

Solubility of Carbon Monoxide and Hydrogen in Dodecane and 1, 4-Dioxane

by

Azwan Fitri Zainal Abidin

Dissertation submitted in partial fulfillment of
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CERTIFICATION OF APPROVAL

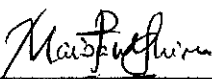
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A project dissertation submitted to the
Chemical Engineering Programme
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BACHELOR OF ENGINEERING (Hons)
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Approved by



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July 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



AZWAN FITRI ZAINAL ABIDIN

ABSTRACT

Solubility of hydrogen and carbon monoxide in dodecane and 1,4-dioxane were measured using the high pressure solubility cell over the temperature range from 303 to 323 K and pressure range from 2 to 10 bar. The measured solubility were correlated and interpreted by activity coefficient models based on regular solution theory (RST) with Yen and McKetta correction for polar solvent. Experimental data and RST shows hydrogen gas and carbon monoxide gas are more soluble in 1, 4-dioxane than dodecane and carbon monoxide gases have greater solubility towards both solvents than hydrogen gases. RST model acting in this particular system with large errors. The RST model might not be suitable for this particular system.

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CHAPTER 1: INTRODUCTION

Thermomorphic solvent system (TMS) or temperature dependent multi-component solvent is considered in the open literature is the best solvent [1] for hydroformylation reaction in the range of temperature and pressure of 303K-323K and 2-10 bar. TMS consists of propylene carbonate (PC), dodecane and 1, 4-dioxane. It is known until now (until this report was done) there is no other open literature study on the dodecane and 1, 4-dioxane as a solvent for hydroformylation individually as been conducted in the range of temperature and pressure study. This chapter summarizes the background of the study, the problem statement and the objectives of the study as well as the scope of the study. The material presented here is intended as a general review for the subsequent chapters. More details specific to the chapter topics are addressed therein.

1.1 BACKGROUND OF THE STUDY

Hydroformylation is the reaction process of an olefin with syngas (H_2/CO) in the presence of the cobalt, platinum or rhodium catalyst to produce an aldehyde. This process has undergone continuous growth since its invention in the 1930's: production capacity reached 6.6×10^6 tons in 1995 and this number still increased. Hydroformylation has provided versatile route for the synthesis of a vast array of bulk and speciality chemicals. The hydroformylation products prepared on the largest scale are butyraldehyde and ethylhexanol [2]. The second largest industrial that applied of hydroformylation is the production of C₈-C₂₀ range of alcohols which are the basic materials of the biodegradable detergents.

In hydroformylation, reaction occurs at the olefinic double bond with synthesis gas CO and H₂ in the presence of the transition metal catalyst like rhodium or cobalt to produce form linear (*n*) and branched (iso) aldehydes containing an

additional carbon as primary products (see next chapter on more data gathered for hydroformylation). Thus, the solubility of the reactant gas in the liquid medium is an important parameter required for the interpretation of kinetics of a gas-liquid reaction for a reactor design. Therefore the solvent that could have higher solubility for CO and H₂ will be advantageous.

For this particular project, the author had narrowed his scope by looking at the 3 solvents that have more attention nowadays. The solvents are propylene carbonate (PC), biphasic mixture of PC and dodecane, and (TMS)-system consisting of. As mentioned earlier, it is found that TMS has the higher affinity with CO and H₂, which is comparable to the single phase PC [1]. All these solvents the data already gathered by other scholars and already published it in the open literature. The author interested to find out what are solubility of the CO and H₂ in the dodecane and 1, 4-dioxane individually since there is no study has been conducted yet in this particular study at the range of the temperature and pressure of study.

TMS-system provides easy separation of the expensive catalyst from the products on cooling of the reaction mixture [3]. TMS-system is preferred because of the high boiling point, thermal stability and inert nature with respect to the homogeneous catalyst. Previous work in the open literature confirmed that the solubility of CO and H₂ in TMS-system is higher compared to the biphasic system, dodecane+PC and single system, PC for the hydroformylation process [1].

The author has decided to choose the working temperature and pressure in the range from 303-323K and 0.2-1.0 bar respectively. This range of temperature and pressure was chosen from the previous work [1]

The measured solubilities will be interpreted by activity coefficient models based on the regular solution theory (RST) and RST with Yen and Mcketta extension for polar solvents (further explanation on next chapter)

1.2 PROBLEM STATEMENT

Since the hydroformylation is one of the common practices in producing the aldehydes, it is required to find the best solvent that can give higher solubility of CO and H₂. PC, biphasic mixture and TMS system data already existed in the open literature.

Thermomorphing multicomponent solvent (TMS) system shows higher affinity for CO and H₂ which is comparable to the propylene carbonate (PC) in temperature and pressure ranges of 298-343K and 0.1-1.5MPa [1]. TMS consists of PC as a polar solvent, dodecane as a nonpolar solvent and 1, 4-dioxane as a semi polar solvent.

The measure of the gas solubilities in the solvent plays a crucially important role due to the reaction kinetics and the reactor design is strongly dependent on it. Thus, it is important to find out the best solvent that can give higher solubility of CO and H₂.

The issue to be address here is to find out whether TMS is better solvent for CO and H₂ compared to dodecane and 1,4-dioxane individually and can proposed what is the solvent that play a major role in TMS whether PC, dodecane and 1,4-dioxane. Hence it is the author hope that by getting the result for dodecane and 1,4-dioxane individually this field of study can be extended to find the best ratio of solvents that can be implied in the TMS solvent.

1.3 OBJECTIVE OF STUDY

The study of this work has three main goals to be achieved. The first objective is to calculate the solubility of CO and H₂ in dodecane and 1, 4-dioxane with RST and RST with correction by Yen and McKetta. With this calculated value,

the solubility of the H₂ in CO in dodecane and 1,4-dioxane can be further predicted with value from the experimental works.

The second objective of this particular study of work is to compare the value calculated by RST and RST with correction by Yen and McKetta with the data getting from the experimental works and the data obtained from the open literature. The result from the open literature than will be extrapolate to analyze whether the RST and RST with correction by Yen and McKetta can be relevant for temperature and pressure that not in the range of the author study

The third objective is to interpret the empirical data with the thermodynamics modeling by RST and RST with Yen and McKetta correction. With this interpretation, we can know how well the empirical data with respect to the thermodynamics modeling. The solubility of the gases later will be analyzed with respect to the data obtained by calculated value, experimental works and by checking with other open literature that available now. The effect of the temperature, pressure and the molecular bonding will be discussed in order to study the solubility effects.

1.4 SCOPE OF STUDY

The scope of this research is divided into the following section:

1.4.1 Determination of Solubility Experimentally

The study of the solubility will be correspondent to the Henry's Law. The Henry's constant will be determine experimentally and the data gathered will be present in the graph manner with partial pressure vs mole fractions plotting will yield the Henry's constant as a slope. The calculation of the mole fraction of the solute gas is follow equation below:

$$X_g = [P_i - (P_f p^v)] V_g / RT V_L \rho_L \quad (1)$$

P_i and P_f is the initial and final pressure reading in the equilibrium cell; p^v is the vapor pressure of the solvents; V_g and V_L are the volumes of the gas and liquids phases respectively; R gas constant; T absolute temperature; ρ_L is the molar density of the liquid. For this particular study with the temperature range from 303K-323K the vapor pressure for the dodecane is negligible. The vapour pressure for the 1, 4-dioxane was calculated with the Antoine equation where the constant are taken from literature [3].

Peng Robinson equation of state (PREoS) has been used to calculate the fugacity coefficient in order to ensure the applicability of the ideal gas law in Eq. (1). The fugacity very close to unity and the vapor phase could consider as an ideal gas [4]. Here it is also assumed under equilibrium conditions the amount of dissolved gas in the liquid has negligible contribution to the liquid volume (details on chapter 3.2.1.3)

1.4.2 Thermodynamics Modelling

The Regular Solution Theory (RST) based model is used to correlate and interpret the experimental solubility data. A comparison shall be made for the prediction accuracy of the models.

RST model is essentially limited to dissolution of non polar gas in non polar solvent. Since in this particular study, with the temperature and pressure range from 303-323K and 2-10bar the 1, 4-dioxane is appearing to be polar solvent. Thus for dodecane and 1, 4-dioxane will follow the equation of RST alone and RST with correction by Yen & McKetta respectively. Thus, in order to extend the RST to polar solvents 1,4-dioxane, the RST proposed by Yen & McKetta was applied [4]

RST

$$-\ln x_2 = \ln \left(\frac{f_2^L}{f_2} \right) + (\phi_1^2 v_2 [\delta_1 - \delta_2]^2) / RT \quad (2)$$

RST with Yen and McKetta correction:

$$\frac{1}{x_2} = \frac{f_2^L}{f_2} \exp \left[\frac{v_2 [\delta_1 - \delta_2]^2 \phi_1^2}{RT} + \frac{\ln \phi_2}{x_2} + 1 - \phi_2 / x_2 \right] \quad (3)$$

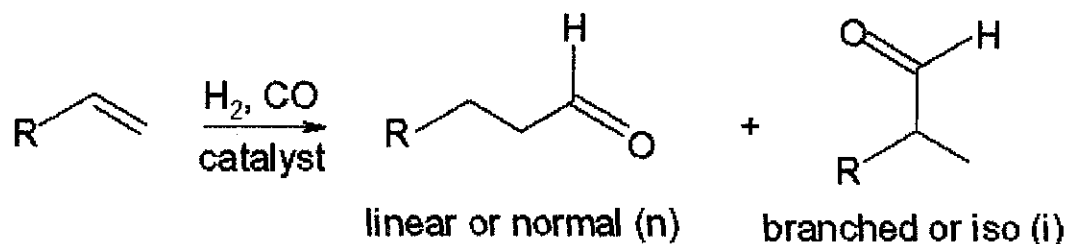
the subscripts 2 and 1 represents the gas and liquid (solvent) respectively; x_2 is the mole fraction of the dissolved solute in the solvent at atmospheric pressure (103.25kPa); f_2 (bar) and f_2^L (bar) are the fugacities of pure gas and hypothetical liquid solute at atmospheric pressure respectively; ϕ_1 and ϕ_2 are the volume fraction of solvent and gas respectively; v_2 ($\text{m}^3 \text{mol}^{-1}$) is the molar volume of gas ; and δ_1 and δ_2 are the solubility parameters (J m^{-3})^{1/2} for the solvent and solute gas respectively; R is the gas constant and T is the absolute temperature. RST also state that the solubility parameters and molar volume of solute are independent of temperature (details on chapter 2.4)

CHAPTER 2: LITERATURE REVIEW/THEORY

This chapter covers all the information needed for better understanding on the field of study. The hydroformylation reaction was further study and presented here. The introduction of the chemicals involved also has been study and the related information was gathered here. The Henry's law and Regular Solution theory also presented here. The author also did discuss the methods for measuring gas solubilities in this particular chapter in order to have better understanding on the definition and application of the solubility.

2.1 HISTORY OF HYDROFORMYLATION

As mentioned in the introduction part, background of the study; hydroformylation is the reaction of an olefin with syngas in the presence of cobalt, rhodium or platinum catalyst to produce an aldehyde. The overall reaction can be best represented by



Hydroformylation was discovered by Otto Roelen in 1938 during an investigation of the origin of oxygenated products occurring in cobalt catalyzed Fischer-Tropsch reactions. Roelen's observation that ethylene, H_2 and CO were converted into propanal, and at higher pressures, diethyl ketone, marked the beginning of hydroformylation.

Cobalt catalysts completely dominated industrial hydroformylation until the early 1970's when rhodium catalysts were commercialized. In 2004, ~75% of all

hydroformylation processes are based on rhodium triarylphosphine catalysts, which excel with C8 or lower alkenes and where high regioselectivity to linear aldehydes is critical. Hydroformylation also is chosen as the best reaction to produce aldehydes.

2.2 INTRO TO ALDEHYDES, PC, DODECANE & 1, 4-DIOXANE

An aldehyde is an organic compound containing a formyl group. This functional group consists of a carbonyl center bonded to hydrogen, O=CH-. This group is called aldehyde group or formyl group. Aldehydes have properties that are diverse and which depend on the remainder of the molecule. Smaller aldehydes are more soluble in water, formaldehyde and acetaldehyde completely so. The volatile aldehydes have pungent odors. Aldehydes are important precursors to commercially useful plasticizers and detergents. Millions of tons of aldehydes are produced industrially each year. There are several methods preparing aldehydes, but the dominant technology is hydroformylation. The method is attractive because the carbon-chain length is extended by one atom [6]. Aldehydes also can be occurred naturally. Traces of many aldehydes are found in the essential oil that contributed to their favourable odours like vanillin.

PC is an organic compound, a twofold ester of propylene glycol and carbonic acid. PC molecular formula is C₄H₆O₃. PC is colourless and odourless liquid. PC melting point and boiling point is 218K and 513K respectively. PC is useful as a highly polar solvent and considered highly inert. PC does not donate the proton like water, thus PC is called as aprotic solvent [7]. Polar aprotic solvents are solvents that share ion dissolving power with protic solvents but lack acidic hydrogen. These solvents generally have high dielectric constants and high polarity. Common characteristics of aprotic solvents are solvents do not display hydrogen bonding, solvents do not have acidic hydrogen and solvents are able to stabilize ions [8].

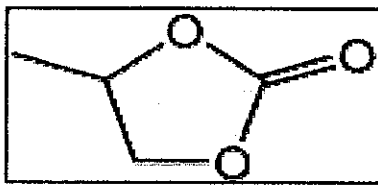


Figure 2.1: PC chemical structure

Dodecane is a liquid alkane hydrocarbon with chemical formula $C_{12}H_{26}$. Dodecane is colourless liquid and has the melting point and boiling point 263.55K and 489.35K respectively. Dodecane is use as nonpolar solvent [9]. Dodecane can cause damage to the lung and may cause central nervous system depression as well. Thus, a precaution steps need to be taken while handling this substance.

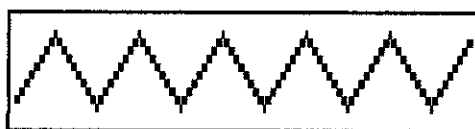


Figure 2.2: Dodecane chemical structure

1, 4-dioxane is a clear, colourless heterocyclic organic compound which is a liquid at room temperature and pressure. It has the molecular $C_4H_8O_2$ and a boiling point of 374.15K. 1, 4-dioxane commonly used as an aprotic solvent.

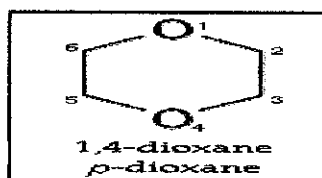


Figure 2.3: chemical structure of 1, 4-dioxane

1, 4-dioxane is a known eye and respiratory tract irritant. It is suspected of causing damage to the central nervous system, liver and kidneys. The precautions actions shall be taken while handling this chemical.

2.3 HENRY'S LAW CONSTANT

Henry's law state that at constant temperature the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid. There are several conventional ways Henry's constants are defined in the literature; the following paragraphs show how to derive the Henry's law constant and infinite dilution activity coefficient based on the definitions used in this work [10]

The Henry's law constant is defines as

$$H_1(T,P) = \lim_{x \rightarrow 0} f_i^L/x_1 \quad (4)$$

Where f_i^L is the fugacity of the gas dissolved in the liquid phase. The Henry's constant depend on the temperature, but is relatively to pressure, especially over the pressure ranges examined in the present work. Knowing the fugacity of the gas in the liquid phase must be equal to the fugacity of the gas in the gas phase and approximating the gas phase fugacity as the gas phase pressure, the following form of Henry's law can be obtained:

$$P_1 = H_1 (T). x_1 \quad (5)$$

Where P_1 is the partial pressure of the gas and $H_1 (T)$ will have units of pressure and is inversely proportional to the mole fraction of the gas in the liquid.

The Henry's constant is also directly related to the infinite dilution activity coefficient and the vapor pressure of the gas. The equilibrium condition for a binary mixture of a gas (1) and solvent (2) can be expressed as [10]

$$\Phi_1 \cdot y_1 \cdot P = \gamma_1 \cdot x_1 \cdot f_1^0 \quad (6)$$

Assuming the vapor phase is ideal ($\Phi_1=1$), the solvents is non volatile ($y_1=1$) and taking $f_1^0 = P_1^{\text{sat}}$ is the vapor pressure of pure gas at temperature T, equation 6 can be re written as

$$P = \gamma_1 \cdot x_1 \cdot P_1^{\text{sat}} \quad (7)$$

The activity coefficient of the gas in the solvent phase, γ_1 , therefore be determined directly by measuring the mole fraction of gas dissolved in the solvent as function of the pressure of gas above the solvent solution. Given the assumption used for equation 4 and 7 can be arranged as:

$$H_1(T) = \lim_{x \rightarrow 0} \gamma_1 \cdot P_1^{\text{sat}} \quad (8)$$

or that

$$\gamma_1 = H_1(T) / P_1^{\text{sat}} \quad (9)$$

The solubility of a gas in a liquid is largely dependent on the intermolecular interactions occurring between both components. Henry's law is an empirical relationship that is used to estimate the solubility of a gas in a liquid at small concentrations. Henry's law is the simplest method could be used to estimate the gas solubility provided the Henry's law constant is known or can be found by fitting experimental solubility data. If the solubility of the CO and H₂ follow the Henry's

law, then a plot of partial pressure vs mole fractions of the gas should be a straight line with a slope of Henry's constant.

2.3.1 Derivation for Enthalpy and Entropy of Absorption

Enthalpy and entropies of absorption can be found by considering the temperature effects on the gas solubilities. The enthalpy yields information about the strength of interaction between the liquid and dissolved gas, whereas the entropy indicates the level of ordering that takes place in the liquid/gas mixture. These properties can be determined from the thermodynamic relations [11]

$$\Delta h_1 = \hat{h}_1 - h_1^{ig} = RT \left\{ \frac{\partial \ln x_1}{\partial \ln T} \right\}_P \left\{ \frac{\partial \ln a_1}{\partial \ln x_1} \right\}_{P,T} \quad (10)$$

$$\Delta s_1 = \hat{s}_1 - s_1^{ig} = R \left\{ \frac{\partial \ln x_1}{\partial \ln T} \right\}_P \left\{ \frac{\partial \ln a_1}{\partial \ln x_1} \right\}_{P,T} \quad (11)$$

Where \hat{h}_1 and \hat{s}_1 are the partial molar enthalpy and entropy of the gas in the solution, h_1^{ig} and s_1^{ig} are the enthalpy and entropy of the pure gas in the ideal gas phase, and a_1 is the activity of the gas in the solution:

$$a_1 = \gamma_1 \cdot x_1 \quad (12)$$

2.4 REGULAR SOLUTION THEORY

Regular solution theory (RST) has been used by several workers to interpret the solubilities of CO and H₂ in different hydroformylation solvents [5]. The average error of prediction has been less than 10% in most cases.

RST is essentially limited to dissolution of non polar gases in non polar, non-associating solvent, the modifications to the RST by Yen and McKetta was applied in order to extend the RST to polar solvents, such as PC and 1, 4-dioxane. The activity models are presented below in the way they used for the solubility calculations:

RST

$$-\ln x_2 = \ln \left(\frac{f_2^L}{f_2} \right) + (\phi_1^2 v_2 [\delta_1 - \delta_2]^2) / RT \quad (13)$$

RST with Yen and McKetta correction:

$$\frac{1}{x_2} = \frac{f_2^L}{f_2} \exp \left[\frac{v_2 [\delta_1 - \delta_2]^2 \phi_1^2}{RT} + \frac{\ln \phi_2}{x_2} + 1 - \phi_2 / x_2 \right] \quad (14)$$

the subscripts 2 and 1 represents the gas and liquid (solvent) respectively; x_2 is the mole fraction of the dissolved solute in the solvent at atmospheric pressure (101.325kPa); f_2 (bar) and f_2^L (bar) are the fugacities of pure gas and hypothetical liquid solute at atmospheric pressure respectively; ϕ_1 and ϕ_2 are the volume fraction of solvent and gas respectively; v_2 ($\text{m}^3 \text{mol}^{-1}$) is the molar volume of gas ; and δ_1 and δ_2 are the solubility parameters (J m^{-3})^{1/2} for the solvent and solute gas respectively; R is the gas constant and T is the absolute temperature. RST also state that the solubility parameters and molar volume of solute are independent of temperature.

The solubility parameter for dodecane and 1, 4-dioxane will be calculated from the heat vaporization as pproposed by Hildebrand and Scott [12]

$$\delta_1 = (\Delta H_v - RT/V_m)^{1/2} \quad (15)$$

ΔH_v represents the heat vaporization and V_m the molar volume of the solvent. Heat of vaporization is generally reported at the normal boiling temperature (T_b). The correlation proposed by the Reid Prausnitz [13] was used to calculate ΔH_v at the chosen temperature of study.

$$\Delta H_{v,T} = \Delta H_{v,T_b} \left(\frac{1 - T_r}{1 - [T_r]T_b} \right)^{0.375} \quad (16)$$

$$T_r = T/T_c \quad \text{and} \quad (T_r)_b = T_b/T_c$$

T_c is the critical temperature of the dodecane and 1, 4-dioxane.

2.5 SOLUBILITY OF CO and H₂ IN TMS

As the TMS system has been said as the better solvent for the CO and H₂ for this process, the solubility of CO and H₂ not yet as been determined experimentally for individual component in TMS except for PC. Thus, solubilities of CO and H₂ in pure solvent of dodecane and 1, 4-dioxane to the hydroformylation process are studied in this work.

TMS system provides easy separation of the expensive catalyst from the products on cooling of the reaction mixture. TMS also preferred because high boiling point, thermal stability and inert nature with respect to the homogeneous catalyst, olefin, hydrogen, carbon monoxide, and the hydroformylation products.

Lecturers/scholars from the Universiti Teknologi PETRONAS have done the experiment to collect the data of solubility CO and H₂ in PC, biphasic mixture and TMS system. The result shows that the TMS systems has higher affinity and solubility of CO and H₂ compared to single phase PC and biphasic mixture in the range of temperature and pressure of 298-343K and 0.1-1.5MPa. However, neither

experimental data nor any theoretical model on solubilities for CO and H₂ of the dodecane and 1, 4-dioxane individually is available in the open literature.

The study of the thermodynamics properties for the dodecane and 1, 4-dioxane might be done by the author to support his findings in the solubility of the CO and H₂ in the dodecane and 1, 4-dioxanes and to make this research more valuable. The absorption of the CO and H₂ with dodecane and 1, 4-dioxane liquid will determine the solubility data and the Henry's constant for each gas in the different solvent will be estimated and reported as a function of temperature. Furthermore, the enthalpy and entropy of absorptions will be obtained from the estimated Henry's constant.

2.5.1 Methods for Measuring Gas Solubility

The following sections will address various experimental methods for measuring gas solubilities and how factors are addressed.

2.5.1.1 Volumetric and Pressure Drop Methods

The most typical methods for measuring the solubility of gases in liquid are modifications on one of two techniques, both occurring at constant temperature. In the first technique, often referred to as the pressure drop method, the volume is held constant, and the pressure is monitored as the gas absorbs into the liquid. In the second case, frequently called the volumetric technique, the pressure is kept constant, and the volume is change needed to maintain the pressure as the gas is absorbed by the liquid is measured. By using either first or second method, the pressure, temperature and volume before absorption and then following absorption are known. Therefore, the amount of gas absorbed by the liquid can be calculated, frequently by using an equation of state to convert pressure, volume and temperature to moles.

Many modifications on the apparatus used for these techniques have been made to improve the different aspects of the measurements, such as improving the equilibration time by changing the stirring method or gas/liquid interface area, improving the degassing of the solvent method, improving the temperature, volume, pressure measurement and control [14] [15]. In general, the majority of the gas solubilities in liquids reported in the literature have been measured using the fundamental concepts involved in either the volumetric (isobaric and isothermal) or the pressure drop (isochoric and isothermal) techniques.

2.5.1.2 Gas Chromatography (GC)

GC can be used to measure gas solubilities in liquids in two different ways [14]. In the extractive technique, the solvent is saturated with the gas of interest and then coated on the column. A non-absorbing carrier gas is passed through the column to extract the gas of interest. The carrier gas phase is analyzed in the GC to determine the amount of solute gas removed. In this technique, it is important to saturate the carrier gas with the solvent prior to flowing it through the column to avoid removing the solvent in the column in the carrier gas phase. In the second GC technique, gas solubilities are measured in the solvent at infinite dilution by first coating the pure (degassed) solvent on a column and then a non-absorbing carrier gas containing the solute of interest is flowed to the column. The amount of gas absorbed by the solvent can be calculated from the retention time of the solute in the column.

2.5.1.3 Gravimetric Method (GM)

In the GM, the gas solubility is determined by measuring the change in weight of the sample upon absorption. This technique is commonly used for absorption of gases onto solids but rarely is used for absorption of gases into liquids because any loss of the liquid due to the evaporation affects the final weight of the sample.

Buoyancy correction is an important factor to account for when measuring gas solubilities by the gravimetric techniques. In the apparatus used in this work, a counterweight side symmetric to the sample side was used to minimize these effects, but still need to be taken into consideration.

2.5.1.4 Other Techniques

Techniques other than those discuss above are occasionally used for measuring gas solubilities in liquid [14]. Mass spectrometry can be used to analyze ratios of gases dissolved in solvents. Chemical analytical techniques can sometimes be used to determine the solubility of specific gases by analyzing for reaction products, but these techniques only apply to specific situations. Some gas-specific sensors are commercially available, such as electrochemical sensors to measure dissolved oxygen content, but again those sensors only work for a specific gas.

CHAPTER 3: METHODOLOGY

In this particular chapter, the author will further explained on the methodology or the procedure that the author might be implement while run his experiment in order to complete his findings in this field of study : Solubility of CO and H₂ in dodecane and 1, 4-dioxane. The author also will briefly state the research methodology that the author had done as well as the Gantt chart or the milestone for this study.

3.1 RESEARCH METHODOLOGY AND GANTT CHART

The author also did the literature review by getting the first literature material by his supervisor Dr Maizatul Shima lecturer of Universiti Teknologi Petronas (UTP). This topic was proposed by Dr Maizatul Shima in conjunction with her previous work: Solubility of CO and H₂ in propylene carbonate and thermomophic multicomponent hydroformylation solvent. With this initial literature review, the author had expands the findings by review other scholars works in other to collect all the information that relevant and related to the field of study. The links and the name of the journal have been stated by the author in the references part.

Please refer to the appendix 1 to see the Gantt chart/milestone of the author planned to complete his findings.

3.2 METHODOLOGY OF THE EXPERIMENT

It is essential for the author to have a correct method or procedure to run his experiment to avoid any delay in time. In this section the author will further explain about the method on determination of the gas solubility, the pressure test method, purging and evacuation method and the solubility experiment. For the details

experiment procedure please refer to the chapter 3.2.1.4. For this particular study three range of temperature has been select for purposed of study which are 303-323K and the pressure is in the range of 3-15bar.

3.2.1 Determination of the Gas Solubility

The solubilities of the pure CO and H₂ in dodecane and 1,4-dioxane are measured by the absorption method as a function of the gas pressure (3-15 bar) and the temperature (303-323K) in a 50mL capacity high pressure gas solubility cell (SOLTEQ model BP 22). As shown in the figure 3, the equipment consists of a gas mixing cell and an equilibrium cell and each of them are immersed in a heating jacket. A PTFE coated magnetic stir-bar placed within the cell in conjunction with an external magnet used to stir the liquid phase inside the cell. Other supporting components include circulation pump, vacuum pump, thermostat heating bath, liquid feed pump, liquid degassing unit and instrumentations such as mass flow controllers, pressure and temperature indicators. High accuracy pressure sensors and platinum RTD sensors are used for high accuracy measurements [16]

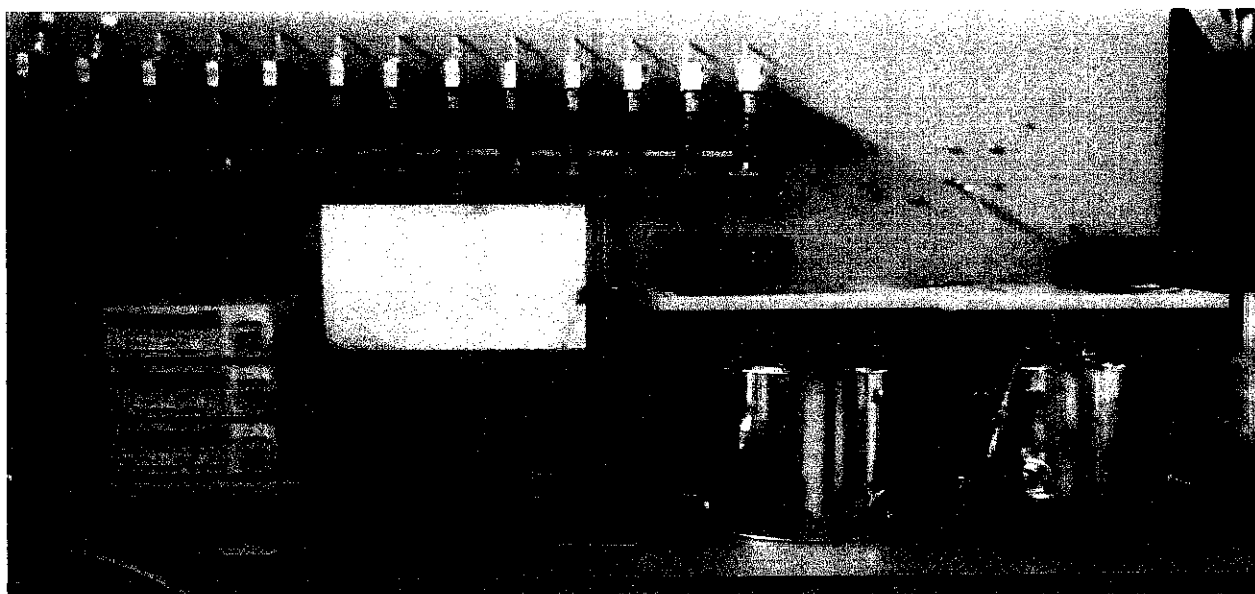


Figure 3.1: High pressure solubility cell unit picture

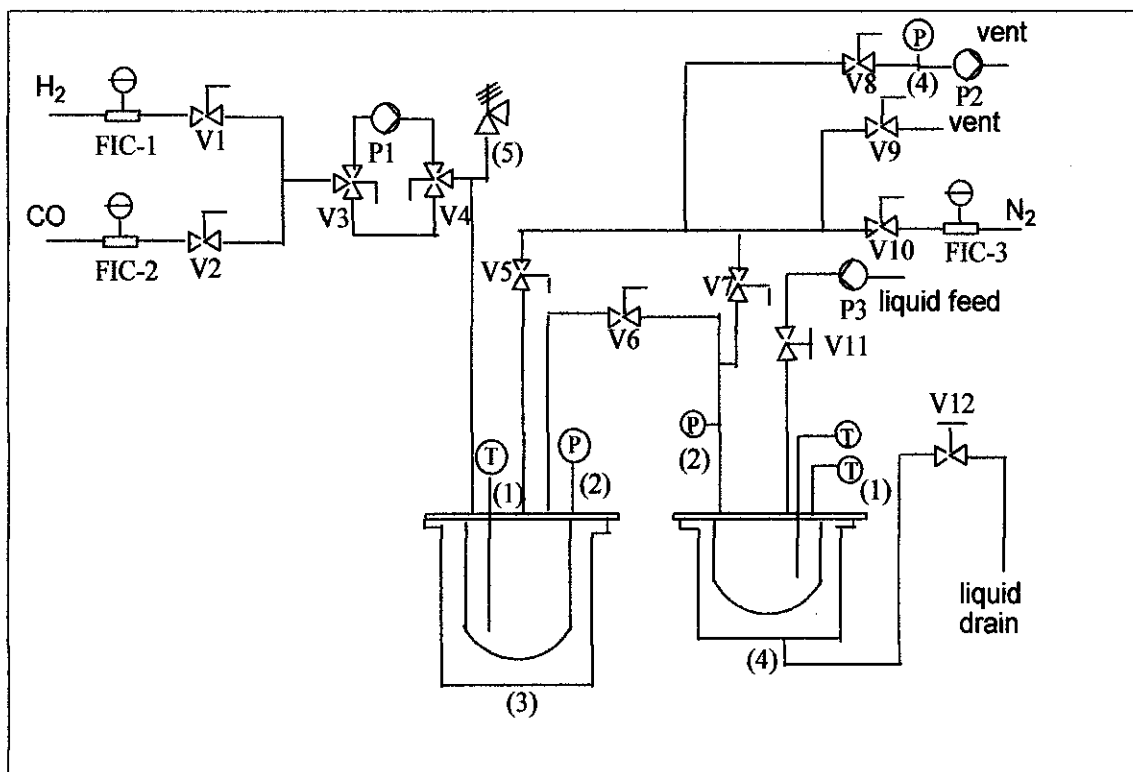


Figure 3.2: Schematic diagram for high pressure solubility cell: 1-thermocouple, 2-pressure transducer, 3-mixing vessel, 4-equilibrium vessel, 5-pressure relief valve

3.2.1.1 Pressure Test

After closing all valves, the gas solubility cell is tested for a leakage by using SNOOP liquid leak detector (SNOOP, Swagelok). The unit was pressurized with N_2 by opening the valves V5, V6 and V10 until the pressure reading reads 6.0MPa. When the visible bubbles are observed, the equipment was de-pressurized before the loose connection was tightened to stop the gas leakage. When the pressure stabilized approximately within 15 minutes, the pressure release valve was set at 3MPa.

3.2.1.2 Purging and Evacuation

The unit supposedly purges with N_2 gas and fully evacuated before carrying out the solubility experiment. Purging was carried out before evacuation to avoid residue gas and liquid from passing through the vacuum pump during evacuation.

Both the mixing and equilibrium cell are purge by allowing N₂ gas to flow through the unit for approximately 10 minutes by setting the flow rate at FIC-3 to 8NL/min. opening valves V5, V7 and V8, the mixing vessel and an equilibrium cell were then evacuated using a turbo molecular vacuum pump (Model DCU-200, Pfeiffer Vacuum). A pressure transducer (Model DPI 150, Druck) having a precision of tolerance 1×10^{-4} bar was used to measure the pressure in the gas reservoir and in the equilibrium cell.

3.2.1.3 Solubility Experiment

After achieving the specified level of vacuum, which is approximately 1×10^{-3} bar, the temperature of the heating bath was set at a desired value and the bath circulation is allow to start. The temperature in the mixing cell and the equilibrium cell is measured by digital thermometers (Model 7563, Yokogawa). Using the maximum flow rate, the gas is charged into the mixing vessel by opening the valves at the mass flow controller. Immediately the air drive supply is turn on to the gas booster P1. The gas booster is air driven, and therefore the air pressure is regulated to control the boosting speed. Once the pressure of the mixing cell has reached the desired pressure, the air drive supply to the gas booster is turn off and valve 4 was switched toward the bypass line. After thermal equilibrium cell is attaining, the pressurized gas is charged into the equilibrium cell up to the desired pressure by slowly opening valve V6. When the pressure and temperature of the mixing vessel and equilibrium cell are equalized, solvent in 50mL capacity was the quickly introduced into the cell using a liquid feed pump, P3. The contents are stir at 1000rpm for about hr to equilibrate the liquid phase with the gas. The total pressure change due to absorption is recorded on line as a function of time till it attained a steady and constant value, indicating saturation of the liquid phase.

From the initial and final pressure readings, the solubility is calculated in mole fraction as in equation 1. As mentioned in the chapter 1.4.1, the vapor pressure of the dodecane is negligible. Only the vapor pressure of the 1,4-dioxane will take

into consideration. The vapor pressure of the 1,4-dioxane is calculated based on Antoine equation:

$$\log_{10}(P) = A - (B/(C+T)) \quad (17)$$

where P is the vapor pressure (kPa), T the temperature (°C) and A, B, C are constants which are 6.5564, 1554.679 and 240.337, respectively [3].

$$\ln \phi_i^f = \frac{b_i}{b_m} (Z-1) - \ln(Z-B) - \frac{A}{2B\sqrt{2}} \times \left[\frac{2 \sum_j y_j \sqrt{a_i a_j} (1 - k_{ij})}{a_m} \right] - \frac{b_i}{b_m} \ln \frac{Z + \frac{(1+\sqrt{2})B}{Z + \frac{(1-\sqrt{2})B}{Z}}}{Z + \frac{(1-\sqrt{2})B}{Z}} \quad (18)$$

Where Z is the compressibility factor and can be written as following:

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B) = 0 \quad (19)$$

Where Z is commonly defined as $Z = (PV/RT)$

$$A = \frac{aP}{R^2 T^2} \quad (20)$$

$$B = \frac{bP}{RT} \quad (21)$$

To calculate the fugacity coefficients, ϕ_i^f using equation 18 or the compressibility factor, Z using equation 19, pure component parameter a_i and b_i were found from equation 20 to equation 24, using critical properties in Table 1, where M is the molecular weight (g mol^{-1}), T_c the critical temperature, P_c the critical pressure and ω the acentric factor.

$$\alpha(T, \omega) = \left[1 + K_i \left(1 - \sqrt{T_{ri}} \right) \right]^2 \quad (22)$$

$$a_i(T) = a_i(T_c) \times \alpha(T, \omega) \quad (23)$$

Where at critical point temperature

$$a_i(T_c) = 0.45724 \frac{R^2 T_{ci}^2}{P_{ci}} \quad (24)$$

$$b_i(T_c) = 0.0778 \frac{R T_{ci}}{P_{ci}} \quad (25)$$

and

$$K_i = 0.3764 + 1.54226\omega_i - 0.26992\omega_i^2 \quad (26)$$

Table 3.1: Critical properties and acentric factors used in the PR EoS

Component	M(gmol ⁻¹)	Tc(K)	Pc(MPa)	ω	Ref
H ₂	2.016	32.98	1.293	-0.217	[17]
CO	28.00	132.9	3.499	0.066	[18]

3.2.1.4 Experimental Procedure

This experimental procedure has been developed by the author with the supervised from his supervisor and with some experience of the author while he is running the equipment with UTP Master Student, Malyana in order for the author to get familiarized with the equipment and to gain experienced in conducting high pressure solubility cell.

Experimental Procedure (solubility study using solubility cell)

1. Switch on main power supply
2. Switch on PC

Username: user

Password: BP22

Purging

1. Open V15 and V18 (if equilibrium cell only: V19)
2. Open V23 to depressurized the unit (venting off)
3. Close V23 and open V22 (N₂ gas)
4. Allow N₂ to flow through the unit by setting the flow rate at FIC-13 to 10NL/min

5. When the P reading is approximate 10bar, switch off FIC-13 and place a beaker beneath V17 to drain off the liquid in the equilibrium cell
6. Introduce 20mL of solvent using the liquid feed pump through V16. Open V16 first, and then switch on the pump. Make sure gas bubbles are not formed in the tubing. Switch off the pump, and then close the valve
7. Repeat step 4 and 5 and then allow N₂ gas to flow through the unit and out from V17 for about 5-10 minutes by setting the flow rate at FIC-13 to 8NL/min
8. Stop the flow at FIC-13 and close V22 and V17
9. Make sure V15 and V17, V18 and V19 are closed.
10. Open V23 to vent the unit to atm pressure.

Evacuation

1. Complete purging first
2. Open V24 (to vacuum pump)
3. Open V18 and V19 to evacuate mixing vessel and equilibrium cell
4. Switch on the vacuum pump and start the vacuum process (till the P reading below than 1×10 milibar)
5. Close valve V24 and stop vacuum pump
6. Close V18 and V19

Introducing gas in the mixing cell

1. Set the pressure regulators on the gas cylinder to be used at 15 barg
2. Switch on heating bath and set the desired heating T
3. Start the bath circulation and open V30 and V31 to allow heating fluid to flow through heating jackets B3 and B4

4. Switch bypass V13 and V14 towards the gas booster P1. Use maximum flow rate of the gas (software)
5. Open the V6
6. Turn on the air drive supply
7. Allow the gas to pressurized until the desired P is reached
8. Turn off the air drive supply and turn off V14 and V13
9. Turn off all the mfc (software) and close valve V1-V12
10. Allow the T in mixing vessel to stabilize

Solubility Study

1. Select the parameters to be recorded by the software and then start the timer
2. Charge equilibrium cell with gas by slowly opening V15 until the pressure are equalized
3. Close V15
4. Allow T in the equilibrium cell to stabilize before proceeding
5. Introduce 20mL of solvent using liquid feed pump through V16
6. Switch on the magnetic stirrer
7. Stop timer and collect sample when P in the equilibrium cell has stabilized

Shut down procedure

1. Switch off magnetic stirrer
2. Reduce T setpoint at the heating bath to room temperature
3. Allow T to drop
4. Perform purging step for mixing vessel and equilibrium cell
5. Once the bath T has dropped to below 50°C, close V30 and V31
6. Stop bath circulation and switch it off

7. Switch of PC, then the control panel
8. Return all valves to the initial position

CHAPTER 4: RESULT AND DISCUSSION

This chapter will be the heart of this report. All the data obtained whether by calculated method, experimental works and by checking with other scholars work in the open literature will be presented here. The calculation of the solubility and fugacity coefficient also will be presented here. The results obtained will be analyze to see the characteristic of the RST based model and RST with correction by Yen and McKetta based model as well as to see the effects of the temperature, pressure and the molecular bonding towards the solubility of the gases. Other parameters that might affects the result also will be take consideration and will be discussed further in this dedicated chapter.

4.1 CALCULATION

The solubility of the H₂ and CO has been predicted by using RST based model and RST with Yen and McKetta correction based model. RST based model has been used to calculate the solubility of the H₂ and CO in dodecane and RST with Yen and McKetta correction based model used to calculate the solubility of H₂ and CO in 1,4-dioxane.

4.1.1 Parameters Gathering Data

The equation of RST without correction (refer to equation 13) can be calculated if the terms in the right hand side is known. Some of the parameters like solubility parameter of the gases and molar volumes of the solute were taken from other scholars work [19-20] and the value as stated below:

$$\delta_{H_2} = 7.835 \cdot 10^3 \text{ J}^{0.5} \text{ m}^{-1.5}$$

$$\delta_{CO} = 6.4 \cdot 10^3 \text{ J}^{0.5} \text{ m}^{-1.5}$$

$$v_{H_2} = 3.73 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$v_{CO} = 3.21 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

4.1.1.1 Fugacity of the Hypothetical Liquid Solute

The parameter f_g^L was calculated from equation 25 and 26 proposed by Yen and McKetta for the temperature interval from 303-323K at atmospheric pressure.

For hydrogen:

$$\ln f_{H_2}^L = -7.4246 \cdot 10^{-2} + 4336T^{-1} - 9.3595 \cdot 10^5 T^{-2} + 6.3853 \cdot 10^7 T^{-3}$$

For carbon monoxide:

$$\ln f_{CO}^L = 4.7475 + 588.52T^{-1} - 1.3151 \cdot 10^5 T^{-2}$$

Table 4.1: fugacity of the hypothetical liquid

Temperature/K	$f_{H_2}^L$ /bar	f_{CO}^L /bar
303	564.999	191.978
313	548.176	197.432
323	530.389	202.151

4.1.1.2 Fugacity of the Pure Gas

The fugacity of the pure gas, f_g can be calculated with the equation given below:

$$f_g = P \cdot e^{bP/RT}$$

P = pressure (bar)

T = temperature (K)

R= gas constant (0.08314 bar.L/mol.K)

The value of the constant b is depending on the gases.

$$b_{H_2} = 2.661 \cdot 10^{-2} \text{ Lmol}^{-1}$$

$$b_{CO} = 3.895 \cdot 10^{-2} \text{ Lmol}^{-1}$$

Table 4.2: Fugacity of the pure gas at 2 bar

Temperature/K	f_{H_2}/bar	f_{CO}/bar
303	2.004229714	2.006337571
313	2.004094442	2.0061334783
323	2.003967553	2.005944569

Refer to the appendix 2 to see fugacity of the pure gas at different pressure of study.

4.1.1.3 Solubility Parameter δ_s For 1,4-Dioxane & Dodecane

The solubility parameter for solvents were calculated from the heat vaporization as proposed by the Hildebrand and Scott [12] as stated in equation 15 and the correlation proposed by the Reid and Prausnitz [13] was used to calculate the heat vaporization at the four chosen temperatures of study. The equation to calculate the heat vaporization as stated in equation 16. The parameters needed for the calculation of heat vaporization for both solvents was getting from the Lange's Handbook [19].

Since the 1,4-dioxane is a polar solvent, the solubility parameter needs to be further corrected by the method given by Lemcoff.

$$(\delta_s)_{\text{corr}}^p = \delta_s / (1.772 \log [\delta_s - \delta_s^2] - 0.509)$$

Table 4.3: solubility parameter for 1,4-dioxane

Temperature/K	$\delta_{1,4\text{-dioxane}}^{\text{H}_2/\text{J}^{0.5} \text{ m}^{-1.5}}$	$\delta_{1,4\text{-dioxane}}^{\text{CO}/\text{J}^{0.5} \text{ m}^{-1.5}}$
303	3023.0577	2986.3396
313	3002.4750	2934.4814
323	2981.3040	2944.0195

Table 4.4: solubility parameter for dodecane

Temperature/K	$\delta_{\text{dodecane}}/\text{J}^{0.5} \text{ m}^{-1.5}$
303	15746.91
313	15647.30
323	15545.42

4.1.1.4 Volume Fraction \square

The volume fraction of the solvent and the gases can be simplified by ratio of the solvent or gases with respect to the total volume. The total volume with respect to the particular equipment used to run the experimental is 50ml. the volume fraction of the solvent and gases as shown in the calculation below:

Volume fraction:

$$\phi_g = \frac{x_g v_g^L}{x_g v_g^L + x_s v_s^L}$$

$$\phi_s = \frac{x_s v_s^L}{x_g v_g^L + x_s v_s^L}$$

Table 4.5: volume fraction for CO-dodecane

T(K)	X_{CO}	v_{CO}	xdodecane	vdodecane	\square_{CO}	$\square_{dodecane}$
303	0.0077687	0.0000321	0.9922313	0.00022712	0.0011054	0.9988946
313	0.0075223	0.0000321	0.9924777	0.00022712	0.0010701	0.9989299
323	0.0072912	0.0000321	0.9927088	0.00022712	0.001037	0.998963

Table 4.6: volume fraction for CO-1,4dioxane

T(K)	X_{CO}	v_{CO}	x1,4-dioxane	v1,4-dioxane	\square_{CO}	$\square_{1,4-dioxane}$
303	0.0029318	0.0000321	0.9970682	8.53E-05	0.0011054	0.9988946
313	0.0028384	0.0000321	0.9971616	8.53E-05	0.0010701	0.9989299
323	0.0027507	0.0000321	0.9972493	8.53E-05	0.001037	0.998963

Table 4.7: volume fraction for H₂-dodecane

T(K)	X_{H_2}	v_{H_2}	xdodecane	vdodecane	\square_{H_2}	$\square_{dodecane}$
303	0.0077687	0.0000373	0.0029318	0.00022712	0.0011054	0.9987158
313	0.0075223	0.0000373	0.0028384	0.00022712	0.0010701	0.9987568
323	0.0072912	0.0000373	0.0027507	0.00022712	0.001037	0.9987952

Table 4.8: volume fraction for H₂-1,4-dioxane

T(K)	X_{H_2}	v_{H_2}	x1,4-dioxane	v1,4-dioxane	\square_{H_2}	$\square_{1,4-dioxane}$
303	0.0029318	0.0000373	0.9970682	8.53E-05	0.0011054	0.9987158
313	0.0028384	0.0000373	0.9971616	8.53E-05	0.0010701	0.9987568
323	0.0027507	0.0000373	0.9972493	8.53E-05	0.001037	0.9987952

4.1.1.5 Solubility Calculation For Dodecane

Since dodecane is non polar solvent, RST equation has been used with no further correction. Refer to the equation number 13 to see the RST equation.

Table 4.9: solubility of H₂ and CO in dodecane solvent at 2bar

Temperature/K	Solubility x_{H_2}	Solubility x_{CO}
303	0.001485714	0.003674429
313	0.001606338	0.00377399
323	0.001740064	0.003881082

Table 4.10: solubility of H₂ and CO in dodecane solvent at 4bar

Temperature/K	Solubility x_{H_2}	Solubility x_{CO}
303	0.002977712	0.007372145
313	0.003219252	0.007571131
323	0.003487031	0.007763118

Table 4.11: solubility of H₂ and CO in dodecane solvent at 6bar

Temperature/K	Solubility x_{H_2}	Solubility x_{CO}
303	0.004450564	0.011093254
313	0.004838762	0.011391528
323	0.005240922	0.011712556

Table 4.12: solubility of H₂ and CO in dodecane solvent at 8bar

Temperature/K	Solubility x_{H_2}	Solubility x_{CO}
303	0.005980638	0.01483787
313	0.00646489	0.01523529
323	0.007001757	0.015663155

Table 4.13: solubility of H₂ and CO in dodecane solvent at 10bar

Temperature/K	Solubility x _{H2}	Solubility x _{CO}
303	0.007491606	0.018606105
313	0.008097655	0.019102523
323	0.008769557	0.019637133

4.1.1.6 Solubility calculation for 1, 4-dioxane

RST based model is essentially limited to dissolution of non polar gases in non polar, non associating solvents. The modification of the RST by Yen and McKetta was applied in order to extend the RST to polar solvent like 1, 4-dioxane. Refer to the equation number 14 to see the RST equation with correction by Yen and McKetta.

Table 4.14: solubility of H₂ and CO in 1,4-dioxane solvent at 2bar

Temperature/K	Solubility x _{H2}	Solubility x _{CO}
303	0.006449054	0.009868127
313	0.006568697	0.00989994
323	0.006694704	0.009938806

Table 4.15: solubility of H₂ and CO in 1,4-dioxane solvent at 4bar

Temperature/K	Solubility x _{H2}	Solubility x _{CO}
303	0.007539558	0.012678334
313	0.00770347	0.012730366
323	0.007877223	0.0127792

Table 4.16: solubility of H₂ and CO in 1,4-dioxane solvent at 6bar

Temperature/K	Solubility x _{H2}	Solubility x _{CO}
303	0.008356311	0.015222287
313	0.008571467	0.015296594
323	0.008786972	0.015388132

Table 4.17: solubility of H₂ and CO in 1,4-dioxane solvent at 8bar

Temperature/K	Solubility x_{H_2}	Solubility x_{CO}
303	0.009079527	0.017758508
313	0.009317918	0.017858682
323	0.009572964	0.017982588

Table 4.18: solubility of H₂ and CO in 1,4-dioxane solvent at 10bar

Temperature/K	Solubility x_{H_2}	Solubility x_{CO}
303	0.009720858	0.020403663
313	0.009994407	0.020534637
323	0.010288198	0.020697318

For experimental data please refer to the appendix 3 until appendix 6.

4.2 RESULT and DISCUSSION

4.2.1 RST Solubility Calculated value

Figure 4.1 until figure 4.4 shows the pattern of the solubility of hydrogen and carbon monoxide with respect to the changes of the pressure and temperature. This data were calculated based on the RST based model and RST with Yen and McKetta extension for both dodecane and 1, 4-dioxane respectively.

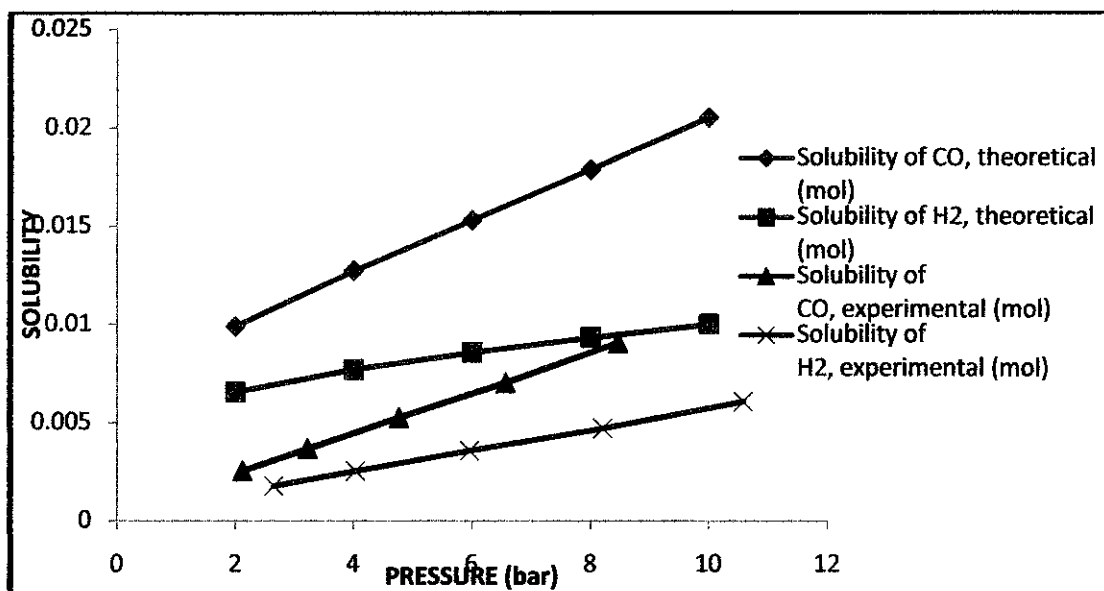


Figure 4.1: solubility of H₂ and CO in 1,4-dioxane at temperature 313K

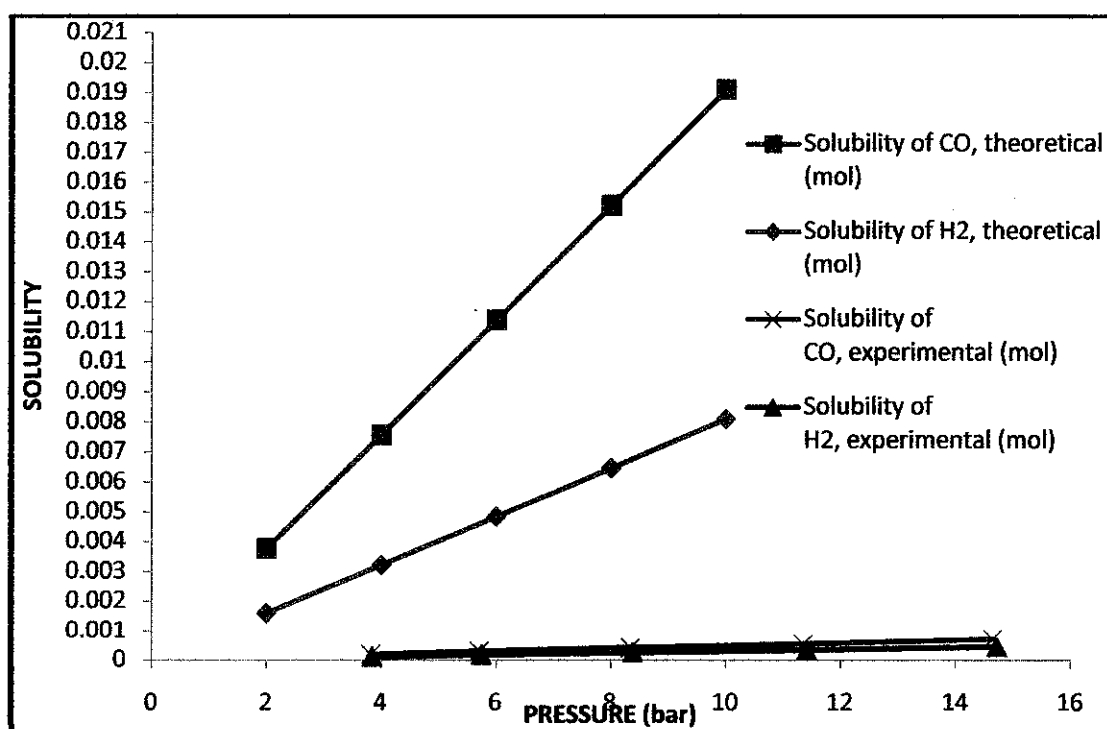


Figure 4.2: solubility of H₂ and CO in I, 4-dioxane at temperature 313K

Figure 4.1 and figure 4.2 shows the solubility of the hydrogen and carbon monoxide are increased as the pressure increased isothermally for both solvents. Increasing the pressure isothermally will result in more collisions of gas molecules per unit time with the surface of the solvents, thus resulting greater solubility.

It is expected that carbon monoxide will soluble more in both solvents compared to the hydrogen gas. This is probably most due to the intermolecular bonding in carbon monoxide is stronger than the hydrogen intermolecular bonding.

Result from this two figure also indicates that 1,4-dioxane is better solvent compared to the dodecane. More carbon monoxide and hydrogen gases soluble in 1,4-dioxane compared to the dodecane. Once reported that the solubility is increased when the solubility parameters in decreased [20]. Since the solubility parameter of 1, 4-dioxane is smaller than the dodecane, it is true for the relationship that the gases is more soluble in 1,4-dioxane compared to dodecane. another reason to this phenomenon, maybe due to the 1,4-dioxane having more smaller chemical structure compared to the dodecane. It is saying that solvents with smaller molecular volume will be thermodynamically better than larger ones having identical solubility parameters [21].

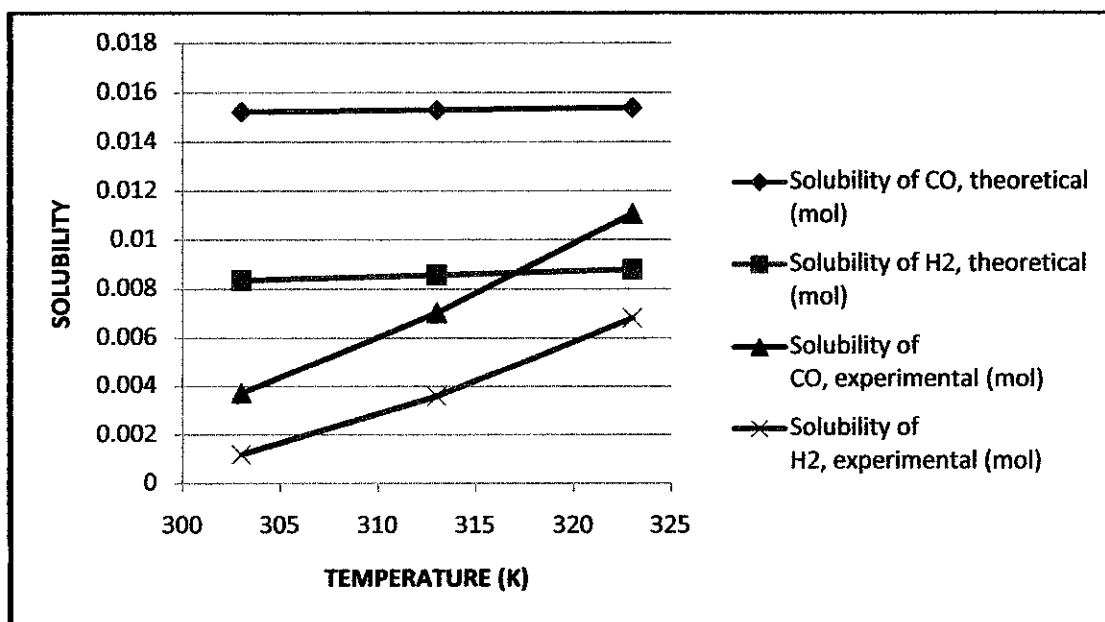


Figure 4.3: solubility of H₂ and CO in 1,4-dioxane at pressure 6bar

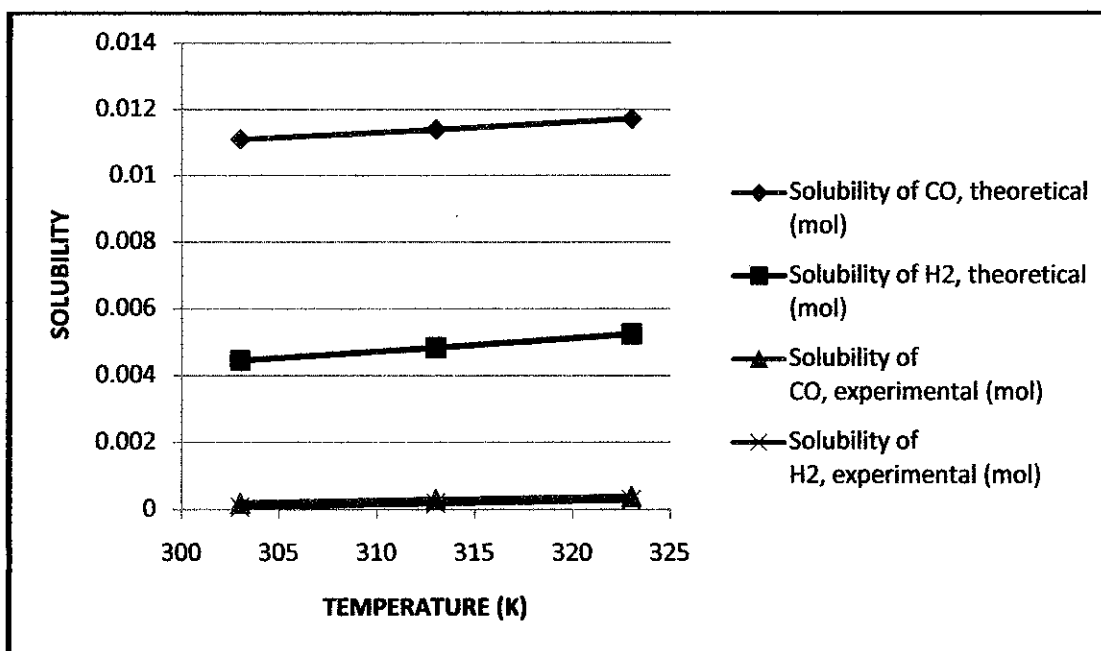


Figure 4.4: solubility of H2 and CO in dodecane at pressure 6bar

Figure 4.3 and figure 4.4 shows that as the temperature increased the solubility also will increased too but except for CO-1, 4-dioxane system. For most gases at ordinary temperature the solubility is decreased as temperature rising. This is most probably due to the rising of the kinetic energy of the gases become larger than its own normal boiling point. As a result, decreasing the tendency of the gases to condense in liquid phase.

Meanwhile, the solubility increasing with increasing temperature most probably due to the decreasing of density. It is shown in the calculation of the Preston [22] suggests that in simple systems, the gas solubility decreases monotonically with temperature when the density of the solvent is held constant [20]

The solubility predicted by the RST model and RST with Yen and McKetta largely deviated from the experiment data for cases, isothermal condition and isobaric condition. This most probably due to the RST model cannot fit with this particular system. Perhaps, the experimental data was not precisely conducted since the data was obtained with one running. Since the time constraint the author cannot redo the

experiment at least to take the data 3 times in order to validate the data obtained and get the average of the data.

It is expected too that the ratio of the solvent and solutes use is not practically suit with the RST model. The author did realize that volume fraction of the solvents and solutes have greater impact on the calculation of the solubility.

CHAPTER 5: CONCLUSION

As shown in the RST model, it is predicted that the solubility of the carbon monoxide and hydrogen is more soluble in 1, 4-dioxane compared to dodecane over the range of temperature and pressure study. The solubilities of the carbon monoxide and hydrogen also increased with increased in pressure and temperature.

The largely error between solubility predicted by the RST model with experimental data can be reduced if the experiment was running at least 3 times to obtained data precisely and to get the average of it. With time constraints, the probability of the author to repeat most of the calculation and experiment works is low; therefore, the author was hope that the data obtained from this field of study can be benchmark for this particular study only. An extensive work can be done if the time is not constraint.

There are so many variables in the RST model that need to be clarified first before the RST model can be used or evaluate. Pressure and temperature is the parameter that initially the author interested in, but by using RST model, parameter such as volume fraction need to be verified at which optimum volume fraction solvents and solutes can give better prediction of the solubility.

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APPENDICES

Appendix 1: Gantt chart

No	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	
1	Project Work Continue	■	■	■					Mid Semester Break								
2	FYP II Briefing	■															
3	Lab Briefing		■														
4	Submission of Progress Report 1				■												
5	Project Work Continue				■	■	■	■									
6	Professional Writing			■													
7	Technical Writing				■												
8	Submission of Progress Report 2										■						
9	Seminar										■	■	■	■			
10	Project Works continue										■	■	■	■			
11	Poster Exhibition												■				
12	Submission of Dissertation (Soft Bound)													■			
13	Oral Presentation															■	
14	Submission of Dissertation (Hard Bound)																■

 Suggested Milestone
 Work Progress

Appendix 2: Fugacity of the pure gas

Calculation of fugacity of the pure gas ($f=P * \exp(P/RT)$)									
	for P=4 bar		for P=6 bar		for P=8 bar		for P=10 bar		
Temperature (K)	for H ₂ /bar	for CO/bar	for H ₂ /bar	for CO/bar	for H ₂ /bar	for CO/bar	for H ₂ /bar	for CO/bar	
303	4.016935	4.025388	6.038145	6.057214	8.067884	8.101875	10.10618	10.15943	
313	4.016393	4.024575	6.036922	6.055378	8.065707	8.0986	10.10277	10.1543	
323	4.015885	4.023812	6.035776	6.053656	8.063664	8.09553	10.09957	10.14949	

Appendix 3: Experimental Data H₂-1,4dioxane

Temperature (K)	Pressure initial (bar)	Pressure final (bar)	Vapor pressure (bar)	Volume of gas (ml)	Gas constant (cm ³ .bar/K.mol)	Volume of liquid (ml)	Molar volume of liquid (cm ³ /mol)	Molar density of liquid (mol/cm ³)	Solubility (mol)
303	3.871897	3.316161	0.06304	15	83.14472	35	85.3	0.011723	0.000898
303	5.791266	5.037158	0.06304	15	83.14472	35	85.3	0.011723	0.001186
303	8.450037	7.444954	0.06304	15	83.14472	35	85.3	0.011723	0.00155
303	11.50377	10.25433	0.06304	15	83.14472	35	85.3	0.011723	0.001905
303	14.84244	13.22517	0.06304	15	83.14472	35	85.3	0.011723	0.002438

Temperature (K)	Pressure initial (bar)	Pressure final (bar)	Vapor pressure (bar)	Volume of gas (ml)	Gas constant (cm ³ .bar/K.mol)	Volume of liquid (ml)	Molar volume of liquid (cm ³ /mol)	Molar density of liquid (mol/cm ³)	Solubility (mol)
313	3.871897	2.652929	0.06304	15	83.14472	35	85.3	0.011723	0.001801
313	5.791266	4.029726	0.06304	15	83.14472	35	85.3	0.011723	0.002563
313	8.450037	5.955963	0.06304	15	83.14472	35	85.3	0.011723	0.003592
313	11.50377	8.203464	0.06304	15	83.14472	35	85.3	0.011723	0.004725
313	14.84244	10.58013	0.06304	15	83.14472	35	85.3	0.011723	0.006076

Temperature (K)	Pressure initial (bar)	Pressure final (bar)	Vapor pressure (bar)	Volume of gas (ml)	Gas constant (cm ³ .bar/K.mol)	Volume of liquid (ml)	Molar volume of liquid (cm ³ /mol)	Molar density of liquid (mol/cm ³)	Solubility (mol)
323	3.871897	2.122343	0.06304	15	83.14472	35	85.3	0.011723	0.002467
323	5.791266	3.223781	0.06304	15	83.14472	35	85.3	0.011723	0.003581
323	8.450037	4.764771	0.06304	15	83.14472	35	85.3	0.011723	0.005102
323	11.50377	6.562771	0.06304	15	83.14472	35	85.3	0.011723	0.006812
323	14.84244	8.464107	0.06304	15	83.14472	35	85.3	0.011723	0.008768

Appendix 4: Experimental Data CO-1,4dioxane

Temperature (K)	Pressure Initial (bar)	Pressure final (bar)	Vapor pressure (bar)	Volume of gas (ml)	Gas constant (cm ³ .bar/K.mol)	Volume of liquid (ml)	Molar volume of liquid (cm ³ /mol)	Molar density of liquid (mol/cm ³)	Solubility (mol)
303	3.871897	2.652929	0.06304	15	83.14472	35	85.3	0.011723	0.00186
303	5.791266	4.029726	0.06304	15	83.14472	35	85.3	0.011723	0.002648
303	8.450037	5.955963	0.06304	15	83.14472	35	85.3	0.011723	0.003711
303	11.50377	8.203464	0.06304	15	83.14472	35	85.3	0.011723	0.004881
303	14.84244	10.58013	0.06304	15	83.14472	35	85.3	0.011723	0.006276

Temperature (K)	Pressure Initial (bar)	Pressure final (bar)	Vapor pressure (bar)	Volume of gas (ml)	Gas constant (cm ³ .bar/K.mol)	Volume of liquid (ml)	Molar volume of liquid (cm ³ /mol)	Molar density of liquid (mol/cm ³)	Solubility (mol)
313	3.871897	2.122343	0.06304	15	83.14472	35	85.3	0.011723	0.002546
313	5.791266	3.223781	0.06304	15	83.14472	35	85.3	0.011723	0.003695
313	8.450037	4.764771	0.06304	15	83.14472	35	85.3	0.011723	0.005265
313	11.50377	6.562771	0.06304	15	83.14472	35	85.3	0.011723	0.007029
313	14.84244	8.464107	0.06304	15	83.14472	35	85.3	0.011723	0.009048

Temperature (K)	Pressure Initial (bar)	Pressure final (bar)	Vapor pressure (bar)	Volume of gas (ml)	Gas constant (cm ³ .bar/K.mol)	Volume of liquid (ml)	Molar volume of liquid (cm ³ /mol)	Molar density of liquid (mol/cm ³)	Solubility (mol)
323	3.871897	1.697874	0.06304	15	83.14472	35	85.3	0.011723	0.003045
323	5.791266	2.579025	0.06304	15	83.14472	35	85.3	0.011723	0.004458
323	8.450037	3.811817	0.06304	15	83.14472	35	85.3	0.011723	0.0064
323	11.50377	5.250217	0.06304	15	83.14472	35	85.3	0.011723	0.008598
323	14.84244	6.771285	0.06304	15	83.14472	35	85.3	0.011723	0.011073

Appendix 5: Experimental Data H₂-dodecane

Temperature (K)	Pressure Initial (bar)	Pressure final (bar)	Volume of gas (ml)	Gas constant (cm ³ .bar/K.mol)	Volume of liquid (ml)	Molar volume of liquid (cm ³ /mol)	Molar density of liquid (mol/cm ³)	Solubility (mol)
303	3.871897	3.859008	15	83.14472	35	227	0.00440529	4.977E-05
303	5.791266	5.769247	15	83.14472	35	227	0.00440529	8.503E-05
303	8.450037	8.421574	15	83.14472	35	227	0.00440529	0.0001099
303	11.50377	11.46825	15	83.14472	35	227	0.00440529	0.0001372
303	14.84244	14.79347	15	83.14472	35	227	0.00440529	0.0001891

Temperature (K)	Pressure Initial (bar)	Pressure final (bar)	Volume of gas (ml)	Gas constant (cm ³ .bar/K.mol)	Volume of liquid (ml)	Molar volume of liquid (cm ³ /mol)	Molar density of liquid (mol/cm ³)	Solubility (mol)
313	3.871897	3.839713	15	83.14472	35	227	0.00440529	0.0001203
313	5.791266	5.740401	15	83.14472	35	227	0.00440529	0.0001901
313	8.450037	8.379466	15	83.14472	35	227	0.00440529	0.0002638
313	11.50377	11.4109	15	83.14472	35	227	0.00440529	0.0003472
313	14.84244	14.7195	15	83.14472	35	227	0.00440529	0.0004596

Temperature (K)	Pressure initial (bar)	Pressure final (bar)	Volume of gas (ml)	Gas constant (cm ³ .bar/K.mol)	Volume of liquid (ml)	Molar volume of liquid (cm ³ /mol)	Molar density of liquid (mol/cm ³)	Solubility (mol)
323	3.871897	3.820515	15	83.14472	35	227	0.00440529	0.0001861
323	5.791266	5.711699	15	83.14472	35	227	0.00440529	0.0002882
323	8.450037	8.337569	15	83.14472	35	227	0.00440529	0.0004074
323	11.50377	11.35385	15	83.14472	35	227	0.00440529	0.0005431
323	14.84244	14.6459	15	83.14472	35	227	0.00440529	0.0007119

Appendix 6: Experimental Data CO-dodecane

Temperature (K)	Pressure Initial (bar)	Pressure final (bar)	Volume of gas (ml)	Gas constant (cm ³ .bar/K.mol)	Volume of liquid (ml)	Molar volume of liquid (cm ³ /mol)	Molar density of liquid (mol/cm ³)	Solubility (mol)
303	3.871897	3.839713	15	83.14472	35	227	0.00440529	0.0001243
303	5.791266	5.740401	15	83.14472	35	227	0.00440529	0.0001964
303	8.450037	8.379466	15	83.14472	35	227	0.00440529	0.0002725
303	11.50377	11.4109	15	83.14472	35	227	0.00440529	0.0003586
303	14.84244	14.7195	15	83.14472	35	227	0.00440529	0.0004747

Temperature (K)	Pressure Initial (bar)	Pressure final (bar)	Volume of gas (ml)	Gas constant (cm ³ .bar/K.mol)	Volume of liquid (ml)	Molar volume of liquid (cm ³ /mol)	Molar density of liquid (mol/cm ³)	Solubility (mol)
313	3.871897	3.820515	15	83.14472	35	227	0.00440529	0.0001921
313	5.791266	5.711699	15	83.14472	35	227	0.00440529	0.0002974
313	8.450037	8.337569	15	83.14472	35	227	0.00440529	0.0004204
313	11.50377	11.35385	15	83.14472	35	227	0.00440529	0.0005605
313	14.84244	14.6459	15	83.14472	35	227	0.00440529	0.0007347

Temperature (K)	Pressure Initial (bar)	Pressure final (bar)	Volume of gas (ml)	Gas constant (cm ³ .bar/K.mol)	Volume of liquid (ml)	Molar volume of liquid (cm ³ /mol)	Molar density of liquid (mol/cm ³)	Solubility (mol)
323	3.871897	3.801412	15	83.14472	35	227	0.00440529	0.0002553
323	5.791266	5.683141	15	83.14472	35	227	0.00440529	0.0003917
323	8.450037	8.295881	15	83.14472	35	227	0.00440529	0.0005584
323	11.50377	11.29708	15	83.14472	35	227	0.00440529	0.0007488
323	14.84244	14.57268	15	83.14472	35	227	0.00440529	0.0009772