

**ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY**

**THE TEMPERATURE DEPENDENCE OF SOLUBILITY  
OF SULFUR DIOXIDE IN HEAT TRANSFER OILS**

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**Department : Chemical Engineering**

**Programme : Chemical Engineering**

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**JULY 2010**



**KÜKÜRT DİOKSİTİN ISI TRANSFER YAĞLARINDAKİ  
ÇÖZÜNÜRLÜĞÜNÜN SICAKLIĞA BAĞLI  
DEĞİŞİMİNİN ARAŞTIRILMASI**

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## **ABBREVIATIONS**

<b>COC</b>	: Cleveland open cup
<b>DMA</b>	: N,N-dimethylaniline
<b>DGM</b>	: Monomethyl ether of diethylene glycol
<b>DMSO</b>	: Dimethyl sulfoxide
<b>FGD</b>	: Flue Gas Desulfurisation
<b>GC-MS</b>	: Gas Chromatography-Mass Spectrometry
<b>IRAPCR</b>	: Industry Related Air Pollution Control Regulation
<b>IUPAC</b>	: International Union of Pure and Applied Chemistry
<b>TBP</b>	: Tributyl phosphate
<b>UV</b>	: Ultraviolet
<b>WHO</b>	: World Health Organization



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## **THE TEMPERATURE DEPENDENCE OF SOLUBILITY OF SULFUR DIOXIDE IN HEAT TRANSFER OILS**

### **SUMMARY**

Sulfur dioxide is one of the most important pollutants arisen from the combustion of coal and from other industrial operations. The concentrations of sulfur dioxide in the atmosphere has increased with increasing energy demands by modern civilization and the highest sulfur dioxide emissions have been recorded in industrial regions. These sulfur dioxide emissions are extremely harmful to the environment and the health of human beings. In order to reduce the adverse effects of sulfur dioxide and decrease sulfur dioxide emissions caused by the combustion of fossil fuels, several control technologies are used. Many of these technologies include the absorption of sulfur dioxide into an alkaline solution and a chemical reaction with amine, limestone or dolomite. However, these type of processes cause the production of large amount of solid waste. One of the alternative processes used for sulfur dioxide removal is physical absorption with polar organic solvents.

In this study, two different non-polar heat transfer oils which belong to BP Company and Mobil Corporation, respectively, have been used. The aim of the present research is to rectify an experimental method for newly installed absorption system and to investigate the solubility of sulfur dioxide in heat transfer oils, Transcal N and Mobiltherm 605, on the base of physical absorption of sulfur dioxide. Since the flash, fire and boiling points of selected oils are relatively high, it is possible to work safely in a wide temperature range. The experiments made with sulfur dioxide and Transcal N were performed in 20°C-140°C temperature interval while those made with sulfur dioxide and Mobiltherm 605 were carried out in a temperature range of 20°C-60°C.

The necessary mass transfer calculations have been made and the solubility of sulfur dioxide has been expressed in mole fraction, Henry's constant, Ostwald's coefficient and solubility in unit volume of oils. The sulfur dioxide absorption capacities of the heat transfer oils have been compared.



# KÜKÜRT DİOKSİTİN ISI TRANSFER YAĞLARINDAKİ ÇÖZÜNÜRLÜĞÜNÜN SICAKLIĞA BAĞLI DEĞİŞİMİNİN ARAŞTIRILMASI

## ÖZET

Kükürt dioksit kömürün yanması ve diğer endüstriyel faaliyetler sonucu ortaya çıkan en önemli kirleticilerden biridir. Atmosferdeki kükürt dioksit konsantrasyonları modern uygarlığın artan enerji ihtiyaçlarıyla birlikte artmıştır ve en yüksek kükürt dioksit emisyonları endüstriyel bölgelerde kaydedilmiştir. Bu kükürt dioksit emisyonları çevreye ve insan sağlığına son derece zararlıdır. Kükürt dioksitin olumsuz etkilerini azaltmak ve fosil yakıtların yanması sonucu açığa çıkan kükürt dioksitin emisyonlarını düşürmek için çeşitli kontrol teknolojileri kullanılır. Bu teknolojilerden birçoğu kükürt dioksitin alkali bir çözeltiliye absorpsiyonunu ve amin, kireç taşı ya da dolomit ile reaksiyonunu içerir. Ancak bu prosesler çok miktarda katı atık oluşumuna sebep olur. Kükürt dioksitin uzaklaştırılması için kullanılan alternatif proseslerden birisi de polar organik çözücülerle yapılan fiziksel absorpsiyondur.

Bu çalışmada, BP ve Mobil firmalarına ait olan iki farklı apolar ısı transfer yağı kullanılmıştır. Bu çalışmanın amacı, yeni kurulan absorpsiyon sistemi için deneysel yöntem geliştirmek ve kükürt dioksitin Transcal N ve Mobiltherm 605 ısı transfer yağlarındaki çözünürlüğünü fiziksel absorpsiyon temelinde incelemektir. Seçilen yağların alevlenme, yanma ve kaynama noktaları oldukça yüksek olduğundan geniş bir sıcaklık aralığında güvenli bir şekilde çalışmak mümkün olmuştur. Kükürt dioksit ve Transcal N ile yürütülen deneyler 20°C-140°C sıcaklık aralığında, kükürt dioksit ve Mobiltherm 605 ile yürütülen deneyler ise 20°C-60°C sıcaklık aralığında yapılmıştır.

Gerekli kütle transfer hesaplamaları yapılarak kükürt dioksit çözünürlüğü mol kesri, Henry sabiti, Ostwald katsayısı ve yağın birim hacmindeki çözünürlük olarak ifade edilmiştir. Isı transfer yağlarının kükürt dioksit absorplama kapasiteleri karşılaştırılmıştır.



## 1.INTRODUCTION

Nowadays, there is a worldwide dependency on energy, especially that originating from fossil hydrocarbons. Oil and gas explorations and existing reserves show that combustion of sulfur-containing fossil fuels will dominate the energy market for the next two decades. Today, more than 80 % of the world energy is supplied by combustion of sulfur-containing fossil fuels, which are primarily oil, gas and coal. The sulfur content in oil varies between low values of 0.5 % to higher values close to 4 % in weight. On the other hand, natural gas fuels are much cleaner and contain sulfur with percentages below 0.5. The sulfur content in coal fuels is the highest with the values between 3 and 7 % [1].

The main anthropogenic reason of sulfur dioxide emissions to the atmosphere is the combustion of these sulfur-containing fossil fuels mentioned above. Other man-made reasons of sulfur dioxide emissions are the smelting of sulfur-containing ores, domestic fires and other industrial processes. In addition to the man-made sources, there are some natural sources of sulfur dioxide such as volcanoes [2]. Moreover, recently a volcano in Iceland has erupted and the experts have warned against the acid rain. Because in atmosphere, sulfur dioxide is oxidized to sulfur trioxide and then sulfur trioxide reacts with water to form sulfuric acid when it is rainy. As a result acid rains occur and it damages the environment. The acid rain is not the only bad effect of the sulfur dioxide on environment, animals and humans. It affects the respiratory system and causes several illnesses such as bronchitis and tracheitis.

In order to reduce the adverse effects of sulfur dioxide and decrease the sulfur dioxide emissions caused by the combustion of fossil fuels, some control technologies are used. These may include the minimising of pollution at source by modifying the combustion process, by removing the pollutants from the fuel or the effluent gas, and by minimising the effects of acidic pollution in receptor areas (e.g. liming of lakes). Flue gases can be scrubbed to remove gaseous pollutants. Flue gas desulfurisation (FGD) is a straight-forward and widely used method for reducing emissions of SO<sub>2</sub> and is currently used in over a thousand plants worldwide [3].

Most of the FGD processes use an alkaline solution to absorb  $\text{SO}_2$  chemically. There are more than 100 FGD processes that can be divided into two categories: the regenerable and non-regenerable systems. In the non-regenerable systems, the  $\text{SO}_2$  is permanently bound by the sorbent and has to be disposed of as a waste or sold as a by-product such as gypsum. In the regenerable systems, the  $\text{SO}_2$  is absorbed and during the regeneration of the absorbent, the  $\text{SO}_2$  is released and further processed to sulfuric acid, liquid  $\text{SO}_2$  or elemental sulfur [4].

Most of the FGD units in operation are of the non-regenerable type using slaked lime ( $\text{Ca}(\text{OH})_2$ ) or limestone ( $\text{CaCO}_3$ ) as sorbent. The new generation processes produce high quality gypsum ( $\text{CaSO}_4$ ). Regenerable processes tend to be fairly complex and hence more costly. Most of the FGD processes are installed in the USA, Germany and Japan [4].

Sulfur dioxide is a colorless, poisonous gas with a pungent odor. At room temperature it is in the gas form, since its boiling point is  $-10^\circ\text{C}$ . It may accumulate at or below ground level since its density is about 2.3 fold of air. It is nonexplosive, noninflammable, tends to put out a fire and in case of contact with a fire is not decomposed into any harmful substances [5]. It has highly corrosive effect on metals in the presence of water. It exists as a liquid between the temperatures  $-10^\circ\text{C}$  and  $-75.5^\circ\text{C}$  and this property provides to use liquid sulfur dioxide as a refrigerant. The solutions of sulfur dioxide show highly acidic properties which place it in the same class as phosphoric acid [6].

Solubility of sulfur dioxide depends on several factors such as temperature and pressure. But one of the most important factors that affects the solubility of sulfur dioxide is the type of solvent. This is important because the interaction between sulfur dioxide and the solvent changes the dissolution mechanism and so the solubility of sulfur dioxide. Solvents mostly used in sulfur dioxide solubility measurements can be divided into two main group:

a) hydrophilic solvents such as water [7], seawater [1], ethylenediamine-phosphoric acid solution [8], aqueous solutions of sodium chloride and ammonium chloride [9], acetic acid, sodium acetate and ammonium acetate [10].

b) organic solvents such as N,N-dimethylaniline [11], quinoline [11], polyglycol ethers [11], N-methylpyrrolidone [12], methyldiethanolamine [12], N,N-(dimethylpropylene)urea [12].

In the first group of solvents or solutions, the dissolution mechanism includes the chemical reaction of sulfur dioxide with water to form sulfurous acid, sulfite and bisulfite ions. However, in organic solvents complex formation between sulfur dioxide and the organic solvent is usually observed. The polar organic solvents have higher absorption capacities for SO<sub>2</sub>. This is because some polar organic solvents are expected to have a high affinity for SO<sub>2</sub> due to their Lewis base properties and strong interacting forces between SO<sub>2</sub> and polar organic solvents lead to the formation of strong complexes. The strength of the complex formed between SO<sub>2</sub> and the organic solvent with respect to solvent group decreases in the order N (amine) > ROR (glycol ether) > ROH (glycol ether) > PO<sub>4</sub> > O=S=O [11]. That's why dimethylaniline and quinoline (or pyridine) have relatively high sulfur dioxide absorption capacities while tributyl phosphate and tetramethylene sulfone have lower absorption capacity. In addition, in solvents having unpaired electrons on oxygen atoms, such as diethyl ether [13], diethylene glycol dimethyl ether [11], solubility of sulfur dioxide increases with an increased number of oxygen atoms.

### **1.1 Scope of the Research**

The aim of this research is to investigate the solubility of sulfur dioxide in two different heat transfer oils, Transcal N and Mobiltherm 605, on the base of physical absorption of sulfur dioxide. Also it is intended to observe the effect of temperature on the solubility of sulfur dioxide.

In order to perform the experiments, a new absorption system has been installed. Simply, the system used consists of a heating circulator which is used to keep absorption medium at desired temperature, a glass jacketed reactor, a speed regulator which is used to adjust the speed of the mechanical stirrer in the reactor, a device showing the pressure instantaneously, a vacuum pump used to suck the air in the reactor, a computer and a software which can record the pressure for each second. Since this system is used for the first time, it is necessary to develop a method to make the experiments. For these purposes, preliminary experiments were performed firstly by using several different methods to find out the convenient way to bring

sulfur dioxide into contact with the oil in new absorption system. After determining the convenient experimental method, actual experiments for the measurements of solubility of sulfur dioxide were performed in a wide temperature range of 20°C to 140°C at atmospheric pressures. The heating circulator with an oil bath provide to work in this wide temperature range and it also provide to fix the temperature in absorption medium at a desired value. Together with the benefits of the heating circulator, the high boiling, fire and flash points of selected solvents enable us to work at high temperatures safely. The software installed in the computer which is connected to the absorption system is used to record the pressure for each second during the experiments. Taking immediate data of pressure against time makes the measurements and calculations more reliable.

For SO<sub>2</sub>-Transcal N system, the experiments were carried out at 20, 30, 40, 50, 60, 70, 80, 100 and 140°C while the experiments were performed at 20, 30, 40, 50 and 60°C for SO<sub>2</sub>-Mobiltherm 605 system. The solubility of sulfur dioxide has been expressed in different terms such as mole fraction, Henry's constant, Ostwald's coefficient and solubility in unit volume of oils. The SO<sub>2</sub> absorption capacities of Transcal N and Mobiltherm 605 have been compared.

## 2. SULFUR DIOXIDE

### 2.1 Formation of Sulfur Dioxide

Sulfur dioxide is a poisonous gas which results from the combustion of sulfur-containing fossil fuels. The formation of  $SO_2$  can be basically represented as follows:



The reaction above is highly exothermic. The ideal gas enthalpy of formation of sulfur dioxide is  $-29.684 \times 10^7$  J/kmol [14].

Available sources of sulfur dioxide are burner gases from the combustion of brimstone and pyrites, smelter gases from the roasting of zinc and copper sulfide ores, hydrogen sulfide from coke oven, refinery and natural gases [6]. Erupting volcanoes are the important natural sources of sulfur dioxide.

### 2.2 Physical and Chemical Properties of Sulfur Dioxide

Sulfur dioxide is colourless, both in liquid and gaseous phases and its odor is pungent. It is in the gas form at room temperature and heavier than air. So, it may accumulate in confined spaces, especially at or below ground level. It reacts with most metals in the presence of moisture by liberating hydrogen. It also reacts with water to form corrosive alkalis [5, 15]. Some physical and chemical properties of sulfur dioxide are given in Table 2.1.

**Table 2.1** : Some physical and chemical properties of sulfur dioxide [5, 14,15].

<b>Molecular weight (g/mol)</b>		64.06
<b>Melting Point (°C)</b>		-75.5
<b>Boiling Point (°C)</b>		-10
<b>Gas Density at Atm. Pressure (g/cm<sup>3</sup>)</b>	at 0°C	$2.9763 \times 10^{-3}$
<b>Relative Liquid Density (referred to water as 1g/cm<sup>3</sup>)</b>	at - 40°C	1.5331
	at - 12.22°C	1.4601
	at 10°C	1.4095
<b>Vapor Pressure (kPa)</b>	at 20°C	330
<b>Latent Heat of Vaporization at 1 atm (kJ/mol)</b>		24.86

Sulfur dioxide absorption mechanism into water can be defined as follows:



A fraction of bisulfite ions may be dissociated to sulfite and metabisulfite ions but they are in negligible proportions [7].

Solubilities of sulfur dioxide in water and vapor pressure of  $\text{SO}_2$  at different temperatures are given in Table 2.2 and Table 2.3, respectively.

**Table 2.2 :** Solubility of sulfur dioxide in water at 101.3 kPa [14].

Temperature (°C)	g $\text{SO}_2$ /100 g $\text{H}_2\text{O}$
0	22.83
10	16.21
20	11.29
30	7.81
40	5.41
50	4.5

**Table 2.3 :** Vapor pressure of sulfur dioxide [16].

Temperature (°C)	Vapor Pressure (kPa)
10	230
20	330
30	462
40	630

Some thermodynamic properties of sulfur dioxide are given in Tables 2.4, 2.5, 2.6 and 2.7, respectively.

**Table 2.4 :** Critical constants of sulfur dioxide [14].

$T_c$ (K)	$P_c$ (MPa)	$V_c$ ( $\text{m}^3/\text{kmol}$ )	$Z_c$
430.75	7.884	0.122	0.269

**Table 2.5 :** Enthalpy, Gibbs energy of formation of  $\text{SO}_2$ , entropy at 298.15K [14].

Ideal gas enthalpy of formation ( $\text{J}/\text{kmol}$ ) $\times 10^{-7}$	Ideal gas Gibbs energy of formation ( $\text{J}/\text{kmol}$ ) $\times 10^{-7}$	Ideal gas entropy ( $\text{J}/\text{kmol}$ ) $\times 10^{-5}$
-29.684	-30.012	2.481

**Table 2.6** : Ideal gas sensible enthalpy( $h_T-h_{298}$ ) of SO<sub>2</sub> [14].

T(K)	Sensible enthalpy(kJ/kmol)
200	-3736
300	74
400	4250
500	8758
600	13544
700	18548

**Table 2.7** : Heat capacity and entropy of SO<sub>2</sub>(g) [16].

T(K)	C <sub>p</sub> (cal/°C)	S <sup>0</sup> <sub>298</sub> (cal/°C)
298.1	9.51	59.40
400	10.35	62.32
500	11.08	64.72
700	12.11	68.62
1000	12.90	73.09
1500	13.42	78.44
1800	13.56	80.90

### 2.3 Atmospheric Chemistry and Reactions of Sulfur Dioxide

Sulfur dioxide is not photosensitive to sunlight radiations in the troposphere despite considerable absorption of SO<sub>2</sub> in the near UV; the absorbed energy is insufficient to break the OS-O bond and the excited states are rapidly quenched without chemical effects. The oxidation of SO<sub>2</sub> to sulfuric acid and sulfates is straightforward and sideproducts are almost absent [17].

Sulfur dioxide has a strong tendency to react with O<sub>2</sub> to form SO<sub>3</sub> at 298 K and 1 atm in air. The equilibrium concentration ratio of SO<sub>3</sub> to SO<sub>2</sub> is equal to 10<sup>12</sup>. In absence of catalysts, the reaction rate in the gas phase is so slow. Therefore oxidation of sulfur dioxide by O<sub>2</sub> can be neglected [17].

Another negligible reaction of sulfur dioxide is the reaction with ozone. Because the rate constant for this reaction at 298K and 1 atm is about 8x10<sup>-24</sup> cm<sup>3</sup>/molecule.s. [17].

One of the significant chemical reactions of sulfur dioxide in the gas phase occurs via the reaction with OH radicals as follows:



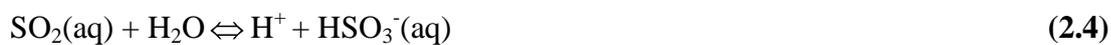
As it is seen as follows the SO<sub>3</sub> reacts with H<sub>2</sub>O to form sulfuric acid:



Another important gas phase reaction of sulfur dioxide occurs in the presence of O<sub>3</sub> and of unsaturated hydrocarbons. The oxidation reaction of SO<sub>2</sub> must be attributed to intermediates, produced in the O<sub>3</sub> olefin reaction [17].



As it is mentioned before, reaction of sulfur dioxide follows the mechanism below:



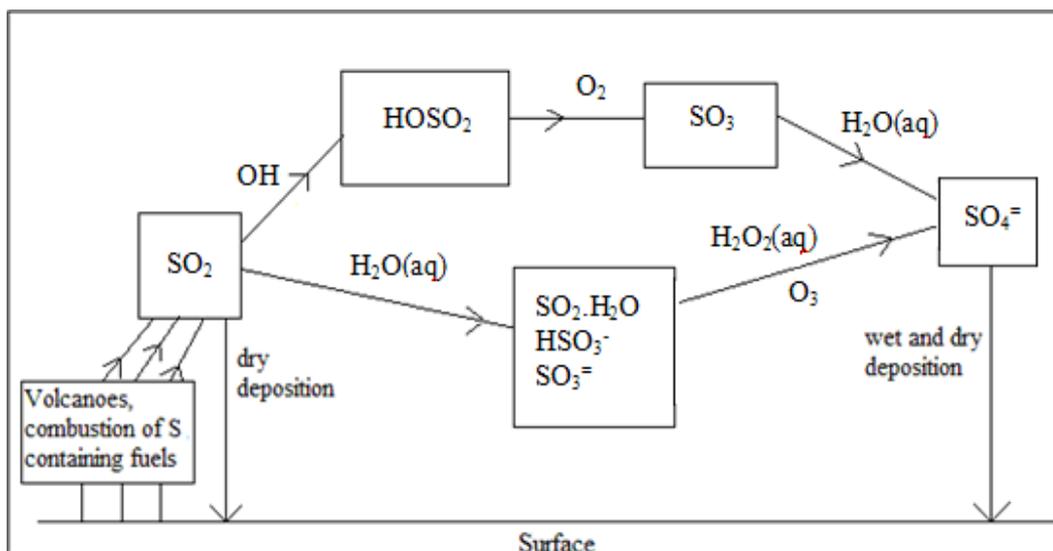
Since sulfurous acid (H<sub>2</sub>SO<sub>3</sub>) is a weak acid, it dissociates into bisulfite (HSO<sub>3</sub><sup>-</sup>) and sulfite (SO<sub>3</sub><sup>2-</sup>) ions as it is seen in equation (2.4) and (2.10) with dissociation constants of 1.3x10<sup>-2</sup> and 6.3x10<sup>-8</sup>, respectively [16].

The most important reaction of sulfur dioxide in atmospheric liquid water is the one occurs with H<sub>2</sub>O<sub>2</sub>. The reaction mechanism of H<sub>2</sub>O<sub>2</sub> and bisulfite ion is generally accepted as below:



The reaction rates for the sulfur dioxide oxidation in the liquid phase increase with decreasing temperature since the solubility of sulfur dioxide increases with decreasing temperature.

Figure 2.1 summarizes principal homogenous gas phase and heterogenous transformation reactions of sulfur dioxide, products and removal paths.



**Figure 2.1** : Principal homogeneous gas-phase and heterogeneous transformation reactions of sulfur dioxide, products and removal paths [17].

#### 2.4 Effects of Sulfur Dioxide on Vegetation, Animal and Human Health

Sulfur dioxide emissions have increased with increasing industrialization, especially after Second World War and peaked in the late 1970s. Although the legislations about the air quality and the emissions have been made and emission control technologies have been used, there are still significant emissions of sulfur dioxide in the atmosphere which affect the vegetation, animal and human health.

As it is mentioned previously, sulfur dioxide, after release to the atmosphere, undergoes a slow oxidation to sulfur trioxide and sulfuric acid; the reaction is catalyzed by sunlight and fine dust particles, especially by minute metallic oxide particles present in smelter smoke [18]. As a result of this mechanism, acid rains occur and they have adverse effects on plants, animals and human. Not only in the form of sulfuric acid, sulfur dioxide affects directly the respiratory system.  $\text{SO}_2$  is captured in the upper respiratory tract during inhalation and virtually it does not penetrate to the lungs during normal breathing. However, during vigorous physical activity, there is less residence time in the upper airways and a shift to oronasal breathing involving partial flow through the less efficient oral passages. Under these conditions, a small fraction of inhaled sulfur dioxide can penetrate to the larger conductive airways of the lungs [3].

### **2.4.1 Effects of sulfur dioxide on vegetation**

Sulfur dioxide and its derivatives affect vegetation in two different ways: directly by uptake through parts of the plants that are above ground and indirectly via soil acidification [3].

The effects of SO<sub>2</sub> on vegetation depend on the plants' structural properties and their abilities to convert dissolved sulfur dioxide into relatively nontoxic forms. For example, higher plants which have boundary layers on their leaves, are more resistant to sulfur dioxide than lower plants such as lichens and mosses which do not have outer cell layers. Legumes such as beans and clover, berry-bearing shrubs and conifers are highly sensitive to sulfur dioxide. The black pine and oak species are relatively resistant to SO<sub>2</sub> [3].

Other criterias that SO<sub>2</sub> effects on plants are dependent on are the exposure amount of sulfur dioxide and exposure time. Within the plastids of plants, the pH is high and this leads to formation of toxic sulfite ions. The high concentrations of these ions cause acute injury in the form of leaf necrosis after short-time exposure to sulfur dioxide and after long-time exposure to sulfur dioxide it may change to chronic injury [3].

In 1940, the effects of low concentrations of sulfur dioxide on plants grown were investigated by Setterstrom, Zimmerman and Crocker [19]. For this purpose, the alfalfa was selected as the test plant. The test plants were grown for periods up to 25 days in a sulfur dioxide concentrations between 0.10 and 0.20 ppm. As a result of the experiments, it was obtained that under most of the conditions there was no significant effect of low concentrations of sulfur dioxide on yield of alfalfa.

Another set of experiments was performed to find out the factors influencing susceptibility of plants to sulfur dioxide injury in Boyce Thompson Institute for Plant Research. According to results of these experiments, it was seen that increase in relative humidity decreased the resistance to SO<sub>2</sub>, plants grown under heavy shade were more susceptible to injury than plants grown without shading young plants were much more resistant to injury than older plants, sulfate sulfur content of nutrient supply and wetting of leaf surfaces had no effect on susceptibility [19].

### **2.4.2 Effects of sulfur dioxide on animal**

There are many researches in literature that have been made to discover the effects of sulfur dioxide on animals.

One of these researches was hold at the Boyce Thompson Institute in 1940. Concentrations of sulfur dioxide between 10 and 1000 ppm were tested on guinea pigs, mice, grasshoppers and cockroaches. Signs in living exposed vertebrate animals (guinea pigs and mice) at the higher concentrations of SO<sub>2</sub> involved lethargy, rhinitis, lachrymation, coughing, conjunctivitis, moderate dyspnea, distention of the abdomen and weakness. Pathologic changes in these animals were general visceral congestion, at higher concentrations edema of the lungs with hemorrhages, acute dilation of the right heart, gross distention of stomach with multiple ulcers and hemorrhages and distention of the gall bladder except at lowest concentrations. Signs in invertebrate animals (grasshoppers and cockroaches) at the highest concentration of sulfur dioxide included lack of coordination of muscular movements and paralysis of posterior legs [19].

Another study in this area is about the effects of sulfur dioxide inhalation on lungs and hearts of mice. In this research, the mice were exposed to sulfur dioxide at various concentrations (22, 56 and 112 mg/m<sup>3</sup>) for 6h/day for a week. According to the results of these experiments, it was stated that SO<sub>2</sub> exposure caused a significant increase in lipid peroxidation process in the lungs and hearts of mice which might lead to cancer. Also it was expressed that SO<sub>2</sub> was toxic not only to the respiratory system but to the entire cardiopulmonary system [20].

### **2.4.3 Effects of sulfur dioxide on human health**

Inhalation is the only route for sulfur dioxide to enter the human body. Absorption of sulfur dioxide in the mucous membranes of the nose and upper respiratory tract occurs as a result of its solubility in aqueous media. The absorption of SO<sub>2</sub> depends on the concentration, that is, 85% absorption occurs in the nose at 4-6 mg/m<sup>3</sup> while it reaches about to 99% at 46 mg/m<sup>3</sup>. From the respiratory tract, sulfur dioxide enters the blood and elimination of it occurs mainly by the urinary route [2].

There is an extremely large variability of sensitivity to sulfur dioxide exposure among individuals. As it can be guessed easily, SO<sub>2</sub> affects asthmatics more than normal persons since it causes problems in the respiratory system.

High concentrations of sulfur dioxide can give rise to bronchitis and tracheitis as acute effects. Repeated short-term occupational exposure to high concentrations of sulfur dioxide combined with long-term exposure to lower concentrations can cause an increased prevalence of chronic bronchitis [2].

As it is mentioned above SO<sub>2</sub> is absorbed through the respiratory tract and subsequently dissociates to form its derivatives (bisulfite and sulfite). These derivatives of sulfur dioxide are suspected to act as a promoter or cocarcinogen. To investigate whether sulfur dioxide derivatives have carcinogenic effects, a study was designed by Qin and Meng [21]. Human bronchial epithelial cells were treated with different concentrations of SO<sub>2</sub> derivatives. It was observed that with increasing concentrations of these derivatives, cell viabilities decreased. Moreover, these derivatives induced a series of genes such as c-fos, c-jun, and c-myc, and H-ras, moreover, suppressed the expression of p53, p16 and Rb. The data obtained after the experiments were supported the hypothesis that SO<sub>2</sub> derivatives could cause the activation of proto-oncogenes and inactivation of tumor suppressor genes and SO<sub>2</sub> derivatives may play a role in the pathogenesis of SO<sub>2</sub>-associated lung cancer.

## **2.5 Air Pollution Standarts**

The increase in global population is inevitably associated with continued industrialization, urbanization and motorization. Increased pollution effects are recorded in industrial regions. Some of these environmental problems are related to the emission of sulfur dioxide. The intensive use of fossil fuels in industrial regions causes a considerable SO<sub>2</sub> emission into the atmosphere. Environmental problems caused by SO<sub>2</sub> emission such as acid rain have resulted worldwide in stringent emission regulations. In order to control the SO<sub>2</sub> emissions, some legislations about air pollution standarts have been enacted [4].

Air pollution standarts can be divided into two main groups: emission standarts and air quality standarts. Emission standards are the permissible quantities of pollutants that are emitted from a source. Air quality standards however, are the admissible

concentrations of pollutants in the atmosphere [22]. The air quality standards for sulfur dioxide in Turkey, in USA, and according to the World Health Organization (WHO) are given in Table 2.8.

**Table 2.8 :** Air quality standards for sulfur dioxide [22].

	<b>in Turkey</b> ( $\mu\text{g} / \text{m}^3$ )	<b>in USA</b> ( $\mu\text{g} / \text{m}^3$ )	<b>WHO</b> ( $\mu\text{g} / \text{m}^3$ )
<b>Annual Average</b>	150	80	50
<b>24 h</b>	400	365	125

The Turkish standards in Table 2.8 were taken from the Air Quality Protection Legislation which was published in Official Gazette (No. 19269) in 1986. However, this legislation has been revoked with the new legislation, Air Quality Evaluation and Management Legislation, which has been published in Official Gazette (No. 26898) in 2008. By making some changes in Air Quality Evaluation and Management Legislation in 2009 (Official Gazette, No. 27219), it is planned to harmonize air quality standards of Turkey with air quality standards of European Union [23]. For this purpose, it is decided to decrease air quality limiting values by progressive stages till 2014. These new limiting values are seen in Table 2.9.

**Table 2.9 :** Air quality standards for SO<sub>2</sub> according to new legislation [23].

<b>Average Time</b>	<b>Limiting Value</b> ( $\mu\text{g} / \text{m}^3$ )	<b>Annual Decrease in Limiting Value</b>
1 h	900	
24h (short-term) (Protection for human health)	400	Limiting value decreases equally in each year till $250 \mu\text{g} / \text{m}^3$ between 2009 and 2014
Average in Winter (1 Oct.-31 March) (Protection for human health)	250	Limiting value decreases equally in each year till $125 \mu\text{g} / \text{m}^3$ between 2009 and 2014
Target Limiting Value (Annual arithmetic average)	60	
Target Limiting Value (Average in Winter) (1 Oct.-31 March)	120	

**Table 2.9 :** (contd.) Air quality standards for SO<sub>2</sub> according to new legislation [23].

<b>Average Time</b>	<b>Limiting Value (<math>\mu\text{g} / \text{m}^3</math>)</b>	<b>Annual Decrease in Limiting Value</b>
1 year (long-term) (Protection for human health)	150	
1 year (long-term) (Protection for Animals, plants and objects)	60	Limiting value decreases equally in each year till $20 \mu\text{g} / \text{m}^3$ between 2009 and 2014

According to the Industry Related Air Pollution Control Regulation (IRAPCR) which came into force in 2004, permissible mass emission of sulfur dioxide is 60 kg/h [24].

## **2.6 Sulfur Dioxide Abatement**

The regulations for sulfur dioxide emissions have become considerably more stringent with time. This has led to the application of various measures to reduce the emission of SO<sub>2</sub>. There are a number of options to realize these reductions:

- i. decreasing the sulfur content of the fuel or switching to other fuels;
- ii. the use of processes to decrease emissions during combustions;
- iii. the application of flue gas desulfurisation (FGD) processes [17].

### **2.6.1 Actions concerning fuel**

Change from high sulfur to low sulfur coal in coal fired power stations, also switching from high sulfur fuel oil to natural gas fired furnaces are the two examples about actions concerning fuel. Such solutions usually require a limited investment compared to the installation of FGD equipment. However, availability and price of the fuels set a limit to the applicability of this alternative for the reduction of SO<sub>2</sub> emissions. The second alternative in this category is the removal of sulfur from the fuel before combustion. This method is called as desulfurisation of coal [17].

### **2.6.2 Actions concerning combustion**

Combustion technologies exist where the control of the emission is an integral part of the process design. Examples include the fluidized bed combustion of coal and the application of sorbent injection. In both cases the intrinsically formed sulfur dioxide

reacts with and is bound to an active solid material, usually calcium or magnesium oxide [17].

In fluidized bed combustion process, the fuel is burned in a furnace containing a bed of finely-divided solid particles at a temperature of 850°C which is several hundred degrees lower than conventional combustion. The addition of a calcium or magnesium mineral like dolomite to the solids can prevent the emission of sulfur dioxide. The formed SO<sub>2</sub> is bound to the solids in the form of sulfate or sulfite and leaves the process together with the spent solids, coal ash and unconverted sorbent. The disadvantages of this method are its high cost and the fact that it is only applicable to new boilers of relatively small size [17].

In sorbent injection method, a dry calcium or sodium based solid sorbent is used. A dry calcium or sodium sulfite/sulfate waste mixed with the fly ash is produced at the end of the process. This method involves low capital cost and is easy to install. However, the degree of desulfurisation obtainable is low [17].

### 2.6.3 Flue gas desulfurisation processes

The most widely used way of reducing the emission of sulfur dioxide is flue gas desulfurisation. The technique consists basically of contacting the flue gas with a liquid or slurry containing a sorbent for SO<sub>2</sub> in specially designed reactors [17].

Flue gas desulfurisation (FGD) processes can be grouped into non-regenerable and regenerable processes. Most of the non-regenerable processes use wet absorption, spray drying and dry injection technologies. With wet scrubbing, a wide range of absorbents are used such as slaked lime, limestone, alkaline solutions, aqueous ammonia and sea water. Table 2.10 gives a survey of the FGD processes.

**Table 2.10 :** Overview of different FGD processes [4].

<b>Non-regenerable Processes</b>	<b>Sorbent</b>	<b>Product</b>
Wet Scrubbers	Lime/Limestone	Gypsum or Calcium Sulfite/Sulfate
	Lime/Fly ash	Calcium Sulfite/Sulfate/Fly ash
Spray-Dry Scrubbers	Lime	Calcium Sulfite/Sulfate
Dual-Alkali	Primary: Sodium Hydroxide Secondary: Lime/Limestone	Calcium Sulfate/Sulfite
Walther	Ammonia	Ammonium Sulfate

**Table 2.10:** (contd.) Overview of different FGD processes [4].

<b>Non-regenerable Processes</b>	<b>Sorbent</b>	<b>Product</b>
Seawater	Primary: Seawater Secondary: Lime	Waste Seawater
<b>Regenerable Processes</b>	<b>Sorbent</b>	<b>Product</b>
Bergbau-Forschung	Activated Carbon	Concentrated SO <sub>2</sub>
Wellman-Lord	Sodium Sulfite	Concentrated SO <sub>2</sub> or Elemental S
Linde-Solinox	Physical Absorption Solvent	Concentrated SO <sub>2</sub>
Spray-Dry Scrubbers	Sodium Carbonate	Elemental S
MgO Process	Magnesium Oxide	Concentrated SO <sub>2</sub>

### 3. THERMODYNAMICS OF SOLUBILITY

Thermodynamics deals with a system. A system can contain a number of phases. A phase is a homogeneous part of a system, which implies that all intensive variables of the system (temperature, pressure, composition, etc.) are uniform within it [25].

The basic terms used to describe any phase which contains more than one component are mixture and solution. A mixture describes a gaseous, liquid or solid phase containing more than one substance, where the substances are all treated in the same way. A solution describes a gaseous, liquid or solid phase containing more than one substance, when for convenience one of the substances, which is called the solvent, and may itself be a mixture, is treated differently than the other substances, which are called solutes [26].

According to IUPAC, the solubility is the analytical composition of a mixture or solution which is saturated with one of the components of the mixture or solution, expressed in terms of the proportion of the designated component in the designated mixture or solution. In this definition, “saturated” implies equilibrium with respect to the process of dissolution and crystallization for solubility of a solid in a liquid, of phase transfer for solubility of a liquid in another liquid, or of vaporization and dissolution for solubility of a gas in a liquid [25].

#### 3.1 Ideal Solutions

Ideality of solutions is analogous to ideality for gases. If gaseous molecules occupy no volume and if the interactions between them are all identical and equal to zero, the equation of state assumes the simple form,

$$PV = nRT \tag{3.1}$$

which is called the ideal-gas equation of state. The solution counterpart of the ideal-gas laws makes a similar assumption that the interactions between all molecules in the solution are identical. However, the magnitude of these interactions cannot be zero [27].

For an ideal solution, the ratio of partial pressure of component A in the solution ( $p_A$ ) to vapor pressure of pure A ( $p_A^*$ ), gives the mole fraction of A in the liquid ( $X_A$ ). This relation is called Raoult's Law [28].

$$p_A = X_A p_A^* \quad (3.2)$$

In ideal solutions the solute, as well as the solvent, obeys Raoult's Law. However, in real solutions at low concentrations, although the vapor pressure of the solute is proportional to its mole fraction, the slope is not equal to the vapor pressure of the pure substance. This linear but different dependence is called Henry's Law [28].

$$p_B = X_B H_B \quad (3.3)$$

In the equation above  $p_B$  denotes the partial pressure of component B while  $X_B$  is representing the mole fraction of B in the liquid.  $H_B$  is the Henry's constant. Mixtures obeying Henry's Law are ideal in a different sense from those obeying Raoult's Law and are called ideal dilute solutions [28].

### 3.2 Chemical Potentials of Ideal Gases and Solutions

For the definition of Gibbs free energy,

$$G = H - TS \quad (3.4)$$

where  $H$ ,  $T$  and  $S$  correspond to enthalpy, temperature and entropy, respectively.

$$H = U + PV \quad (3.5)$$

By inserting equation (3.5) into equation (3.4) and complete differentiation of this yields,

$$dG = dU + PdV + VdP - TdS - SdT \quad (3.6)$$

For a reversible change,

$$dU = TdS - PdV \quad (3.7)$$

Substituting equation (3.7) in equation (3.6) gives,

$$dG = VdP - SdT \quad (3.8)$$

For an isothermal system, temperature change is equal to zero. Therefore, the second term on the right-side of equation (3.8) becomes zero.

$$dG = VdP \quad (3.9)$$

Dividing equation (3.9) by mole number ( $n$ ) yields,

$$d\mu = V_m dP \quad (3.10)$$

where  $V_m$  is the molar volume. With the assumption of ideal-gas law,  $V_m$  can be defined as,

$$V_m = \frac{RT}{P} \quad (3.11)$$

Inserting equation (3.11) into equation (3.10) yields,

$$d\mu = RT \frac{dP}{P} \quad (3.12)$$

By integrating equation (3.12) between two states, 1 and 2, gives,

$$\mu_2 = \mu_1 + RT \ln \frac{P_2}{P_1} \quad (3.13)$$

If “1” represents a reference state, using “ $\theta$ ” instead of “1” is more convenient. After rewriting equation (3.13), equation below is obtained and it gives the chemical potential of an ideal gas.

$$\mu = \mu^\theta + RT \ln \frac{P}{P^\theta} \quad (3.14)$$

The chemical potential of a pure liquid A can be written as,

$$\mu_A^*(l) = \mu_A^\theta + RT \ln \frac{P_A^*}{P^\theta} \quad (3.15)$$

where  $P_A^*$  denotes the vapor pressure of pure liquid A.

If another substance is also present in the liquid the chemical potential of A in the liquid is  $\mu_A(l)$  and its vapor pressure is  $p_A$ . In this case,

$$\mu_A(l) = \mu_A^\theta + RT \ln \frac{P_A}{P^\theta} \quad (3.16)$$

Combining equations (3.15) and (3.16) yields equation (3.17).

$$\mu_A(l) = \mu_A^*(l) + RT \ln \frac{p_A}{p_A^*} \quad (3.17)$$

As it is mentioned before, ideal solutions obey Raoult's Law which states that the ratio  $p_A / p_A^*$  is the mole fraction of A in the liquid ( $X_A$ ). Inserting  $X_A$  into equation (3.17) gives the chemical potential for ideal solutions.

$$\mu_A(l) = \mu_A^*(l) + RT \ln X_A \quad (3.18)$$

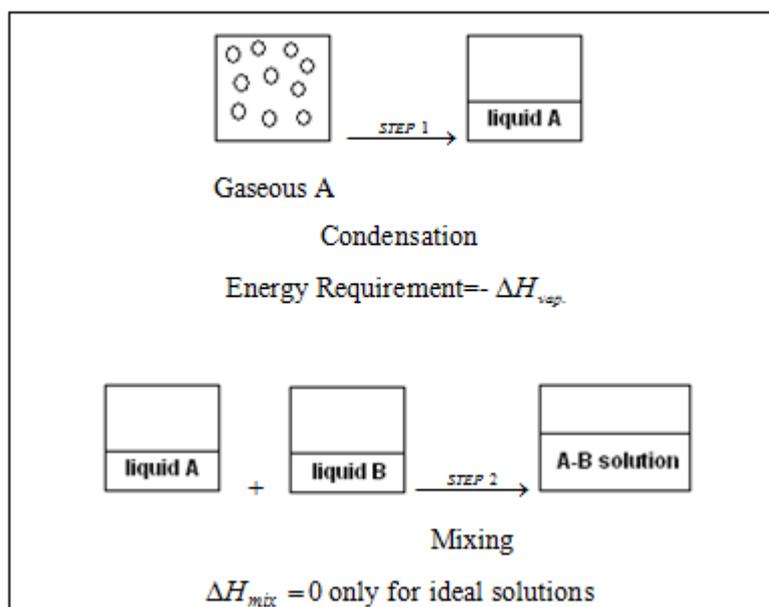
### 3.3 Solubility of Gases in Liquids

The solubility of gases in liquids has been under quantitative investigation since the beginning of the nineteenth century. Gas solubilities have become increasingly more important for both the theoretical understanding of the liquid state and solutions, and for practical applications from the solubility of gases in human tissues to the solubility of gases in molten salts and metals.

Experiments on the solubility of gases can be divided into two groups: (a) the solubility of a gas in a liquid is measured directly at a particular temperature and pressure; (b) liquid-vapor equilibria are determined, either as vapor pressures of a liquid mixture at a fixed temperature, or as the boiling point of the liquid mixture at a given pressure, with or without determination of the composition of the vapor phase [25].

The distinction between vapor-liquid equilibria and the solubility of gases in liquids depends on the physical state of the pure component. If the pure saturating component is a gas under the stated conditions, then the equilibrium is gas-liquid solubility (e.g., between argon and water at 300 K), whereas if the pure saturating component is a liquid under the stated conditions, then the equilibrium is vapor-liquid equilibrium (e.g., between hexane and cyclohexane at 350 K) [25].

Dissolution process of gases in liquids can be explained in two steps. In the first step, the gas is condensed to a liquid, after which the two liquids are mixed in the second step. This process is illustrated in Figure 3.1 [27].



**Figure 3.1** : Steps involved in solution formation of a gas in a liquid solvent [27].

For an ideal solution,  $\Delta H_{mix} = 0$ , so that the total energy requirement for the process is simply the negative of the enthalpy of vaporization of gaseous A [27].

The solubility of gases in liquids decreases with decreasing pressure and increasing temperature. The increasing solubility of gases at higher partial pressures is seen in everyday life by examining bottles containing carbonated beverages. When the bottle is sealed, no  $CO_2(g)$  bubbles are visible on the walls of the container. All the  $CO_2(g)$  is in solution. When the seal is broken, however, the pressure of the  $CO_2$  is released and the  $CO_2(g)$  solubility decreases. For the temperature effect on solubility of gases in liquids again the carbonated beverages can be given as an example. When the can of a carbonated beverage is taken from the refrigerator and opened, most of the  $CO_2(g)$  carbonation is in solution, and very little gas escapes as the can is opened. However, if the can is opened while it is hot, the beverage often spews out under the force of escaping  $CO_2(g)$  that was under high pressure because the gas had come out of solution as the temperature increased [27].

### 3.3.1 Quantities and units used to describe solubilities of gases

Gas solubilities have been expressed in a great many ways. Some of them are mol fraction, Henry's constant, Ostwald's coefficient and weight of solute in unit volume of solvent.

Mol fraction of component  $i$  in a solution is defined as its amount of substance ( $n_i$ ) divided by the total amount of substance in the solution ( $n_T$ ).

$$X_i = \frac{n_i}{n_T} \quad (3.19)$$

For ideal dilute solutions, Henry's constant is another alternative way of expressing the gas solubility. According to Henry's Law, the ratio of partial pressure of gas B to mole fraction of B in the liquid gives the Henry's constant in pressure units.

$$H_B = \frac{P_B}{X_B} \quad (3.20)$$

The Ostwald's coefficient,  $L$ , is defined as the ratio of the volume of gas absorbed ( $V_g$ ) to volume of the absorbing liquid ( $V_L$ ), all measured at the same temperature and pressure. Unit of Ostwald's coefficient may be mL gas abs./mL liquid or L gas abs./L liquid [29].

$$L = \frac{V_g}{V_L} \quad (3.21)$$

Weight of solute in unit volume of solvent can be symbolized as  $s$ . If the density of gas is known at experiment temperature it is possible to convert this term to Ostwald's coefficient or with the known molecular weight of gas and density of solvent, number of moles of gas per gram solvent which is called weight solubility ( $C_w$ ) can be calculated [29].

### 3.4 Van't Hoff Equation

The Van't Hoff equation relates the change in temperature ( $T$ ) to the change in equilibrium constant ( $K$ ).

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (\text{constant temperature}) \quad (3.22)$$

where  $\Delta H^0$  and  $\Delta S^0$  are standard enthalpy and entropy changes, respectively. In equation (3.22),  $\Delta H^0$  and  $\Delta S^0$  may be regarded as constant over small ranges of temperature, and so the equation simply shows the variation of  $K$  with temperature [30].

$$\ln K = -\frac{\Delta H^0}{R} \cdot \frac{1}{T} + C \quad (\text{constant temperature}) \quad (3.23)$$

where  $C$  is a constant, equal to  $\Delta S^0 / R$ .

Since equation (3.23) has the classic form of the  $y = mx + c$  relationship, it is seen that  $y$  corresponds to  $\ln K$ ,  $x$  to  $1/T$  and  $m$  to  $-\Delta H^0 / R$ . That is, the slope of the graph of  $\ln K$  vs  $1/T$  gives  $-\Delta H^0 / R$ . It is possible to obtain  $\Delta H^0$  [30].

### 3.5 Solubility of Sulfur Dioxide in Different Solvents

Sulfur dioxide concentrations in the atmosphere increase with increasing population, industrialization, motorization and urbanization. The most of the sulfur dioxide emissions are recorded in industrial areas. Since sulfur dioxide and its derivatives have adverse effects on vegetation, animal and human health and cause to air pollution, many legislations and regulations have been made by the governments. In order to meet the necessities of the laws and to decrease the adverse effects of sulfur dioxide on the environment, industrial plants have been forced to develop processes to decrease  $\text{SO}_2$  emissions. For these reasons, many studies have been made. Most of these studies aim to reduce sulfur dioxide in flue gases by absorbing it physically or chemically into an solvent. The type of the solvents used as absorbents show a great variety in most of the researches. Some of these solvents used in sulfur dioxide removal are water [7] and seawater [1], organic solvents such as N-methylpyrrolidone [12], N,N-(dimethylpropylene)urea [12], methyldiethanolamine [12], phosphoric and phthalic acid esters [31], poly(ethylene glycols) [31], poly(ethylene glycol) dialkyl ethers [31], N,N-dimethylaniline [11], quinoline [11], dimethyl ethers of diethylene glycol, triethylene glycol, and tetraethylene glycol [11], heptadecane [13], hexadecane [13,32], phenol [13], nitrobenzene [13], aqueous alcohol solutions [33], aqueous solutions of sodium chloride and ammonium chloride [9], and of acetic acid, sodium acetate and ammonium acetate [10], water-acetonitrile solutions [34], and heat transfer oil (Transcal N) [35].

One of the researches that included the solubility of sulfur dioxide in polar organic solvents were made by Härtel in 1985 [31]. In this research, the solubilities of  $\text{SO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{COS}$  in several phosphoric and phthalic acid esters, poly(ethylene glycols)

and poly(ethylene glycol) dialkyl ethers were measured in the temperature range of 20°C-100°C and pressures between 1 kPa and 100 kPa. During the experiments, the dissolution of the gas in the solvent was noted by the decrease in the pressure of the system until the equilibrium was established. According to the results of the experiments, it was obtained that phthalic acid esters such as dibutyl phthalate, dibutyl glycol phthalate and dimethyl glycol phthalate showed good solubility properties for sulfur dioxide. However, the polyethylene dialkyl ethers (such as tetraethylene glycol dimethyl ether, pentaethylene glycol methyl isopropyl ether) were found to be better absorbents for SO<sub>2</sub> than others.

In 1987, an alternative study was performed by Demyanovich et al. to determine the vapor-liquid equilibria of sulfur dioxide in polar organic solvents [11]. For this purpose, N,N-dimethylaniline (DMA), quinoline, dimethyl ethers of diethylene glycol, triethylene glycol and tetraethylene glycol, monomethyl ether of diethylene glycol (DGM), tetramethylene sulfone and tributyl phosphate (TBP) were used as solvents. The experiments were run over the temperature range 30°C-95°C and a concentration range of 0.02-0.16 weight fractions of SO<sub>2</sub>. The experimental total pressures ranged from 4.0 to 130 kPa. A recirculating still connected with a condenser was used for vapor-liquid equilibrium measurements. The obtained data were neither isobaric nor isothermal, but were at constant SO<sub>2</sub> concentration. The solutions of sulfur dioxide in these organic solvents were prepared (generally 350-400 g of solvent were used with varying amounts of SO<sub>2</sub> between 10 to 70 g). The prepared solution was introduced to the system and heated to the boiling point of the solution. Since the selected solvents had relatively low vapor pressures, it was assumed that the vapor evolved was largely SO<sub>2</sub>. The curves plotted by using partial pressures of sulfur dioxide corresponding to weight fractions of SO<sub>2</sub> showed that DMA was the best solvent for absorption of SO<sub>2</sub>. Quinoline was the second best pure solvent followed by the polyglycol ethers. However, TBP and sulfolane had relatively low sulfur dioxide absorption capacities. These results allowed to workers to draw a few general conclusions about the solvents tested: 1) The absorption capacity for SO<sub>2</sub> with respect to solvent group decreases in the order N (amine) > ROR (glycol ether) > ROH (glycol ether) > PO<sub>4</sub> > O=S=O. 2) DGM, which is very similar to dimethyl ether of diethylene glycol except that the end monomer unit is CH<sub>2</sub>OH instead of CH<sub>2</sub>OCH<sub>3</sub>, has significantly less absorption capacity for SO<sub>2</sub>. It

appears that the presence of the alcohol group does not increase the solubility of SO<sub>2</sub>, perhaps because of increased hydrogen bonding between neighboring solvent molecules.

Van Dam et al. studied selective sulfur dioxide removal by using organic solvents [12]. The study included preselection of solvents, investigation of SO<sub>2</sub>-solvent interactions and measurement of solubility steps. In the preselection of solvents, N-methylpyrrolidone, N,N-(dimethylpropylene)urea and methyldiethanolamine were chosen as absorbents due to their good capacity, selectivity, low vapor pressure and toxicity. The interactions between SO<sub>2</sub> and the solvents were investigated by the melting point measurement of SO<sub>2</sub>-solvent mixtures, infrared, ultraviolet-visible and nuclear magnetic resonance spectroscopy. These analysis showed that the interactions between SO<sub>2</sub> and methyldiethanolamine was so strong that a stable reaction product was formed. According to infrared spectroscopy results, the acid-base interaction of N-methylpyrrolidone and N,N-(dimethylpropylene)urea with SO<sub>2</sub> was located at the carbonyl group. For the solubility measurements, two different experimental installations were used: an agitated stirred tank reactor with a water jacket for the measurements up to 0.6 kPa and a bubble column reactor for the measurements between 2 to 100 kPa. The solubility experiments were performed at 25°C for N-methylpyrrolidone and N,N-(dimethylpropylene)urea. Three approaches, which consisted of only physical interaction, only chemical interaction and combination of physical and chemical interactions, were proposed for the solubility of sulfur dioxide, in order to describe deviations of Raoult's Law. However, the resultant solubility data showed the best agreement with the model including combination of physical and chemical interactions. The high solubility of sulfur dioxide in these solvents indicated the adequacy of these solvents for sulfur dioxide removal processes.

Another study which investigated the solubility of sulfur dioxide in various solvents was conducted by Lenoir et al. in 1971 [13]. In this study, Henry's constants of 12 gases in 19 solvents were determined by gas-liquid chromatography. For sulfur dioxide 12 different solvents were tested. These solvents were benzyl alcohol, decahydronaphthalene, dimethyl sulfoxide, ethylene glycol, heptadecane, hexadecane, nitrobenzene, phenol, propylene carbonate, triethyl phosphate, trisobutyl phosphate and tripropyl phosphate. Experiments run with benzyl alcohol,

decahydronaphthalene, dimethyl sulfoxide, ethylene glycol, hexadecane, nitrobenzene and propylene carbonate at 25°C showed that dimethyl sulfoxide had the highest absorption capacity of SO<sub>2</sub>, followed by propylene carbonate, nitrobenzene, benzyl alcohol, ethylene glycol, hexadecane and decahydronaphthalene, respectively. Experiments performed with decahydronaphthalene, heptadecane, phenol, propylene carbonate and tripropyl phosphate at 50°C resulted that the highest solubility of sulfur dioxide was obtained in tripropyl phosphate with the lowest Henry's constant, 62.92 kPa. Some of the experiments were carried out with triethyl phosphate and trisobutyl phosphate at 52°C. According to data obtained in these experiments, it might be said that trisobutyl phosphate had greater absorption capacity of SO<sub>2</sub> than triethyl phosphate.

In 1976, Tremper et al. investigated the solubilities of seven inorganic gases in four different high-boiling hydrocarbon solvents in the temperature range of 25°C-200°C [32]. Used gases and solvents were ammonia, nitrogen, carbon monoxide, hydrogen sulfide, hydrogen chloride, carbon dioxide and sulfur dioxide; n-hexadecane, diphenylmethane, bicyclohexyl and 1-methylnaphthalene. The solubility values were given in terms of Henry's constants in atm. Solubility of sulfur dioxide was tested only in n-hexadecane and resultant Henry's constants showed increment with increasing temperature, which meant that solubility of sulfur dioxide decreased with increasing temperature. This expected situation was explained as the increment of kinetic energy of the gas with increasing temperature prevented gas to condense into liquid phase.

Dimethyl sulfoxide (DMSO) is one of the popular solvents in sulfur dioxide absorption, which was used for the investigation of SO<sub>2</sub> solubility by Li et al. in 2002 [36]. In this work, solubility of sulfur dioxide in DMSO was determined at temperatures between 293.15 K and 313.15 K at partial pressures of SO<sub>2</sub> from 0.15 kPa to 2.62 kPa. The solubility apparatus involved saturation and absorption flasks, magnetic stirrer, constant temperature bath and heater, burette. The principle for this method was to bring a known volume of liquid into contact with a gas in a closed system at constant temperature and pressure. It was possible to calculate the volume of the sulfur dioxide absorbed by DMSO via the difference between the measured volume change of the buret and injected solvent volume. The resultant data obtained from this research showed that there was a great solubility for dilute SO<sub>2</sub> in DMSO at

working temperature range, and the dissolving process of dilute SO<sub>2</sub> in DMSO obeyed Henry's law.

As it is mentioned at the beginning of this section, water and aqueous solutions of different solvents are alternative solvents which are used as absorbents in sulfur dioxide absorption. However, the absorption mechanism in water or aqueous solutions differs from the mechanism in organic solvents. Because, SO<sub>2</sub> dissociates instantaneously and reversibly to form H<sup>+</sup> and HSO<sub>3</sub><sup>-</sup> ions in aqueous solutions. Mondal investigated the sulfur dioxide solubility in water by using a bubble column containing fixed volume of water [7]. The effect of temperature (temperature range: 293 K – 303 K) on SO<sub>2</sub> absorbed and gas bubble-liquid interfacial area, the effect of partial pressure on SO<sub>2</sub> absorbed at 303 K and the relations between temperature and Henry's constant, temperature and dissociation constant were studied. According to the data obtained, it was said that interfacial area slightly decreased as the temperature was increased at the temperature range between 293 K and 303 K. A graph of SO<sub>2</sub> absorbed versus SO<sub>2</sub> passed unit volume of liquid was plotted for working temperatures at 0.831 kPa SO<sub>2</sub> partial pressure. This plot showed that there was no effect of temperature till 0.005 kmol SO<sub>2</sub>/m<sup>3</sup> liquid. But, after that at any temperature the amount of SO<sub>2</sub> absorbed increased slowly and became constant at saturation point. The amount of SO<sub>2</sub> absorbed was high at lower temperatures at saturation. Another graph of SO<sub>2</sub> absorbed versus SO<sub>2</sub> passed unit volume of liquid was drawn at 303 K for different partial pressures of sulfur dioxide ranged from 0.447 kPa to 0.963 kPa. According to this plot, it was possible to say that up to 0.008 kmol SO<sub>2</sub>/m<sup>3</sup> liquid, amount of SO<sub>2</sub> absorbed was irrespective of partial pressure. But after that point more sulfur dioxide was absorbed for high partial pressures. Two equations were proposed for the relations between temperature and Henry's constant and dissociation constant. According to these equations, Henry's constant decreased while dissociation constant increased with increasing temperature between 293 K and 303 K. In this work, all obtained and calculated data were found to agree well with the data reported by other workers in the literature.

In 2001, Al-Enezi et al. studied the solubility of sulfur dioxide in seawater of the Arabian Gulf [1]. Solubility measurements were made as a function of the seawater temperature and salinity at atmospheric conditions. Water samples involved distilled water, seawater, mixtures of distilled water and seawater, and brine blowdown from

the multistage flash desalination plants in Kuwait. Each set of water samples varied in salinity, pH and conductivity. Experiments were performed in a water jacketed mixing cell at temperatures of 10, 20, 30 and 40°C and the rotation speed was adjusted to 1600 rpm. In light of the measured data and results analysis, it was seen that the solubility of sulfur dioxide increased upon reduction of the system temperature and increase of the water sample salinity. In this context, for the same conditions, solubility of SO<sub>2</sub> in brine blowdown solution, whose salinity was about 65100 ppm, was much more greater than in distilled water containing 5 ppm of salt. This was related to inclusion of chemical reactions with the salt content in the water as well as physical absorption of SO<sub>2</sub> in water.

Byerley et al. studied solubility of sulfur dioxide in water-acetonitrile solutions [34]. The experiments were carried out in 50 mL buret equipped with a water jacket at 25 and 50°C and total pressure of 101.3 kPa. The solubilities were expressed in grams of sulfur dioxide dissolved in 100 grams of solute gas-free solution. In order to investigate the interactions between SO<sub>2</sub>-CH<sub>3</sub>CN and SO<sub>2</sub>-H<sub>2</sub>O, ultraviolet spectra of solutions of SO<sub>2</sub> in acetonitrile and in water was examined. As a result of UV spectra, strong interactions and complex formation was obtained between SO<sub>2</sub> and CH<sub>3</sub>CN both at 25 and 50°C. However, the interaction between SO<sub>2</sub> and water was very low relative to SO<sub>2</sub>-CH<sub>3</sub>CN interaction. Resultant data obtained from the experiments showed that when the acetonitrile content of mixture was between 20 and 80% by weight, two liquid phases existed in the mixture at 25°C. However, the two-phase system was not observed at 50°C. The solubility data of SO<sub>2</sub> at 50°C increased as the acetonitrile percentage by weight was increased.

Another study about the solubility of sulfur dioxide was performed with sulfuric acid solutions containing hydrogen peroxide by Colle et al. in 2008 [37]. The effect of temperature and acidity on overall kinetic parameter was investigated at 35 and 50°C. A cables-bundle laboratory scrubber was used as an absorption reactor. The data analysis showed that at a given temperature Henry's law constant increased sharply with the increment of the concentration of sulfuric acid, that is, the solubility of the SO<sub>2</sub> species reduced. An increase in temperature enhanced the overall kinetic parameter for the global process of sulfur dioxide absorption (solubility+diffusion+reaction) whereas an increase in sulfuric acid content decreased it.

Aydin et.al studied the solubility of sulfur dioxide in a heat transfer oil (Transcal N) which was a mixture of saturated hydrocarbons [35]. The reason of selecting this solvent was its high flash, fire and boiling points which enabled to work in a wide temperature range. The experiments were performed in the temperature range of 293.15 - 313.15 K and at 101.3 kPa. The principle of solubility measurements was to bring a known amount of gas into contact with the known amount of solvent in the absorption flask settled into the water bath. Experimental procedure basically included the keeping the system under vacuum for a while in order to suck the air in the system, then loading of gas into the absorption flask, followed by the injection of the oil (three times with time intervals of 15 minutes) and recording the pressure change during the absorption process. The solubility of sulfur dioxide in Transcal N was expressed in terms of mol fraction, Henry's constant, Ostwald's coefficient and grams of SO<sub>2</sub> absorbed by unit volume of oil. As a result of this study it was obtained that the SO<sub>2</sub> absorption capacity of Transcal N was not as high as that of other organic solvents studied in the literature such as dimethylaniline, dimethylacetamide, diethylene glycol dimethyl ether. However, it was stated that its high fire, flash and boiling points, wide range of working temperature made it preferable to use for SO<sub>2</sub> absorption.



## 4. EXPERIMENTAL

### 4.1 Chemicals

In this research, two different heat transfer oils, Transcal N and Mobiltherm 605, were used as absorbing liquid. These oils are stable at high temperatures such as the temperatures at which flue gases come out of the chimney.

Transcal N is a commercial product of British Petroleum. It is a high quality heat transfer oil possessing low vapor pressure, good thermal stability, high specific heat and high thermal conductivity. The excellent thermal stability of the fluid gives long life. It is possible to work with Transcal N in a temperature range of  $-10^{\circ}\text{C}$  to  $320^{\circ}\text{C}$ . Some chemical and physical properties of Transcal N are given below.

**Table 4.1** : Typical characteristics of Transcal N [16].

Property	Unit	Value
Specific Gravity at $15^{\circ}\text{C}$	$\text{kg/m}^3$	875
Viscosity at $40^{\circ}\text{C}$	cSt	31
Viscosity at $100^{\circ}\text{C}$	cSt	5.2
Flash Point (COC)	$^{\circ}\text{C}$	221
Pour Point	$^{\circ}\text{C}$	-12
Fire Point	$^{\circ}\text{C}$	243
Autoignitin Point	$^{\circ}\text{C}$	350
Neutralization Value	mg KOH/g	<0.05
Coefficient of Expansion	for every $1^{\circ}\text{C}$	0.00077
Operating Temperature Range	$^{\circ}\text{C}$	-10 to 320
Boiling Point Range	$^{\circ}\text{C}$	355-365

Transcal N is a hydrocarbon mixture which contains linear and cyclic hydrocarbons in the range of 14C-30C. The most abundant hydrocarbons are cyclotetradecane ( $\text{C}_{14}\text{H}_{28}$ ), tricosane ( $\text{C}_{23}\text{H}_{48}$ ), hexacosane ( $\text{C}_{26}\text{H}_{54}$ ), octacosane ( $\text{C}_{28}\text{H}_{58}$ ) and triacontane ( $\text{C}_{30}\text{H}_{62}$ ). The average molecular weight of Transcal N is 337.74 g/mole [16].

Other heat transfer oil is Mobiltherm 605 which belongs to Mobil Corporation. It is very thermally stable and is capable of an extremely long service life without deposit

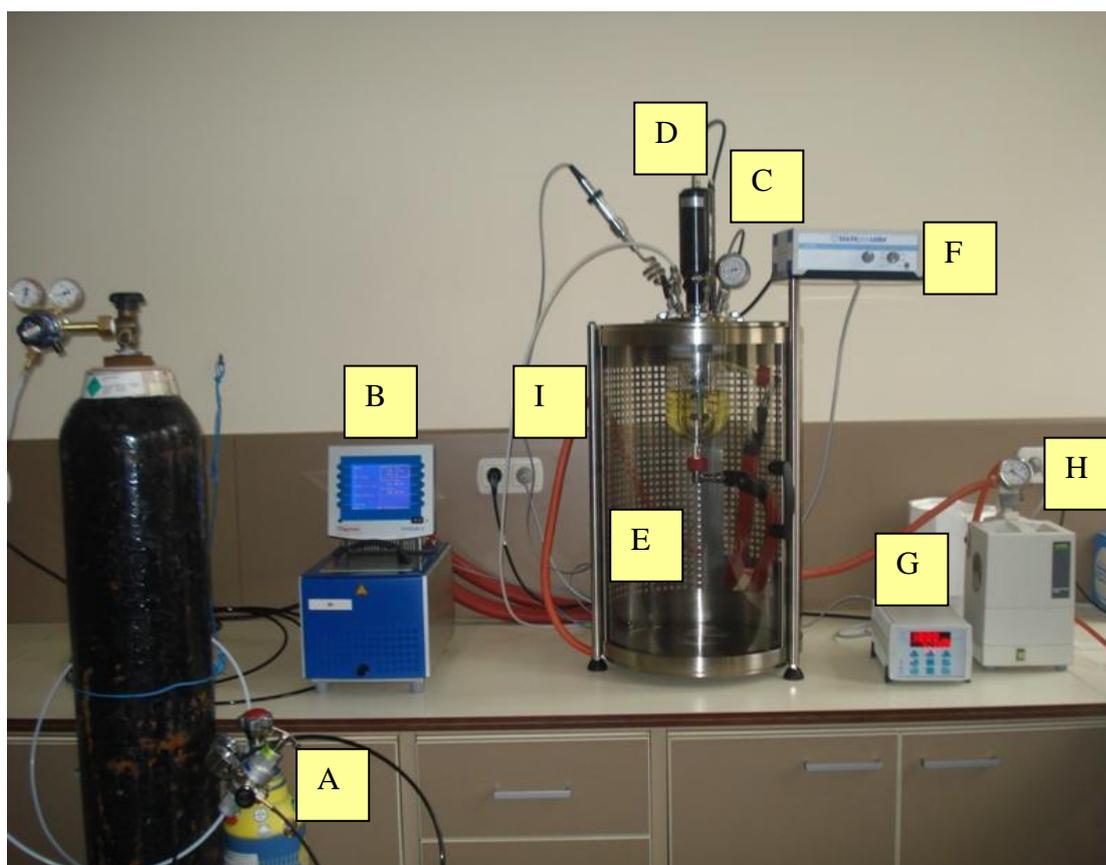
formation or viscosity increase. Typical properties of Mobiltherm 605 can be seen in Table 4.2.

**Table 4.2 :** Typical properties of Mobiltherm 605 [38].

Property	Unit	Value
Specific Gravity at 15°C	g/cm <sup>3</sup>	0.872
Viscosity at 40°C	cSt	29
Viscosity at 100°C	cSt	5.1
Flash Point (COC)	°C	210
Pour Point	°C	-15
Maximum Operating Temperature	°C	320
Boiling Point	°C	>316

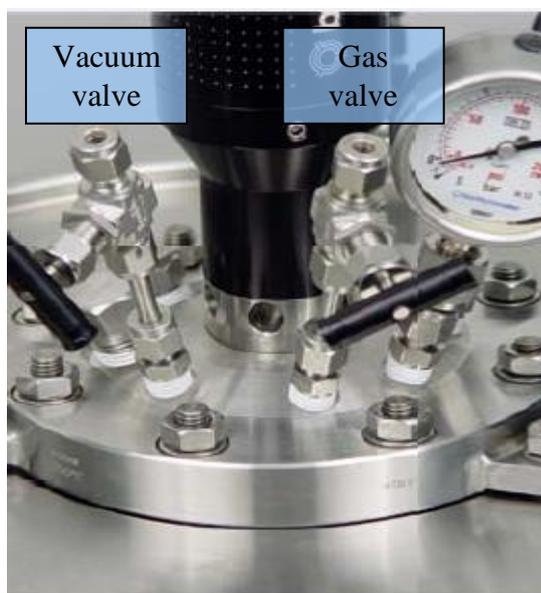
Sulfur dioxide (3.8) was used as a solute. It is acquired from Linde AG with a gas cylinder at 99.9 % purity.

#### 4.2 Experimental Setup



**Figure 4.1 :** Experimental setup.

A display of the experimental system is shown in Figure 4.1. The system involves a heating circulator (B) connected with a thermocouple (C) entering the jacketed vessel (E). A protecting frame (I) with a sliding door encloses the jacketed vessel. There are seven openings on the upper part of the vessel. Four of these openings are the spaces of drive with mechanical stirrer, manometer, thermocouple connected to the heating circulator and pressure transmitter connected to device (G). Another opening is septum which provides to inject liquid material into the vessel. Last two openings seen in Figure 4.2, are valves which are connected to vacuum pump and SO<sub>2</sub> cylinder with thin pipes. In addition to these openings, there is a bursting disc which sets in when the pressure exceeds 6 bar. There is a magnetic stirrer connected with a drive (D). The speed controller (F) provides to adjust the speed of rotation of mechanical stirrer. The device denoted as (G) shows the pressure in the vessel in mbar. The vacuum pump (H) is used to sweep the air in the vessel. There is a software installed in computer connected with this system, which records the pressure for each second. In addition, a balance is present to use for mass measurements of oil. The sulfur dioxide is fed into the system by a gas cylinder (A).



**Figure 4.2 :** Vacuum and gas valves.

The system involving glass vessel for pressure reactions, protecting frame with stainless steel construction and polycarbonate sliding door, stirrer drive, is called ecoclave. This system was bought from Büchi AG. The “Type 1” glass stirrer vessel with heating jacket is available both in 0.25 L and 0.5 L. It is heatable up to

maximum 200°C and usable for maximum 600 kPa in laboratory and maximum 1200 kPa in autoclave room. One of the most important properties of this vessel is being hydrogen tight, that is, even if H<sub>2</sub> is working gas, the vessel does not leak gas. Since the vessel is made of glass, visual supervision of the reaction medium is possible. The type of the drive is “cyclone 075” and it consists of an electric motor and a speed controller “cc 075”. It is manually adjustable between 100 rpm and 3000 rpm.

The device (G) which is called “bds.sc” with model “pr 94”, was provided by Büchi AG. It is a single channel instrument displaying pressure.

The installed software “Büchi bls 2” in the computer provide the documentation of experimental data and simple transfer to Microsoft Excel document.

Vacuum pump with model “V-700” is also a product of Büchi AG. It serves to evacuate the vessel down to 10 mbar.

The heating circulator, HAAKE Phoenix II P2-B5, was provided by Thermo Fischer Scientific. The net volume of bath of the circulator is 4.5 L. Distilled water, water with antifreeze, and silicone oil (SIL 180) can be used as bath liquids. The recommended bath liquid temperature depends on the sort of the bath liquid. For distilled water, water with antifreeze and silicone oil, the bath temperature ranges are between 5°C-95°C, -10°C-80°C and -40°C-200°C, respectively. The temperature accuracy is ± 0.01K.

The balance with model “ML204/01” is a product of Metler-Toledo AG. Maximum measurement capacity is 220 g with 0.1 mg readability.

GC-MS used in determination of the composition of Mobiltherm 605, is a product of Agilent HP. The models of gas chromatograph, mass spectrometer and automatic sampler are 6890 N, 5975 B and 7683 B, respectively.

### **4.3 Experimental Procedure**

The principle of these experiments is to bring a known amount of oil into contact with sulfur dioxide gas within the glass jacketed vessel at constant temperature. Decrease in the pressure gives how much gas is absorbed by the oil indirectly.

Since the absorption system is new one, in order to find out the convenient method for the absorption measurements two different methods were tried. In the first tested

method, vessel was evacuated down to 1 kPa by vacuum pump in order to suck the air in the vessel. During the evacuation, gas valve was closed while vacuum valve was opened. Then SO<sub>2</sub> with a pressure around 40 kPa was sent to the vessel and the vessel was evacuated again. This was done to make sure that the only gas in the vessel was sulfur dioxide with 1 kPa pressure in the vacuum. After that, SO<sub>2</sub> was sent to the vessel up to 120-130 kPa. Then the oil with a volume about 1.5-2 mL was injected to the system. However, no significant pressure decrease was observed. The reason of this situation was explained as the amount of injected oil was so small to provide a contact between oil and mechanical stirrer. To provide an effective mixing of oil, it was necessary to load the vessel with oil about 40 mL. Since it was not possible to sent 40 mL oil into the vessel by injection, the experimental procedure was changed. According to the new method, first 40 mL oil was fed to the vessel by a graduated cylinder as if in batch system instead of injection and then SO<sub>2</sub> was sent to the system. The details of new experimental method is explained below.

Experimental procedure can be summarized as follows:

First of all, 40 mL of oil is fed into the reactor and air in the reactor is sucked by the vacuum pump. It is better to wait for a few seconds to see that the vacuum pressure is constant in order to be sure that there is no leakage in the system. Then, SO<sub>2</sub> is sent to the system up to 120-130 kPa and temperature is set. After the temperature of the system comes at setted value, mechanical stirrer is started up. Pressure change with time during the absorption is recorded by a software.

It was noticed that the most of the absorption occurred in the first 1.5 minutes and then a flatness was reached. Although the most of the absorption occurred in first 1.5 minutes each experiment was carried out until 30 minutes passed in order to see whether there is desorption or not.

The experiments with SO<sub>2</sub> and Transcal N were carried out at 20, 30, 40, 50, 60, 70, 80, 100 and 140°C while those of with SO<sub>2</sub> and Mobiltherm 605 were made at 20, 30, 40, 50 and 60°C. Experiments for each temperature were run three times to show the repetition of experimental results. For each experiment rotational speed is fixed at 2000 min<sup>-1</sup>.

Although the new selected experimental method provides an effective mixing of oil and a good contact between gas and oil, there are some limitations of the system. The

most important restriction of the system is about the liquid material fed to the vessel. This problem exists since liquid material is fed to the vessel before the evacuation. If the boiling point of the liquid material is relatively low and vapor pressure is relatively high, it is not possible to evacuate the system down to 1 kPa. In this study, silicone oil was tested together with Transcal N and Mobiltherm 605. However, when the system was evacuated down to 30 kPa, bubbles rising upward were observed in the silicone oil. This was because the silicone oil started to vaporize with decreasing pressure in the vessel. When Transcal N and Mobiltherm 605 were used, there was no problem about the vaporization of oils since their boiling points (about 350°C) were relatively higher than that of silicone oil (about 200°C).

## **5. RESULTS AND DISCUSSION**

### **5.1 Comparison of New Absorption System With Previous Study**

Since the study conducted by A. Alper Aydin [16] is assumed as the starting point of present study, it is necessary to state the differences of experimental setups and procedures between two studies.

Although the absorption systems in two researches are basically similar, there are some differences between them. In previous study [16], the absorption system was designed manual. It consisted of preheating and absorption flasks settled in a water bath, water pump on the exit line, digital and mercury manometers, an electrical heating device with contact thermometer, magnetic and mechanical stirrers. However, the newly installed absorption system used in present work is equipped with advanced devices. The most important advantage of new absorption system is being able to record the pressure data for each second by a computer software. Thereby, it is possible to observe the pressure change from the beginning to the end of the absorption. However, in absorption system used in previous study, there was no software recording the pressure changes by time. Therefore, the pressure changes were recorded manually just at 3<sup>rd</sup>, 5<sup>th</sup>, 10<sup>th</sup> and 15<sup>th</sup> minutes after each injection of oil.

Another difference between the systems is in calculation of mole fraction of sulfur dioxide in oil at atmospheric pressure. In previous research, three injections were done for each experiment and mole fractions of sulfur dioxide in oil were calculated. Then, by using these mole fractions and pressure values obtained after equilibrium was reached, the graphs of pressure versus mol fraction were plotted for each experiment. According to these graphs, the mole fractions at atmospheric pressure were obtained by interpolating for 101.3 kPa. However, in present research oil was fed once for each experiment and according to the pressure changes, mol fraction of sulfur dioxide in oil was calculated. These calculated values of mole fractions were

assumed to be mole fractions at atmospheric pressure since the working pressure was about 120 kPa which was close to atmospheric pressure 101.3 kPa.

## **5.2 Determination of Composition and Average Molecular Weight of Mobiltherm 605**

The chemical composition of Mobiltherm 605 is just given as petroleum hydrocarbons. Therefore, to obtain further details about the chemical composition and to determine the average molecular weight of the oil, GC-MS analysis has been performed in Forensic Toxicology Laboratory of the Institute of Forensics Sciences in Istanbul University. According to GC-MS spectral data, it is found out that Mobiltherm 605 is composed of linear long-chain hydrocarbons such as n-eicosane ( $C_{20}H_{42}$ ), n-heneicosane ( $C_{21}H_{44}$ ), n-docosane ( $C_{22}H_{46}$ ), n-tricosane ( $C_{23}H_{48}$ ), n-tetracosane ( $C_{24}H_{50}$ ), n-pentacosane ( $C_{25}H_{52}$ ), n-hexacosane ( $C_{26}H_{54}$ ), n-heptacosane ( $C_{27}H_{56}$ ) and n-octacosane ( $C_{28}H_{58}$ ). Since the peak areas in the GC-MS spectrum give the percentages of existence of these hydrocarbons in the oil, it is possible to calculate the average molecular weight of the oil. Thus, the average molecular weight of Mobiltherm 605 has been evaluated as 350.44 g/mol. GC-MS spectrum is available in Appendix Part, Figure A.1.

## **5.3 Solubility of Sulfur Dioxide in Transcal N and Mobiltherm 605**

The solubility of sulfur dioxide has been determined both in Transcal N and in Mobiltherm 605. The experiments were made in the jacketed reactor at constant temperatures and change in gas pressure by time was observed. Since the boiling points of these heat transfer oils are above 300°C, their vapor pressures at working temperature range are assumed to be negligible. For  $SO_2$ -Transcal N system, the experiments were performed at 20, 30, 40, 50, 60, 70, 80, 100 and 140°C. There is no significant change in pressure by time for the temperatures above 70°C. The graphs of pressure versus time are given in Appendix part, in Figure A.2-Figure A.10.

The experiments with  $SO_2$  and Mobiltherm 605 were made at 20, 30, 40, 50 and 60°C. The changes in gas pressure by time are seen in Figure A.11-Figure A.15 in Appendix part.

According to the results of these experiments, solubilities of sulfur dioxide in heat transfer oils have been expressed in four different ways. These are mol fractions of sulfur dioxide in heat transfer oils, Henry's constants, Ostwald's coefficients and solubility of sulfur dioxide in unit volume of both oils. Beside the calculation of these solubility terms, the relations between temperature and these terms have been stated and also heat of the dissolution has been evaluated.

### 5.3.1 Calculation of mole fractions of sulfur dioxide in heat transfer oils

Known amount of oil by weight is fed into the reactor in the experiments. Dividing mass of oil by its density gives volume of oil that is fed into the reactor. Since the reactor volume is 0.25L, the difference between volumes of reactor and oil gives the volume of Sulfur dioxide that is fed into the reactor.

$$V_{OIL\ FED} = \frac{m_{OIL\ FED}}{\rho_{OIL}} \quad (5.1)$$

$$V_{SO_2} = V_{REACTOR} - V_{OIL\ FED} \quad (5.2)$$

Sulfur dioxide is assumed as ideal gas and all calculations were worked out in light of the ideal gas theory. It is possible to evaluate mole number of SO<sub>2</sub> that is fed to the reactor since the pressure and temperature is known at feeding conditions. According to the ideal gas equation  $n_{SO_2,1}$  (mole number of SO<sub>2</sub> that is fed to the reactor) is calculated as follows:

$$P_{SO_2,1} \cdot V_{SO_2} = n_{SO_2,1} \cdot R \cdot T_1 \quad (5.3)$$

$$n_{SO_2,1} = \frac{P_{SO_2,1} \cdot V_{SO_2}}{R \cdot T_1} \quad (5.4)$$

In equation (5.4)  $P_{SO_2,1}$ ,  $V_{SO_2}$  and  $T_1$  correspond to pressure, volume and temperature of SO<sub>2</sub> that is fed to the reactor, respectively. R is the ideal gas constant with a value of 0.08205746 L.atm/mol.K.

It is possible to evaluate the mole number of SO<sub>2</sub> in the gas phase after absorption is complete. In order to calculate  $n_{SO_2,2}$  (mole number of SO<sub>2</sub> in the gas phase after absorption), ideal gas equation is used once more.

$$P_{SO_2,2} \cdot V_{SO_2} = n_{SO_2,2} \cdot R \cdot T_2 \quad (5.5)$$

$$n_{SO_2 2} = \frac{P_{SO_2 2} \cdot V_{SO_2}}{R \cdot T_2} \quad (5.6)$$

$P_{SO_2 2}$ ,  $V_{SO_2}$  and  $T_2$  denote pressure, volume and temperature of  $SO_2$  after absorption is complete. Since the volume of  $SO_2$  absorbed by the oil is so small compared with the initial volume of  $SO_2$  ( $V_{SO_2}$ ), the volume of  $SO_2$  after absorption is assumed to be same as the initial volume of  $SO_2$ .

The difference between the initial and final mole numbers of  $SO_2$  in the gas phase gives the mole number of  $SO_2$  absorbed by the oil.

$$n_{SO_2 abs.} = n_{SO_2 1} - n_{SO_2 2} \quad (5.7)$$

Mole fractions of sulfur dioxide in oil are calculated as follows:

$$X_{SO_2} = \frac{n_{SO_2 abs.}}{(n_{SO_2 abs.} + n_{OIL})} \quad (5.8)$$

The evaluated mole fractions of Sulfur dioxide in Transcal N and in Mobiltherm 605 are given in Tables 5.1 and 5.2, respectively.

Although pressure is read in milibar and given as such in Tables 5.1 and 5.2, while making calculations all necessary unit conversions, such as from milibar to atm for pressure, from centigrade to Kelvin for temperature, are made.

Since the experiments were performed at pressures about atmospheric pressure, the evaluated mol fraction values can be assumed as mol fractions at standard pressure.

As it is seen in Tables 5.1 and 5.2, mol fractions of sulfur dioxide in heat transfer oils decrease with increasing temperature. When the solubilities of  $SO_2$  in Transcal N and in Mobiltherm 605 are compared, it is seen that the solubility values in Mobiltherm 605 are slightly greater than those in Transcal N. This means that the  $SO_2$  absorption capacity of Mobiltherm 605 is greater than that of Transcal N.

**Table 5.1 : Mole fractions of sulfur dioxide in Transcal N.**

		$V_{SO_2} (L)$	$\Sigma oil (g)$	$n_{oil}$ (mole)	$P_{SO_2 1}$ (mbar)	$T_1 (^{\circ}C)$	$n_{SO_2 1}$ (mole)	$P_{SO_2 2}$ (mbar)	$T_2 (^{\circ}C)$	$n_{SO_2 2}$ (mole)	$n_{SO_2 abs.}$ (mole)	$X_{SO_2}$	$X_{SO_2 mean}$
<b>20°C</b>	<b>1</b>	0.2110	34.1608	0.1011	1288	20.6	0.0111	856	21.2	0.0074	0.0037	0.0357	0.0353
	<b>2</b>	0.2103	34.7479	0.1029	1314	20.8	0.0113	892	21.7	0.0077	0.0037	0.0343	
	<b>3</b>	0.2101	34.9427	0.1035	1360	18.7	0.0118	918	19.4	0.0079	0.0038	0.0358	
<b>30°C</b>	<b>1</b>	0.2090	35.9178	0.1063	1311	21.3	0.0112	967	30.9	0.0080	0.0032	0.0292	0.0287
	<b>2</b>	0.2099	35.0935	0.1039	1198	23.1	0.0102	862	31.3	0.0071	0.0031	0.0286	
	<b>3</b>	0.2088	36.0472	0.1067	1258	17.7	0.0109	938	31.3	0.0077	0.0031	0.0284	
<b>40°C</b>	<b>1</b>	0.2088	36.0835	0.1068	1257	21.2	0.0107	987	39.5	0.0079	0.0028	0.0255	0.0255
	<b>2</b>	0.2107	34.3879	0.1018	1281	21.7	0.0110	1044	41	0.0084	0.0026	0.0248	
	<b>3</b>	0.2109	34.2004	0.1013	1231	20.9	0.0106	974	39.6	0.0079	0.0027	0.0262	
<b>50°C</b>	<b>1</b>	0.2098	35.1984	0.1042	1112	20.9	0.0095	922	49.4	0.0072	0.0023	0.0219	0.0220
	<b>2</b>	0.2101	34.8772	0.1033	1248	33.8	0.0103	1023	50.6	0.0080	0.0023	0.0217	
	<b>3</b>	0.2102	34.8483	0.1032	1232	18.4	0.0107	1066	50.4	0.0083	0.0024	0.0223	
<b>60°C</b>	<b>1</b>	0.2094	35.49	0.1051	1210	28.6	0.0101	1042	57.5	0.0079	0.0022	0.0202	0.0208
	<b>2</b>	0.2096	35.388	0.1048	1250	23.2	0.0106	1108	60.1	0.0084	0.0023	0.0210	
	<b>3</b>	0.2113	33.8715	0.1003	1168	22	0.0101	1035	60.1	0.0079	0.0022	0.0211	
<b>70°C</b>	<b>1</b>	0.2092	35.6634	0.1056	1130	26.9	0.0095	1051	69.9	0.0077	0.0018	0.0165	0.0174
	<b>2</b>	0.2112	33.9786	0.1006	1232	33.9	0.0102	1123	69.9	0.0083	0.0019	0.0183	
	<b>3</b>	0.2090	35.8472	0.1061	1166	24.2	0.0099	1089	70.4	0.0080	0.0019	0.0175	

**Table 5.2 : Mole fractions of sulfur dioxide in Mobiltherm 605.**

		$V_{SO_2} (L)$	$\Sigma oil (g)$	$n_{oil}$ (mole)	$P_{SO_2 1}$ (mbar)	$T_1 (^\circ C)$	$n_{SO_2 1}$ (mole)	$P_{SO_2 2}$ (mbar)	$T_2 (^\circ C)$	$n_{SO_2 2}$ (mole)	$n_{SO_2 abs.}$ (mole)	$X_{SO_2}$	$X_{SO_2 mean}$
<b>20°C</b>	<b>1</b>	0.2106	34.3627	0.0981	1288	19.9	0.0111	884	20.8	0.0076	0.0035	0.0346	0.0364
	<b>2</b>	0.2105	34.4308	0.0983	1296	19.7	0.0112	877	21.1	0.0075	0.0037	0.0359	
	<b>3</b>	0.2103	34.6299	0.0988	1367	19.2	0.0118	911	20.5	0.0078	0.0040	0.0387	
<b>30°C</b>	<b>1</b>	0.2113	33.7207	0.0962	1281	20.5	0.0111	950	30	0.0080	0.0031	0.0314	0.0316
	<b>2</b>	0.2106	34.3834	0.0981	1263	21.4	0.0109	931	30.8	0.0078	0.0031	0.0306	
	<b>3</b>	0.2108	34.1933	0.0976	1299	16.3	0.0114	964	29.6	0.0081	0.0033	0.0328	
<b>40°C</b>	<b>1</b>	0.2110	33.9915	0.0970	1276	16.1	0.0112	1043	41.3	0.0084	0.0028	0.0278	0.0282
	<b>2</b>	0.2106	34.3415	0.0980	1332	18.9	0.0116	1065	40.8	0.0086	0.0030	0.0293	
	<b>3</b>	0.2098	35.0421	0.1000	1303	26.2	0.0110	1015	40.6	0.0082	0.0028	0.0274	
<b>50°C</b>	<b>1</b>	0.2105	34.4728	0.0984	1281	16.6	0.0112	1113	51.7	0.0087	0.0025	0.0250	0.0234
	<b>2</b>	0.2106	34.3354	0.0980	1146	21.3	0.0099	962	50.8	0.0075	0.0023	0.0233	
	<b>3</b>	0.2095	35.3580	0.1009	1232	37.6	0.0100	992	50.9	0.0077	0.0023	0.0221	
<b>60°C</b>	<b>1</b>	0.2101	34.8086	0.0993	1319	29.2	0.0110	1166	60.8	0.0088	0.0022	0.0217	0.0213
	<b>2</b>	0.2108	34.2196	0.0976	1149	14.7	0.0101	1048	60.2	0.0080	0.0021	0.0215	
	<b>3</b>	0.2106	34.3736	0.0981	1158	16.2	0.0101	1064	61	0.0081	0.0021	0.0207	

### 5.3.2 Henry's constant

The equation below is used in order to calculate Henry's constant at standard pressure which is equal to 101.3 kPa.

$$H(kPa) = \frac{P}{X_{SO_2}} \quad (5.9)$$

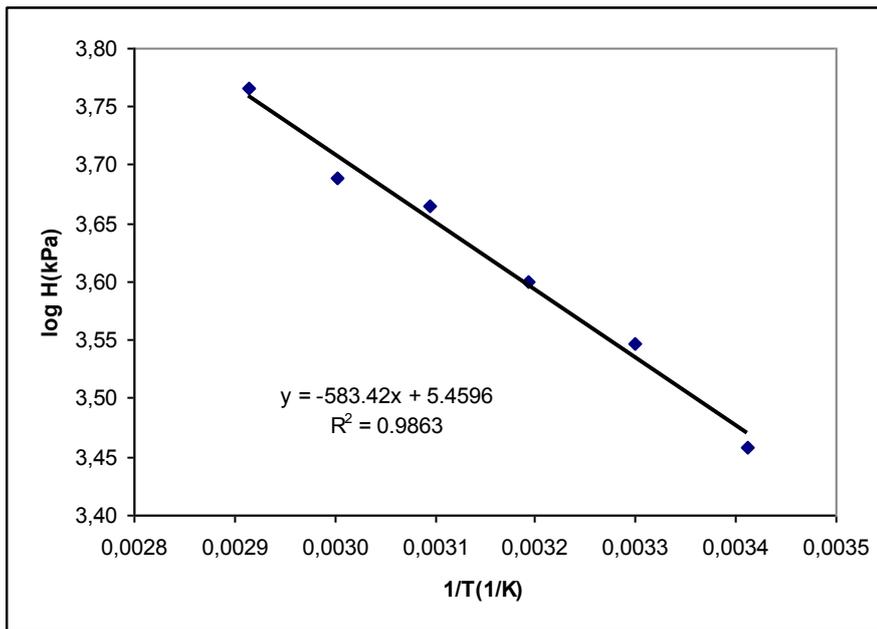
In Table 5.3 it is possible to see Henry's constants at each temperature for SO<sub>2</sub>-Transcal N and SO<sub>2</sub>-Mobiltherm 605 systems. Henry's constants in Table 5.3 increase with increasing temperature as being in accordance with the gas solubility theory. When Henry's constant values for both systems are compared with each other, it is seen that mean values of Henry's constants for SO<sub>2</sub>-Transcal N system are greater than those for SO<sub>2</sub>-Mobiltherm 605 system. This is an expected case since solubility of sulfur dioxide in Mobiltherm 605 is greater than that in Transcal N.

**Table 5.3 :** Henry's constants for SO<sub>2</sub>-Transcal N and SO<sub>2</sub>-Mobiltherm 605.

		$P_{atm}$ (kPa)	Transcal N			Mobiltherm 605		
			$X_{SO_2}$	$H(kPa)$	$H_{mean}$ (kPa)	$X_{SO_2}$	$H(kPa)$	$H_{mean}$ (kPa)
20°C	1	101.3	0.0357	2836.2	2872.1	0.0346	2927.1	2788.4
	2	101.3	0.0343	2953.3		0.0359	2821.6	
	3	101.3	0.0358	2826.8		0.0387	2616.6	
30°C	1	101.3	0.0292	3471.5	3524.2	0.0314	3222.8	3206.7
	2	101.3	0.0286	3540.0		0.0306	3305.2	
	3	101.3	0.0284	3561.3		0.0328	3091.9	
40°C	1	101.3	0.0255	3972.2	3977.3	0.0278	3638.5	3595.3
	2	101.3	0.0248	4086.4		0.0293	3454.7	
	3	101.3	0.0262	3873.3		0.0274	3692.7	
50°C	1	101.3	0.0219	4633.8	4615.5	0.0250	4058.3	4333.3
	2	101.3	0.0217	4669.9		0.0233	4348.9	
	3	101.3	0.0223	4542.7		0.0221	4592.7	
60°C	1	101.3	0.0202	5023.2	4878.6	0.0217	4673.6	4758.6
	2	101.3	0.0210	4816.4		0.0215	4704.1	
	3	101.3	0.0211	4796.1		0.0207	4898.1	
70°C	1	101.3	0.0165	6153.1	5826.1			
	2	101.3	0.0183	5532.7				
	3	101.3	0.0175	5792.4				

For SO<sub>2</sub>-Transcal N system, the effect of temperature on Henry's constant can be seen in Figure 5.1 obviously. Equation (5.10) gives any value of Henry's constant for desired temperature between 20°C and 70°C.

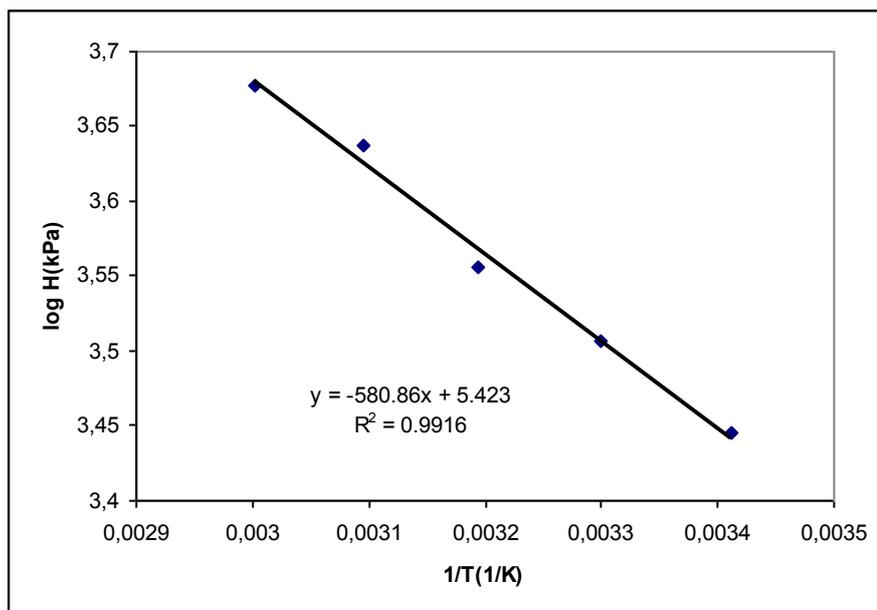
$$\log H(kPa) = -583.42(1/T)(1/K) + 5.4596 \quad (5.10)$$



**Figure 5.1 :** Temperature dependence of Henry's constant for SO<sub>2</sub>-Transcal N.

Figure 5.2 shows the relation between temperature and Henry's constant for SO<sub>2</sub>-Mobiltherm 605 system. It is possible to evaluate Henry's constant for temperatures between 20°C and 60°C by using Equation (5.11).

$$\log H(kPa) = -580.86(1/T)(1/K) + 5.4523 \quad (5.11)$$



**Figure 5.2 :** Temperature dependence of Henry's constant for SO<sub>2</sub>-Mobiltherm 605.

### 5.3.3 Ostwald's coefficient

The Ostwald's coefficient is the ratio of volume of gas absorbed to the volume of absorbing oil. While evaluating these values solvent expansion due to dissolving gas is assumed to be negligible.

$$L = \frac{V_{SO_2 abs.}}{V_{OIL}} \quad (5.12)$$

As it is mentioned before it is possible to evaluate the volume of absorbing oil by using Equation (5.1). The volume of sulfur dioxide absorbed by the oil can be calculated with the help of ideal gas equation since the temperature and pressure during the absorption are known. The mole numbers of sulfur dioxide absorbed by the oil have been already calculated for each temperature. The evaluated Ostwald's coefficients are seen in Table 5.4.

$$V_{SO_2 abs.} = \frac{n_{SO_2 abs.} \cdot R \cdot T_2}{P_{SO_2}} \quad (5.13)$$

**Table 5.4 :** Ostwald's coefficients at different temperatures.

		<b>Transcal N</b>		<b>Mobiltherm 605</b>	
		$L$ $(\frac{mL SO_2}{mL oil})$	$L_{mean}$ $(\frac{mL SO_2}{mL oil})$	$L$ $(\frac{mL SO_2}{mL oil})$	$L_{mean}$ $(\frac{mL SO_2}{mL oil})$
<b>20°C</b>	<b>1</b>	2.7436	2.6080	2.4662	2.5790
	<b>2</b>	2.5291		2.5849	
	<b>3</b>	2.5514		2.6858	
<b>30°C</b>	<b>1</b>	2.0358	2.1080	2.1425	2.1596
	<b>2</b>	2.2412		2.1356	
	<b>3</b>	2.0470		2.2009	
<b>40°C</b>	<b>1</b>	1.7857	1.7636	1.7863	1.8108
	<b>2</b>	1.6477		1.8423	
	<b>3</b>	1.8575		1.8039	
<b>50°C</b>	<b>1</b>	1.6842	1.5623	1.5459	1.5772
	<b>2</b>	1.5115		1.6615	
	<b>3</b>	1.4912		1.5243	
<b>60°C</b>	<b>1</b>	1.4068	1.4318	1.3128	1.3778
	<b>2</b>	1.3919		1.4483	
	<b>3</b>	1.4965		1.3721	
<b>70°C</b>	<b>1</b>	1.1769	1.2046		
	<b>2</b>	1.2273			
	<b>3</b>	1.2096			

When the results are compared for two different heat transfer oils, it can be said that Ostwald's coefficients decrease with increasing temperature and the results are so close to each other for both oils.

Correlations between Ostwald's coefficient and temperature for both SO<sub>2</sub>-Transcal N and SO<sub>2</sub>-Mobiltherm 605 systems are obtained by plotting Ostwald's coefficient versus temperature graphs in Figures 5.3 and 5.4, respectively.

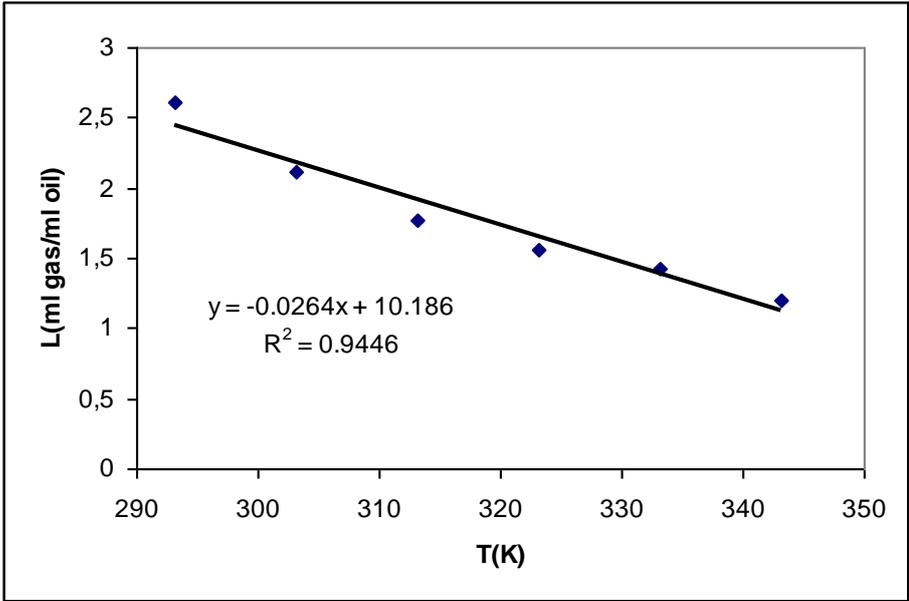


Figure 5.3 : Temperature dependence of Ostwald's coefficient for SO<sub>2</sub>-Transcal N.

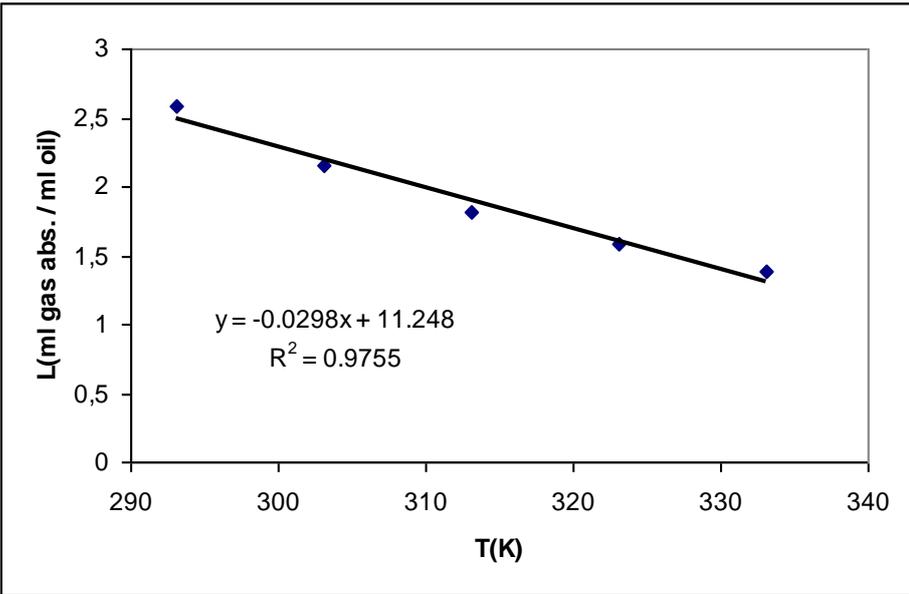


Figure 5.4 : Temperature dependence of Ostwald's coefficient for SO<sub>2</sub>-Mobiltherm 605.

Ostwald's coefficients can be calculated in the working temperature range by using the equations (5.14) and (5.15). These equations belong to SO<sub>2</sub>-Transcal N and SO<sub>2</sub>-Mobiltherm 605 systems, respectively.

$$L(\text{ml SO}_2 \text{ abs.} / \text{ml oil}) = -0.0264T(K) + 10.186 \quad (5.14)$$

$$L(\text{ml SO}_2 \text{ abs.} / \text{ml oil}) = -0.0298T(K) + 11.248 \quad (5.15)$$

### 5.3.4 Solubility of SO<sub>2</sub> in unit volumes of Transcal N and Mobiltherm 605

Solubility values of sulfur dioxide in unit volumes of heat transfer oils have been calculated from Ostwald's coefficients by making necessary unit conversions.

$$L(L \text{ SO}_2 \text{ abs.} / L \text{ oil}) = \frac{V_{\text{SO}_2 \text{ abs.}}}{V_{\text{OIL}}} \quad (5.16)$$

Inserting equation (5.13) into equation (5.16) yields:

$$L(L \text{ SO}_2 \text{ abs.} / L \text{ oil}) = \frac{n_{\text{SO}_2 \text{ abs.}} \cdot R \cdot T_2}{V_{\text{OIL}} \cdot P_{\text{SO}_2 2}} \quad (5.17)$$

Mole number of sulfur dioxide absorbed by the oil can be written as below since its molecular weight is 64g/mole.

$$n_{\text{SO}_2 \text{ abs.}} = \frac{m_{\text{SO}_2 \text{ abs.}}}{MW_{\text{SO}_2}} \quad (5.18)$$

Combining equations (5.17) and (5.18) gives the mass of sulfur dioxide absorbed by one liter oil. Here, 8.314472 L.kPa/mol.K, which is one of the gas constant values, is used for unit conformity.

$$L(L \text{ SO}_2 \text{ abs.} / L \text{ oil}) = \frac{m_{\text{SO}_2 \text{ abs.}} \cdot R \cdot T_2}{MW_{\text{SO}_2} \cdot V_{\text{OIL}} \cdot P_{\text{SO}_2 2}} \quad (5.19)$$

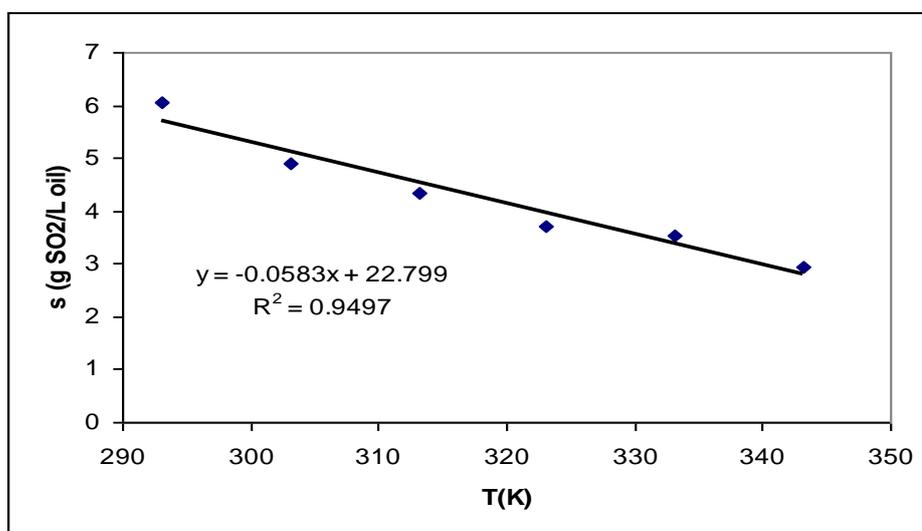
$$\frac{m_{\text{SO}_2 \text{ abs.}}}{V_{\text{OIL}}} = \frac{L \cdot MW_{\text{SO}_2} \cdot P_{\text{SO}_2 2}}{R \cdot T_2} \quad (5.20)$$

The evaluated data are given in Table 5.5. Figures 5.5 and 5.6 shows the relation between temperature and solubility of sulfur dioxide in unit volumes of Transcal N and Mobiltherm 605, respectively.

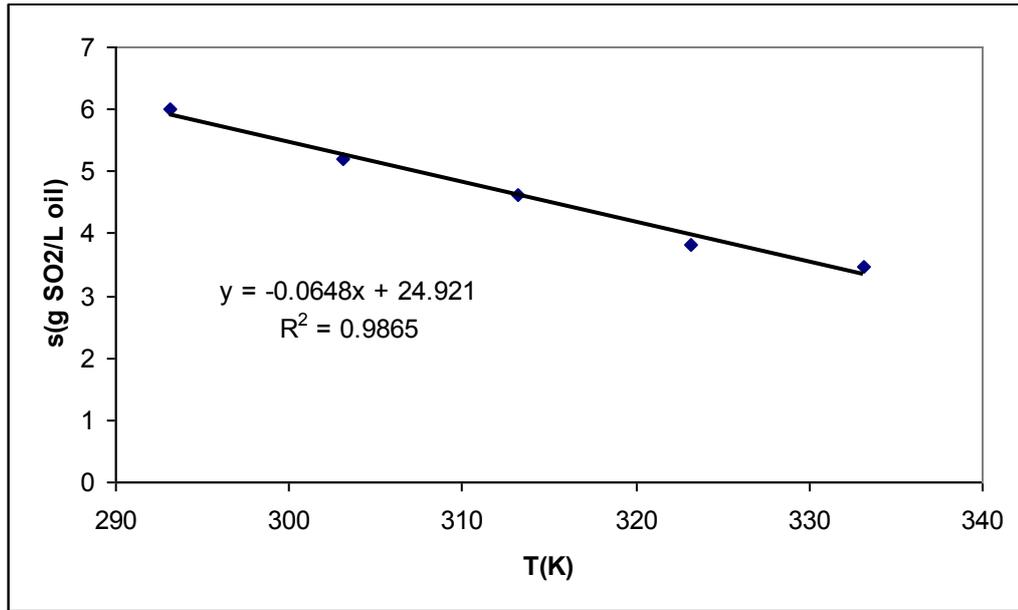
**Table 5.5 :** Solubility of sulfur dioxide in unit volumes of heat transfer oils.

		Transcal N		Mobiltherm 605	
		$s$ $(\frac{g SO_2 abs.}{Loil})$	$s_{mean}$ $(\frac{g SO_2 abs.}{Loil})$	$s$ $(\frac{g SO_2 abs.}{Loil})$	$s_{mean}$ $(\frac{g SO_2 abs.}{Loil})$
20°C	1	6.1416	6.0645	5.7090	6.0176
	2	5.8894		5.9302	
	3	6.1626		6.4137	
30°C	1	4.9839	4.9076	5.1680	5.1991
	2	4.8845		5.0351	
	3	4.8544		5.3943	
40°C	1	4.3391	4.3356	4.5607	4.6211
	2	4.2148		4.8107	
	3	4.4529		4.4919	
50°C	1	3.7057	3.7213	4.0769	3.8222
	2	3.6765		3.7980	
	3	3.7818		3.5918	
60°C	1	3.4126	3.5175	3.5282	3.4654
	2	3.5623		3.5049	
	3	3.5777		3.3631	
70°C	1	2.7754	2.9397		
	2	3.0924			
	3	2.9513			

Solubilities of sulfur dioxide in unit volumes of Transcal N and Mobiltherm 605 decrease with increasing temperature. When the results are compared, it is seen that the solubility values are very similar to each other for both SO<sub>2</sub>-Transcal N and SO<sub>2</sub>-Mobiltherm 605 systems.



**Figure 5.5 :** Temperature dependence of solubility of SO<sub>2</sub> in Transcal N.



**Figure 5.6 :** Temperature dependence of solubility of SO<sub>2</sub> in Mobiltherm 605.

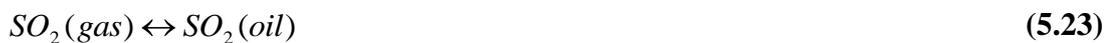
Correlations between temperature and solubility of SO<sub>2</sub> in Transcal N and in Mobiltherm 605 are stated by equations below, respectively.

$$s(\text{g } SO_2 \text{ abs./ } L \text{ oil}) = -0.0583T(K) + 22.799 \quad (5.21)$$

$$s(\text{g } SO_2 \text{ abs./ } L \text{ oil}) = -0.0648T(K) + 24.921 \quad (5.22)$$

#### 5.4 Equilibrium Between SO<sub>2</sub> and Heat Transfer Oils and Heat of Dissolution

Since the absorption of sulfur dioxide by the oils is a physical absorption, a physical equilibrium is established between the phases. This equilibrium condition can be represented as follows:



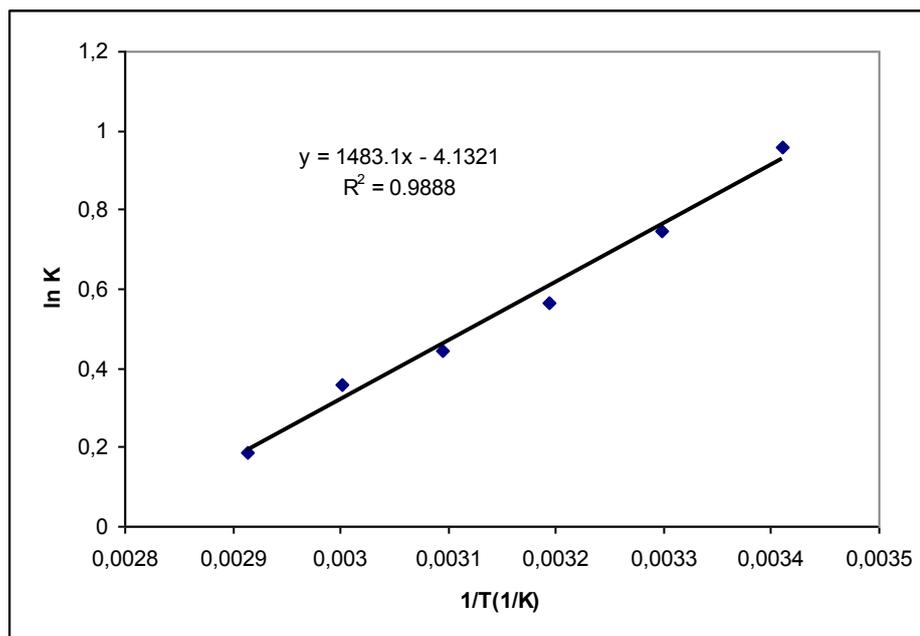
At equilibrium, no mass transfer occurs between gas and liquid phases. Equilibrium constant, K, is defined as below:

$$K = \frac{[SO_2]_{oil}}{[SO_2]_{gas}} = \frac{n_{SO_2, oil} / V_{oil}}{n_{SO_2, gas} / V_{gas}} \quad (5.24)$$

In equation (5.24),  $n_{SO_2, oil}$  corresponds to mole number of SO<sub>2</sub> absorbed by the oil and these values have been already calculated at previous parts.  $V_{oil}$  and  $V_{gas}$  values are the volumes of oil and sulfur dioxide fed into the reactor, respectively. Since the

volume of SO<sub>2</sub> absorbed by the oil is so small, the expansion of oil due to dissolving gas is assumed to be negligible.

To find out the relation between equilibrium constant and temperature, the graph of (ln K) versus (1/T) is plotted according to the Van't Hoff equation. Figures 5.7 and 5.8 show these relations for SO<sub>2</sub>-Transcal N and SO<sub>2</sub>-Mobiltherm 605 systems, respectively.



**Figure 5.7 :** Temperature dependence of equilibrium constant for SO<sub>2</sub>-Transcal N.

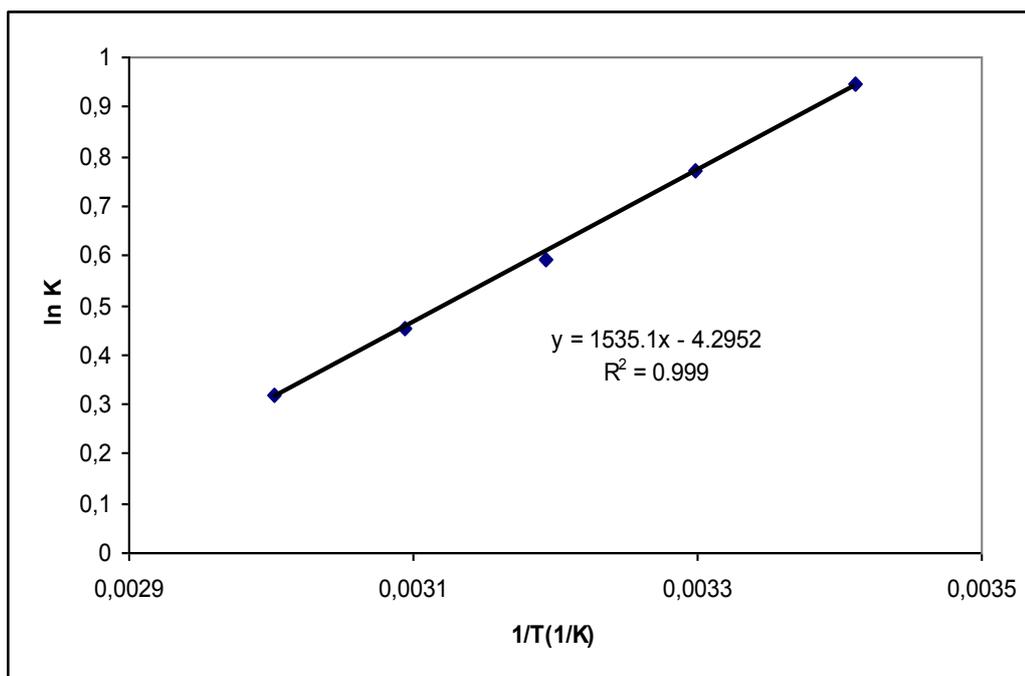
The slope of the graph in Figure 5.7 is equal to  $-\Delta H^0 / R$ . Replacing the value of R, 1.987 cal/mol.K, in the expression gives the heat of dissolution of Sulfur dioxide in Transcal N. The equation of the line above is as follows:

$$\ln K = 1483.1(1/T)(1/K) - 4.1321 \quad (5.25)$$

$$\text{slope} = 1483.1 = -\frac{\Delta H^0}{R} \quad (5.26)$$

$$\Delta H^0 = -2946.9 \text{ cal/mol} \quad (5.27)$$

Negative sign shows the dissolution of sulfur dioxide in Transcal N is an exothermic process.



**Figure 5.8 :** Temperature dependence of equilibrium constant for SO<sub>2</sub>-Mobiltherm 605.

The equation that relates temperature and equilibrium constant is written below. By following the same procedure as in the SO<sub>2</sub>-Transcal N system, the heat of dissolution of sulfur dioxide in Mobiltherm 605 is evaluated as follows:

$$\ln K = 1535.1(1/T)(1/K) - 4.2952 \quad (5.28)$$

$$slope = 1535.1 = -\frac{\Delta H^0}{R} \quad (5.29)$$

$$\Delta H^0 = -3050.24 \text{ cal/mol} \quad (5.30)$$

### 5.5 Comparison of Sulfur Dioxide Solubility in Different Solvents

In this research solubilities of sulfur dioxide in two different oils have been investigated. According to the results of this research, it is obvious that the solubilities of sulfur dioxide in Transcal N and in Mobiltherm 605 are so close to each other.

In literature, there are many researches in which solubility of sulfur dioxide is studied in different solvents. One of these solvents is n-hexadecane. In Table 5.6, the comparison between Henry's constants in n-hexadecane, Transcal N and Mobiltherm 605 at different temperatures are given.

**Table 5.6** : Henry's constants for different solvents [32].

<b>n-hexadecane</b>	<b>T(°C)</b>	<b>27</b>	<b>52</b>	<b>77</b>	<b>102</b>	<b>127</b>	<b>152</b>	<b>177</b>	<b>202</b>
	<b>H(atm)</b>	15.1	22.3	30.8	40.2	50.1	60.1	69.8	77.1
<b>Transcal N*</b>	<b>T(°C)</b>	<b>20</b>	<b>30</b>	<b>40</b>	<b>50</b>	<b>60</b>	<b>70</b>		
	<b>H(atm)</b>	28.4	34.8	39.3	45.6	48.2	57.5		
<b>Mobiltherm 605*</b>	<b>T(°C)</b>	<b>20</b>	<b>30</b>	<b>40</b>	<b>50</b>	<b>60</b>			
	<b>H(atm)</b>	27.5	31.7	35.5	42.8	47.0			

\*These results have been calculated according to data obtained in this research.

As it is mentioned before, solubility of sulfur dioxide in Transcal N has also been studied in the temperature range of 20°C to 40°C by A. Alper Aydin [16]. The comparison of the mole fractions at 20°C, 30°C and 40°C for the previous and the present study are given in Table 5.7.

**Table 5.7** : Mole fractions of SO<sub>2</sub> in previous and present study at 101.3 kPa [16].

	<b>Previous Study*</b>	<b>Present Study**</b>
<b>T(°C)</b>	<b>X<sub>SO<sub>2</sub></sub> in Transcal N</b>	<b>X<sub>SO<sub>2</sub></sub> in Transcal N</b>
20	0.1298	0.0353
30	0.1051	0.0287
40	0.0862	0.0255

\*These results have been calculated by A. Alper Aydin in previous research [16]

\*\*These results have been calculated according to data obtained in this research.

As it is seen in Table 5.7, mole fractions calculated in previous study are greater than those calculated in present study. There are some reasons of these differences between mole fractions of two studies. Firstly, the difference between the absorption system can be said as one of these reasons. In previous study, SO<sub>2</sub> was sent to the absorption flask firstly and then oil about 3-5 mL was injected to the flask by three injections for each experiment. Since the magnetic stirrer at the bottom of the flask provided an effective mixing of oil and SO<sub>2</sub>, small amount of oil was enough to observe a significant pressure change and absorption of SO<sub>2</sub>. Since the ratio of gas volume to oil volume was so high, the absorption observed in these experiments were defined as gas-phase controlled absorption. On the other hand, in new absorption system used in present study, a mechanical stirrer, located at a higher point from the bottom of the absorption vessel, is present instead of a magnetic stirrer at the bottom. Therefore, in order to provide an effective mixing of oil, it was necessary to feed oil at about 40 mL which was considerably higher than the amount used in previous study. This high amount of oil fed to the vessel causes a relatively low ratio of gas volume to oil volume which is the main reason of these low mole

fractions in present study. The low ratio of gas volume to oil volume and the high amount of oil fed to the vessel mean that the sulfur dioxide absorption in present study occurred on the base of liquid-phase controlled absorption.

Another reason of the differences between mole fractions of two studies is related with the calculation of mole fractions at 101.3 kPa. In previous study, three injections were done for each experiments and the pressures at equilibrium were recorded. Then mole fractions at equilibrium were calculated and by using these values, graphs of pressure versus mole fraction were plotted. With the help of these graphs, the mole fraction at 101.3 kPa was calculated by interpolating for 101.3 kPa. On the other hand, in present study, for each experiment oil was fed once instead of injecting by three times and the equilibrium mole fractions were calculated according to the pressure change. Since the working pressure was about 120 kPa which was close to atmospheric pressure 101.3 kPa, the calculated mole fractions were assumed to be mole fractions at atmospheric pressure.



## 6. CONCLUSION

This study involves the determination of the convenient experimental method for newly installed absorption system and measurements of solubility of sulfur dioxide in two different heat transfer oils, Transcal N and Mobiltherm 605, at atmospheric pressures. For SO<sub>2</sub>-Transcal N system, experiments were performed in a temperature range of 20°C to 140°C and no significant pressure change has been observed at temperatures above 70°C. In the temperature range of 20°C to 70°C, the calculated mole fractions of sulfur dioxide in Transcal N decrease from 0.0353 to 0.0174 with increasing temperature. The experiments for SO<sub>2</sub>-Mobiltherm 605 system, were carried out in the temperature range of 20°C to 60°C with 10°C increments. As the temperature is increased the mole fractions of sulfur dioxide in Mobiltherm 605 fall from 0.0364 to 0.0213 in the working temperature range. When the sulfur dioxide absorption capacities of Transcal N and Mobiltherm 605 are compared with each other, it can be said that their absorption capacities are so comparable.

The solubility of SO<sub>2</sub> in Transcal N in the temperature range of 20°C to 40°C were also investigated in previous study by A. Alper Aydin [16]. However, for previous and present researches the calculated mole fractions of sulfur dioxide in Transcal N are not close to each other. This is mainly resulted from the differences between the absorption systems used in previous and present studies. In previous study, SO<sub>2</sub> was sent to the absorption flask and then 3-5 mL oil was fed to the flask by three injections. Since the volume ratio of gas to oil is about 90, the absorption observed in these experiments were defined as gas-phase controlled absorption. However in new absorption system used in present work, 40 mL oil has to be fed to the vessel in order to provide a good contact between the mechanical stirrer and the oil. This high amount of oil reduces the volume ratio of gas to oil too much, which leads to liquid-phase controlled absorption. This study presents mole fractions at atmospheric pressure, so the ratio of gas to liquid is relatively low since 40 mL oil was used. However, if the working pressure range is changed up to 300 kPa, the absorption of

sulfur dioxide by the oil will be possibly greater. This is because more SO<sub>2</sub> molecules will be forced to diffuse into the oil with increasing pressure.

The newly installed absorption system has many advantages compared with the system in previous study. It is equipped with many devices which provide to control and to monitor the system parameters. The most important advantage of this system is being able to record the pressure for each second by a computer software. This makes possible to obtain more data and watch pressure change of the system instantaneously. Moreover, the system is suitable to work at pressures up to 300 kPa. Thus, it is possible to obtain solubility data of gases in liquids at higher pressures. Furthermore, the heating circulator with an oil bath provides to investigate the solubility of a gas in a wide temperature range. By using this system it is possible to obtain solubility data for gases such as SO<sub>2</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>S in a wide temperature and pressure range.

In this research, during the experiments the speed of the stirrer was fixed at 2000 min<sup>-1</sup>. However, in the studies that followed, the effect of the stirrer speed on the gas absorption may be investigated.

Although the new absorption system has many advantages, there is a limitation of this system about the solvent used in solubility experiments. At the beginning of the experiment, liquid is fed to the vessel and then the vessel is evacuated. If the boiling point of the liquid is relatively low, it starts to vaporize as the system is evacuated. The data obtained from this solubility measurement do not reflect the actual solubility of the gas since a fraction of the solvent exists in the gas form. Therefore, for this new absorption system it is necessary to use high-boiling solvents such as heat transfer oils in order to prevent the vaporization of the solvent under vacuum.

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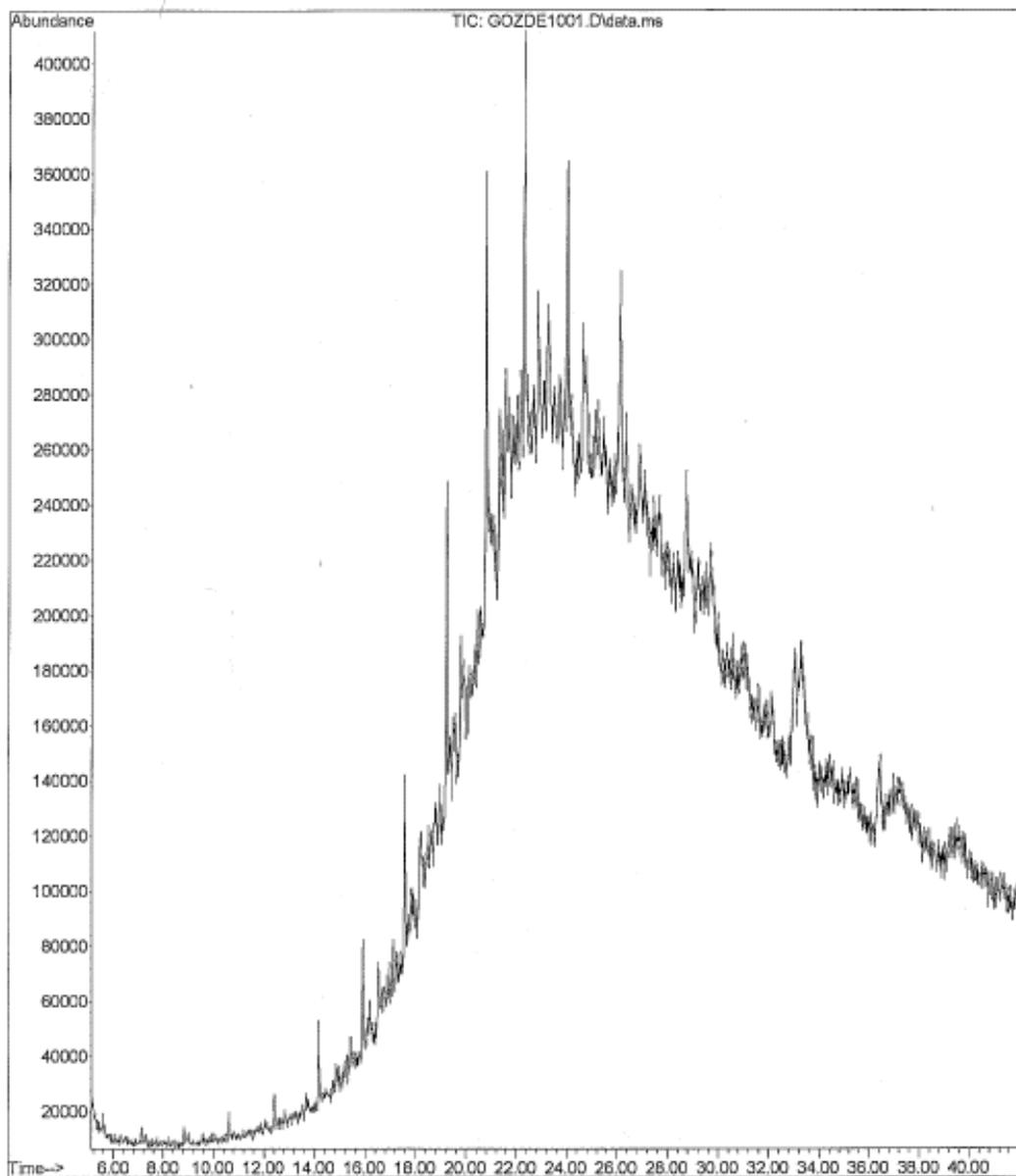


## **APPENDICES**

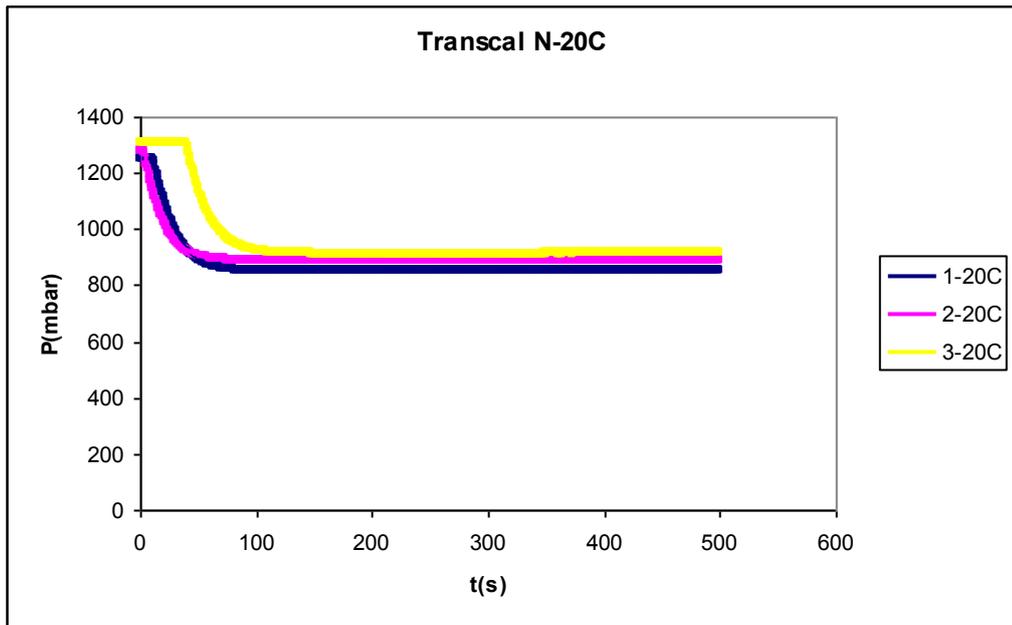
### **APPENDIX A.1 : GC-MS Spectrum of Mobiltherm 605 and Pressure vs. Time Graphs for SO<sub>2</sub>-Transcal N and SO<sub>2</sub>-Mobiltherm 605 Systems**

## APPENDIX A.1

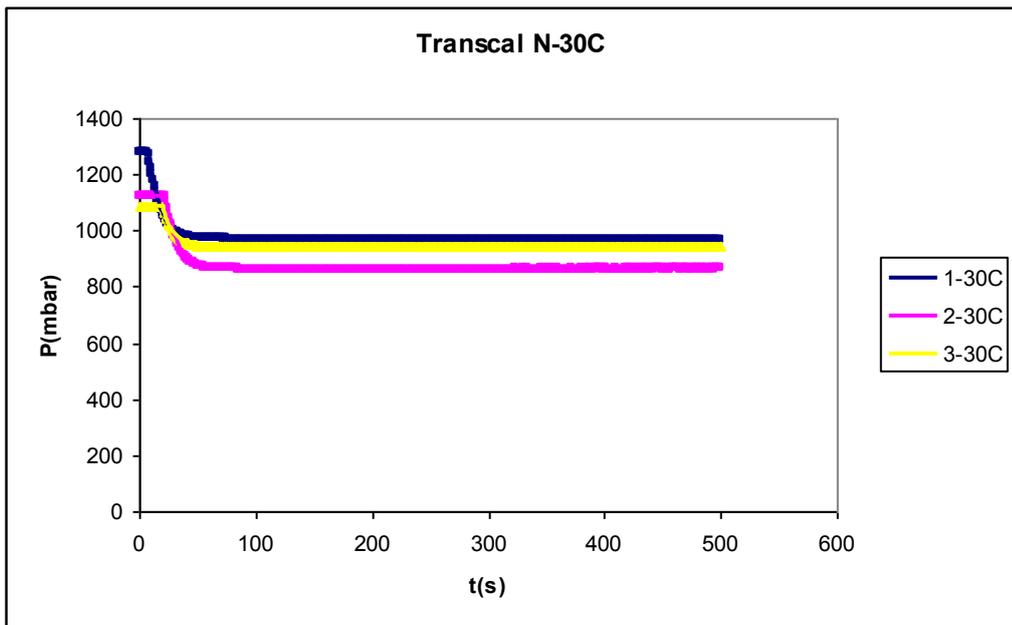
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Vial Number: 1



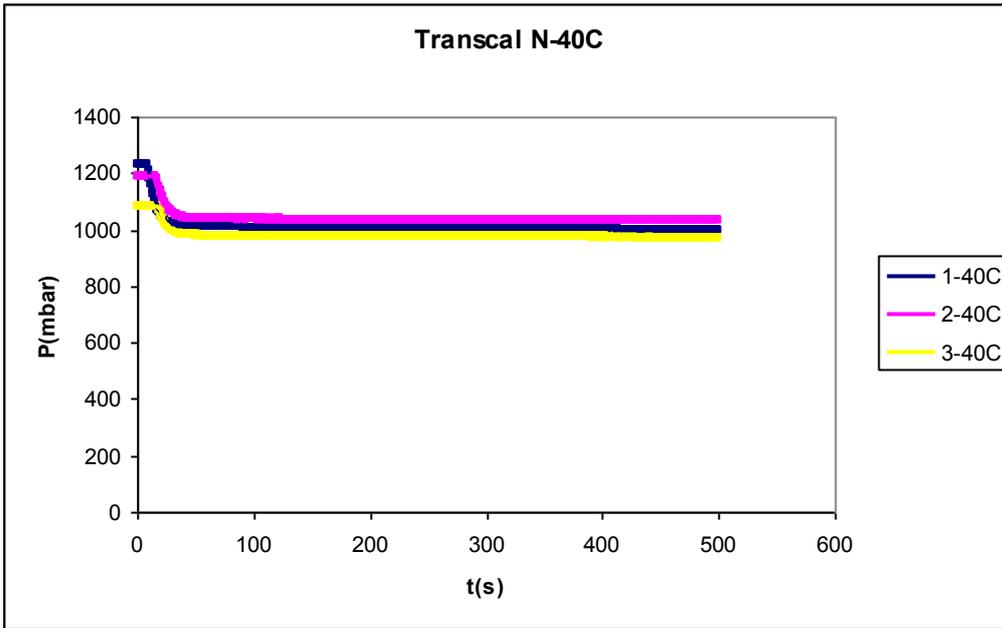
**Figure A.1** : GC-MS spectrum of Mobiltherm 605.



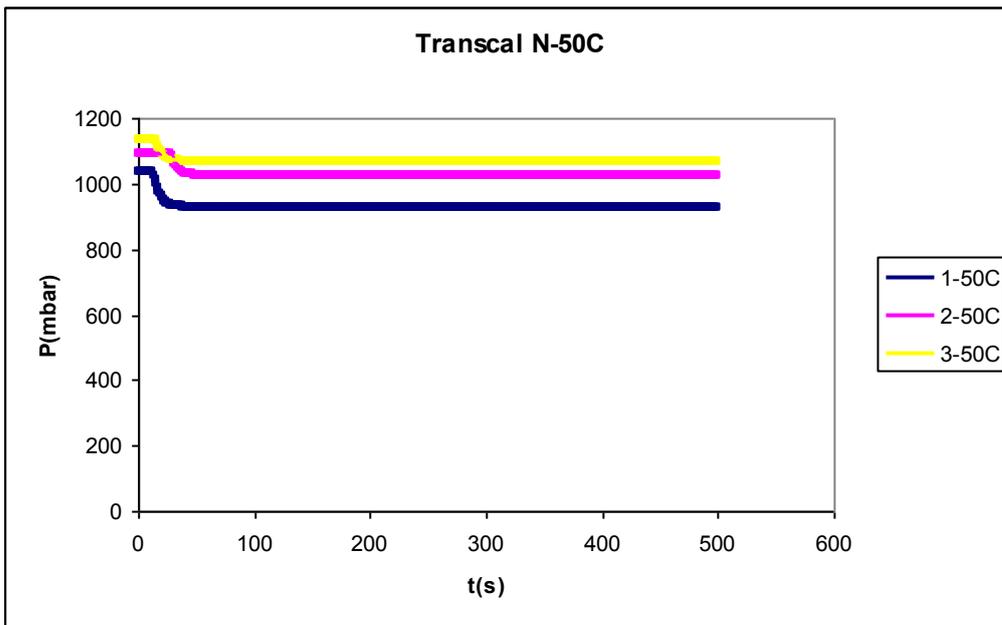
**Figure A.2 :** Pressure change by time at 20°C for SO<sub>2</sub>-Transcal N system.



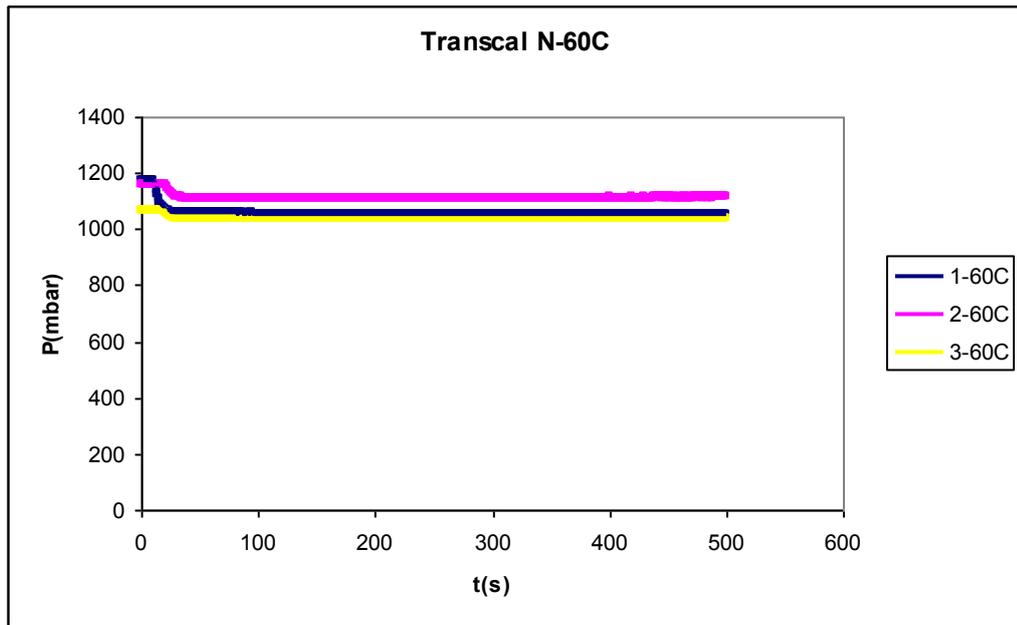
**Figure A.3 :** Pressure change by time at 30°C for SO<sub>2</sub>-Transcal N system.



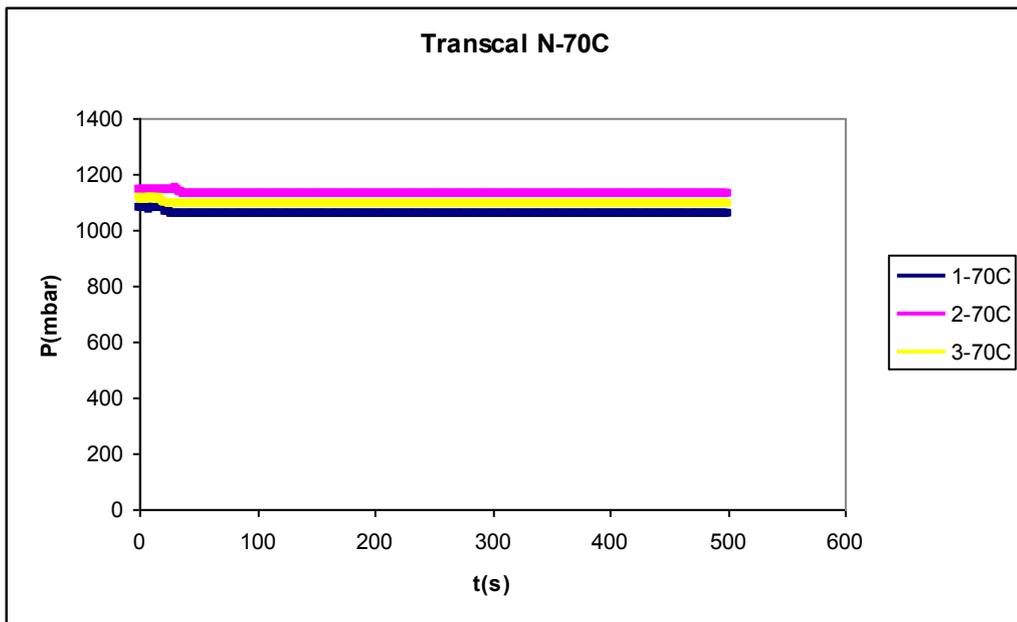
**Figure A.4** : Pressure change by time at 40°C for SO<sub>2</sub>-Transcal N system.



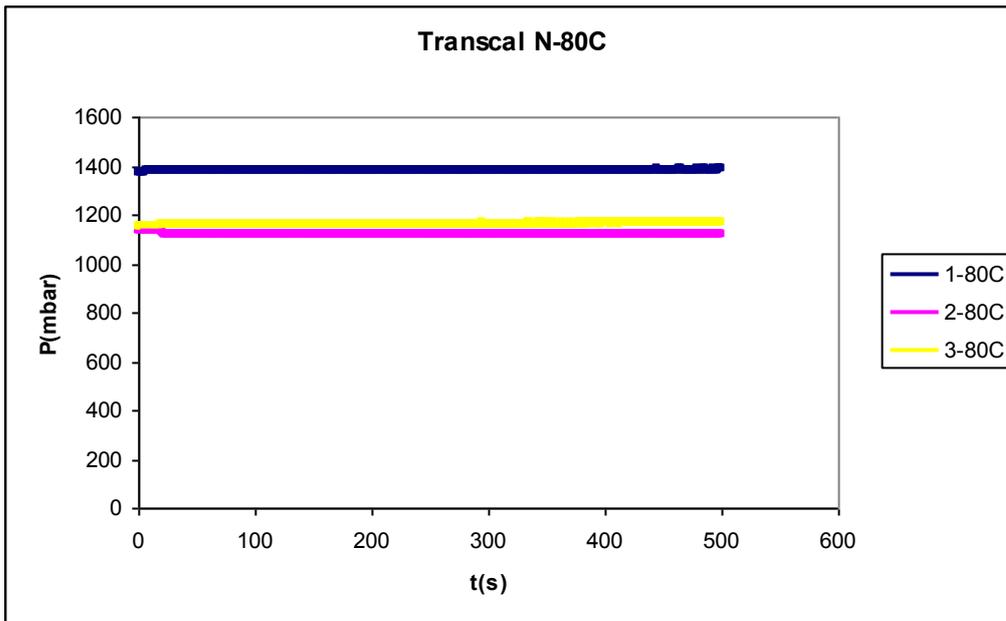
**Figure A.5** : Pressure change by time at 50°C for SO<sub>2</sub>-Transcal N system.



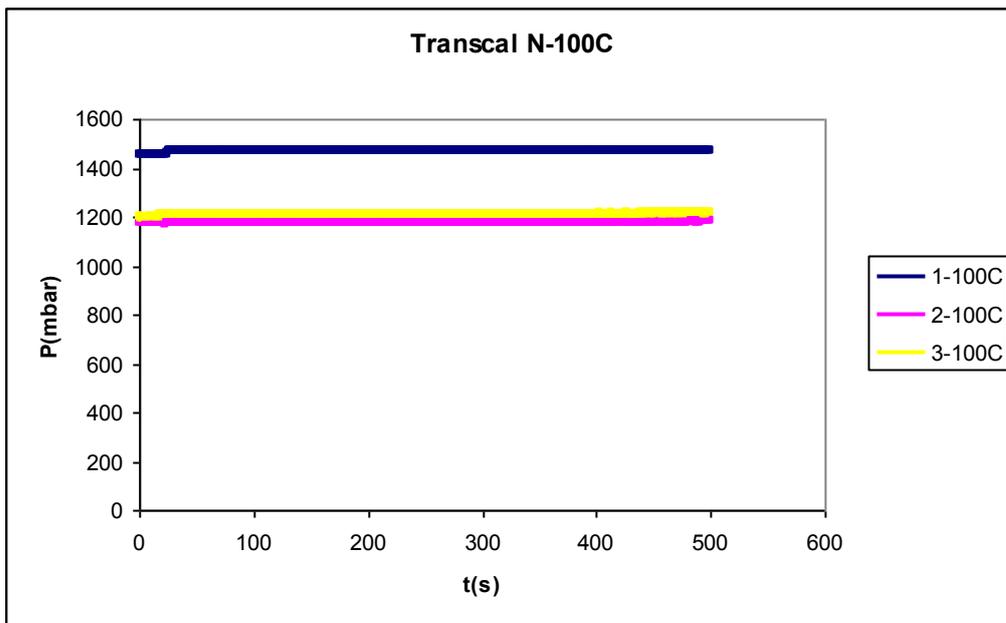
**Figure A.6 :** Pressure change by time at 60°C for SO<sub>2</sub>-Transcal N system.



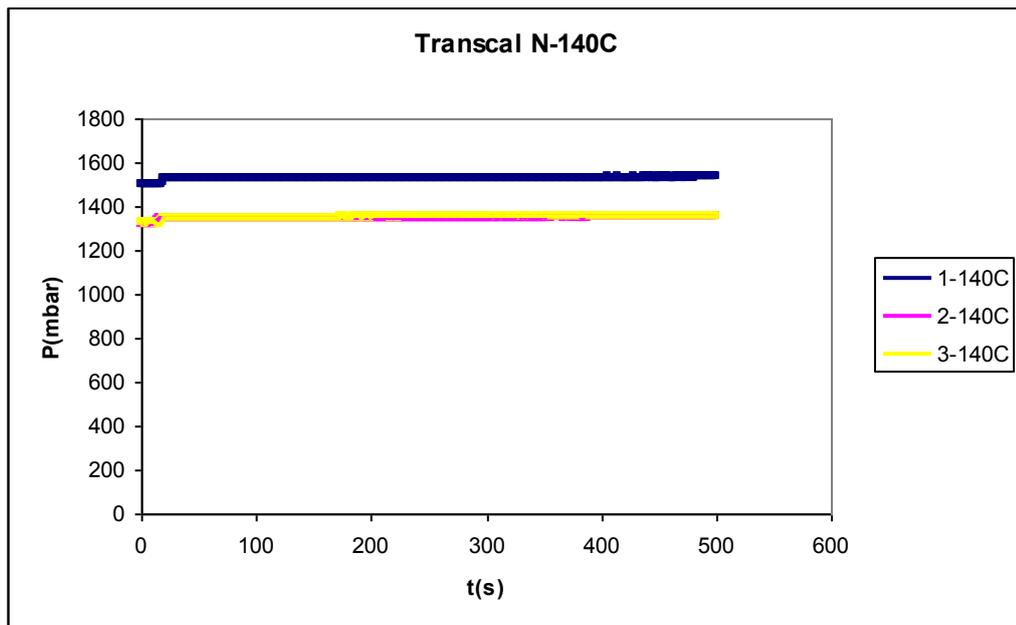
**Figure A.7 :** Pressure change by time at 70°C for SO<sub>2</sub>-Transcal N system.



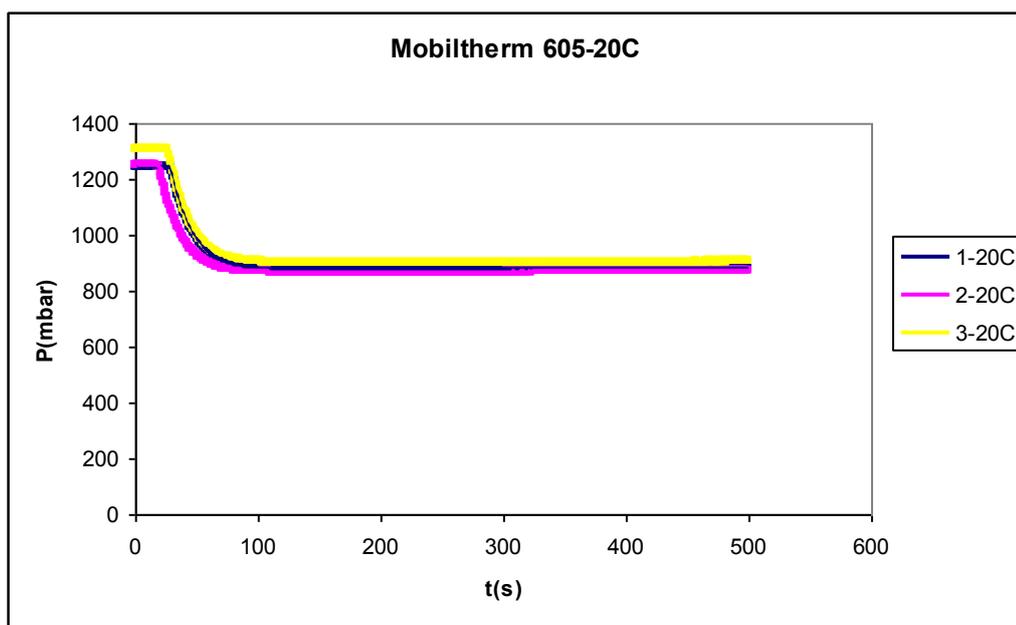
**Figure A.8** : Pressure change by time at 80°C for SO<sub>2</sub>-Transcal N system.



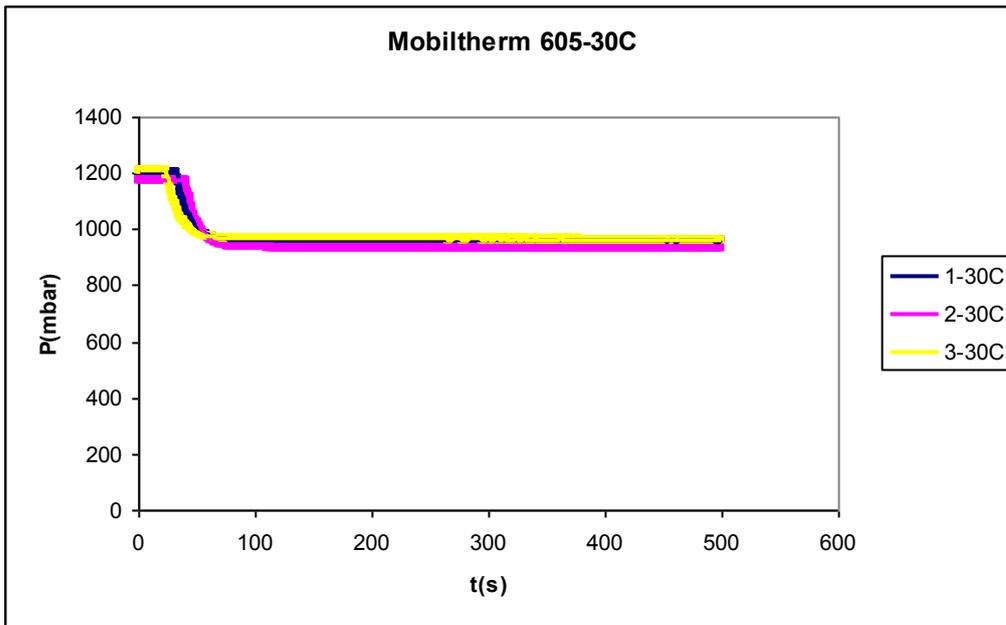
**Figure A.9** : Pressure change by time at 100°C for SO<sub>2</sub>-Transcal N system.



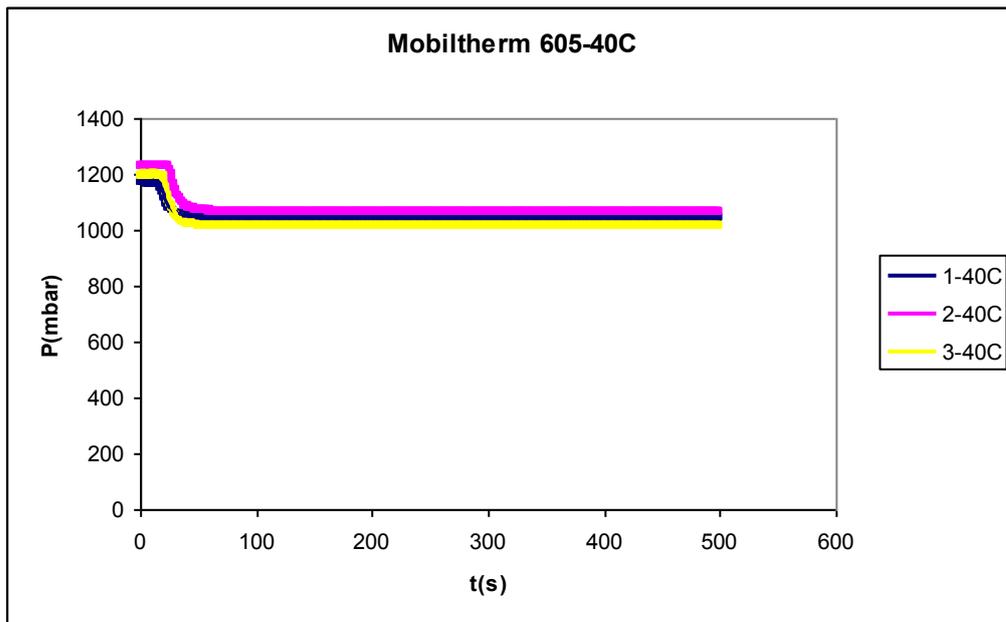
**Figure A.10 :** Pressure change by time at 140°C for SO<sub>2</sub>-Transcal N system.



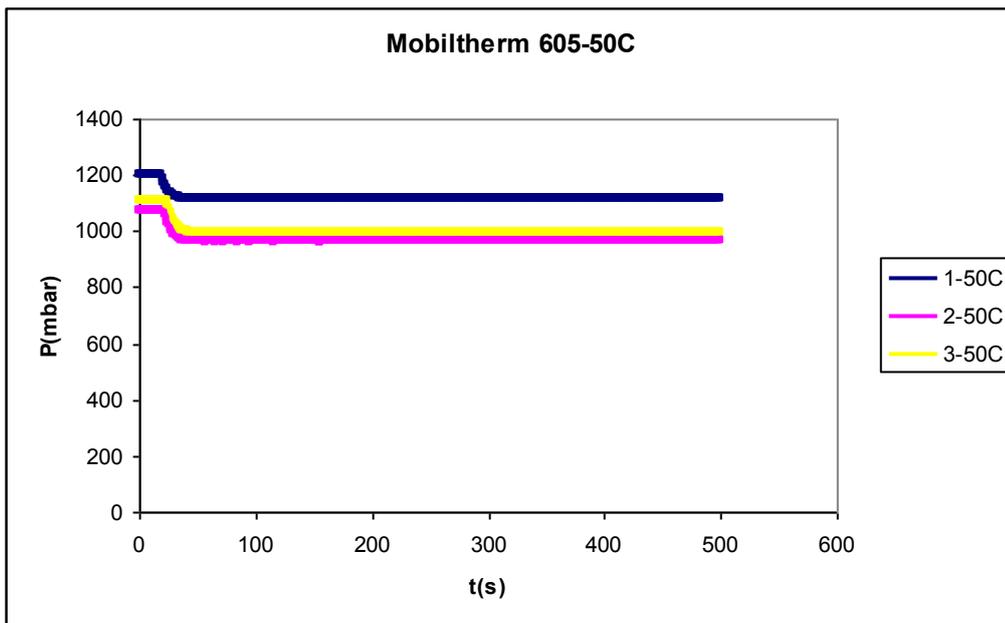
**Figure A.11:** Pressure change by time at 20°C for SO<sub>2</sub>-Mobiltherm 605 system.



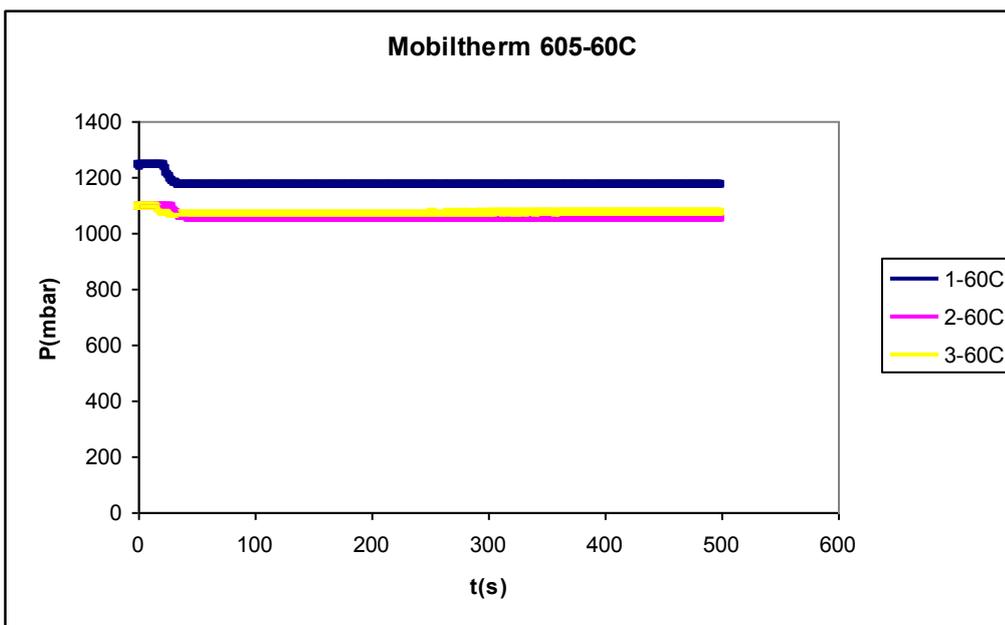
**Figure A.12** : Pressure change by time at 30°C for SO<sub>2</sub>-Mobiltherm 605 system.



**Figure A.13** : Pressure change by time at 40°C for SO<sub>2</sub>-Mobiltherm 605 system.



**Figure A.14** : Pressure change by time at 50°C for SO<sub>2</sub>-Mobiltherm 605 system.



**Figure A.15** : Pressure change by time at 60°C for SO<sub>2</sub>-Mobiltherm 605 system.



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