4	39.28 to -31.52	35.4 to -35.4	36.43 to -34.37	35.4 to -35.4	35.56 to -35.24
					ΔG values (kJ/mol)	
	G_p at 300°C, 70 br	-1.6	G_p at 300°C, 90 br	-4		
Species	ΔG (Species = 0)	ΔG (Species > 0)	ΔG (Species = 0)	ΔG (Species > 0)		
$\mathcal{E}_1 = 0$	35.4 to -35.4	35.24 to -35.56	35.4 to -35.4	35 to -35.8		
$\mathcal{E}_2 = 0$	3.2 to -3.2	1.43 to -4.97	8 to -8	6.23 to -9.77		
CO	-49.9 to 14.5	-48.13 to 16.27	-45.1 to 9.7	-43.33 to 11.47		
H ₂	127.1 to -20.9	123.56 to -24.44	131.9 to -25.7	128.36 to -29.24		
H ₂ O	-5.65 to -12.05	-3.88 to -10.28	-0.85 to -16.85	0.92 to -15.08		
CO ₂	20.9 to 14.5	19.13 to 12.73	25.7 to 9.7	23.93 to 7.93		
CH ₃ OH	35.4 to -35.4	35.24 to -35.56	35.4 to -35.4	35 to -35.8		

ΔH is the enthalpy of the reaction in kJ/mol, ΔG is the free energy of reaction in kJ/mol, $G_{(p)}$ is the free energy (ΔG , in kJ/mol) of the reaction at a pressure, P, in bars (br). \mathcal{E}_1 and \mathcal{E}_2 are extents of reaction 1 and 2, respectively.