

Solubility of Cyclohexane  
and Benzene in  
Liquid Sulphur Dioxide

by.

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1922. A8  
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SOLUBILITY OF CYCLOHEXANE AND BENZENE  
IN LIQUID SULPHUR DIOXIDE.

by

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A Thesis submitted for the Degree of  
MASTER OF ARTS  
in the Department  
of  
CHEMISTRY

THE UNIVERSITY OF BRITISH COLUMBIA.

April, 1922.

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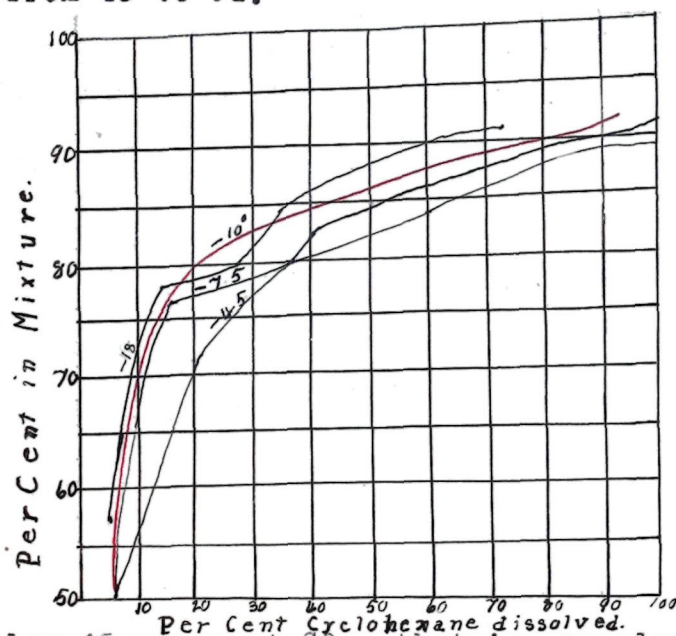
In 1899, Walden published an article in volume 32 of the *Berichte* on liquid sulphur dioxide as a new inorganic solvent in which dissociation occurs. In this article he says, "Liquid sulphur dioxide has a remarkable power of dissolving the most varied substances, both inorganic and organic, the solutions often showing a characteristic colour; thus potassium, sodium, and ammonium iodide all dissolve readily forming yellow solutions. Among soluble organic substances are benzene, naphthalene, ethyl alcohol, benzoic acid, phenol, ethyl acetate, aniline, diphenylamine and Bnaphthylamine. The fact that the dissolved substances react readily with each other points to their being electrolytically dissociated. The conductivity of sulphur dioxide solutions is considerable, and in some cases greater than that of equally concentrated aqueous solutions".

This property, possessed by liquid sulphur dioxide, of dissolving certain organic substances, was used by Edeleanu, and later by Browery in the refining of crude petroleums. According to their results the naphthines were found to be insoluble.

In the *Metallurgical and Chemical Engineering Journal*

of 1918, an article appeared, by J. Moore, J. Morrell and Gustav Egloff on the solubility of paraffins, aromatics, naphthenes and olefins in liquid  $\text{SO}_2$ . In it they stated that the paraffins were insoluble, the aromatics and olefins, soluble, and that the solubility of the naphthenes varied. The following is an extract from this article:

"Edeleanu and Browery both state that naphthenes are entirely insoluble in liquid sulphur dioxide and after treatment are left with the paraffins. The present work, however, indicates that naphthenes vary in solubility from 0 to 100 per cent depending on the temperature, and concentration of the liquid  $\text{SO}_2$ . Graph I shows the solubility of pure Cyclohexane at temperatures of  $-18^\circ$ ,  $-10^\circ$ ,  $-7.5^\circ$  and  $-4.5^\circ$  C, and at percentages  $\text{SO}_2$  ranging from 45 to 91.



Graph I.

Below 45 per cent  $\text{SO}_2$ , that is, nearly an equal volume there is no solubility at  $-18^\circ\text{C}$ , and only 3 per cent at  $-4.5^\circ$ .

With about 70 per cent  $\text{SO}_2$ , however, the solubility shows a marked increase. The solubility also increases rapidly with temperature; with 89.4 per cent  $\text{SO}_2$  the solubility is about 58 per cent at  $18^\circ$ , and 100 per cent at  $-4.5^\circ$ . One marked peculiarity of the naphthene action with  $\text{SO}_2$  is that as the concentration of the  $\text{SO}_2$  reached a point between 83 and 87 per cent, white crystals appeared in the oils, remaining upon addition of more  $\text{SO}_2$ .

This peculiarity of behavior together with the rather marked increase in solubility at about 70 per cent seems to point to some compound between the  $\text{SO}_2$  and the naphthenes".

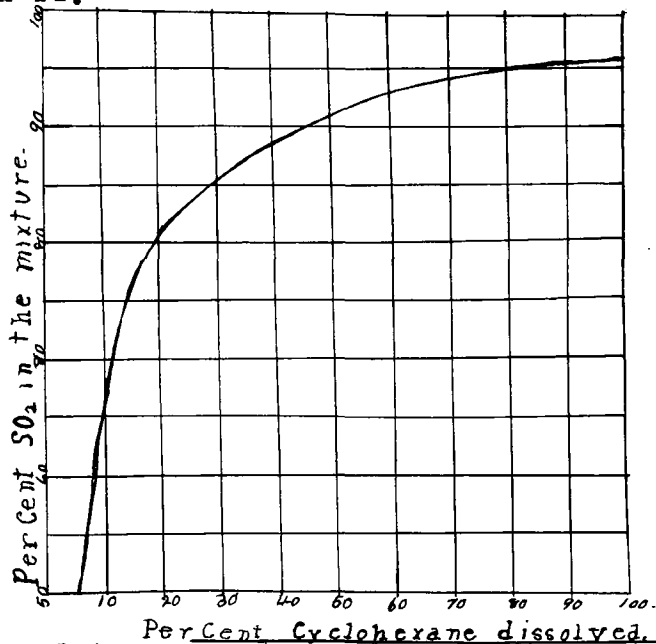
The statement that the solubility varies with the concentration of the solvent, when both temperature and pressure are constant, is contrary to the principles of the phase rule.

A theoretical curve can be plotted from the fact that, a mixture containing 50%  $\text{SO}_2$ , dissolves 5% of the oil present. The other points on the curve are plotted from this ratio.

For example:-

Am't dissolved.	Am't of oil	Am't $\text{SO}_2$	% $\text{SO}_2$
.5	10	10	50
1.	10	20	66.6
1.5	10	30	75
2.	10	40	80
2.5	10	50	83.3
10.	10	200	90.9

The curve obtained by using these figures is shown in Graph II.



Graph II

This curve is very similar to the one at  $-10^{\circ}$  in Graph I. The curves plotted at  $-4.5^{\circ}$  and  $-7.5^{\circ}$  are above the boiling point of the liquid dioxide. Therefore it is very difficult to make accurate measurements of the solubility at these temperatures. Also the fact that only a few points were determined renders it impossible to draw any accurate conclusions from these curves.

The inconsistency between their results and their conclusions, and the fact that the latter are contrary to the phase rule were the reasons for redetermining the solubility of Hexamethylene.

#### Cyclohexane.

The above mentioned experimenters obtained their results by a volumetric method. Attempts therefore were made

to determine the solubility of Hexamethylene in liquid  $\text{SO}_2$  by a similar volumetric method. The following is a brief description of the method used.



The oil was poured into the upper graduated half of the apparatus, the reading taken, and the oil was then allowed to flow into the lower part. The  $\text{SO}_2$  was added by a similar method. The mixture was then kept in a bath at  $-14^\circ\text{C}$  for 40 minutes, and the whole apparatus shaken frequently. The lower layer consisting of the liquid  $\text{SO}_2$  containing dissolved oil, was then run off into a small erlenmeyer flask, and the  $\text{SO}_2$  allowed to evaporate. The oil dissolved in the sulphur dioxide was thus left behind.

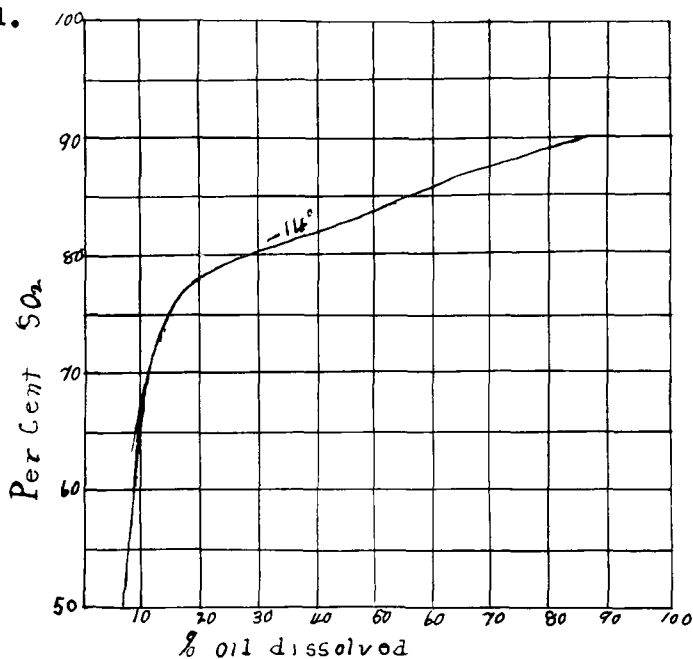
This method was inaccurate for the following reasons:

1. Hexamethylene evaporates fairly rapidly at room temperature, so that while the sulphur dioxide was evaporating from the mixture, some of the oil vaporized and caused an error of considerable magnitude, if the per cent of Cyclohexane in the mixture was large.

2. If the reading of the  $\text{SO}_2$  in the graduated tube is taken at  $-14^\circ$ , the difficulty is to run the  $\text{SO}_2$  into the lower part before it begins to boil. If on the other hand the read-

ing is taken at a lower temperature, the correct volume is not obtained.

Graph II shows the solubility curve obtained by this method.



Graph 3.

Crystals appeared, but always after the mixture of sulphur dioxide and oil had been standing for some weeks. Apparently the  $\text{SO}_2$  was oxidizing the cyclohexane, because free sulphur was deposited, and the Hexamethylene turned brown before the crystals appeared. The crystals obtained in the experiment quoted above were probably due to moisture in the  $\text{SO}_2$ , as several sulphur dioxide hydrates are known to exist.

Since the volumetric method did not prove very successful a gravometric method was tried.

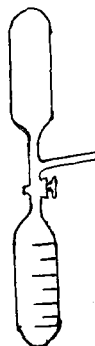
Before being condensed the  $\text{SO}_2$  was thoroughly dehydrated, by being bubbled through several  $\text{H}_2\text{SO}_4$  drying bottles, passed over phosphorous pentoxide and by standing



over concentrated sulphuric acid in large cylinders for several days. On the following page is a diagram of this apparatus. The  $\text{SO}_2$  was condensed in a flask of this type,,



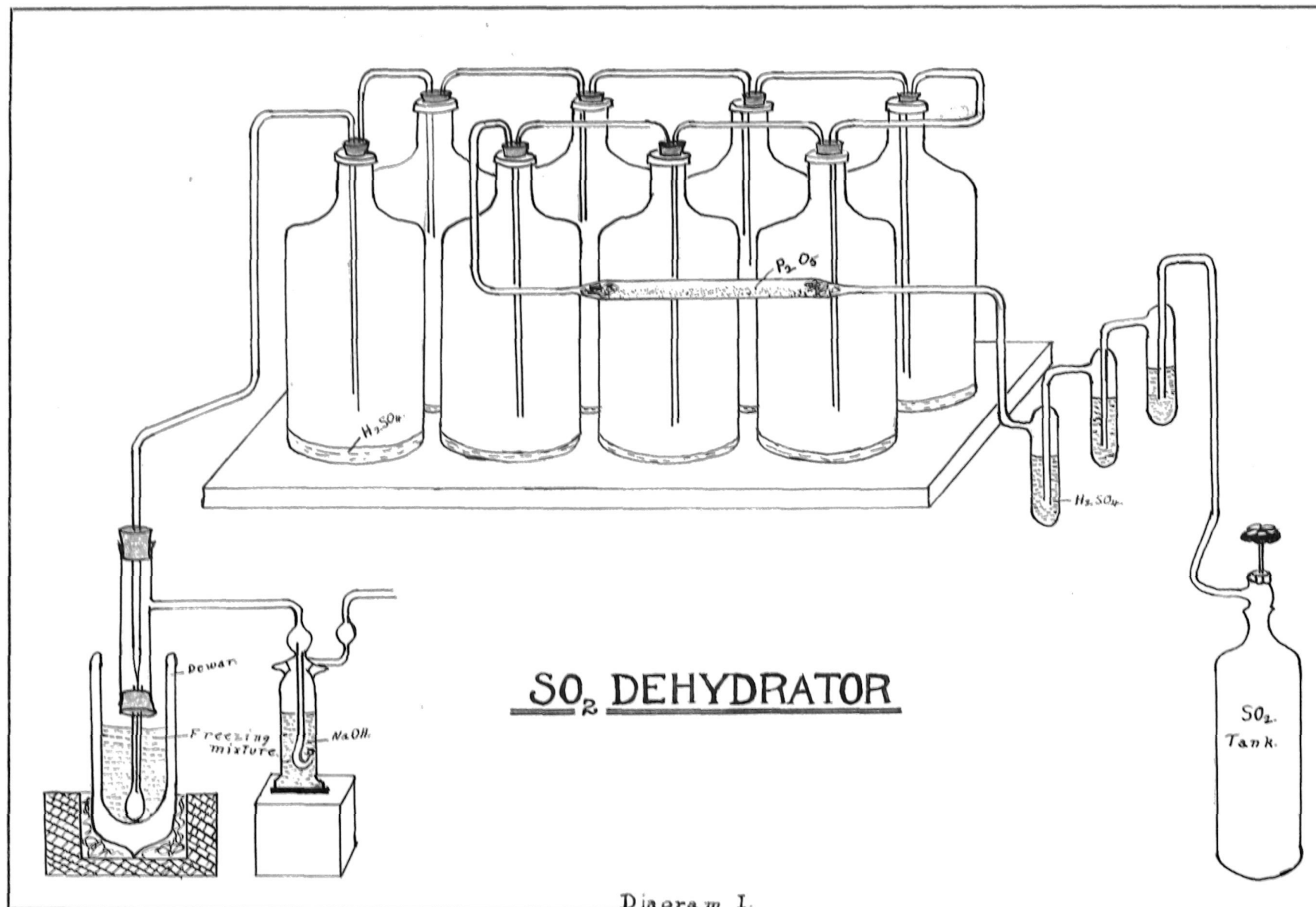
into which a known quantity of oil had been put. When sufficient  $\text{SO}_2$  had been condensed the capillary was removed, and the temperature of the bath allowed to rise to  $-14^\circ$ . A second flask was then sealed on to the top of the first, and evacuated by means of the side tube.



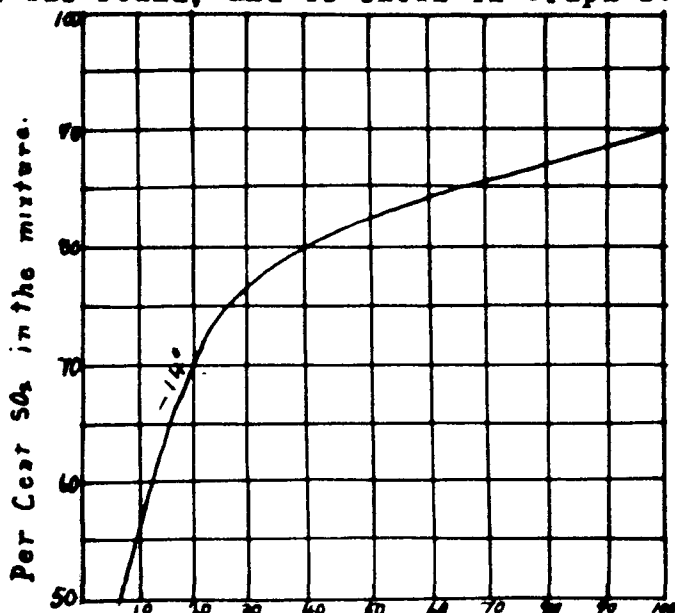
By inverting the whole apparatus, the  $\text{SO}_2$  layer was run into flask B which was kept in a bath at a very low temperature. Flask B was then sealed off. By reweighing A, the loss in weight of oil was obtained, and hence the weight of Cyclohexane dissolved in the sulphur dioxide. B was weighed, when full of the mixture and when empty.

There were two difficulties met with in this method.

1. To run the  $\text{SO}_2$  from A into B at a temperature of  $-14^\circ$ .
2. To prevent the sulphur dioxide from escaping through the stopper.



A curve similar to that obtained by the volumetric method was found, and is shown in Graph IV.



Graph 4

There was no sign of crystal formation at any concentration.

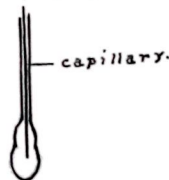
The curves obtained by both the volumetric and gravimetric method are very similar to the theoretical curve. In that curve it is clear that solubility does not increase with concentration, therefore curves in Graph I, III, and IV, do not show any peculiar behavior, in spite of the fact that it was clearly stated in the article quoted above, that naphthenes vary in solubility from 0 to 100 per cent depending on the concentration of the liquid SO<sub>2</sub>.

However, neither the volumetric nor the gravimetric method is sufficiently accurate to enable one to say conclusively that there is no formation of compounds.

The principles of the Phase Rule have been applied

to the investigation of the equilibria between compounds. An application of this rule to the system sulphur dioxide and Cyclohexane is the best and easiest method of determining the compounds formed.

Obviously owing to the fact that liquid sulphur dioxide boils at  $-10^{\circ}$  the ordinary freezing point method with a Beckmann apparatus cannot be used.



Bulbs of about a 15 cc. volume were made as shown, and into these were run various amounts of cyclohexane. The bulbs were then filled with liquid  $\text{SO}_2$  which had been dehydrated by the method described above, and while the temperature of the bath was still low, the tops of the bulbs were sealed off. Three weighings were made, first when the bulbs were empty, secondly after the oil had been put in, and the third when they were full of  $\text{SO}_2$ .

At room temperature the two liquids were miscible at all concentrations, but upon slight cooling two layers formed. The temperature at which these two distinct layers just disappeared was accurately recorded and is given in Table I.

TABLE I.

Solubility of the Two Liquids.

per cent  $\text{SO}_2$

Temp.

1.      2.      3.

table con't.

<u>per cent SO<sub>2</sub></u>	<u>Temp.</u>		
	<u>1.</u>	<u>2.</u>	<u>3.</u>
18	-1	-1	-1
22	2	1.5	1.5
35.1	11	11.5	11
40.9	11.3	11.3	11.3
59.2	13.5	13.6	13.4
65.4	13.3	13.5	13.0
83.2	9	8.6	--
87.9	4.2	4	4
92.2	-6	-6	-6
94	-8	-8.5	-8.5

If the temperature be lowered still more the Hexamethylene begins to separate out in the form of white crystals, but the super cooling was very great, being in some cases as much as 15°, and in all cases as much as 10°. The temperature was allowed to rise until the point was reached where the solid phase neither increased nor decreased. The temperature at which the crystals disappeared was taken as the freezing point, and these temperatures are recorded in Table II.

TABLE II.

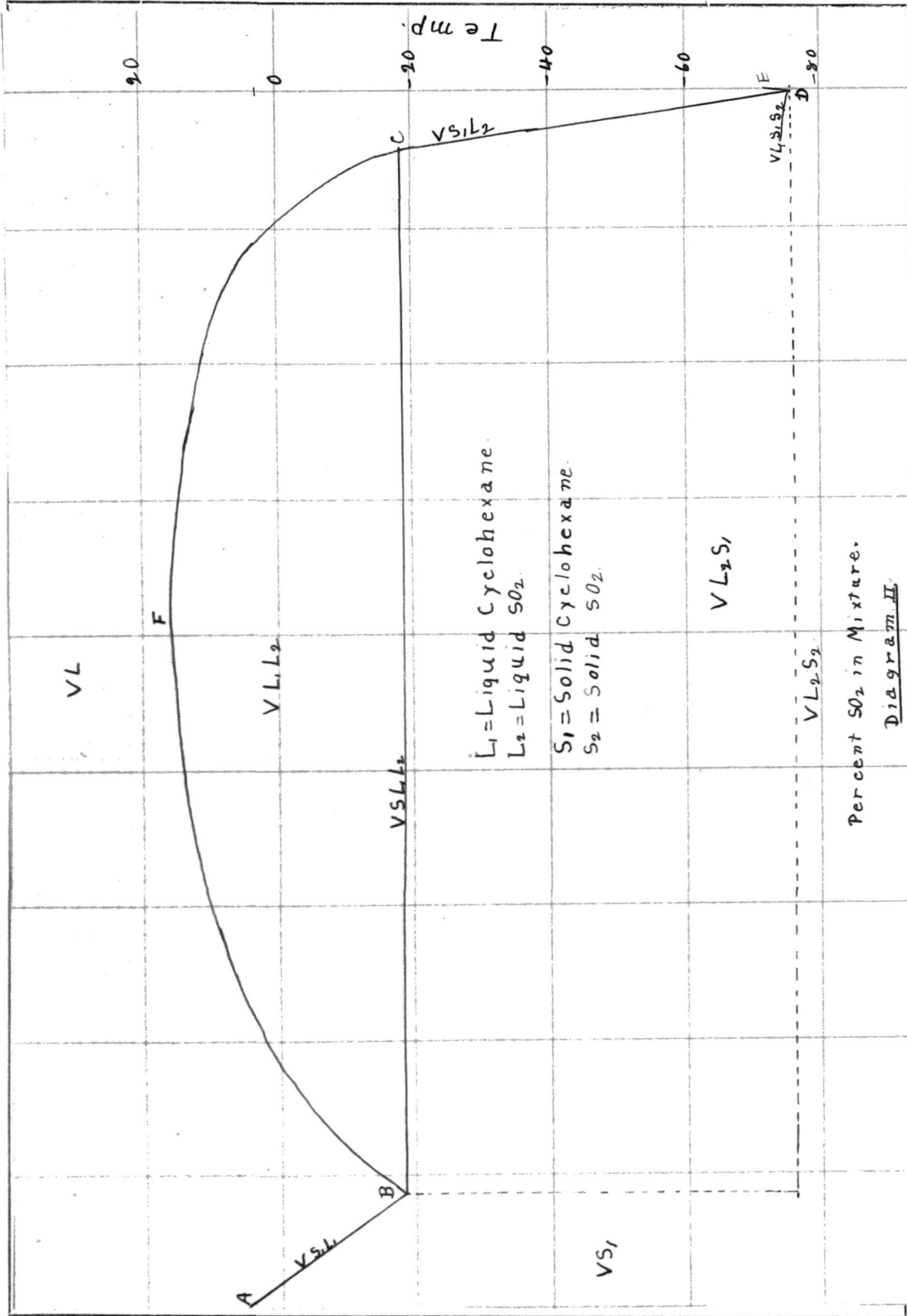
Temperature at which Cyclohexane crystals appear.      ear  
per cent SO<sub>2</sub>      Temp. at which crystals disapp

	<u>1.</u>	<u>2.</u>
4	-4.5	-4
18	-17	-17

table con't.

<u>per cent SO<sub>2</sub></u>	<u>Temp. at which crystals disappear.</u>	
	<u>1.</u>	<u>2.</u>
22	-17	-
35	-	-
40.9	-	-
59.2	-	-
65.4	-	-
83.2	-	-
87.9	-	-
92.2	-	-
94	-	-
96.7	-24.5	-24
97.5	-34.4	-34.1
98.4		about -51
99	-57	-55
99.2	-61	-59
99.5	-65	-64

Diagram II shows the curve as plotted by using the figures in both Table I and II. If to the system, Cyclohexane at 6.4° liquid sulphur dioxide is added, the temperature will fall; and continued addition of the SO<sub>2</sub> will lead at last to the transition point B where the maximum solubility of sulphur dioxide in oil is reached, and it begins to separate out as a separate layer. As there are now four phases present, vapor, solid and liquid Cyclohexane and liquid SO<sub>2</sub> the system is in-



variant, and a further increase in the amount of liquid sulphur dioxide can only cause a change in the relative amounts of the phases. Therefore continued addition of  $\text{SO}_2$  will cause an increase in the amount of the liquid phase containing excess of  $\text{SO}_2$ , whereas the other liquid phase will gradually disappear. When it has completely disappeared the system will be represented by the point C, where there are again three phases. As the amount of solid Cyclohexane is diminished the equilibrium temperature will fall until at D the eutetic point is reached. The temperature of the euryhydric point is approximately  $76^\circ$  but the composition of the solution was not accurately determined owing to the fact that the Hexamethylene is almost completely insoluble in liquid  $\text{SO}_2$  at these low temperatures. 1 part of oil showed no signs of dissolving in 200 parts of  $\text{SO}_2$  at  $-72^\circ$ .

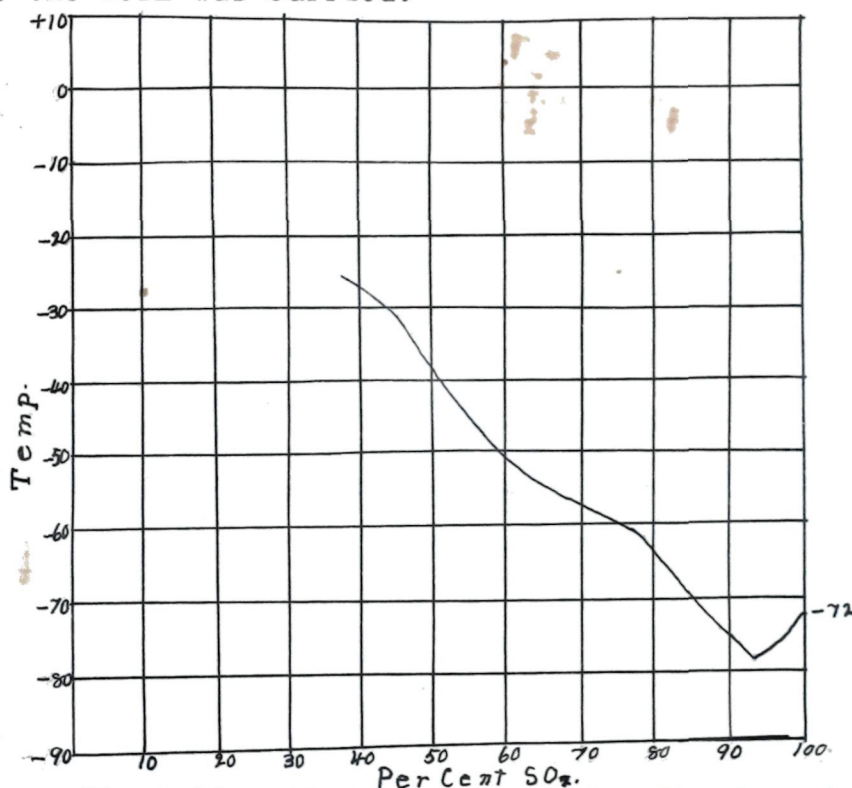
If the amount of the Cyclohexane is diminished still more the temperature rises until at  $-72.3$  the freezing point of pure liquid sulphur dioxide is reached.

Along line B C., there exists four phases, vapor, two liquids and one solid, but if heat be added the solid Hexamethylene will disappear leaving a univariant system of vapor and two liquids. In general the solubility curve of two partially immiscible liquids is of a somewhat parabolic shape, and it is seen that the curve B F C has the general form of a parabola. Above  $13.6$  the critical temperature the liquids are miscible in all proportions. This curve shows no evidence of any compound formation.



Benzene.

In one of the BSc thesis of last year work was done on the freezing points of Benzene in liquid sulphur dioxide. The sulphur dioxide was weighed in a freezing point tube, and the benzene added as in the ordinary freezing point determinations. Difficulty was experienced in getting accurate weights of the sulphur dioxide. Graph V. shows the curve obtained as far as the work was carried:



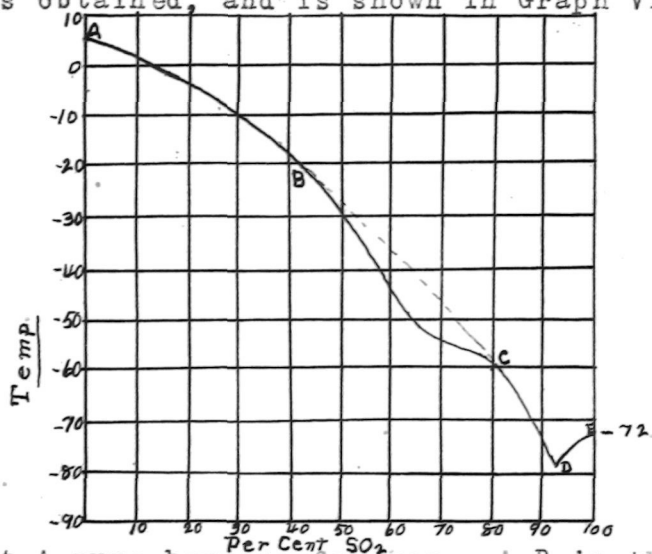
The bulb method of determining the freezing points was also tried with benzene. Table III shows the results obtained.

<u>per cent SO<sub>2</sub></u>	<u>Freezing Point.</u>	
	<u>1.</u>	<u>2.</u>
3.7	3.5	4
14.6	-3	-3.8
15.5	-3.5	-4.5
27	-9.5	-9

table cont'd.

<u>per cent SO<sub>2</sub></u>	<u>Freezing Point.</u>	
	<u>1.</u>	<u>2.</u>
29.5	-1.2	-11
50.6	-26	-26
58.2	-40	-41
65.8	-53	-53
67.1	-53	-53.5
79	-59	-59.5
84.9	-66	-66
85.2	-66.5	-67
92.9	-77	-76.5
96.8	-72	-73.5
99.1	-72	-72

If these figures are plotted a curve similar to that in Graph V. is obtained, and is shown in Graph VI.



Graph VI.

At A pure benzene freezes. A B is the freezing point curve of benzene in the presence of liquid sulphur dioxide, and D E that of SO<sub>2</sub> in the presence of benzene. The curve B C

shows compound formation, but the compound undergoes transition to another solid phase at a temperature below its melting point. It is therefore unstable and can exist only in contact with solutions containing excess of one of the components. The point A and B represent the limits of the existence of the compound AB.

Summary.

1. The solubility of Cyclohexane in liquid sulphur dioxide was redetermined.
2. The freezing point curve of the system Hexamethylene and  $\text{SO}_2$  was plotted, but there was no sign of any compound formation.
3. A freezing point curve of benzene in the same solvent was also plotted, and a very unstable compound shown to exist.