İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SULFUR DIOXIDE ABSORPTION IN HEAT TRANSFER OIL AND RELATED MASS TRANSFER CALCULATIONS

MASTER OF SCIENCE THESIS

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Department : Chemical Engineering

Programme: Chemical Engineering

JUNE 2005

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ISI TRANSFER YAĞINDA KÜKÜRT DİOKSİT ABSORPSİYONU VE KÜTLE İLETİMİ HESAPLAMALARI

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SUMMARY

Sulfur dioxide is one of the major pollutants arisen from combustion processes and today, it is probably the most widespread air pollutant. Some sulfur dioxide streams are scrubbed with an alkali solution performing a chemical reaction with an amine or a solid substance such as limestone or dolomite, which in turn generates wastes that pose other pollution problems. While the conversion of sulfur dioxide to elemental sulfur has many environmental advantages, no processes exist that are environmentally acceptable and economically viable. An alternate purification process for sulfur dioxide is physical absorption with polar organic solvents.

In this research, a non-polar absorbing solvent has been selected. The solvent is heat transfer oil, commercial product of BP Company, with high flash, fire and boiling points that can be used at high flue gas temperatures.

The aim of this research is to determine the sulfur dioxide absorption capacity of heat transfer oil and make necessary mass transfer calculations in 293 K to 313 K temperature interval.

Determination of the chemical composition, average molecular weight and boiling range of the heat transfer oil, Transcal N, have also been studied in this research.

In this study, the sulfur dioxide solubility in heat transfer oil is expressed in four different units; mole fraction of sulfur dioxide at standard pressure, Henry’s constant, Ostwald’s coefficient and solubility in unit volume of solvent.

ISI TRANSFER YAĞINDA KÜKÜRT DİOKSİT ABSORPSİYONU VE KÜTLE İLETİMİ HESAPLAMALARI

ÖZET

Kükürt dioksit yanma prosesleri sonucu açığa çıkan başlıca kirleticilerdendir ve günümüzde en yaygın olan kirleticidir. Bazı kükürt dioksit çıkışları alkali çözeltilerle yıkanarak ve amin, kireçtaşı veya dolomit gibi malzemelerle kimyasal reaksiyona sokularak kükürt dioksit doğaya zararlı başka forma çevrilmektedir. Kükürt dioksitin elementel kükürde çevrilmesinin çevresel büyük avantajları olmasına karşılık, bunun için çeveresel açıdan kabul edilebilir ve ekonomik bir proses bulunmamaktadır. Diğer bir alternatif proses polar çözücüler ile fiziksel absorpsiyonun yapılmasıdır.

Bu çalışmada, apolar bir çözücü seçilmiştir. Çözücü BP firmasının ticari olarak sattığı yüksek yanma ve kaynama noktasına sahip ısı transfer yağı Transcal N'dir. Bu çalışmanın amacı 293 K – 313 K sıcaklıları arasında yağın absorpsiyon kapasitesini belirlemek ve gerekli kütle iletimi hesaplamalarını yapmaktır.

Ayrıca, yağın kimyasal yapısının netlik kazanması, ortalama molekül ağırlığının ve kaynama aralığının belirlenmesi de bu çalışmanın hedeflerindendir.

Bu çalışmada yağın absorpsiyon kapasitesi dört farklı şekilde ifade edilmiştir: standard basınçta mol kesri, Henry sabiti, Ostwald katsayısı ve birim hacim çözücüdeki kükürt dioksit çözünürlüğü olarak ifade edilmiştir.

1. INTRODUCTION

Sulfur dioxide is one of the major pollutants arisen from combustion processes and metallurgical operations and today, it is probably the most widespread air pollutant. An area of major interest in recent years is the control of sulfur dioxide emissions from power plant and industrial plant processes. The sulfur dioxide concentration in waste gases from metallurgical operations is normally relatively high, and many smelters have installed processes which recover many hundreds of tons of valuable sulfur products per day. The concentration of sulfur dioxide waste gases in sulfuric acid plant and in stack gases from the combustion of fuels is quiet low. In such cases, the economical removal and recovery of sulfur dioxide is difficult, and only a few processes for the removal of sulfur dioxide at these low concentrations exist.

The major and the most widespread source of sulfur dioxide is derived from the combustion of high sulfur fuels, most of which are treated to produce sulfuric acid with accompanying problems of market shortage and transportation difficulties. Some sulfur dioxide streams are scrubbed with an alkali solution performing a chemical reaction with an amine or a solid substance such as limestone or dolomite, which in turn generates wastes that pose other pollution problems. While conversion of sulfur dioxide to elemental sulfur has many environmental advantages, no processes exist that are environmentally acceptable and economically viable. An alternate purification process for sulfur dioxide is physical absorption with polar organic solvents. Physical absorption with a polar solvent provides a convenient and economical method for removing acid gases. Today, more stringent laws may require for removal of sulfur dioxide from these gases to a far greater extent than in the past.

The control of industrial smog hinges on the removal of sulfur from fuels and the control of sulfur dioxide emissions where they do occur. Many processes have been proposed for the removal of sulfur dioxide from stack gases. None has yet proved superior to all others, and none has proved totally effective in removing sulfur dioxide under all circumstances.

In designing an absorption system to purify flue gases, it is crucial to know the solubility values of sulfur dioxide in the absorbing solvent, and necessary to use such a solvent with high flash, fire and boiling points due to high gas outlet temperature in the stack. The effective and economical regeneration of the absorbing solvent is very important to be able to recycle the solvent stream in the installed process and lower the treatment process expenses. Minor loss of the absorbing solvent during regeneration and due to vaporization may increase the process efficiency with easy process control.

In this research, a non-polar absorbing solvent has been selected. The solvent is heat transfer oil, commercial product of BP Company, with high flash, fire and boiling points that can be used at high flue gas temperatures.

The aim of this research is to determine the sulfur dioxide absorption capacity of heat transfer oil and make necessary mass transfer calculations in 293 K to 313 K temperature interval.

This research can be represented as a starting point and contains the data at low temperatures for determining the absorption capacity of heat transfer oil.

2. SULFUR DIOXIDE

2.1. Formation of Sulfur Dioxide

The overall reaction for the formation of sulfur dioxide from sulfur in fossil fuels is simply:

$$S + O_2 \rightarrow SO_2 \qquad (2.1)$$

This reaction is highly exothermic with a heat release of 296800 kJ/kg.mole at 298 K. In addition to sulfur dioxide, a small quantity of sulfur trioxide, SO_3, is formed in combustion reaction. In combustion of fossil fuels the SO_2/SO_3 ratio is typically 40:1 to 80:1.

Some of the industrial processes use sulfur containing starting materials. In most of the metallurgical processes, sulfur dioxide appears as a by-product. Many modern plants burn pyrite and other metallic sulfide ores in fluid-bed roasters. The stack gas from smelting often contains sufficient sulfur dioxide (*ca*. 6% by weight) for economical conversion to sulfuric acid, whereas the lower concentration in power plant stack gases generally requires concentration of sulfur dioxide.

2.1.1. Thermodynamics and kinetics of sulfur dioxide formation

The formation processes for SO_2 and SO_3 cannot be explained quantitatively by the simple overall reactions,

$$S + O_2 \rightarrow SO_2 \qquad (2.2)$$

$$SO_2 + \tfrac{1}{2} O_2 \leftrightarrows SO_3 \qquad (2.3)$$

The sulfur monoxide and S_2O are important kinetically in the oxidation scheme. Since both are unstable and reactive at atmospheric temperatures, they are not found among the normal products of combustion processes.

The conventional sulfur oxides found as stable products of combustion are SO_2 and SO_3. The thermodynamic relationships between them are summarized in Table 2.1.

Table 2.1 Equilibrium Constants for The SO_2-SO_3 Oxidation Reaction [1]

$\mathbf{SO_2 + \frac{1}{2} O_2 \leftrightarrows SO_3}$	**T (°K)**	$\mathbf{K_P}$
$K_P = \frac{p_{SO_3}}{p_{SO_2}(p_{O_2})^{1/2}}$	298	2.6×10^{12}
	500	2.6×10^{5}
	1000	1.8
	1500	3.8×10^{-2}
	2000	5.6×10^{-3}

The K_P values show that equilibrium favors SO_3 at low temperatures and SO_2 at high temperatures in lean mixtures. This means that small amounts of sulfur trioxide can be found at the flame zone, and large amounts in the cooled flue gases as the equilibrium shifts with the temperature. It has shown that opposite effect is observed in power plant furnaces. In the flame zone the sulfur trioxide level exceeds the predicted equilibrium value, while in the cooled flue gas near the exit the sulfur trioxide level is far below the equilibrium value for that temperature [2].

This behavior of sulfur trioxide is because of the role of kinetics in determining the rate of formation of intermediate species. It has been claimed that the sulfur monoxide is an important intermediate product in the reaction scheme. It is assumed that sulfur monoxide is produced early in the reaction zone. The next step is to examine the reactions which first sulfur monoxide is oxidized to sulfur dioxide, and then to sulfur trioxide. The major sulfur dioxide formation reactions are thought to be,

$$SO + O_2 \rightarrow SO_2 + O \tag{2.4}$$

$$SO + OH \rightarrow SO_2 + H \tag{2.5}$$

These reactions are also producing oxygen and hydrogen atoms, which are highly reactive and may enter the overall reaction scheme later.

The major concern is the formation and removal of sulfur trioxide. The major formation reaction is the three-body process,

$$SO_2 + O + M \rightarrow SO_3 + M \tag{2.6}$$

M is a third body acting as an energy absorber. Three body processes are fairly slow; however, this reaction proceeds rapidly in the hot reaction zone because the concentration of oxygen atoms is at maximum. The major steps for the removal of sulfur trioxide are thought to be,

$$SO_3 + O \rightarrow SO_2 + O_2 \tag{2.7}$$

$$SO_3 + H \rightarrow SO_2 + OH \tag{2.8}$$

$$SO_3 + M \rightarrow SO_2 + O + M \tag{2.9}$$

The last step, which is simply the reverse reaction, is a thermal decomposition process [1].

In hot reaction zone, where high levels of oxygen atoms occur, it is possible to assume that reactions 2.6 and 2.7 dominate the overall reaction mechanism. With basic kinetic concepts, the following equation can be written,

$$\frac{d[SO_3]}{dt} = k_{1.6}[SO_2][O][M] - k_{1.7}[SO_3][O] \tag{2.10}$$

The maximum sulfur trioxide concentration is found by setting $\frac{d[SO_3]}{dt} = 0$. As a result,

$$[SO_3]_{\max} = \frac{k_{1.6}[SO_2][M]}{k_{1.7}} \tag{2.11}$$

It is found that the maximum sulfur trioxide level can be between 1 to 5 percent of sulfur dioxide concentration [3].

In hydrocarbon rich flames, the removal reaction is 2.8. Oxygen atom concentration is much lower under this condition. If the rate of sulfur trioxide concentration is now rewritten in terms of reactions 2.6 and 2.8, and then set equal to zero, it is found that,

$$[SO_3]_{\max} = \frac{k_{1.6}[SO_2][M][O]}{k_{1.8}[H]} \tag{2.12}$$

The ratio of [O]/[H] controls the value of maximum sulfur trioxide concentration. Since this ratio is small, the conversion of sulfur dioxide to sulfur trioxide is suppressed significantly.

As the products of combustion leave the hot reaction zone, the temperature drops and atom concentrations decay rapidly by recombination. With low atom concentrations, the formation and removal steps of sulfur trioxide, such as reactions 2.6, 2.7, and 2.8, become negligible. Some sulfur trioxide may thermally decompose by reaction 2.9 as the temperature decreases. However, this reaction has large activation energy; the significant temperature decrease makes it negligible. Kinetics predicts superequilibrium levels of sulfur trioxide in the flame zone of lean hydrocarbon mixtures with modest drop in concentration as the gases cool. The predicted final level of sulfur trioxide is a few percent of the sulfur dioxide concentration. This result is parallel with industrial experience, where SO_3/SO_2 values are between 1:40 and 1:80. In fuel rich combustion, sulfur trioxide levels are negligible [1].

2.1.2. Properties of Sulfur Dioxide

Sulfur dioxide is a poisonous and colorless gas. It has a sharp and irritating odor.

The polar nature of sulfur dioxide is reflected in the ease with which it may be liquefied. It liquefies at -10^{o}C (the normal boiling point) under 1 atm pressure and at 293 K a pressure of 3 atm will liquefy the gas. This property of SO_2 makes it useful as a refrigerant.

Critical temperature and critical pressure of SO_2 are 430.3 K and 77.7 atm, respectively [4].

Table 2.2 Physical Constants of Sulfur Dioxide [4,5]

Melting Point (°C)	-75.46
Heat of Fusion (cal/mole)	1769 (7.40 kJ/mole)
Boiling Point (°C)	-10.02
Heat of Vaporization (cal/mole)	5960 (-10.0°C; 24.92 kJ/mole)
Density (liq., 0°C)	1.434
Heat of Formation (18°C; cal/mole)	70920
Free Energy of Formation (cal/mole)	-69660
Standard Entropy (cal/deg; S^o_{298})	59.40 (g)
Molecular Size and Shape	S-O, 1.46 A° < O-S-O, 120 A°
Fundamental Frequencies (cm^{-1})	525, 1152, 1361

SO_2 (liq) $\leftrightarrows$ SO_2 (g)

Table 2.3 Vapor Pressures [4,5]

T (°C)	**P (kPa)**
10°C	230 kPa
20°C	330 kPa
30°C	462 kPa
40°C	630 kPa

Table 2.4 Molar Heat Capacity of SO_2 (liq) [4,5]

T (K)	**C_p (cal/deg)**
200	20.97
210	20.91
220	20.86
230	20.81
240	20.76
250	20.71
260	20.66

Table 2.5 Heat Capacity and Entropy of SO_2 (g) [4,5]

T (K)	**C_p (cal/deg)**	**S^o_{298}(cal/deg)**
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

Table 2.6 Solubility in Water at 101.3 kPa [4,5]

T(°C)	**g/100g H_2O**
0°C	22.971
10°C	16.413
20°C	11.577
30°C	8.247
40°C	5.881

Other thermodynamic properties of SO_2 and partial pressures of water and SO_2 over aqueous solutions of sulfur dioxide can be found in Chemical Engineers' Handbook [5].

Sulfur dioxide is moderately soluble in water, producing solutions of sulfurous acid, H_2SO_3. The acid is not very stable, and pure H_2SO_3 cannot be isolated. The extent of the reaction between dissolved SO_2 molecules and water is not known. Probably, both H_2SO_3 and SO_2 molecules exist in the solution in equilibrium:

$$SO_2\,(aq) + H_2O \leftrightarrows H_2SO_3\,(aq) \qquad (2.13)$$

Sulfurous acid is a weak, diprotic acid. The first dissociation is

$$H_2SO_3\ (aq) \rightleftarrows H^+\ (aq) + HSO_3^-\ (aq) \qquad Ka_1 = 1.3x10^{-2} \qquad (2.14)$$

which is sometimes written as

$$SO_2\ (aq) + H_2O \rightleftarrows H^+\ (aq) + HSO_3^-\ (aq) \qquad (2.15)$$

The second dissociation is

$$HSO_3^-\ (aq) \rightleftarrows H^+\ (aq) + SO_3^{2-}\ (aq) \qquad Ka_2 = 6.3x10^{-8} \qquad (2.16)$$

Sulfurous acid forms two series of salts; normal salts, Na_2SO_3, sodium sulfite, and acid salts, $NaHSO_3$, sodium bisulfite or sodium hydrogen sulfite.

Sulfites are often prepared by bubbling SO_2 gas through a solution of a hydroxide,

$$2OH^- + SO_2\ (g) \rightarrow SO_3^{2-}\ (aq) + H_2O \qquad (2.17)$$

If the SO_2 addition is continued, acid sulfites are produced:

$$H_2O + SO_3^{2-}\ (aq) + SO_2(g) \rightarrow 2\ HSO_3^-\ (aq) \qquad (2.18)$$

Sodium metabisulfite, $Na_2S_2O_5$, is produced by the evaporation of sulfur dioxide saturated solution of boiling hydroxide or carbonate solutions. Sodium metabisulfite is a white solid and is more safely and easily transported than $NaHSO_3$ solutions. The reaction for the sodium metabisulfite production is as follows:

$$2\ NaHSO_3 \rightarrow Na_2S_2O_5 + H_2O \qquad (2.19)$$

Except ammonium and alkali metal sulfites, sulfites are insoluble.

The salts of sulfurous acid is unstable, the addition of an acid to a sulfite or to an acid sulfite liberates SO_2 gas, which is a convenient way to prepare the gas in the laboratory:

$$SO_3^{2-}\ (aq) + 2\ H^+\ (aq) \rightarrow SO_2\ (g) + H_2O \qquad (2.20)$$

2.1.2.1. Redox reactions of sulfur dioxide

Sulfur dioxide, sulfurous acid, and sulfites can function as mild oxidizing agents, but reactions in which these compounds react as reducing agents (and are oxidized to sulfate ion, SO_4^{2-}) are more numerous and more important. Many substances such as potassium permanganate, manganese dioxide, potassium dichromate, chlorine, and bromine, oxidize sulfite to sulfate. However, not only sulfate but also many other oxygen containing sulfur anions, polytionates such as dithionates $S_2O_6^{2-}$, $S_4O_6^{2-}$, etc., are formed with the oxidants. Sulfites are usually contaminated by traces of sulfates because of oxidation by the oxygen of air:

$$2\ SO_3^{2-} + O_2\ (g) \rightarrow 2\ SO_4^{2-} \qquad (2.21)$$

In the presence of some reducing agents, for example, Fe(II) and arsenites AsO_3^{2-}, sulfites are much more rapidly oxidized by oxygen than in the absence of these substances. Some substances inhibit the oxidation of sulfites by oxygen, for example, small concentrations of phenol, glycerine, mannitol, benzaldehyde, and especially stannous chloride greatly decrease the rate of conversion to sulfate.

Sulfurous acid may also act as an oxidizing agent. Hydrogen sulfide, H_2S is oxidized to elementary sulfur by H_2SO_3. By the action of metallic zinc Zn, sulfurous acid H_2SO_3 is reduced to dithionite containing acid, $H_2S_2O_4$ (former name: hyposulfurous acid) which is very strong reducing agent and its salt sodium dithionite, $Na_2S_2O_4$, an anhydrous white powder, is used in vat dyeing. [4]

2.2.Effects of Sulfur Oxides and Related Compounds on Environment

Sulfur dioxide occurs in industrial and urban atmospheres at 1 ppb-1 ppm range and in remote areas of earth at 50-120 parts per trillion (10^{12}). Natural sources for SO_2 include volcanoes, decaying organic matter, and solar action on seawater.

Sulfur dioxide can act both as a reduction agent and an oxidizing agent at atmospheric conditions. The reaction between H_2S and SO_2 in the presence of catalyst is an example of SO_2 acting as an oxidizing agent. This reaction is:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \tag{2.22}$$

The problem of sulfur dioxide pollution is its ability to react either photochemically or catalytically with other atmospheric contaminants, forming sulfur trioxide, sulfuric acid, and various salts of sulfuric acid. For example, in the presence of a metallic oxide as a catalyst in the atmosphere,

$$SO_2 + \frac{1}{2} O_2 \rightarrow SO_3 \tag{2.23}$$

Sulfur dioxide oxidation occurs by the action of particulate matters in the atmosphere with oxygen, ozone, oxides of nitrogen or hydrogen peroxides in aqueous micro-droplets and hydrometeors and this oxidation has been suggested as a non-photolytic pathway for the production of sulfuric acid in humid atmosphere [6,7].

Some metal oxides oxidize sulfur dioxide directly to sulfate. As an example,

$$4MgO + 4SO_2 \rightarrow 3MgSO_4 + MgS \tag{2.24}$$

Two other reactions take place in the atmosphere when high humidity present,

$$2SO_2 + 2H_2O + O_2 \rightarrow 2H_2SO_4 \tag{2.25}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{2.26}$$

The first oxidation reaction occurs rapidly in the presence of metal salts, such as the sulfates and chlorides of iron and manganese. These metal salts act as catalyst for the reaction. The droplets of sulfuric acid formed, which are highly corrosive, tend to reduce visibility. These reactions are also partially responsible for the acid rain phenomenon.

Industrial smog consists primarily of particles (ash and smoke), SO_2, and H_2SO_4 mist.

As it is mentioned previously, the SO_2 can undergo air oxidation to SO_3, especially when catalyzed on the surface of airborne particles or through reaction with NO_2. Then, SO_3 reacts with water vapor to produce H_2SO_4 mist. A further reaction may occur with ammonia to produce particles of ammonium sulfate, $(NH_4)_2SO_4$. Effects of air pollution on the environment along with the acid rains cause not only the metal corrosion but also leaching of polluting compounds from contaminated soils. Thus, net result is the contamination of ground and surface waters, and food chains [8].

2.2.1. Effects of sulfur dioxide on human health

As a major pollutant, sulfur dioxide is responsible from many negative developments in environmental health. Sulfur dioxide undergoes several reactions, especially radical and catalytic reactions, in atmosphere.

Sulfur dioxide, despite the thermodynamic forces, pushes the reaction with oxygen toward the sulfur trioxide. The conversion of sulfur dioxide to sulfur trioxide in atmosphere would be a slow process, because of small rates of conversion at atmospheric temperatures. However, once sulfur dioxide is in atmosphere, the rate is affected by heterogeneous catalysis on the surface of suspended particles. This results in an increased rate of sulfur dioxide conversion to sulfur trioxide. It also leads to an increase in sulfate aerosol formation, and these aerosols are dangerous for human health. Thus, assessment of the human health effects of sulfur dioxide in polluted atmospheres is complicated by the simultaneous presence of particulates, sulfuric acid, sulfates and other pollutants.

The exact physiological effects of SO_2 and H_2SO_4 mist at low concentrations are not well understood, but these substances are respiratory irritants and levels above 0.10 ppm are generally considered harmful. Acute exposures to concentrations of approximately 50 ppm promptly irritate the nose and throat and cause coughing and nasal discharge. Most persons would not tolerate them more than 15 minutes. By 24 hours exposure to 0.52 ppm, especially accompanied by particulate, increased mortality may occur. Acutely toxic levels can cause bronchitis and astmalike and influenzalike symptoms. At very high levels of sulfur dioxide, asphyxia leading to death can result or a chemical bronchopneumonia may develop which can be fatal after several days. Chronic exposure to sulfur dioxide has been widespread in certain industries, notably smelting and paper manufacture.

Since, chronic effects and resulting cumulative effects after long term exposure are very important from the human health point of view, not only the acute bronchitis but also heart and vein diseases are claimed to be started or supported by sulfur oxide pollutants. Chronic plant injury is also seen by the presence of 0.03 ppm SO_2 for a year period [8].

2.2.2. Effects of sulfur dioxide on plants

The higher the SO_2 concentration, the exposure times for the similar injury effects on the plants get shorter. Against sulfur dioxide; spinach, lettuce, and other leafy vegetables are very sensitive, as are cotton and alfalfa. Pine needles are also affected, with either the needle tip or the whole needle become brown and brittle as it has been seen at the suburbs of Yatağan, Muğla.

Sulfur dioxide produces two types of injury on the leaves of plants, acute and chronic. The former is characterized by the killing of sharply defined marginal or interveinal areas of the leaf. Immediately following the fumigation, these areas take on a dull, water-soaked appearance. They dry up and bleach to an ivory color. The leaf tissue surrounding the acutely injured areas is usually green and apparently normal. Chronic markings are caused by the absorption of an amount of gas somewhat less than that necessary to cause acute injury, or they may be caused by the slow, long-continued absorption of sub-lethal amounts of gas which accumulate until the buffer capacity of the leaf is exceeded or a salt effect is produced. The leaf does not collapse because of its type of injury, but histological examination reveals that some of the mesophyll and palisade cells may be shattered or the chloroplasts in some cells may be ruptured. Photosynthesis measurements of cotton leave indicate that the chronically injured areas are about one-half as active as normal areas.

Maximum sensitivity to sulfur dioxide occurs in the late spring or early summer, paralleling the physiological activity of the plant. Acute lesions consist of reddish discoloration of the needles with subsequent shrinkage of the tissue. The discolorations may involve the whole leaf or limited areas of any portion of the leaf. Abscission may follow after a variable interval. In winter, the first symptom is a general change from the normal dark green to a lighter green. Then, definite areas turn yellow-brown and finally red-brown.

Chronic markings do not appear immediately after fumigation. Their first appearance delay for 2 to 4 days, and they continue to develop for several days. Chronic markings due to long-continued exposure to sub-lethal concentration of the gas may require several weeks to develop. A large amount of sulfate is found in the latter leaves, whereas leaves that have been injured either acutely or chronically by a single fumigation show only a small increase in the sulfate content [9].

“Invisible injury” of sulfur dioxide is reduced vigor of plants and reduced level of photosynthetic activity [10]. There may be a temporary partial inhibition of photosynthesis while the gas is present, but if the leaves are not permanently injured, the normal level, or even a slightly higher than normal level, of photosynthesis is rapidly regained after the fumigation is stopped, so that no appreciable reduction of assimilation is found. Investigations indicate that fumigations with sulfur dioxide, which do not injure the leaves visibly, do not reduce the yield [9,11].

Sulfur is an essential element in plants, because the amino acids cystine and methionine are essential constituents of some plant proteins. Sulfur is also a constituent of many plant hormones and enzymes such as thiamine biotin, lipoic acid [12]. The organic sulfur level of the leaves of most broad-leaved plants ranges from about 0.15 to 0.3 percent on dry basis. Conifer needles contain about 0.1 percent and some plants contain as much as 0.6 percent. Little or no sulfate is present if the leaf contains only its normal quota or less of organic sulfur, and a large excess of sulfate does not raise the organic sulfur level above normal [13].

Sulfur deficiency in plants, manifested by a general yellowing of the leaves and retarded grow rate. Deficiency can be corrected by supplying the sulfur as sulfur dioxide to the leaves, but because the element introduced is not readily translocated from the leaves it is less effective to supply the sulfur in this way than as sulfate through roots [14].

A number of suggestions have been made as to the mechanisms of sulfur dioxide injury. It is assumed that the gas reacts with such compounds as aldehydes and sugars in the leaf, forming additional products that slowly release sulfuric acid, causing injury to the cells. This mechanism cannot be more than partly correct because injury due to the given quantity of absorbed gas is greater in the morning, when sugar concentrations are low [15]. Another theory is that the sulfur dioxide inactivates the iron in the chloroplasts, causing interference with its catalytic properties in assimilation. Then, secondary changes affect the photo-oxidative processes of the leaf so that bleaching and death of the cells result [16].

2.2.2.1.Proof of sulfur dioxide injury on plants

A possible method of chemical analysis of the leaves for total and sulfate sulfur is present if the leaves have been analyzed before the fumigation. An increase in the total sulfur, together with an equal increase in sulfate fraction of 0.1 to 0.2 percent sulfur or more, means that the injury was probably because of sulfur dioxide. A large amount of sulfate sulfur would suggest a long-continued low concentration fumigation, which might induce sulfate toxicity. However, it must be noted that a similar sulfate build-up in the leaves can be due to soluble sulfate in the soil [17].

It is claimed that leaves injured by sulfur dioxide could be identified by the presence of pheophytin, which would be formed in the leaves by acidification of chlorophyll. Leaves injured by frost, insects, and diseases do not give pheophytin reaction [18].

2.2.3. Air quality criteria and standards

Air Quality Criteria describe effects that can be expected to occur when pollutant levels reach or exceed specific figures for a specific time period. Air Quality Criteria has been an essential step in providing a quantitative basis for air quality standards. Standards prescribe the pollutant levels that cannot be legally exceeded during a specific time period in a specific geographical region. In many countries, standards are given as primary and secondary standards. Primary standards have a purpose of protecting the public health within a specified time limit. Secondary standards are given to protect the public from known or anticipated adverse effects Air pollution control is a very important task directed to the governments and local municipalities.

Table 2.7 Ambient Air Quality Standards for Sulfur Dioxide [19-21]

	EPA[*]	**WHO**[**]	**Turkish Standards**
Annual Average	80 μg/m^3(0.03 ppm)	40-60 μg/m^3	150 μg/m^3
24 h	365 μg/m^3 (0.14 ppm)	100-150 μg/m^3	400 μg/m^3

[*] U.S. Environmental Protection Agency

[**] World Health Organization

Secondary standards for sulfur dioxide given by EPA are 60 μg/m^3 (0.02 ppm) for annual average; 260 μg/m^3 (0.1 ppm) for 24 hour average and 1300 μg/m^3 (0.5 ppm) for 3 hour exposure [19].

2.2.4. Pollutant emission standards

According to the clean air policy of governments, the emission standards have been established for the pollutants. In Turkey, regulations are given in Air Quality Protection Legislation appeared in 1986. The sulfur dioxide standards for stationery sources are given in Table 2.8.

Table 2.8 Sulfur Dioxide Standards for Stationary Sources [19,21]

	EPA Regulations	**Turkish Regulations**
Power Plant		
a) Coal fired unit	520 g/10^{6}kJ * 260 g/10^{6}kJ **	2000 mg/m$^{3\ ***}$
b) Gas and liquid fuel fired units	86 g/10^{6}kJ	Liq.Fuel**** 1700 mg/m^3 (new plants) 3200 mg/m^3 (old plants) Gas Fuel****100 mg/m^3
Sulfuric Acid Plant	2000 g/ton acid	400gSO_3/ton acid 30mg/m^3(alkaline scrub.)

*For 90% reduction of potential SO_2 emissions
**For 70% reduction of potential SO_2 emissions
***Based on 5% O_2 content in flue gas
****Based on 3% O_2 content in flue gas

2.3. Removal Processes of Sulfur Dioxide

Several processes can be used to recover sulfur dioxide in one or more forms of sulfuric acid, elemental sulfur, ammonia sulfate, or gypsum. Generally, when pure or concentrated sulfur dioxide is recovered, it is converted to sulfuric acid with small amounts of liquid sulfur dioxide.

Four possible methods may be used to reduce sulfur dioxide emissions from fossil fuel combustion. These potential methods are:

- Change to low sulfur fuel
    - Natural gas
    - Liquefied natural gas
    - Low sulfur coal
    - Low sulfur oil
- Use desulfurized coal and oil
- Build tall stacks to increase atmospheric dispersion
- Use flue gas desulfurization systems [1]

2.3.1. Flue gas desulfurization systems

Progress in developing satisfactory desulfurization process for flue gases has been extremely slow because of the complexity and magnitude of the problem. For example, a 1000 MW electric power plant using coal containing between 2.5 and 3 percent sulfur will discharge 48 to 60 thousand m^3/min of flue gas with a sulfur dioxide content between 0.2 and 0.3 percent by volume. It seems unlikely that a single desulfurization method will be developed that is capable of controlling effluents from all types of sources. The control techniques to be employed depend upon such factors as boiler size, configuration, load pattern, geographical location, etc.

Regenerative processes are applied by physical or chemical methods. Physical regeneration is applied to the sulfur dioxide absorbed medium to recover the absorbing material. In chemical regeneration, absorbed sulfur dioxide has been converted into other sulfur forms containing compounds and the reagent is circulated [1].

2.3.1.1 Regenerative processes by physical means

In these processes, sulfur dioxide is adsorbed or reacted with the reagent and the reagent is simply regenerated by heat. Various regenerative processes for sulfur dioxide removal from waste gases have been developed; the media used for the absorption can be polyethers, as in Solinox-Linde process, amines [22,23], ketones, glycol ethers [24,25], esters, ureas [26-28], or heterocyclic compounds [26-29]. Besides some amines, the regenerative absorption depends on the reversible formation of a complex between sulfur dioxide and the solvent molecule at low/ambient temperature which can decompose at higher temperatures.

Some of the regenerative physical processes are given below:

- Dimethylaniline process
- Sulfidine process
- Magnesium oxide scrubbing
- Basic aluminum sulfate process
- Single alkali scrubbing

2.3.1.2 Regenerative processes by chemical means

In chemical regenerative processes sulfur dioxide is oxidized or reduced in the solution and the reagent has been converted into its reactive form by chemical means. For example, in an indirect electrochemical process, reductants, such as Ti^{3+}, V^{2+} or Cr^{2+} ions, are electrogenerated in aqueous solutions and the absorbed sulfur dioxide is reduced to elemental sulfur. The oxidized forms of metal ions are electrochemically reduced after separation and recovery of the sulfur product [30].

Some of the regenerative chemical processes are given below:

- Sodium sulfite- zinc sulfite process
- Double alkali scrubbing
- Wet thiogen process
- Dry limestone scrubbing in fluidized beds

2.3.1.3 Non-regenerative processes

Some of the non-regenerative processes involve the oxidation of sulfur dioxide. Sulfur dioxide oxidation occurs by the action of oxygen [6], ozone, nitrogen dioxide or hydrogen peroxide [7] in aqueous solutions in the presence of Mn(II), Cu(II), Co(II), or Fe(II) ions [6,31]. Some metal complex catalysts, such as cobalt(II) tetrasulfonated phtalocyanine complex, are also used in sulfur dioxide oxidation [31].

Some non-regenerative chemical processes are summarized below:

- Ammonia-sulfuric acid process
- Lime and limestone scrubbing
- Wet limestone scrubbing modified with magnesium sulfate
- Dry scrubbing
- Citric acid scrubbing
- Absorption by alkaline water
- Catalytic oxidation to sulfuric acid

3. THERMODYNAMICS OF SOLUBILITY

A solution is a system of different substances which has the same chemical composition and physical properties in every part. The systems composed of two components are called binary solutions. The substance in larger quantity is usually called the solvent and the other called the solute.

The official IUPAC definition for solubility: 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 [32].

3.1.Vapor Pressure of Ideal and Non-Ideal Solutions

For an ideal solution the partial pressure of a component is directly proportional to its mole fraction X in the liquid and the proportionality constant is the vapor pressure of the pure substance. This relation is called Raoult's Law. Then, p_1 representing the partial pressure of component 1 and p_2 the partial pressure of component 2, with p^0_1 and p^0_2 the vapor pressures of components respectively,

$$p_1 = X_1 p_1^0 \tag{3.1}$$

$$p_2 = X_2 p_2^0 \tag{3.2}$$

Non-ideal solutions are much more common and the total vapor pressure is not a linear function of the composition expressed in the mole fractions. The vapor pressure of the component present at the higher concentration approaches the values given by Raoult's law as the mole fraction approaches 1.

In an ideal solution of A and B, the interaction between molecules is the same as between A molecules and other A molecules or B molecules and other B molecules. However, in a non-ideal solution the intermolecular attractive energies are different. If

A-B interaction energy is higher than the A-A and B-B interaction energies, the tendency of each component to pass into the vapor phase is reduced and there are negative deviations from Raoult's law.

The interaction between acetone and chloroform which leads to negative deviations from Raoult's law is due to the formation of weak hydrogen bond between the oxygen of the acetone and the hydrogen of chloroform [33].

3.2.The Chemical Potential of Ideal Solutions and Henry's Law

The Gibbs energy *G* at any pressure *p* with a perfect gas in its standard state, p^{Θ}=1 bar, is

$$G = G^{\Theta} + nRT \ln \frac{p}{p^{\Theta}} \tag{3.3}$$

The molar Gibbs energy can be expressed as $G_m = G/n$ and the chemical potential μ of a pure substance is defined as

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{p,T} \tag{3.4}$$

In other words, chemical potential shows how the Gibbs energy of a system changes when the substance is added to it. The chemical potential of a perfect gas is

$$\mu = \mu^{\Theta} + RT \ln \frac{p}{p^{\Theta}} \tag{3.5}$$

The chemical potential of pure liquid A, with vapor pressure of p^*_A, is

$$\mu_A^*(l) = \mu_A^{\Theta} + RT \ln \frac{p_A^*}{p^{\Theta}} \tag{3.6}$$

If another substance is present in the liquid, then the chemical potential of A is

$$\mu_A(l) = \mu_A^{\Theta} + RT \ln \frac{p_A}{p^{\Theta}} \tag{3.7}$$

These two formulas can be combined to give

$$\mu_A(l) = \mu_A^*(l) + RT \ln \frac{p_A}{p_A^*} \tag{3.8}$$

According to the Raoult's Law the ratio p_A/p^*_A is proportional to mole fraction of A in the liquid and it can be written as

$$p_A = x_A p_A^* \tag{3.9}$$

Some mixtures obey Raoult's Law very well when the components are very similar. Mixtures that obey the law througout the composition range from pure A to pure B are called ideal solutions.

For an ideal solution,

$$\mu_A(l) = \mu_A^*(l) + RT\ln x_A \tag{3.10}$$

However, in real solutions at low concentrations, although the vapour pressure of the solute is proportional to its mole fraction, the slope is not equal to the vapour pressure of the pure substance. This linear but different dependence is called Henry's Law.

$$p_B = x_B H_B \tag{3.11}$$

X_B is the mole fraction of the solute and H_B is a constant with the dimensions of pressure [34].

3.3.Solubility of Gases in Liquids

The solubility of gases in liquids has been a subject of great practical and theoratical importance since the start of modern science.

A gas dissolves in a liquid until the rate of escape of gas molecules from the surface is just equal to the rate at which gas molecules enter the liquid phase and the gas solubility of a liquid at this stage can be expressed in different ways, such as mole fraction at standard pressure, the Henry's constant, the Ostwald's coefficient or amount of solute in unit volume of solvent by weight.

The mole fraction of a component in a solution is

$$x_B = \frac{n_B}{\Sigma n_i} \tag{3.12}$$

where n_i is the amount of substance of components i=1, 2, .., c. For a system of solute 2 gas in solvent 1 the mole fraction is

$$x_2 = \frac{n_2}{(n_1 + n_2)} \tag{3.13}$$

The temperature and gas pressure must be specified with the given mole fraction values. For low values of mole fraction, the value can be accepted to be equal to mole ratio [32]. For dilute solutions the solubility of a gas in a liquid expressed as its mole fraction depends upon the pressure of the gas according to the Henry's law. Mixtures obeying this law are called ideal dilute solutions.

The Henry's constant, for gases dissolving in liquids at the equilibrium state, can be expressed as a proportion constant between the partial pressure of the gas and the mole fraction of the gas in the solution at a constant temperature. Henry's law holds very well where the partial pressure of the solute gas does not exceed 1 atm. For partial pressures of solute gas greater than 1 atm, Henry's constant is seldom independent of the partial pressure of the solute gas, and a given value of it can be used over only a narrow range of partial pressures. In defining gas solubility at these higher pressures, the partial pressure of the solute gas and temperature must be specified with the given value of Henry's constant. Henry's constants for several gases are given in Table 3.1 [35].

Table 3.1 Henry's Law Constants for Gases at 298 K (mmHg/m.f.) [35]

	Solvent	
Gas	**Water**	**Benzene**
H_2	$5.34\text{x}10^7$	$2.75\text{x}10^6$
N_2	$6.51\ \text{x}10^7$	$1.79\ \text{x}10^6$
O_2	$3.30\ \text{x}10^7$	
CO	$4.34\ \text{x}10^7$	$1.22\ \text{x}10^6$
CO_2	$1.25\ \text{x}10^7$	$8.57\ \text{x}10^6$
CH_4	$31.4\ \text{x}10^7$	$4.27\ \text{x}10^6$

The Ostwald's coefficient can be defined as a volumetric ratio of the solute. One of the mathematical definition of the Ostwald's coefficient is

$$L_V^0 = \left({V_g}\big/{V_L^0} \right)_{equil} \tag{3.14}$$

where V_g is the volume of gas absorbed by a volume $V^0{}_L$ of pure liquid at a specified temperature and a total pressure p.

The second mathematical definition of Ostwald’s coefficient is

$$L_V = \left(V_g / V_L \right)_{equil} \tag{3.15}$$

where V_g is the volume of gas absorbed by a volume V_L of saturated liquid at a specified temperature and a total pressure p.

The differences between these definitions are negligible as long as ideal gas behavior without expansion of the solvent upon dissolving gas is assumed.

Amount of solute in unit volume of solvent by weight can be obtained by making unit conversions of Ostwald’s coefficient values. From the mathematical definition of the Ostwald’s coefficient, it can be seen that the unit of the resulting value will be $mL_{solute}/mL_{solvent}$ at a specific temperature and pressure. With the known density of the solute, it is possible to evaluate the amount of gas dissolved in unit volume of liquid by weight, $g_{solute}/L_{solvent}$, at a specific temperature and pressure [32].

3.4.Enthalpy

When a system is free to change its volume against a constant external pressure, the change in internal energy is no longer equal to the energy supplied as heat. Some of the energy supplied as heat is converted into the work required to drive back the surroundings. At constant pressure the heat supplied is equal to the change in enthalpy.

$$H = U + pV \tag{3.16}$$

3.4.1. Standard enthalpy changes

Changes in enthalpy during physical or chemical change are calculated for the process taking place under standard conditions. The standard state of a substance at a specified temperature is its pure form at 1 bar pressure.

The standard enthalpy of dissolution of a substance is the standard enthalpy change when it dissolves in a specified amount of solvent. The limiting enthalpy of dissolution is the standard enthalpy change when the substance dissolves in an infinite amount of solvent and the interaction between the ions are negligible.

$$HCl(g) \rightarrow HCl(aq) \qquad \Delta H^{\Theta}_{sol} = -75.14 kJmol^{-1} \tag{3.17}$$

75 kJ of energy is released as heat when 1 mole of HCl (g) dissolves to produce an infinitely dilute solution [34].

4. EXPERIMENTAL

4.1 Chemicals

The heat transfer oil, Transcal N, is a commercial product of British Petroleum and it was kindly supported by BP.

Transcal N has properties of relatively high flash and fire points of 221^{o}C and 243^{o}C, respectively. During its use, the temperature of the liquid body should not exceed 320^{o}C, and the thin film temperature on the heated surfaces should not exceed 340^{o}C. Its chemical composition has been given as a mixture of normal and branched alkanes with some additives for corrosion inhibition. However, its average molecular formula or weight has not been specified.

Determination of the chemical composition, average molecular weight and boiling range of the heat transfer oil, Transcal N, have also been studied in this research. In order to determine the chemical composition of the oil, several analyses have been performed, such as elemental analysis, infrared and gas chromatography-mass spectroscopy. Average molecular weight of heat transfer oil is evaluated with the help of GC-MS spectral and elemental analyses data.

Transcal N is very slightly acidic in nature with the neutralization value of <0.05 mg KOH/g. As it is given in Table 4.1, its kinematic viscosities at different temperatures make it sprayable through nozzles.

Table 4.1 Typical Characteristics of Transcal N

		ASTM Method
Relative Density at 15.5ºC	0.875	ASTM D 1298
Flash Point (COC)	221ºC	ASTM D 92
Fire Point	243ºC	ASTM D 92
Kinematic Viscosity	30 cSt at 40ºC 5.1 cSt at 100ºC	ASTM D 445
Pour Point	-12ºC	ASTM D 97
Autogenious Ignition Point	350ºC	ASTM D 2155
Neutralization Value	<0.05 %wt	ASTM D 664
Coefficient for Thermal Expansion	0.00077	
Normal Operating Range Of Bulk Temperature	-10 to 320ºC	

Sulfur dioxide was provided by Burtaş A.Ş. with a 10 liter of sulfur dioxide gas cylinder at 99% purity.

4.2 Experimental Setup

Experimental setup consists of pre-heating (B) and absorption (G) flasks with water pump on the gas exit line, digital (M2) and mercury (M1) manometers, an electrical heating device (D) with contact thermometer (I), magnetic (E) and mechanical (F) stirrers and a water bath (C). The absorption process is performed in the absorption flask of 0.3115 L. The sulfur dioxide is fed into the system by a 10 liter of sulfur dioxide gas cylinder (A). The heat transfer oil is injected through the septum at the top of the absorption flask.

Experimental setup is given in Figure 4.1.

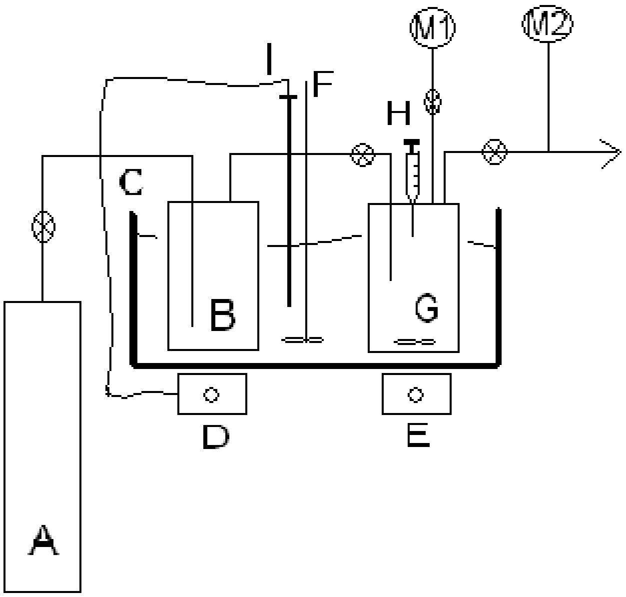

Figure 4.1 Experimental Setup

4.3 Sulfur Dioxide Absorption Experiment

Experiments were performed within the absorption flask, totally filled with sulfur dioxide. The principle of this method is to bring a known amount of liquid into contact with a gas in a closed system at a constant temperature.

The air in the system should be swept effectively to be able to fill the absorption flask completely with sulfur dioxide. Water pump, at the end of the gas exit line, is let to suck air and decrease the system pressure below 760 mm Hg pressure. Although the system is kept under vacuum, it is also necessary to let sulfur dioxide flow during suction in order to sweep all air in the absorption flask.

During suction, the mercury manometer line is closed in order to prevent any counter flow of mercury into the absorption flask being under vacuum, as a precaution. The digital manometer measures the vacuum pressure and helps setting the system pressure to a starting value. The precise pressure inside the absorption flask is measured by the mercury manometer after the inlet and outlet taps are closed and gate to the manometer is opened.

Pressure changes during absorption process were recorded after a known amount of oil is injected into the system at a constant temperature. In order to get more precise results at the evaluation of records, three injections with different amounts of oil were done in every experiment, resulting in drop of inside pressure below 760 mm Hg pressure. At each temperature, experiments were performed three times to be able to evaluate a statistical data and prove the repetition of the resulting values.

Sulfur dioxide absorption in the heat transfer oil has also been proven with infrared spectroscopy.

At each temperature, several pre-experiments have been performed in order to determine the pressure recording times. It has been noticed that most of the absorption had occurred in the first three minutes and a decreasing absorption capacity had been seen till the equilibrium reached at the end of the 15th minute.

The sensivity of the differential pressure read at the mercury manometer was 0.5 mm Hg and the pressure changes were recorded at 3rd, 5th, 10th and 15th minutes after each injection.

The sensivity of mass of oil injected was 0.0001 g.

The experiments were performed between 293 K and 313 K temperature interval. The temperature of the experimental setup was kept constant with the help of the contact thermometer in a water bath.

5. RESULTS AND DISCUSSION

5.1 Chemical Structure Determination of The Heat Transfer Oil

The BP Company stated that the heat transfer oil, Transcal N, is a mixture of saturated linear and cyclic hydrocarbons. However, detailed chemical composition of the oil has not been disclosed. Therefore, several analyses have been performed in order to determine the chemical structure, average empirical formula and average molecular weight of Transcal N to be used in related mass transfer calculations. These additional data are given as follows:

Boiling Range: 355 – 365 ^{0}C

Infrared (NaCl, neat) (cm^{-1}): 2921 (strong, C-H stretching);
2854 (s, C-H str., cycloalkane);
1461 (m, C-H deformation);
1377 (m, C-H deformation)

Elemental Analysis: C%: 87.36; H%: 13.48; N%: 0.00; S%: 0.00

Empirical Formula: $(CH_{1.838})_n \approx C_nH_{2n}$

The elemental analysis and GC-MS data indicate that the heat transfer oil is a hydrocarbon mixture with high molecular weights. It does not contain any N or S containing moieties, such as non-cyclic or heterocyclic groups, by which its non-polar and hydrophobic character appears.

Since the presence of unsaturated group containing chemicals would make the oil unstable against heat, the heat transfer oil contains saturated moieties which are proven by infrared spectroscopy and chemical means such as addition reactions. The infrared spectrum is given in Figure A.21 in Appendix.

GC-MS data and library comparisons indicated the hydrocarbon mixture had linear and cyclic hydrocarbons in the carbon range of 14 C-30 C. Also, empirical formula indicates the presence of cyclic hydrocarbons. The most abundant hydrocarbons are cyclotetradecane (C_{14}), tricosane (C_{23}), hexacosane (C_{26}), octacosane (C_{28}) and triacontane (C_{30}).

5.1.1 Average molecular weight of heat transfer oil

Average molecular weight of heat transfer oil has been evaluated from the abundance of the most probable hydrocarbons found in GC-MS data and by use of elemental analysis results.

Thus, the average empirical formula giving the C and H ratios is $C_{24.36}\,H_{44.79}$.

Average molecular weight of the heat transfer oil is 337.74 g/mole.

5.2 Sulfur Dioxide Solubility in Heat Transfer Oil

Sulfur dioxide solubility in heat transfer oil has been determined at five different temperatures in 293 K to 313 K interval. The experiments have been repeated three times and the results regarding the pressure changes by time are given in Appendix Table A.1-3 and plotted graphs in Figures A.1-5.

In the experiments, the pressure of the gas phase is observed. The vapor pressure of the oil is assumed to be negligible due to its high boiling point and vapor pressure lower than 1 mmHg at working temperatures.

5.2.1 Mole fractions of sulfur dioxide in the solvent

In order to calculate the number of moles of sulfur dioxide in the gas and liquid phases correctly, a volumetric adjustment coefficient, z', should be used at the equations due to decrease in gas volume after each oil injection.

If the initial mole number of sulfur dioxide in gas volume of V_0 is n_{0g}; and the unabsorbed sulfur dioxide moles in the gas phase is n_{ng}, for the initial stage and first oil injection:

$$P_0.V_0 = n_{0g}.R.T \quad , \tag{5.1}$$

$$P_1.V_1 = n_{1g}.R.T \tag{5.2}$$

can be written, respectively. Dividing each equation side by side,

$$\frac{P_0}{P_1}.\frac{V_0}{V_1} = \frac{n_{0g}}{n_{1g}} = z \tag{5.3}$$

is obtained. If, $V_0/V_1=z'$, then (5.4)

$$\frac{P_0}{P_1}.z' = \frac{n_{0g}}{n_{1g}} = z \tag{5.5}$$

can be written.

Thus, by use of the sulfur dioxide mole numbers in the gas phase before and after the injection, the number of moles of sulfur dioxide absorbed by oil, n_1(oil), can be calculated as follows:

$$n_{0g} - n_{1g} = n_1(oil) \tag{5.6}$$

$$n_{0g} - \frac{n_{0g}}{z} = n_1(oil) \tag{5.7}$$

$$n_{og}(1 - \frac{1}{z}) = n_1(oil) \tag{5.8}$$

where $z = \dfrac{P_0}{P_1}.z'$ (5.9)

Sulfur dioxide mole fraction in oil is calculated by use of number of moles of solute, n_n(oil), and total number of moles of solute and solvent, N_n oil, in the liquid phase:

$$X_{SO_2} = \frac{n_n(oil)}{(N_n + n_n)(oil)} \tag{5.10}$$

The evaluated data is given in Table 5.1.

Table 5.1 Evaluated Mole Fractions Data of Sulfur Dioxide

V_n (L)	**Z'**	**T (K)**	**Σ Inj. (g)**	**P_0 (mmHg)**	**P_n (mmHg)**	**$Z'.P_0/P_n$**	**n_0 SO_2 (gas)**	**n_n SO_2 (gas)**	**ΣN_n Oil**	**Σn_n SO2 (oil)**	**$\Sigma(N_n + n_n)$ (oil)**	**X_{S02}**
0.3100	1.0050	293	1.3440	814	783.0	1.0448	0.0139	0.0133	0.0040	0.00059	0.00457	0.13001
0.3090	1.0082		2.2142		765.0	1.0728		0.0129	0.0066	0.00094	0.00750	0.12562
0.3087	1.0090		2.4264		760.5	1.0800		0.0128	0.0072	0.00103	0.00821	0.12520
0.3098	1.0054	293	1.4598	811	775.0	1.0521	0.0138	0.0131	0.0043	0.00068	0.00501	0.13678
0.3091	1.0078		2.0982		759.5	1.0761		0.0128	0.0062	0.00098	0.00719	0.13604
0.3088	1.0088		2.3724		753.0	1.0865		0.0127	0.0070	0.00110	0.00813	0.13552
0.3101	1.0045	293	1.2250	828	797.5	1.0430	0.0141	0.0135	0.0036	0.00058	0.00421	0.13816
0.3087	1.0090		2.4060		771.5	1.0828		0.0130	0.0071	0.00108	0.00820	0.13164
0.3075	1.0130		3.4750		750.0	1.1183		0.0126	0.0103	0.00149	0.01178	0.12677
0.3100	1.0049	298	1.3228	814	786.0	1.0407	0.0136	0.0131	0.0039	0.00053	0.00445	0.11991
0.3090	1.0082		2.1962		768.5	1.0679		0.0128	0.0065	0.00087	0.00737	0.11765
0.3082	1.0107		2.8587		755.0	1.0896		0.0125	0.0085	0.00112	0.00959	0.11709
0.3099	1.0053	298	1.4239	828	797.5	1.0437	0.0139	0.0133	0.0042	0.00058	0.00480	0.12121
0.3083	1.0104		2.8002		770.5	1.0858		0.0128	0.0083	0.00110	0.00939	0.11688
0.3069	1.0151		4.0289		750.0	1.1207		0.0124	0.0119	0.00149	0.01342	0.11132
0.3099	1.0051	298	1.3729	830	800.0	1.0428	0.0139	0.0133	0.0041	0.00057	0.00464	0.12313
0.3083	1.0102		2.7472		772.5	1.0854		0.0128	0.0081	0.00110	0.00923	0.11865
0.3070	1.0147		3.9179		752.0	1.1199		0.0124	0.0116	0.00149	0.01309	0.11380
0.3098	1.0054	303	1.4542	815.5	789.0	1.0392	0.0134	0.0129	0.0043	0.00051	0.00481	0.10528
0.3087	1.0089		2.3965		772.5	1.0651		0.0126	0.0071	0.00082	0.00792	0.10376
0.3079	1.0116		3.1059		760.0	1.0855		0.0124	0.0092	0.00106	0.01025	0.10322
0.3099	1.0052	303	1.4042	816	789.0	1.0396	0.0135	0.0129	0.0042	0.00051	0.00467	0.10974
0.3089	1.0085		2.2713		772.5	1.0652		0.0126	0.0067	0.00082	0.00755	0.10914
0.3081	1.0110		2.9588		759.5	1.0863		0.0124	0.0088	0.00107	0.00983	0.10867
0.3098	1.0053	303	1.4361	828	799.5	1.0412	0.0137	0.0131	0.0043	0.00054	0.00479	0.11263
0.3081	1.0109		2.9302		774.0	1.0815		0.0126	0.0087	0.00103	0.00970	0.10595
0.3066	1.0159		4.2370		752.5	1.1178		0.0122	0.0125	0.00144	0.01398	0.10288

Table 5.1 Evaluated Mole Fractions Data of Sulfur Dioxide (continued)

V_n (L)	Z'	T (K)	Σ Inj. (g)	P_0 (mmHg)	P_n (mmHg)	$Z'.P_0/P_n$	n_0 SO_2 (gas)	n_n SO_2 (gas)	ΣN_n Oil	Σn_n SO2 (oil)	$\Sigma(N_n + n_n)$ (oil)	X_{S02}
0.3096	1.0062	308	1.6781	816	787.5	1.0426	0.0132	0.0127	0.0050	0.00054	0.00551	0.09824
0.3085	1.0096		2.5757		772.5	1.0664		0.0124	0.0076	0.00082	0.00845	0.09757
0.3075	1.0129		3.4442		758.5	1.0897		0.0121	0.0102	0.00109	0.01129	0.09647
0.3096	1.0062	308	1.6600	815	787.0	1.0420	0.0132	0.0127	0.0049	0.00053	0.00545	0.09771
0.3085	1.0098		2.6168		771.0	1.0674		0.0124	0.0077	0.00083	0.00858	0.09721
0.3074	1.0133		3.5458		756.0	1.0923		0.0121	0.0105	0.00112	0.01162	0.09618
0.3098	1.0055	308	1.4759	817	792.0	1.0372	0.0133	0.0128	0.0044	0.00048	0.00485	0.09811
0.3080	1.0112		3.0139		768.5	1.0751		0.0123	0.0089	0.00093	0.00985	0.09394
0.3066	1.0158		4.2257		751.5	1.1044		0.0120	0.0125	0.00125	0.01376	0.09098
0.3092	1.0074	313	1.9849	820	790.5	1.0450	0.0131	0.0125	0.0059	0.00056	0.00644	0.08745
0.3075	1.0129		3.4457		769.5	1.0794		0.0121	0.0102	0.00096	0.01116	0.08617
0.3066	1.0160		4.2794		757.5	1.0999		0.0119	0.0127	0.00119	0.01386	0.08574
0.3099	1.0051	313	1.3848	811.5	790.0	1.0325	0.0130	0.0125	0.0041	0.00041	0.00451	0.09041
0.3083	1.0104		2.7939		769.5	1.0656		0.0122	0.0083	0.00080	0.00907	0.08787
0.3073	1.0137		3.6654		756.5	1.0874		0.0119	0.0109	0.00104	0.01189	0.08753
0.3098	1.0055	313	1.4702	819.5	795.5	1.0358	0.0131	0.0126	0.0044	0.00045	0.00480	0.09405
0.3080	1.0114		3.0510		773.5	1.0715		0.0122	0.0090	0.00087	0.00991	0.08813
0.3064	1.0167		4.4512		755.0	1.1036		0.0119	0.0132	0.00123	0.01441	0.08519

5.2.2 Expressions of sulfur dioxide solubility in heat transfer oil

In this study, the sulfur dioxide solubility in heat transfer oil is expressed in four different ways; such as mole fraction of sulfur dioxide at standard pressure, Henry's constant, Ostwald's coefficient and solubility in unit volume of solvent.

5.2.2.1 Mole fraction of sulfur dioxide in heat transfer oil at standard pressure

Linear correlations have been calculated with the help of graphs plotted between the pressure and sulfur dioxide mole fractions for each experiment. The correlation equations are given on the figures A6-20 at Appendix.

Sulfur dioxide mole fractions are calculated at standard pressure, 760 mmHg, and the solubility mole fractions at five different temperatures are given in Table 5.2.

The mole fraction expresses the sulfur dioxide solute percentage on the total molar bases of solute and solvent. This mole fraction expression is almost equal to mole ratio of reactants [(n_n(oil)/N_n oil)] for low values, such as x = 0.01. However, for higher mole fractions, as in this research, such as x = 0.12 at 298 K, they can not be taken as same.

Table 5.2 Mole Fractions of Sulfur Dioxide at 760 mmHg

TEMPERATURE	**20^0C**	**25^0C**	**30^0C**	**35^0C**	**40^0C**
Exp. #1	0.1247	0.1171	0.1029	0.0965	0.0856
Exp. #2	0.1358	0.1137	0.1085	0.0963	0.0873
Exp. #3	0.1289	0.1155	0.1037	0.0923	0.0857
Mean	0.1298	0.1154	0.1051	0.0950	0.0862
Standard Deviation	0.0056	0.0017	0.0030	0.0024	0.0009
95% Conf. Interval	0.1298±0.0140	0.1154±0.0043	0.1051±0.0076	0.0950±0.0058	0.0862±0.002

5.2.2.2 Henry’s constant

Henry’s constant has been calculated by the equation,

$$H(mmHg\ /\ molefrac.) = \frac{P}{X} \tag{5.11}$$

at 760 mmHg (1 atm). The results are given in Table 5.3. The correlation between Henry’s constant and temperature is observed to be linear in 293 K to 313 K temperature interval in Figure 5.1. The following equation expresses the Henry’s constant change, H (mmHg/m.f.), by temperature, T (K).

$$H(mmHg\ /\ X_{SO_2}) = 146.49T(K) - 37085 \tag{5.12}$$

$$R^2 = 0.9984 \tag{5.13}$$

Table 5.3 Henry’s Constants (mmHg/m.f.)

TEMPERATURE	20^{0}C	25^{0}C	30^{0}C	35^{0}C	40^{0}C
Exp. #1	6096.45	6490.08	7384.89	7876.96	8873.98
Exp. #2	5595.12	6686.36	7001.52	7891.33	8706.70
Exp. #3	5894.63	6580.20	7327.47	8231.98	8870.25
Mean	5862.06	6585.55	7237.96	8000.09	8816.98
Standard Deviation	252.24	98.25	206.76	200.95	95.52
95% Conf. Interval	5862.06±626.65	6585.55±244.08	7237.96±513.66	8000.09±499.23	8816.98±237.30
Relative SD	4.30%	1.49%	2.85%	2.51%	1.08%

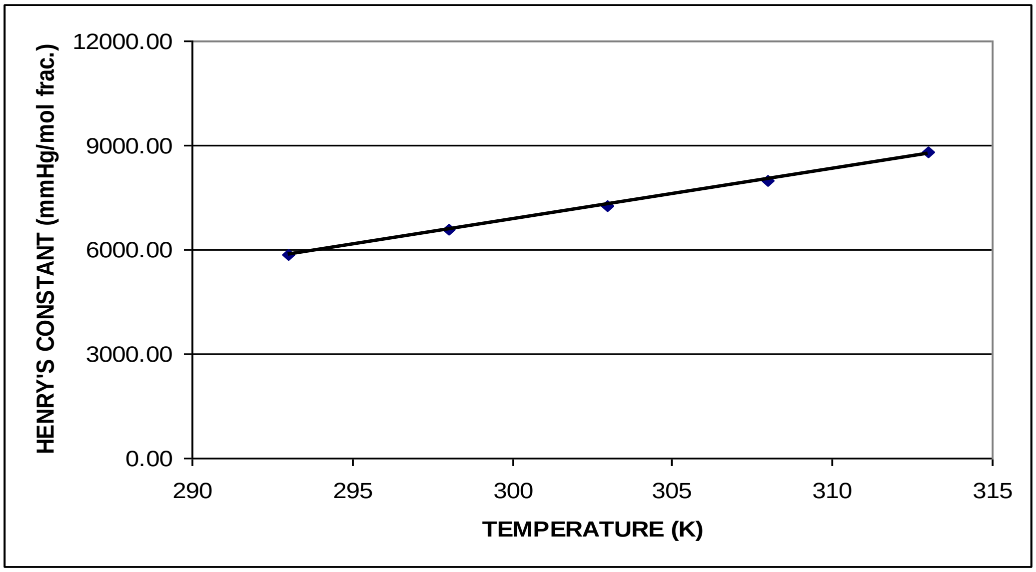

Figure 5.1 Temperature Dependence of Henry's Constant

The plot between Log H and 1/T is linear. This linearity is a typical of solutions with decreasing solubility by increasing temperature [36]. Figure 5.2 shows this relation.

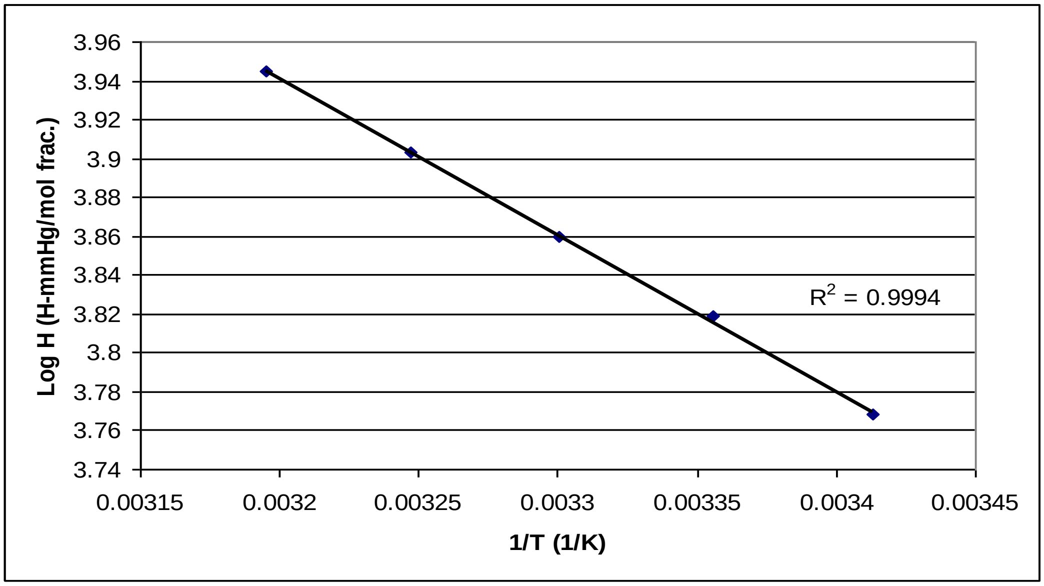

Figure 5.2 Henry's Constant for Sulfur Dioxide Solubility in Heat Transfer Oil

5.2.2.3 Ostwald's coefficient

Ostwald's coefficient is calculated with the acceptable ideal gas behavior in which solvent expansion upon dissolving gas is negligible. If V^0_{oil} is the volume of pure oil at a specified temperature and total p pressure, and V_{gas} is the absorbed gas volume, L^0_V, Ostwald's coefficient is calculated by:

$$L_V^0\,(mL/mL_{oil}) = \left(\frac{V_{gas}}{V_{oil}^0}\right)_{equil.} \tag{5.14}$$

The results for total 760 mmHg pressure are given in Table 5.4 and the correlation showing the decrease of Ostwald's coefficient by increasing temperature can be seen in Figure 5.3. The correlation is observed to be linear in 293 K to 313 K temperature interval. The following equation expresses the Ostwald's coefficient, L^0_V (mL_{SO2}/mL_{oil}), change by temperature, T (K). This coefficient can be defined as a volumetric ratio of sulfur dioxide absorption.

$$L_V^0\,(mL_{SO_2}/mL_{oil}) = -0.1469\,T(K) + 52.113 \tag{5.15}$$

$$R^2 = 0.9881 \tag{5.16}$$

Table 5.4 Ostwald's Coefficients at 760 mmHg Total Pressure (mL/mL_{oil})

TEMPERATURE	20⁰C	25⁰C	30⁰C	35⁰C	40⁰C
Exp. #1	8.8167	8.3713	7.3547	6.9549	6.1985
Exp. #2	9.7356	8.0675	7.7977	6.9419	6.3790
Exp. #3	9.1654	8.2179	7.4024	6.6212	6.1955
Mean	9.2393	8.2189	7.5183	6.8393	6.2576
Standard Deviation	0.4639	0.1519	0.2430	0.1890	0.1051
95% Conf. Interval	9.24±1.15	8.22±0.38	7.52±0.60	6.84±0.47	6.26±0.26

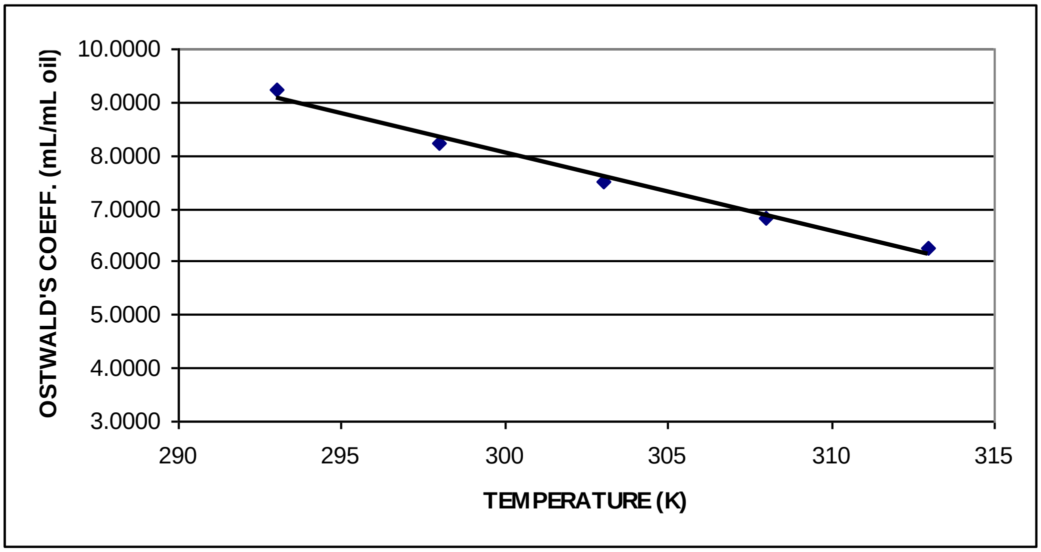

Figure 5.3 Temperature Dependence of Ostwald's Coefficient

5.2.2.4 Solubility of sulfur dioxide in unit volume of oil

Solubility values of sulfur dioxide in unit volume of oil are calculated from Ostwald's coefficient and are given in Table 5.5.

The correlation is observed to be linear in 293 K to 313 K temperature interval in Figure 5.4. The following equation expresses the solubility, s (g_{SO2}/L_{oil}), change by temperature, T (K).

$$s(g_{SO_2}/L_{oil}) = -0.4439T(K) + 154.18 \tag{5.17}$$

$$R^2 = 0.9874 \tag{5.18}$$

Table 5.5 Solubility Data (g_{SO2}/L_{oil}) at 760 mmHg Total Pressure

TEMPERATURE	**20^0C**	**25^0C**	**30^0C**	**35^0C**	**40^0C**
Exp. #1	23.4704	21.9108	18.9322	17.6125	15.4462
Exp. #2	25.9166	21.1155	20.0726	17.5795	15.8961
Exp. #3	24.3986	21.5093	19.0550	16.7674	15.4386
Mean	24.5952	21.5120	19.3533	17.3198	15.5936
Standard Deviation	1.2348	0.3977	0.2430	0.4786	0.2619
95% Conf. Interval	24.59±3.07	21.51±0.99	19.35±1.55	17.32±1.19	15.59±0.65

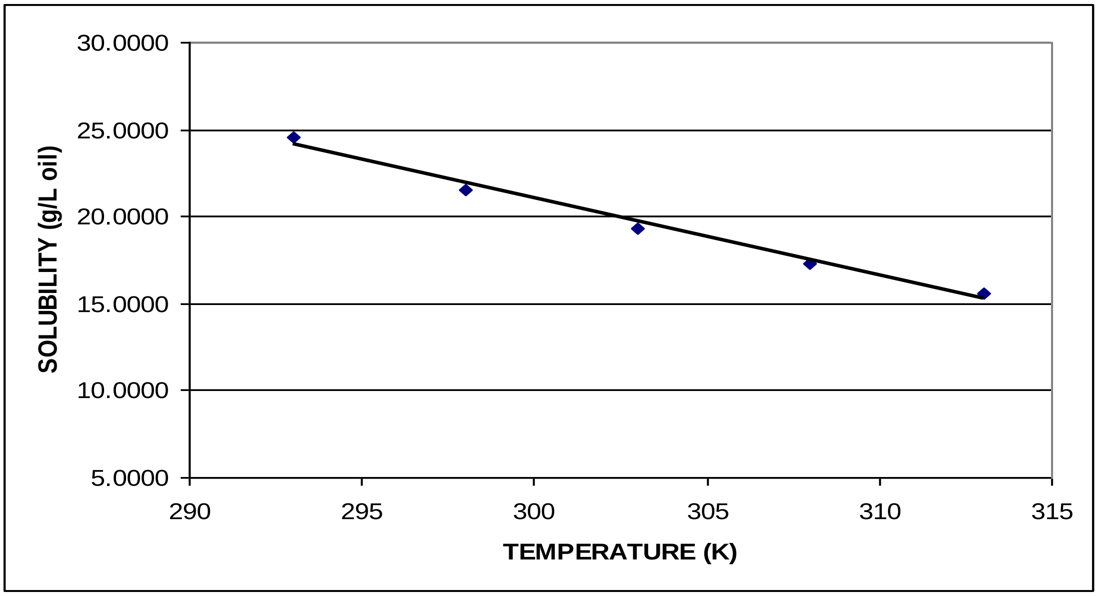

Figure 5.4 Temperature Dependence of Solubility

5.2.3 Infrared data of sulfur dioxide in heat transfer oil

Sulfur dioxide absorption in the heat transfer oil has also been proven with infrared spectroscopy. The infrared spectrum is given in Figure A.22 in Appendix.

Infrared (NaCl, neat) (cm^{-1}): 2921 (strong, C-H stretching);
2853 (s, C-H str., cycloalkane);
2357, 2340 (m, S=O str.);
1459 (m, C-H deformation);
1122 (w, S-O bending).

5.2.4 Equilibrium between gas and liquid phases and heat of dissolution

At a specified temperature and pressure, sulfur dioxide is dissolved in heat transfer oil to reach equilibrium. The mass transfer equilibrium can be written as:

$$SO_2 \text{ (gas)} \leftrightarrows SO_2 \text{ (oil)} \qquad (5.19)$$

At equilibrium, the initial n_0 mole sulfur dioxide is reduced by the absorption of n_{SO_2} (oil) mole sulfur dioxide. Thus, the equilibrium constant, K, of heat transfer oil with non-volatile character at working temperatures can be calculated as follows:

$$K = \frac{[SO_2]_{oil}}{[SO_2]_{gas}} = \frac{n_{SO_2}(oil) \big/ V_{oil}}{n_0 - n_0(oil) \big/ V - V_{oil}} \tag{5.20}$$

The equilibrium constants, $K_{1,2,..,5}$, are dependent on temperature (T) and the slope of the plot between Log K and 1/T has been evaluated to calculate the heat of dissolution according to the following equation.

$$\Delta H^0(cal) = -slope 2.303 R \tag{5.21}$$

The correlation is observed to be linear in 293 K to 313 K temperature interval in Figure 5.5. The following equation expresses the logarithm of equilibrium constant, Log K, change by temperature, 1/T, with the slope of 767.82.

$$LogK = 767.82(1/T) - 4.6578 \tag{5.22}$$

$$R^2 = 0.9973 \tag{5.23}$$

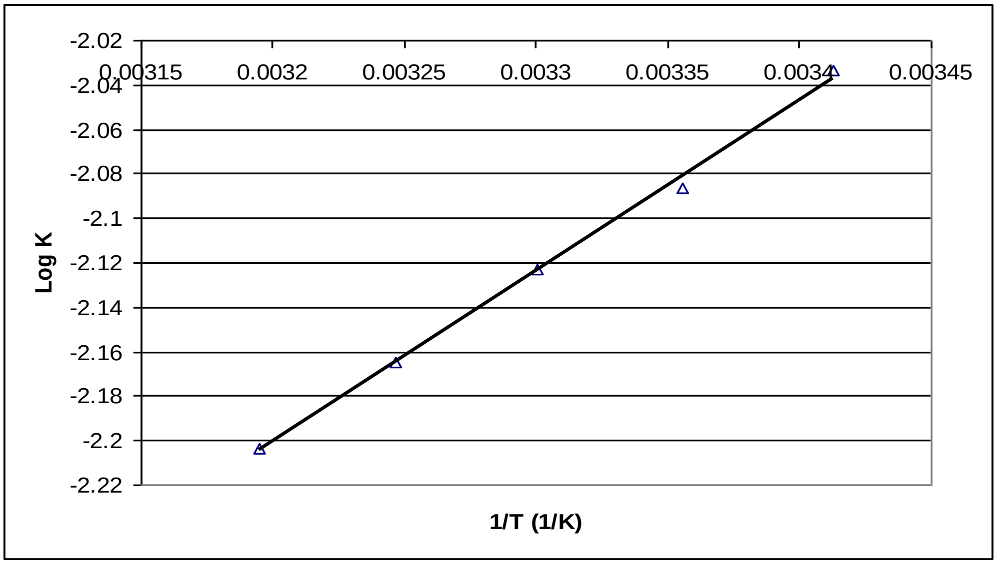

Figure 5.5 Log K – 1/T

The sulfur dioxide heat of dissolution in heat transfer oil is calculated to be -3513.6 calorie.

5.3 Discussion

Sulfur dioxide solubilities in several solvents have been investigated from literature. In some of the solvents such as pure water [37] or aqueous electrolyte solutions of sodium chloride or ammonium chloride [38], sulfuric and hydrochloric acids [39], seawater [40], and ammonia [41] sulfur dioxide gives ionic species, by which the dissolution mechanisms differ.

Sulfur dioxide solubilities in different organic solvents and heat transfer oil at 298 K are given in terms of Henry's constant in mmHg/m.f. in Table 5.6.

Table 5.6 Henry's Constants of Sulfur Dioxide in Different Organic Solvents [27] and Heat Transfer Oil at 298 K

SOLVENT	H_{SO2}, mmHg/m.f.
Heat Transfer Oil	6585.55
1,2-dichloroethane	3210.00
1,2-ethanediol	2588.00
diethyl ether	1776.00
nitrobenzene	1245.00
tetrahydrofuran	294.00
tributyl phosphate	258.80
diethylene gylcol-dimethyl ether	201.00
triethylene gylcol-dimethyl ether	192.75
tetraethylene gylcol-dimethyl ether	163.50
dimethyl formamide	129.00
dimethyl acetamide	89.20
dimethyl sulfoxide	89.20
dimethylaniline	69.76
pyridine	66.01

Sulfur dioxide solubility of the heat transfer oil is observed to be the minimum among all other organic solvents due to non-polar chemical composition of the oil. Sulfur dioxide can easily be dissolved in polar solvents which also act as Lewis base. Sulfur dioxide with electronic structures of its resonance forms can act both as a Lewis acid and also a Lewis base.

It can be stated that polar groups in organic solvents increase the sulfur dioxide solubility due to strong chemical interaction with sulfur or oxygen atoms of sulfur dioxide. On the other hand, with chemicals having unpaired electrons on oxygen atoms in their chemical structure, like diethyl ether, diethylene gylcol-dimethyl ether or tributyl phosphate, sulfur dioxide solubility increases with the increased number of oxygen atoms due to increased interaction strength with sulfur dioxide.

In spite of the higher solubility capacity of each of the above organic solvents, their physical properties are not suitable to be used at high flue gas temperatures. Most of them have low boiling and flash points affecting the maximum working temperature and are soluble in water making the regeneration process more difficult and expensive. Some give explosive mixtures at several limits which may cause explosion during absorption process. However, the heat transfer oil has very high boiling and flash points, safe to be used at high flue gas temperatures and is insoluble in water which is an advantage for an effective regeneration process to be developed. In the following, physical properties of the organic solvents and the heat transfer oil are given in Table 5.7.

Table 5.7 Physical Properties of The Organic Solvents [42] and The Heat Transfer Oil

SOLVENT	BOILING POINT	VAPOR PRESSURE	FLASH POINT	SOLUBILITY	EXPLOSION LIMIT
Heat Transfer Oil	355-365^{0}C		221^{0}C	insoluble	
1,2-dichloroethane	83^{0}C	387 mmHg@25^{0}C	15^{0}C	slightly	6.2% - 15.6%
1,2-ethanediol	197^{0}C	0.08 mmHg@20^{0}C	110^{0}C	miscible	3.2% - 15.3%
diethyl ether	34.6^{0}C	400 mmHg@18^{0}C	-40^{0}C	6.90%	1.7% - 48%
nitrobenzene	210^{0}C	0.15 mmHg@20^{0}C	87^{0}C	insoluble	1.8% - 40%
tetrahydrofuran	66^{0}C	129 mmHg@20^{0}C	-14^{0}C	miscible	1.5% - 12%
tributyl phosphate	289^{0}C	0.8 mmHg@114^{0}C	120^{0}C	slightly soluble	***
diethylene gylcol-dimethyl ether	162^{0}C	1.7 mmHg@20^{0}C	56^{0}C	miscible	
triethylene gylcol-dimethyl ether	216^{0}C		113^{0}C	miscible	
tetraethylene gylcol-dimethyl ether	276^{0}C	<0.01mmHg@20^{0}C	141^{0}C	miscible	
dimethyl formamide	153^{0}C	2.6 mmHg @ 20^{0}C	58^{0}C	miscible	2.2% - 15.2%
dimethyl acetamide	166^{0}C	9.0 mmHg @ 60^{0}C	70^{0}C	moderate	***
dimethyl sulfoxide	189^{0}C	0.42 mmHg @20^{0}C	85^{0}C	moderate	3.5% - 42%
dimethylaniline	194^{0}C	10 mmHg @20^{0}C	63^{0}C	<0.1%	1% - 7%
pyridine	115^{0}C	16 mmHg @20^{0}C	19^{0}C	miscible	1.8% - 12.4%

*** gives explosive vapor-air mixtures above flash point

The sulfur dioxide solubility in the heat transfer oil has been compared with the data given at different temperatures for dimethyl sulfoxide (DMSO) [43]. The sulfur dioxide solubility in DMSO has been reported over a limited temperature and partial pressure ranges of sulfur dioxide by Benon [44] and Lenoir [45] at 298 K; Kurochkin [46] have worked at one partial pressure of sulfur dioxide. Li [43] and co-workers have studied at temperature range of 293 K- 313 K and partial pressures of sulfur dioxide from 1.125 mm Hg - 19.65 mm Hg.

Comparison with the Li's results [43] can be done by making related unit conversions because the constant used in their work is referred as a proportionality constant which can be used as Henry's constant according to their study.

DMSO, CH_3-SO-CH_3, is a polar solvent and interactions between sulfur dioxide and DMSO is stronger than the interactions between non-polar hydrocarbons and sulfur dioxide. The molecular interaction explanation can be seen by numbers in Table 5.8.

Table 5.8 Comparison of The Sulfur Dioxide Solubility in DMSO [43] and Heat Transfer Oil

Temperature (K)	**H* (kPa.kg.mol^{-1})**	**H** (kPa.kg.mol^{-1})**
293	0.9591	229.4
298	1.0787	262.2
303	1.2203	291.6
308	1.4661	325.7
313	1.8659	361.8

*DMSO
**Heat Transfer Oil
H is proportionality constant, $H=P_{SO2}(kPa)/n_{so2}(mol/kg)$

Since, DMSO is hydrophilic its sulfur dioxide dissolving property would not help in removing sulfur dioxide from flue gases, which also contain water. Re-use of DMSO would not be possible.

Only example for polar and hydrophobic solvent of sulfur dioxide is R227ea(1,1,1,2,3,3,3-heptafluoropropane), a refrigerant. However, it gives azeotropic mixture with sulfur dioxide [47].

The presented research deals with the sulfur dioxide dissolving capability of the non-polar and hydrophobic solvent mixture, heat transfer oil, in temperature range of 293 K - 313 K.

Sulfur dioxide solubility is dependent on temperature and the Henry's constant can be calculated with the help of the following relation, in the working temperature range:

$$H(mmHg / X_{SO_2}) = 146.49T(K) - 37085 \tag{5.24}$$

Ostwald's coefficient can be calculated with the help of the following relation, in the working temperature range:

$$L_V^0 (mL / mL_{oil}) = -0.1469\,T(K) + 52.113 \tag{5.25}$$

The solubility in grams per liter oil can be calculated with the equation:

$$s(g / L_{oil}) = -0.4439\,T(K) + 154.18 \tag{5.26}$$

The sulfur dioxide dissolution in heat transfer oil is exothermic ($\Delta H<0$) and the solubility of the gas decreases with increasing temperature in the working temperature interval (293 K – 313 K).

Although the chemical composition of heat transfer oil contains linear and cyclic alkanes with high molecular weight, it has significant sulfur dioxide dissolution capacity. The solubility data of sulfur dioxide in heat transfer oil indicated that the hydrophobic and non-polar properties of the oil would not be a disadvantage for its use in sulfur dioxide absorption processes. The oil with its high flash and boiling points is safe and dissolves sulfur dioxide at remarkable ratios. Sulfur dioxide can be transferred into water and the oil can be re-used without significant loss. This research can be represented as a starting point and contains the data at low temperatures for determining the absorption capacity of heat transfer oil.

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APPENDIX

Table A.1 Differential Pressure Changes by Time at 293 K

	PRESSURE (mmHg)					
TIME (min.)	**20 ^{0}C**					
	$W_{injection}$ (g)	**Exp. # 1**	**$W_{injection}$ (g)**	**Exp. # 2**	**$W_{injection}$ (g)**	**Exp. # 3**
0	-	54.0	-	51.0	-	68.0
	1.3440		1.4598		1.2250	
3		30.0		23.0		43.0
5		27.5		20.0		41.5
10		24.0		16.0		38.5
15		23.0		15.0		37.5
	0.8702		0.6384		1.1810	
3		8.0		3.5		16.0
5		6.0		2.0		14.5
10		6.0		0.0		12.5
15		5.0		-0.5		11.5
	0.2122		0.2742		1.0690	
3		2.5		-4.5		-6.0
5		2.0		-5.0		-8.0
10		1.0		-6.5		-9.0
15		0.5		-7.0		-10.0

Table A.2 Differential Pressure Changes by Time at 298 K

	PRESSURE (mmHg)					
TIME (min.)	**25 ^{0}C**					
	W$_{injection}$ (g)	**Exp. # 1**	**W$_{injection}$ (g)**	**Exp. # 2**	**W$_{injection}$ (g)**	**Exp. # 3**
0	-	54.0	-	68.0	-	70.0
	1.3228		1.4239		1.3729	
3		31.0		42.5		45.0
5		30.0		40.5		43.0
10		27.0		38.5		41.0
15		26.0		37.5		40.0
	0.8734		1.3763		1.3743	
3		12.0		15.5		17.5
5		11.5		13.5		16.0
10		9.5		12.0		14.0
15		8.5		10.5		12.5
	0.6625		1.2287		1.1707	
3		-2.0		-6.5		-5.5
5		-2.0		-8.0		-6.5
10		-3.0		-9.0		-7.0
15		-5.0		-10.0		-8.0

Table A.3 Differential Pressure Changes by Time at 303 K

	PRESSURE (mmHg)					
TIME (min.)	**30 ^{0}C**					
	W$_{injection}$ (g)	**Exp. # 1**	**W$_{injection}$ (g)**	**Exp. # 2**	**W$_{injection}$ (g)**	**Exp. # 3**
0	-	55.5	-	56.0	-	68.0
	1.4542		1.4042		1.4361	
3		33.0		33.0		43.5
5		32.0		32.0		43.0
10		30.0		30.0		41.0
15		29.0		29.0		39.5
	0.9423		0.8671		1.4941	
3		15.0		14.5		17.0
5		15.0		14.5		16.5
10		14.0		13.0		15.0
15		12.5		12.5		14.0
	0.7094		0.6875		1.3068	
3		3.0		1.5		-4.5
5		2.0		1.0		-5.0
10		0.0		0.0		-7.0
15		0.0		-0.5		-7.5

Table A.4 Differential Pressure Changes by Time at 308 K

	PRESSURE (mmHg)					
TIME (min.)	**35 ^{0}C**					
	$W_{injection}$ (g)	**Exp. # 1**	**$W_{injection}$ (g)**	**Exp. # 2**	**$W_{injection}$ (g)**	**Exp. # 3**
0	-	56.0	-	55.0	-	57.0
	1.6781		1.6600		1.4759	
3		33.0		31.5		36.0
5		32.0		31.0		35.0
10		28.5		28.5		33.5
15		27.5		27.0		32.0
	0.8976		0.9568		1.5380	
3		16.0		15.0		13.0
5		15.5		14.5		12.0
10		14.0		12.0		10.0
15		12.5		11.0		8.5
	0.8685		0.9290		1.2118	
3		0.5		-0.5		-5.5
5		0.0		-1.0		-6.0
10		-0.5		-3.0		-7.5
15		-1.5		-4.0		-8.5

Table A.5 Differential Pressure Changes by Time at 313 K

	PRESSURE (mmHg)					
TIME (min.)	**40 ^{0}C**					
	$W_{injection}$ (g)	**Exp. #1**	**$W_{injection}$ (g)**	**Exp. # 2**	**$W_{injection}$ (g)**	**Exp. # 3**
0	-	52.0	-	51.5	-	59.5
	1.6685		1.3848		1.4702	
3		33.0		35.0		40.0
5		32.0		34.0		39.5
10		31.0		31.5		36.5
15		30.5		30.0		35.5
	1.1209		1.4091		1.5808	
3		15.5		12.0		16.5
5		15.0		11.5		16.5
10		10.0		10.0		14.5
15		9.5		9.5		13.5
	0.9367		0.8715		1.4002	
3		0.0		-0.5		-3.0
5		-0.5		-1.5		-3.5
10		-2.0		-2.5		-4.5
15		-3.0		-3.5		-5.0

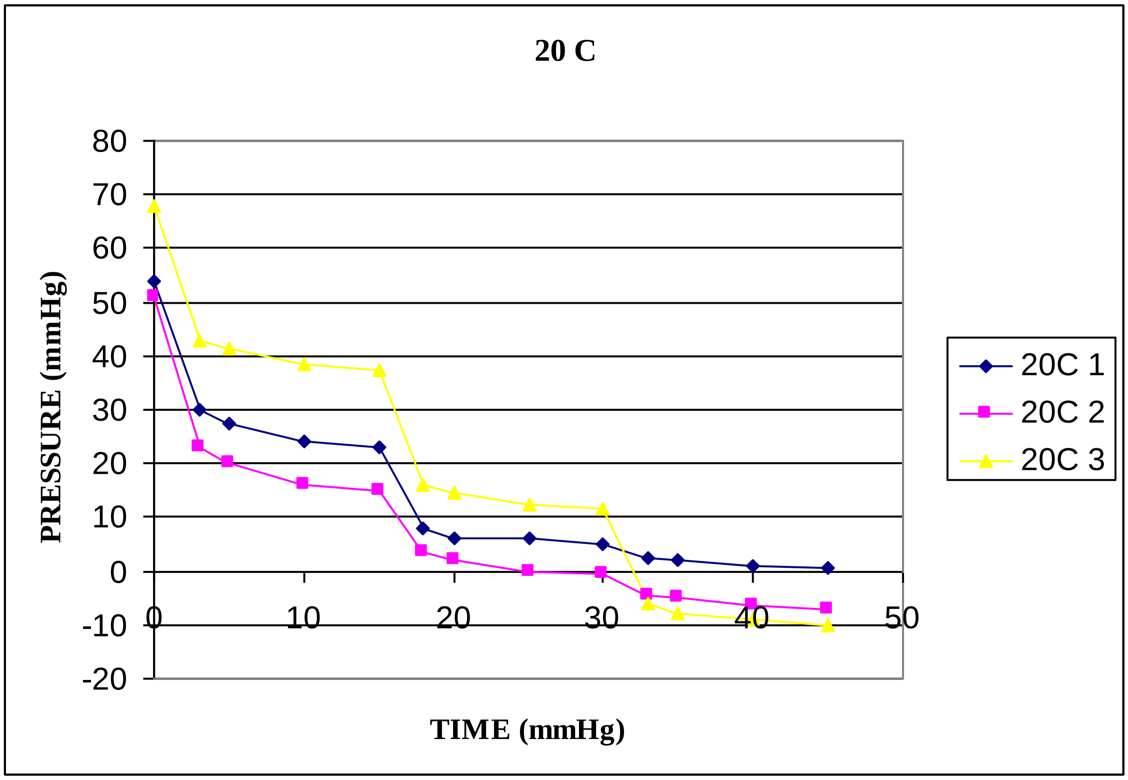

Figure A.1 Differential Pressure Change by Time at 293 K

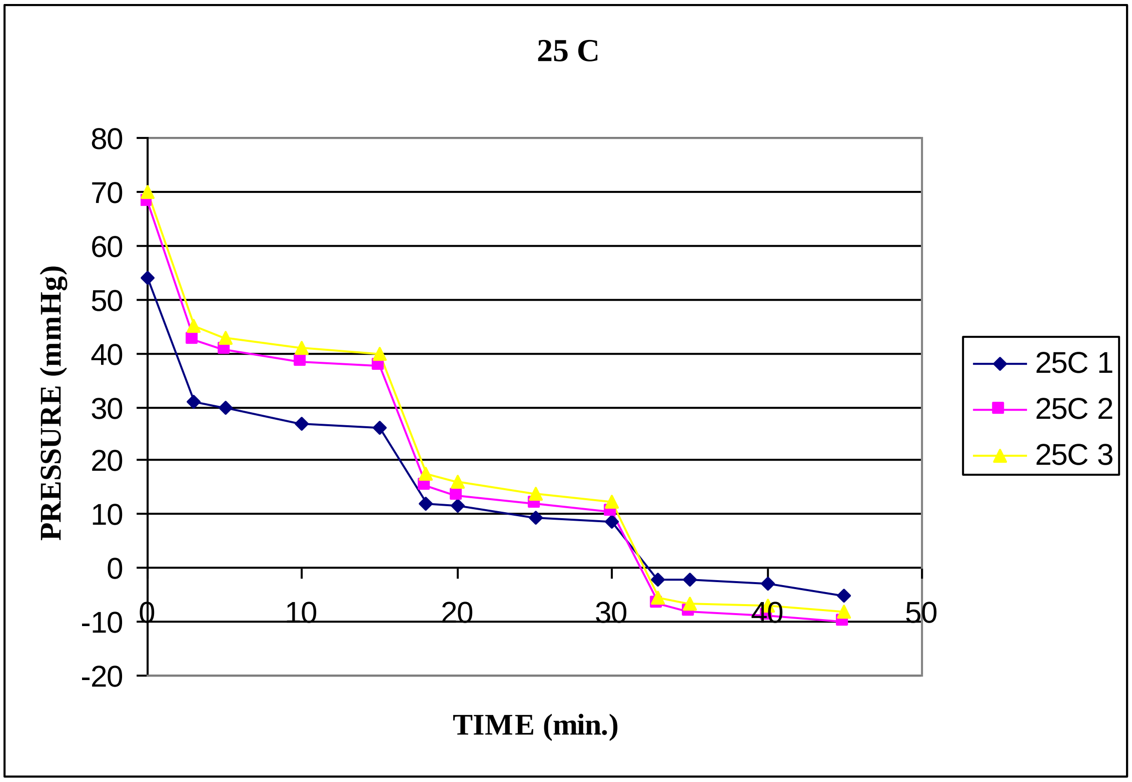

Figure A.2 Differential Pressure Change by Time at 298 K

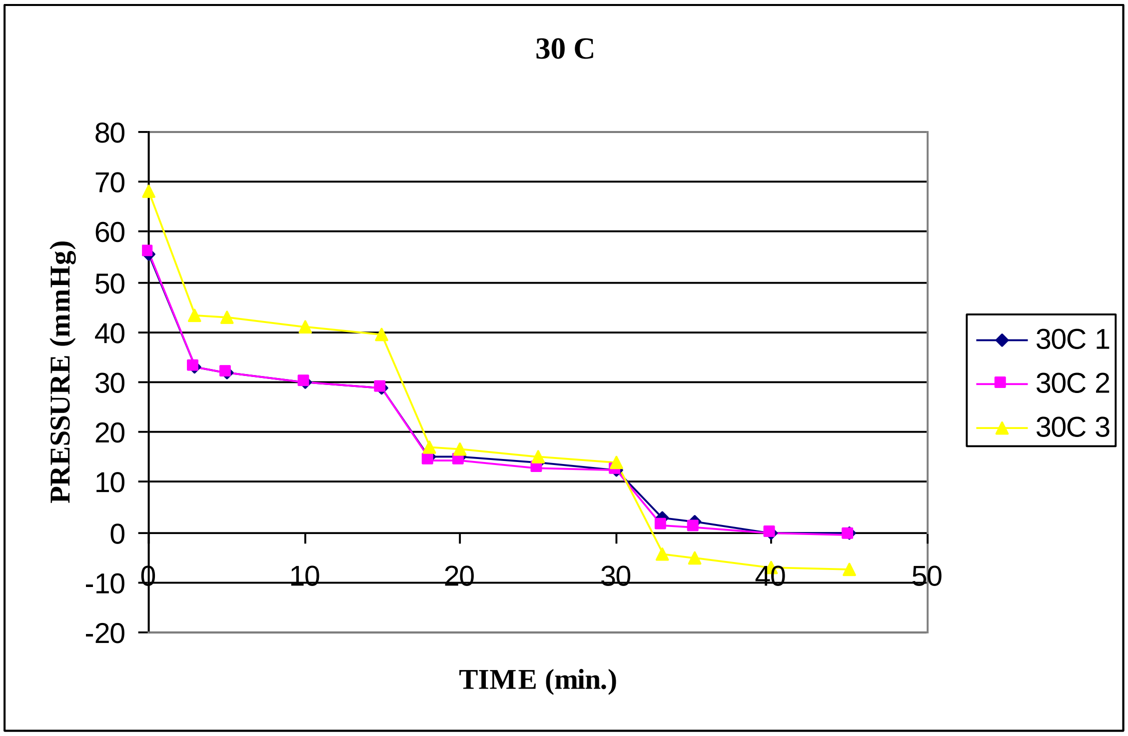

Figure A.3 Differential Pressure Change by Time at 303 K

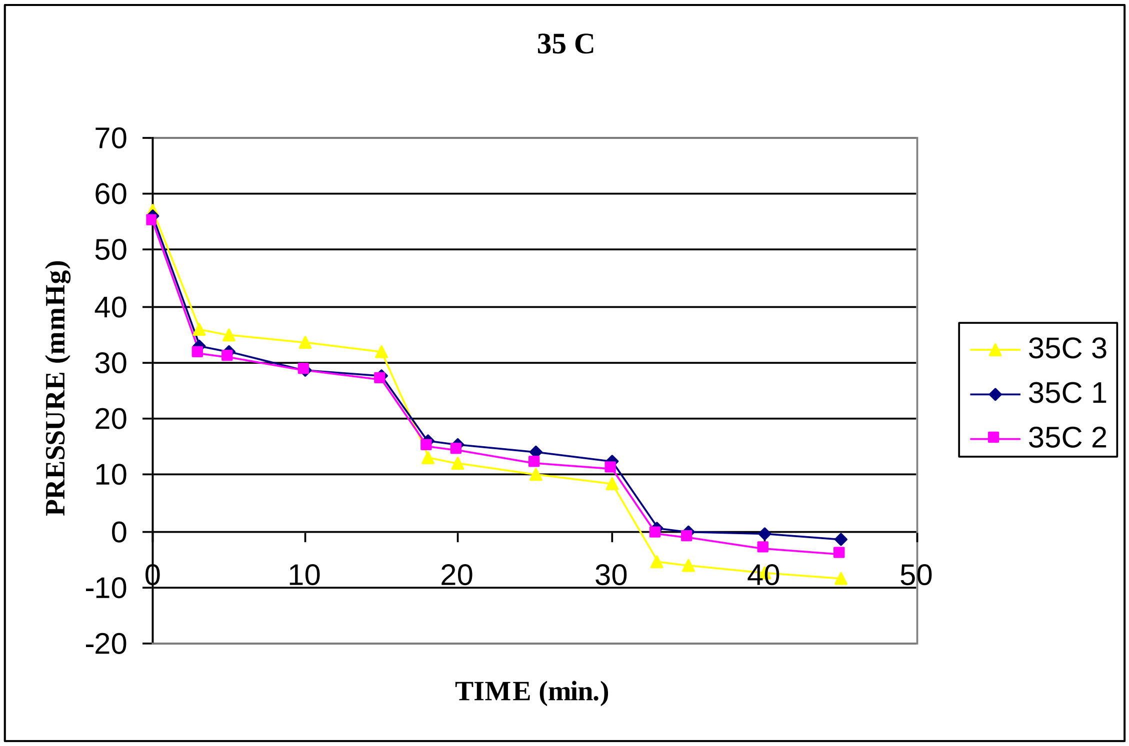

Figure A.4 Differential Pressure Change by Time at 308 K

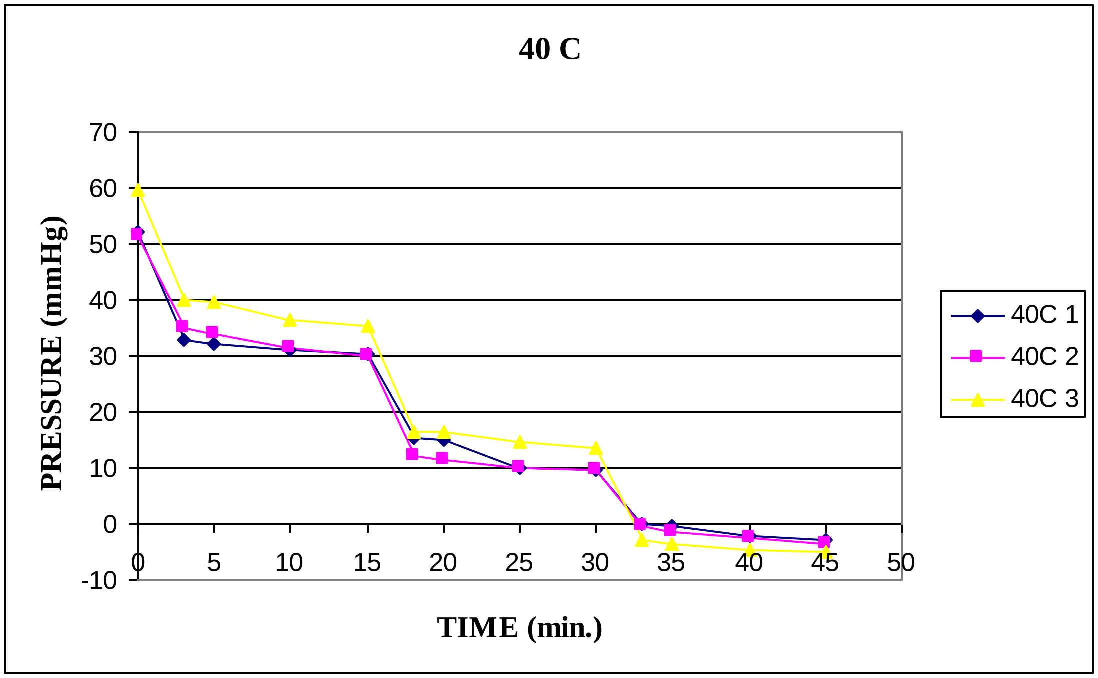

Figure A.5 Differential Pressure Change by Time at 313 K

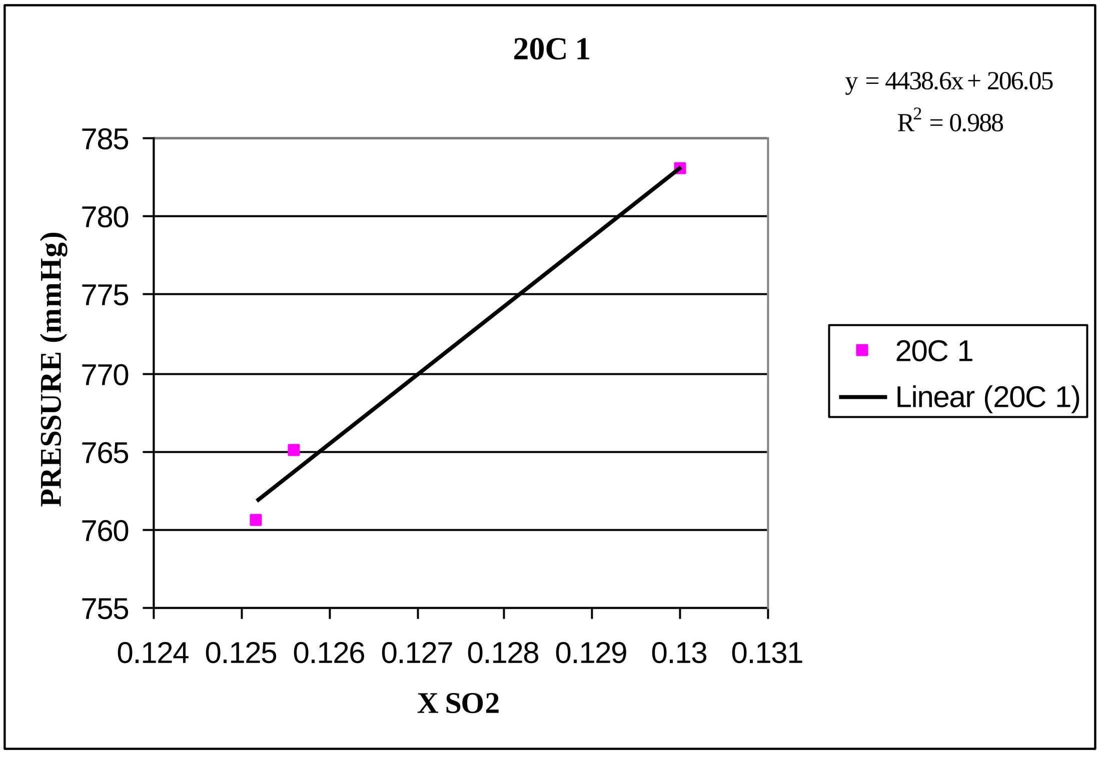

Figure A.6 Pressure vs. Sulfur Dioxide Mole Fraction at 293 K (1)

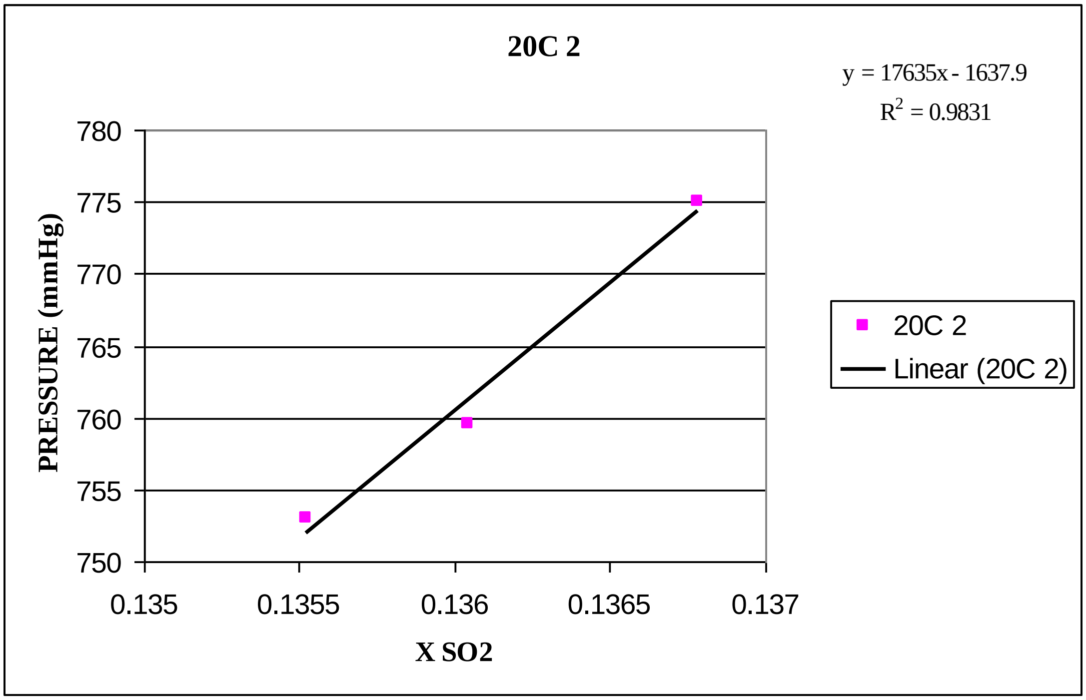

Figure A.7 Pressure vs. Sulfur Dioxide Mole Fraction at 293 K (2)

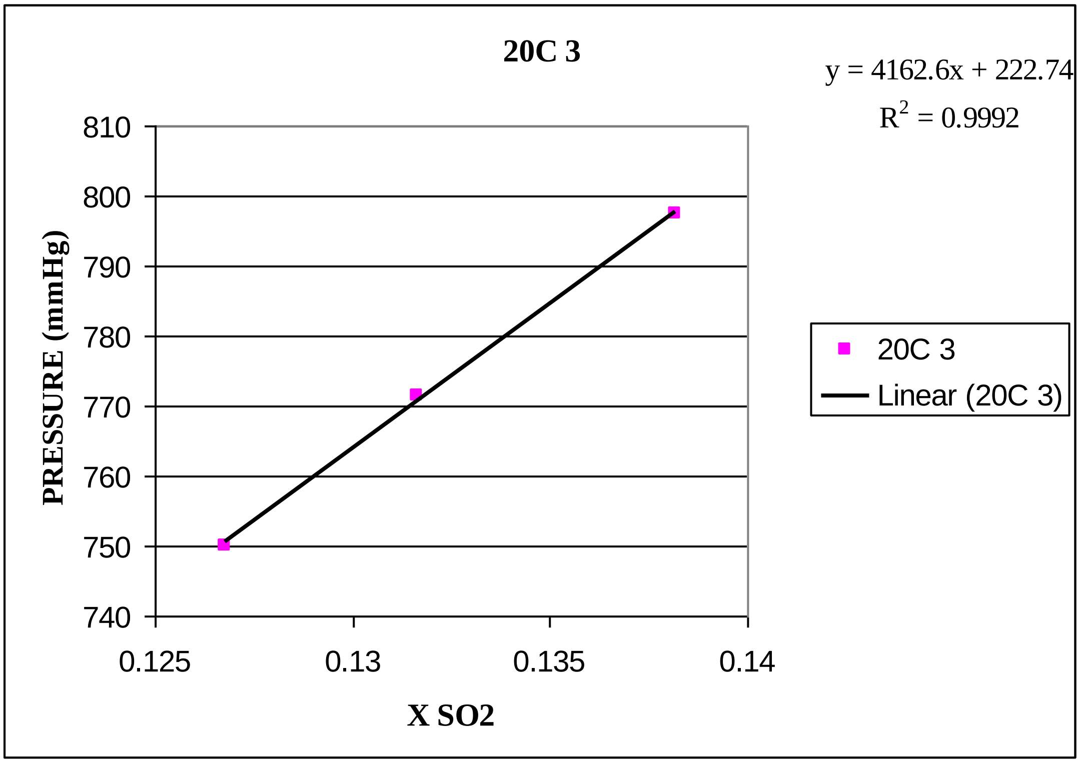

Figure A.8 Pressure vs. Sulfur Dioxide Mole Fraction at 293 K (3)

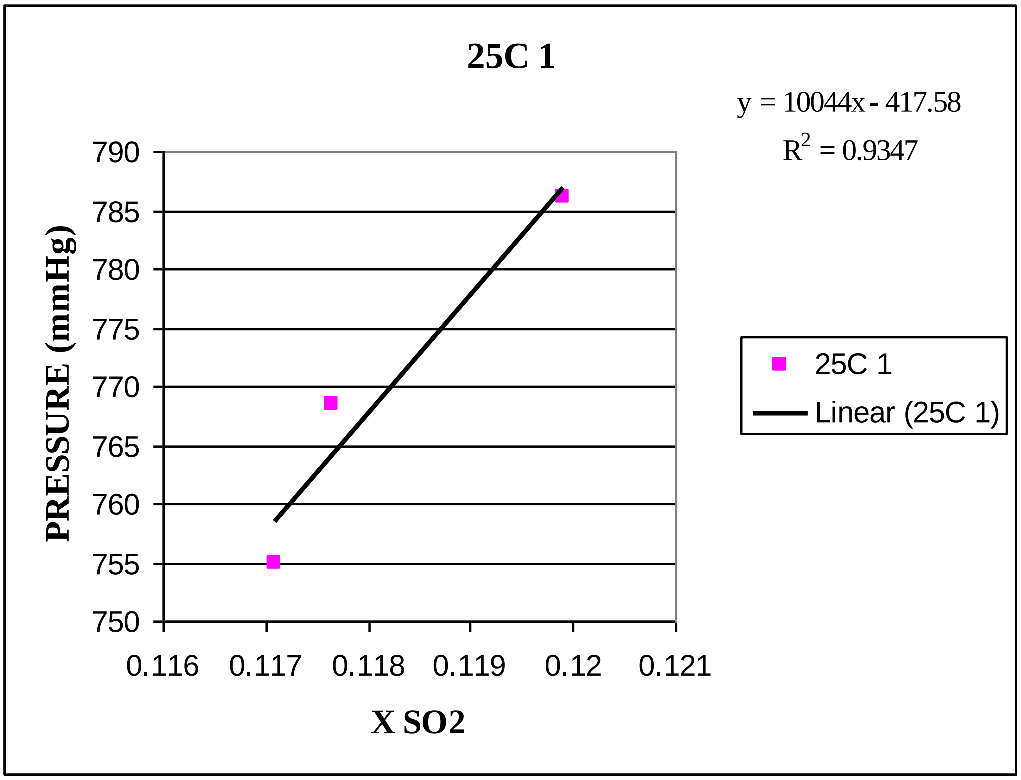

Figure A.9 Pressure vs. Sulfur Dioxide Mole Fraction at 298 K (1)

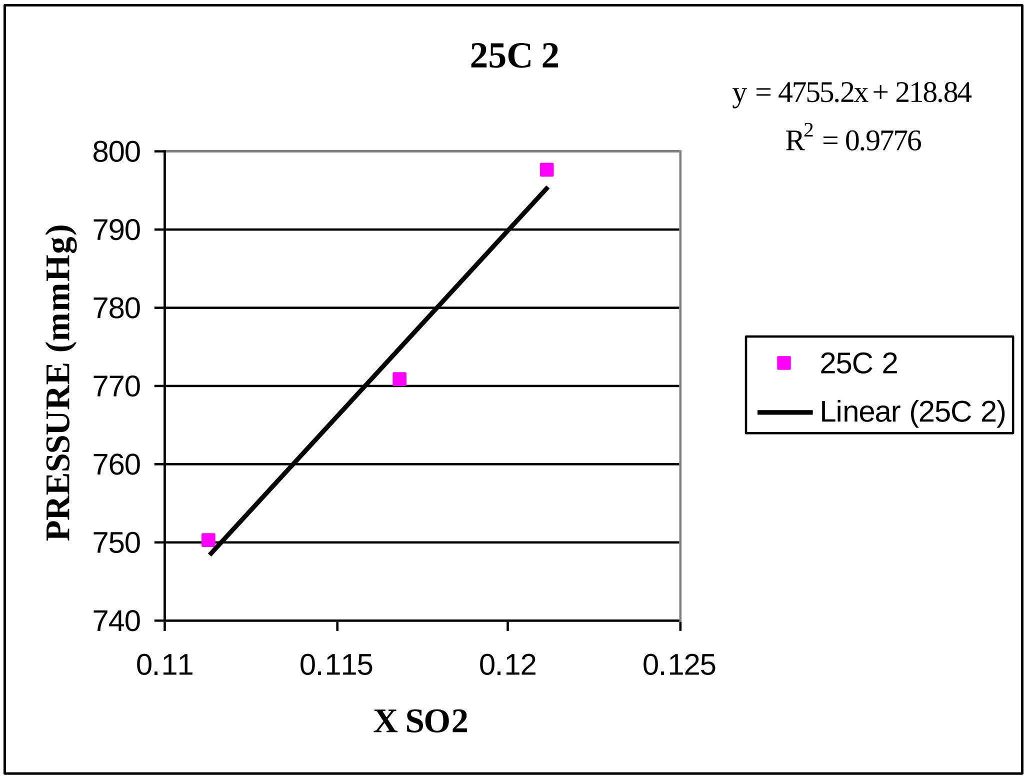

Figure A.10 Pressure vs. Sulfur Dioxide Mole Fraction at 298 K (2)

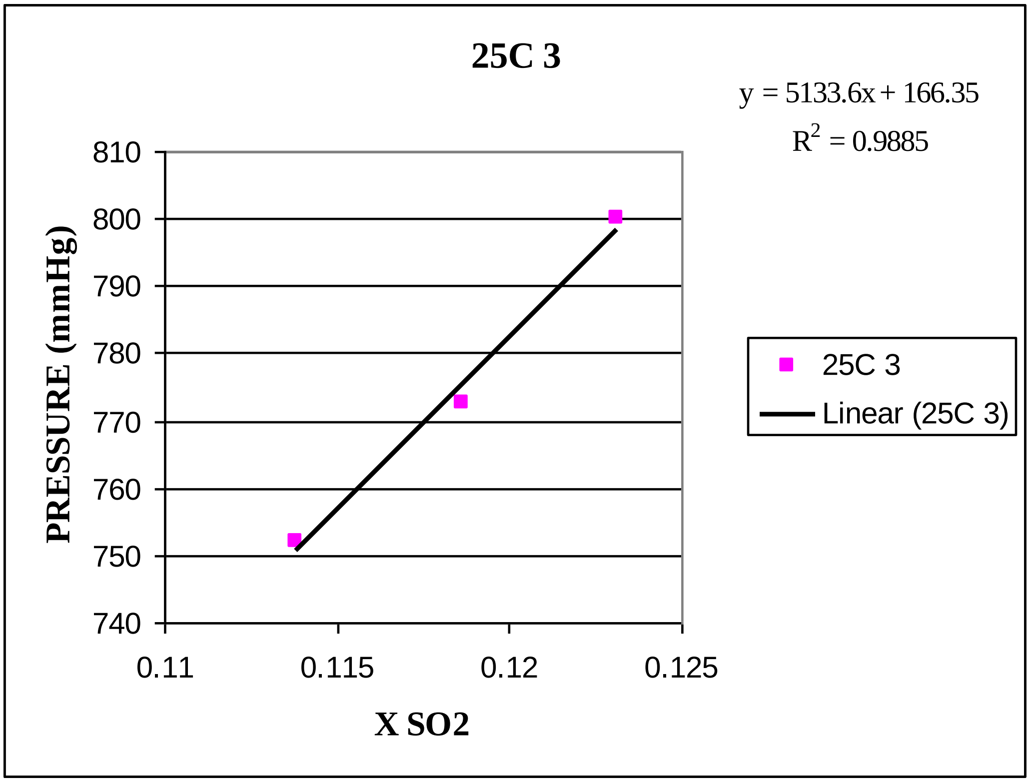

Figure A.11 Pressure vs. Sulfur Dioxide Mole Fraction at 298 K (3)

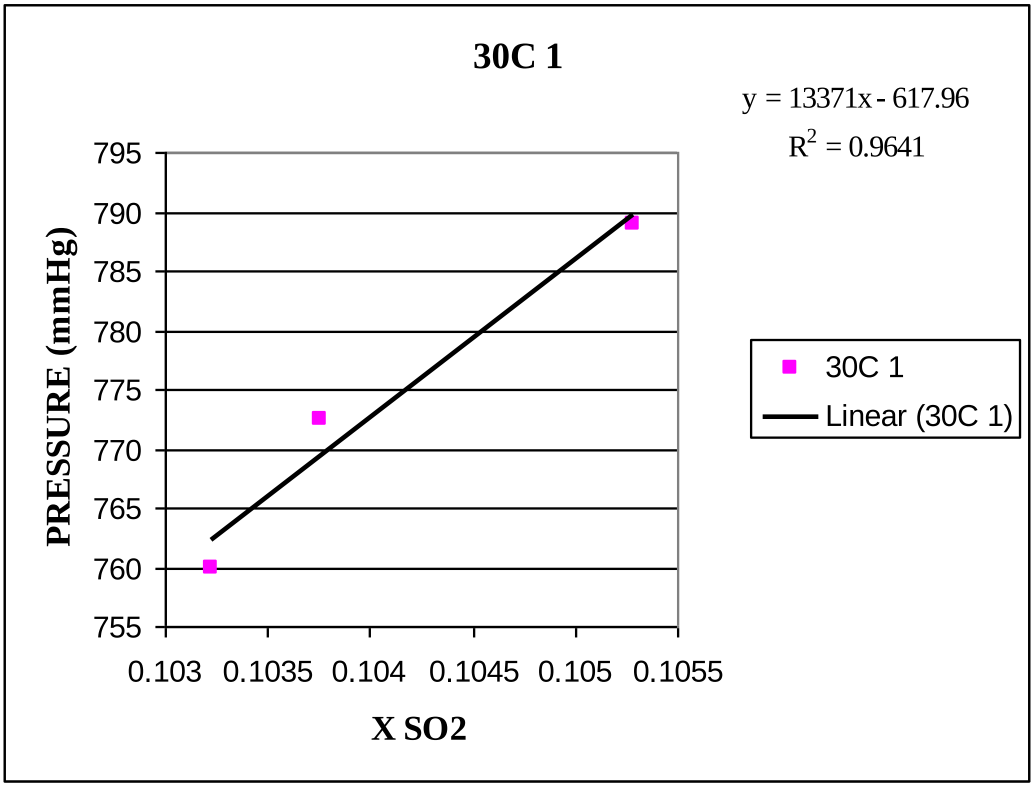

Figure A.12 Pressure vs. Sulfur Dioxide Mole Fraction at 303 K (1)

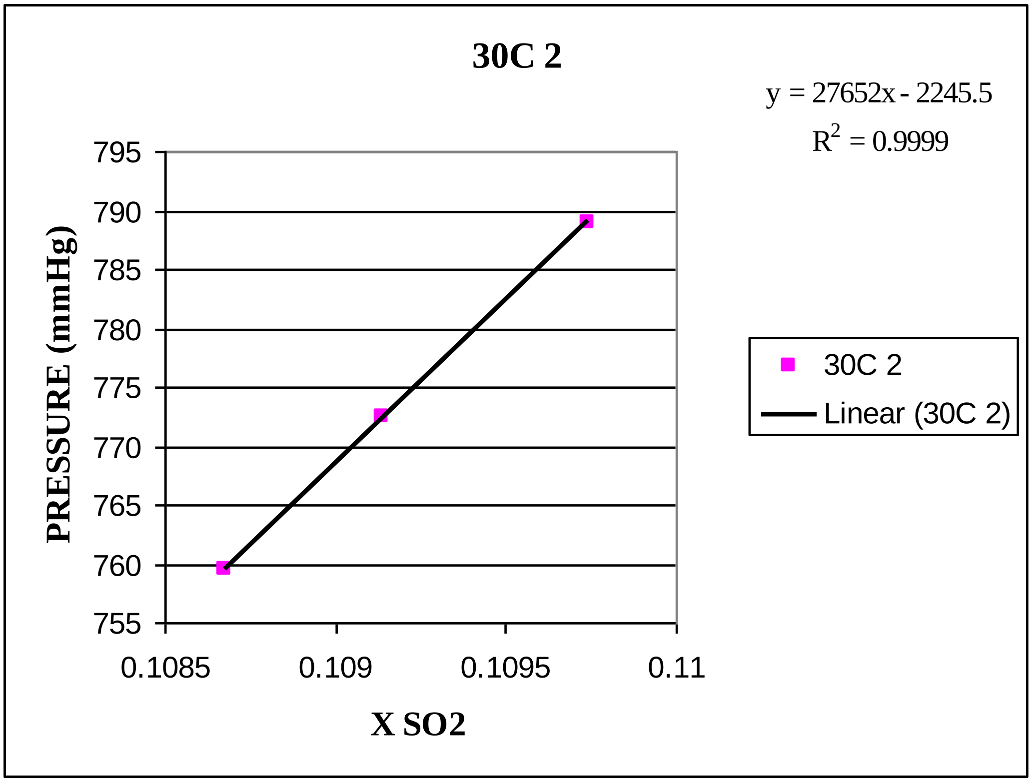

Figure A.13 Pressure vs. Sulfur Dioxide Mole Fraction at 303 K (2)

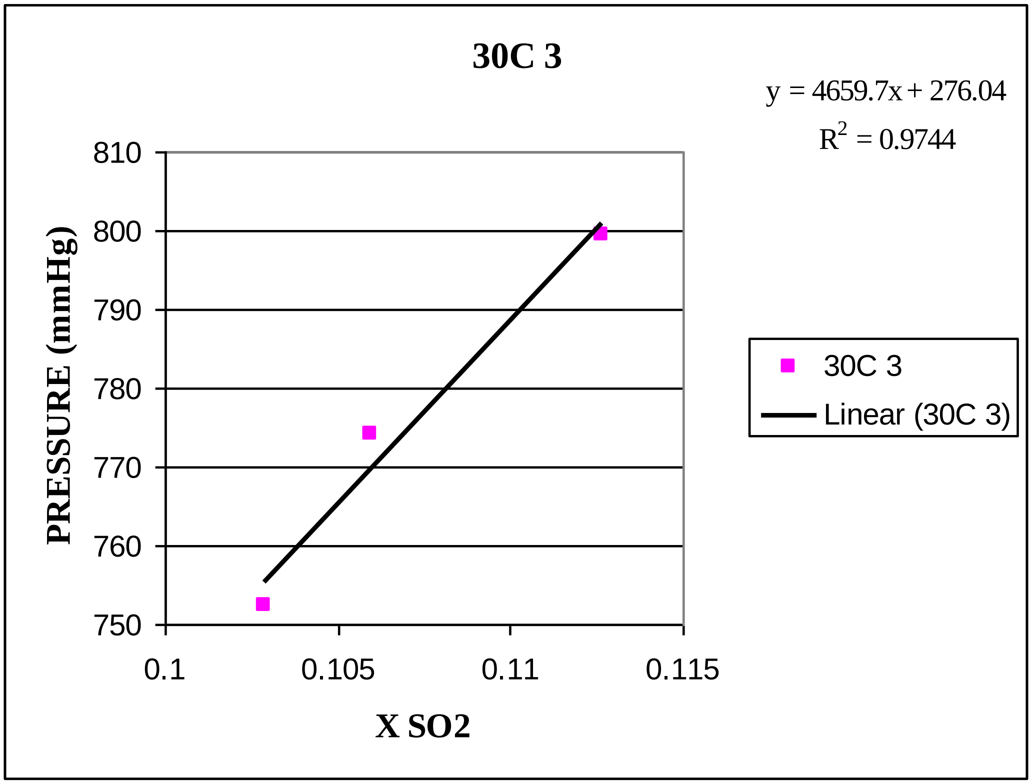

Figure A.14 Pressure vs. Sulfur Dioxide Mole Fraction at 303 K (3)

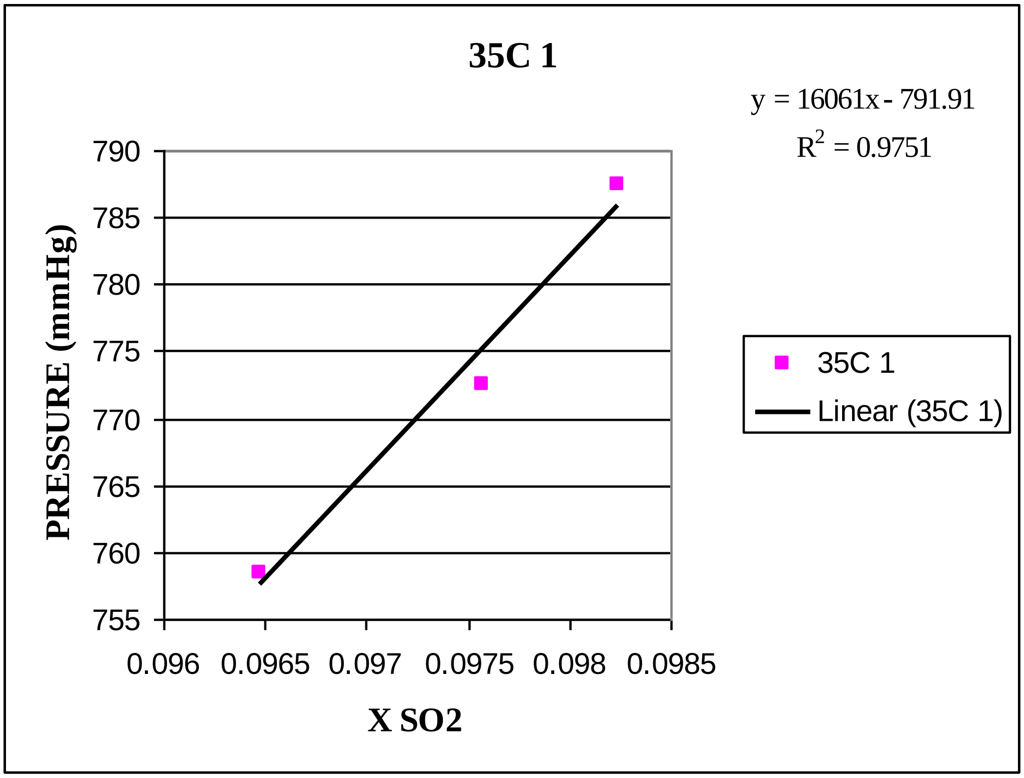

Figure A.15 Pressure vs. Sulfur Dioxide Mole Fraction at 308 K (1)

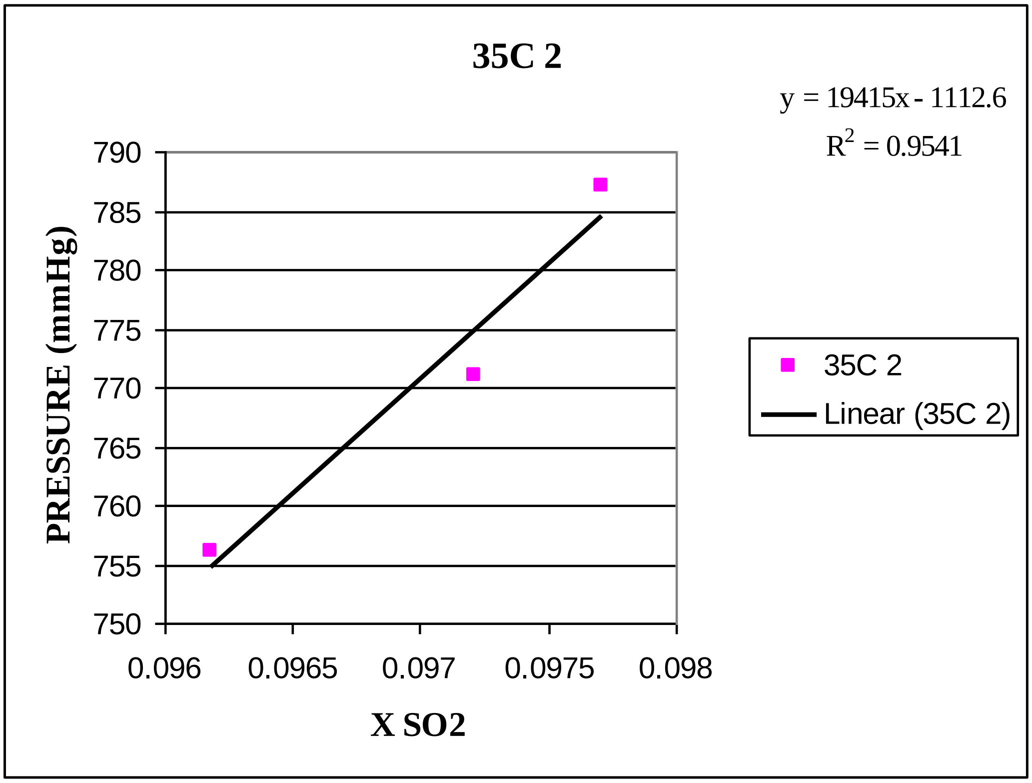

Figure A.16 Pressure vs. Sulfur Dioxide Mole Fraction at 308 K (2)

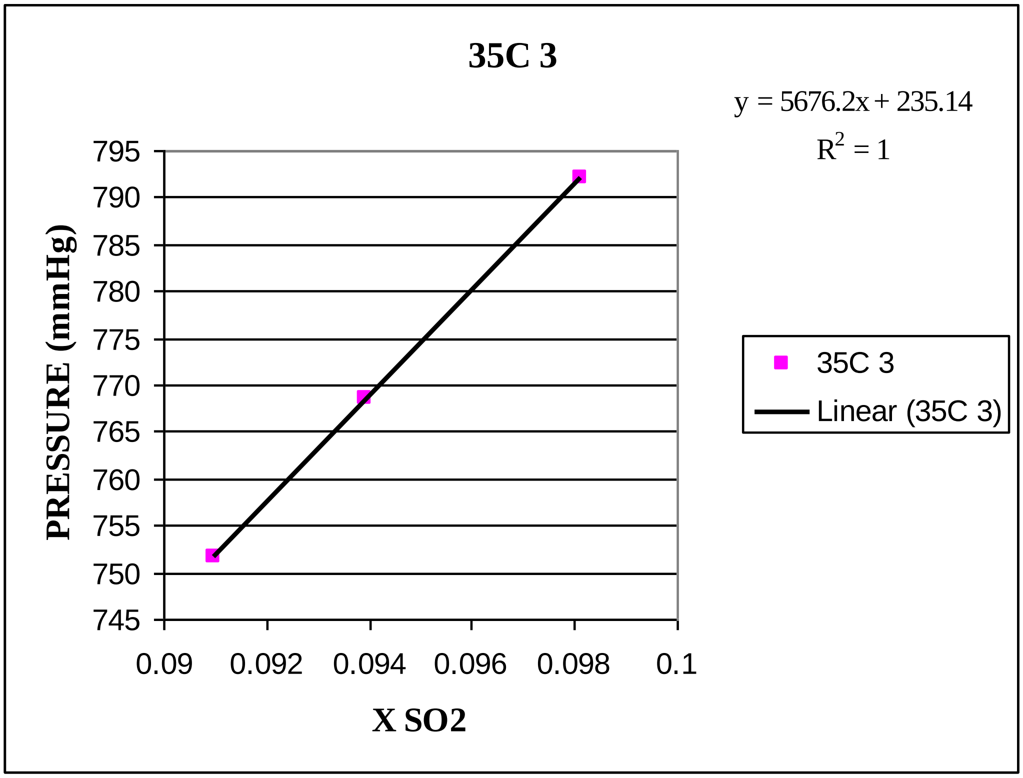

Figure A.17 Pressure vs. Sulfur Dioxide Mole Fraction at 308 K (3)

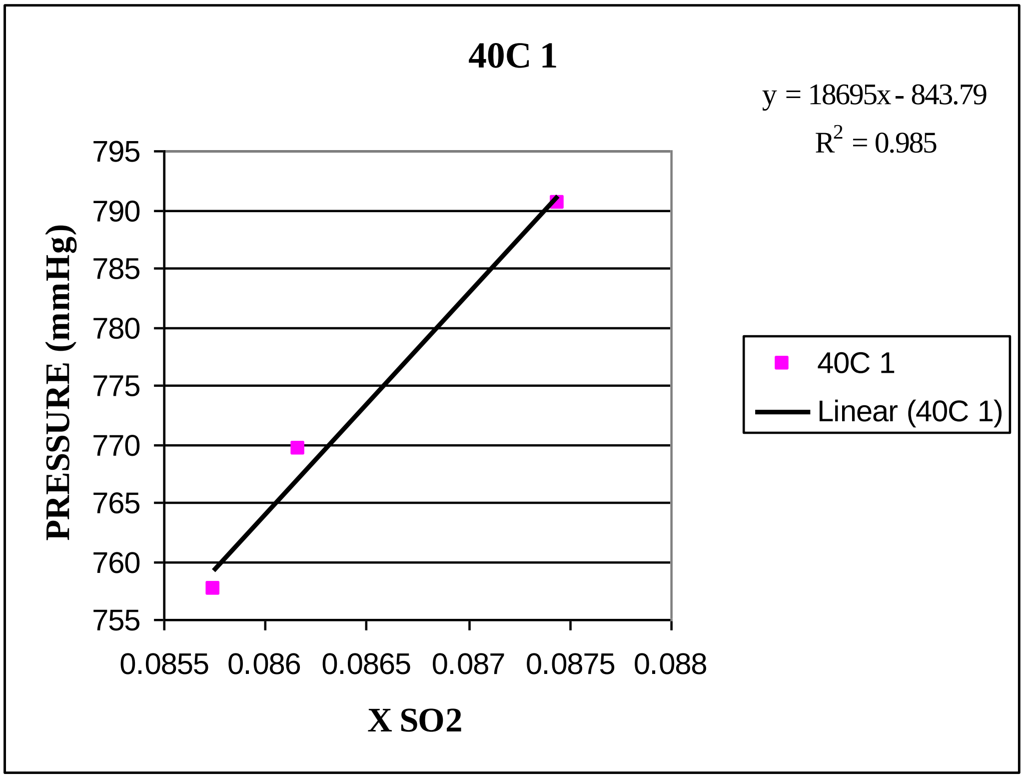

Figure A.18 Pressure vs. Sulfur Dioxide Mole Fraction at 313 K (1)

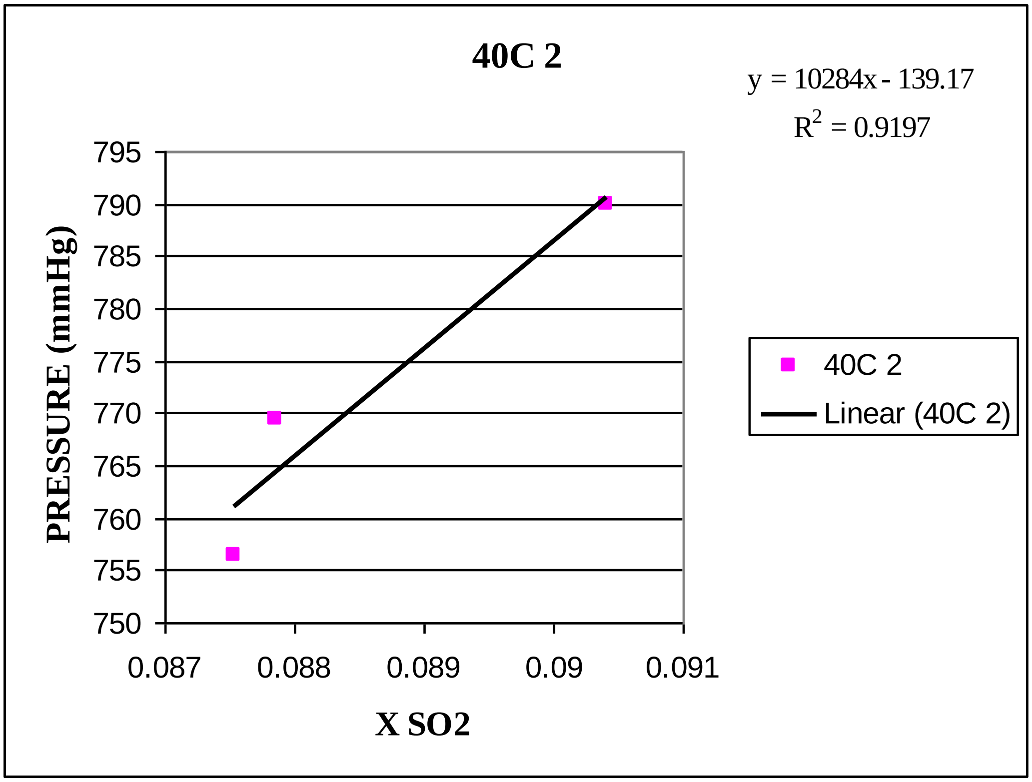

Figure A.19 Pressure vs. Sulfur Dioxide Mole Fraction at 313 K (2)

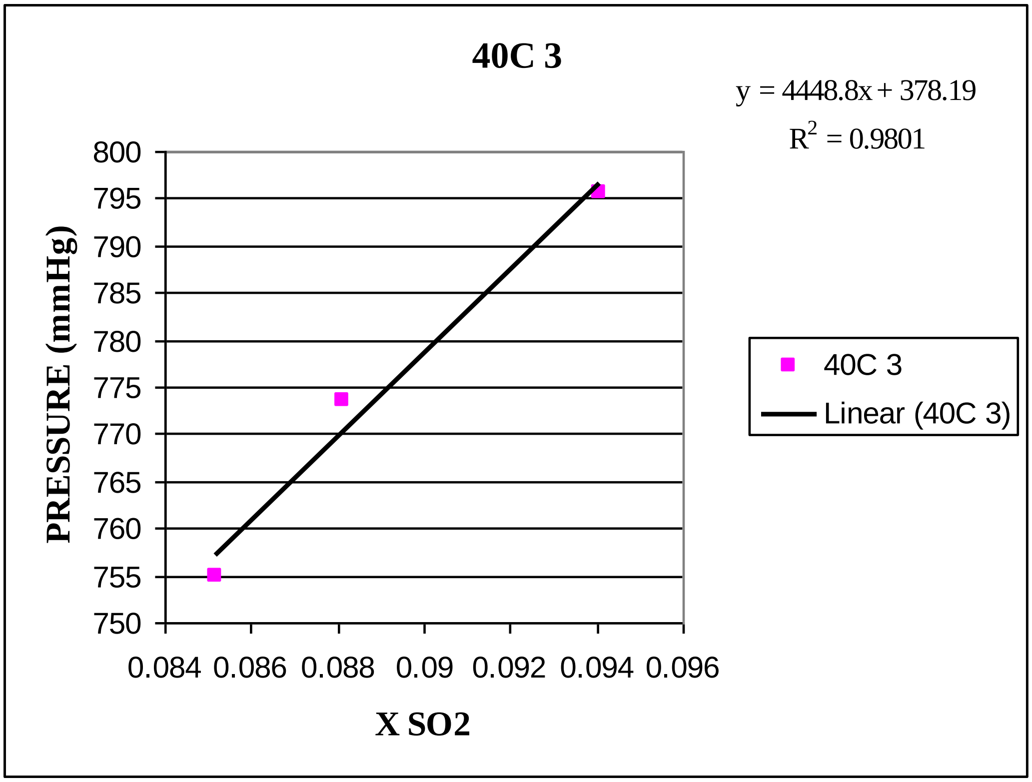

Figure A.20 Pressure vs. Sulfur Dioxide Mole Fraction at 313 K (3)

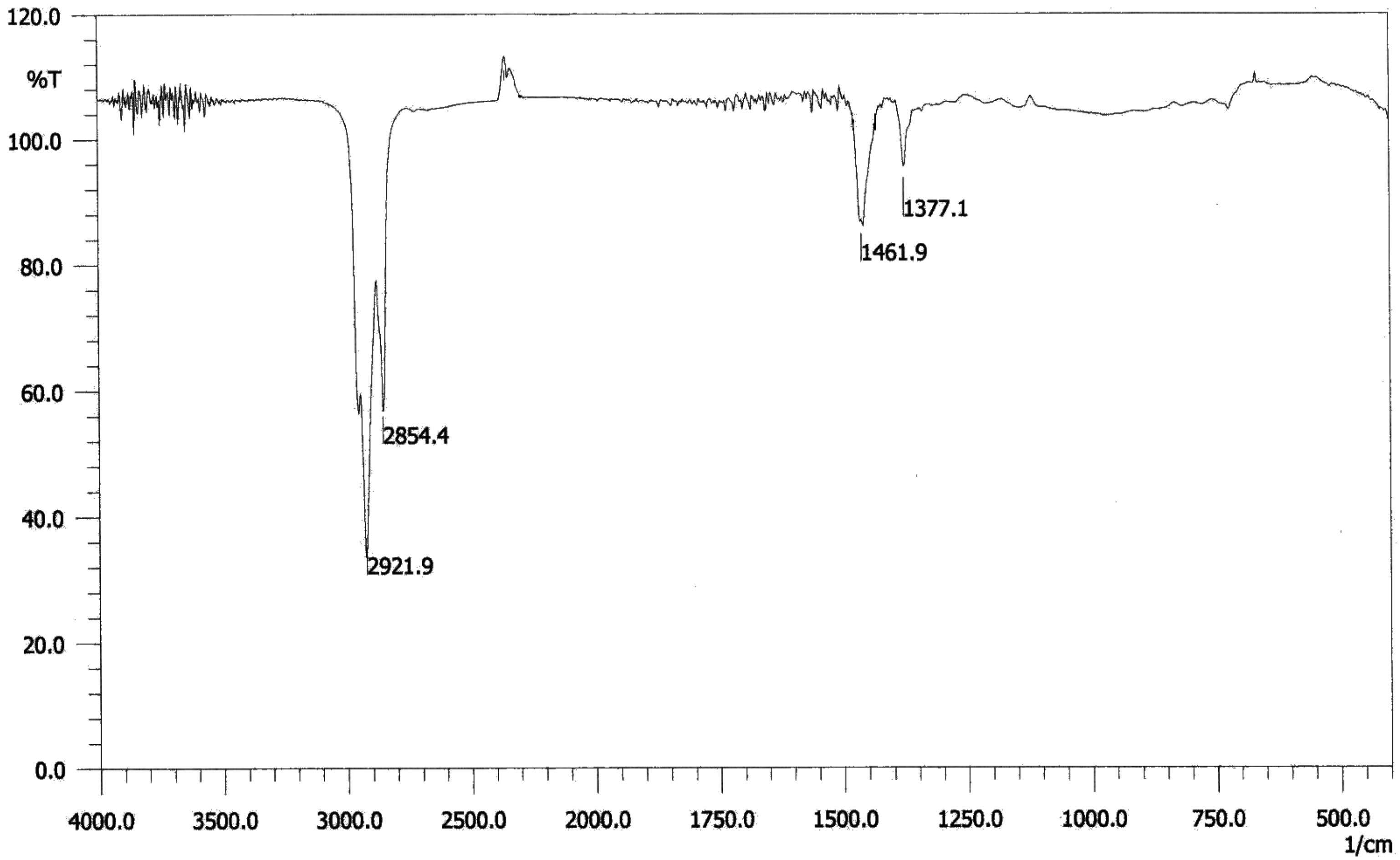

Figure A.21 IR Spectrum of The Heat Transfer Oil

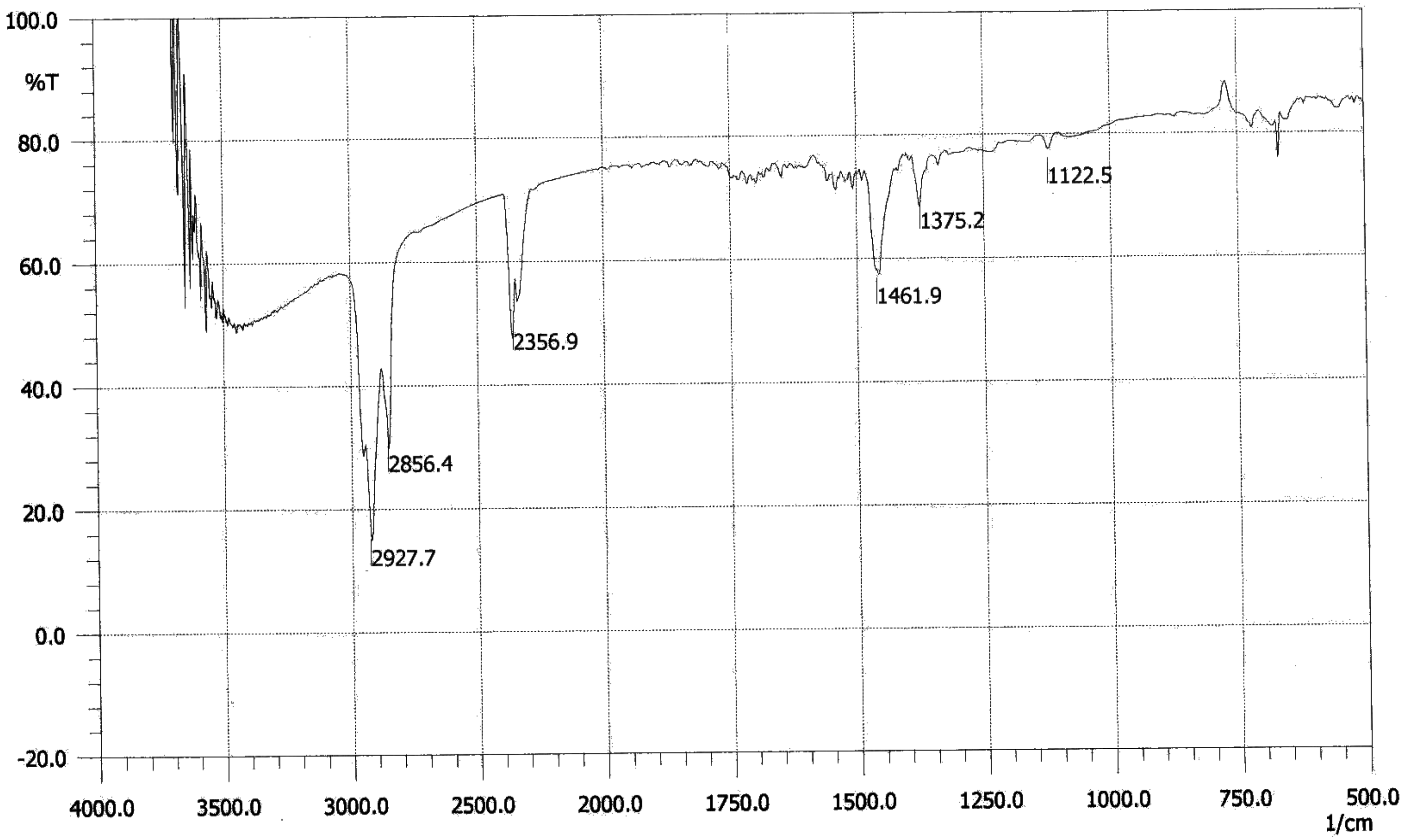

Figure A.22 IR Spectrum of The Sulfur Dioxide Absorbed Heat Transfer Oil

RESUME

Ahmet Alper AYDIN was born in 1981. He graduated from F.M.V. Ayazağa Işık High School in 1999. In the same year, he was enrolled to The Chemical Engineering Department of Faculty of Chemical and Metallurgical Engineering, Istanbul Technical University.

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