

1953

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Recommended Citation

Reed, Robert H. and Osburn, James O. (1953) "The Equilibrium Vapor Pressures of Some Carbon Disulfide Solutions," *Proceedings of the Iowa Academy of Science*, 60(1), 308-314.

Available at: <https://scholarworks.uni.edu/pias/vol60/iss1/38>

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The Equilibrium Vapor Pressures of Some Carbon Disulfide Solutions

By ROBERT H. REED AND JAMES O. OSBURN

The problem of recovering carbon disulfide from a mixture of air and carbon disulfide is encountered in the manufacture of viscose rayon. The completeness of the removal must be high, both because of the expense of the material and also from the standpoint of health and safety.

One method for the removal of carbon disulfide from air is that of absorption in a suitable liquid. This method was studied, and one part of this study, the choice of solvents and measurement of equilibrium vapor pressures, is reported here.

Choice of Solvents

The choice of solvents which might be suitable for absorbing carbon disulfide depends on several factors. The cost of the solvent should be low, to minimize the initial investment; the solvent itself should have a low vapor pressure, to keep down the replacement costs; and finally, the solvent should be a good solvent for carbon disulfide. Stated in another way, the last requirement means that solutions should exert a low vapor pressure of carbon disulfide. In the absence of data of this kind, theoretical considerations were used to screen a list of possible solvents, and to choose three for experimental study.

A widely-used correlation for vapor pressure above solutions is Raoult's Law, which states that the vapor pressure of a component is equal to the vapor pressure of the pure substance times its mol fraction in the solution. An ideal solution obeys Raoult's Law, whereas non-ideal solutions may give either positive or negative deviations. A positive deviation means that the vapor pressure is higher than predicted from Raoult's Law, and a negative deviation means that it is lower. For absorption, it is an advantage to have as low a vapor pressure as possible, so a negative deviation is desirable.

Hildebrand (1) and Ewell, Harrison and Berg (2) show that for non-polar solutes, which includes carbon disulfide, one cannot expect negative deviations from Raoult's Law. The best one can hope for, then, is an ideal solution.

There are certain criteria by which one can predict whether or not a solution will behave ideally. Lewis (3) has shown that in

the formation of an ideal solution from its components there is no change in volume and no heat of mixing. It has also been shown (4) that only liquids whose intermolecular forces in the pure state are equal can form ideal solutions. These forces are referred to as "internal pressure."

Hildebrand (1), in a discussion of the factors influencing solubility, concludes that deviations from Raoult's Law may be ascribed to the inequality of internal pressures or to a difference in polarity. Mixtures of non-polar liquids having approximately equal internal pressures usually obey Raoult's Law, while both mixtures of two liquids having different internal pressures, and mixtures of a polar and a non-polar liquid show positive deviations. Ewell, *et al* (2) also mention the importance of hydrogen bonds in producing positive deviations from Raoult's Law.

Using these theories as a guide, solvents were chosen as follows: First, data on the vapor pressure of about 1500 substances compiled by Stull (5) were inspected and liquids which have low vapor pressures were listed. Second, compounds which might form strong hydrogen bonds in solution were eliminated from the list. Third, very expensive solvents were eliminated. Eight solvents remained on the list at this point.

Heats of mixing of equimolar amounts of carbon disulfide and each of the remaining solvents were then measured. Those which had a high heat of mixing were eliminated. The solvents remaining were absorption oil, tetralin, decalin, and o-dichlorobenzene. Tetralin and decalin are similar compounds, so only one was investigated. Tetralin was chosen because it has the lower molecular weight.

Apparatus

Figure 1 shows the arrangement of the apparatus. A vacuum manometer (M2) measures the pressure in the system. A 2-liter bottle (H) acts as a surge tank. A vent valve (V5) permits adjustment of the pressure in the system.

A sampling trap was added to the isotenoscope of Smith and Menzies (6) to permit the withdrawal of samples without disturbing the equilibrium. The isotenoscope is shown in Figure 2. The large chamber has a capacity of 200 ml., the U-tube is 10 mm. in diameter, and the bulbs hold about 25 ml. each. Below the large chamber is a sampling trap.

The apparatus was tested to determine the accuracy of the measured vapor pressure and the length of time required to reach equilibrium. These tests showed that equilibrium was reached in 15

minutes. The vapor pressures of three pure materials were measured, with satisfactory results, as shown in Table I.

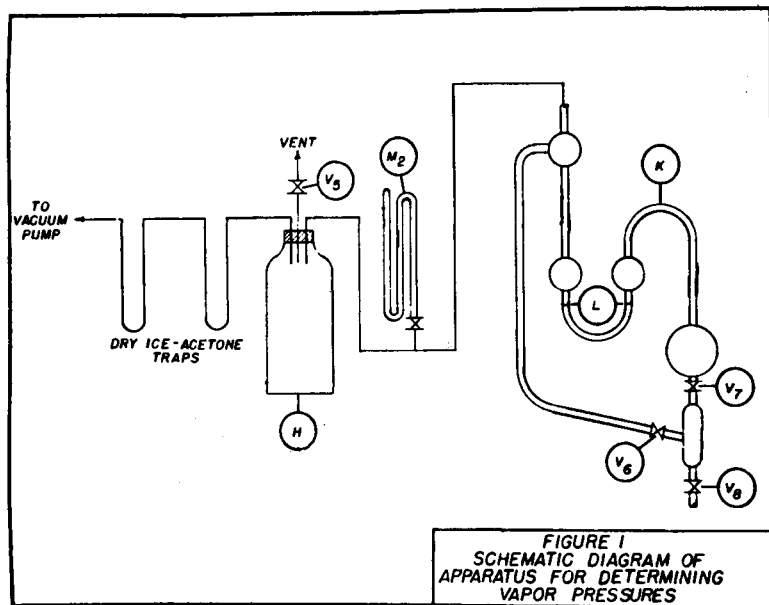


Figure 1. Diagram of Apparatus for Determining Vapor Pressures.

Table 1
 Vapor Pressures of Pure Substances.

Substance	Observed	Literature
O-dichlorobenzene	1.8	1.75
Water	23.8	23.76
Benzene	96.0	95.8

Materials

Since application to industrial operations was envisioned, technical grade materials were used. The carbon disulfide was obtained from Merck and Company, Inc., and was distilled immediately before using.

The absorption oil was obtained from the Phillips Petroleum Company. A 5% "top cut" was removed by vacuum distillation. The A.P.I. gravity of the oil was 40.6 at 60°/60° F. The molecular weight was estimated from the molal average boiling point and the specific gravity by the correlation of Watson and Nelson (7). The average molecular weight found in this manner was 210.

The o-dichlorobenzene was obtained from the Monsanto Chemical Company; the tetralin from the Eastman Kodak Company.

Traces of low-boiling impurities were removed from each of these materials by vacuum distillation.

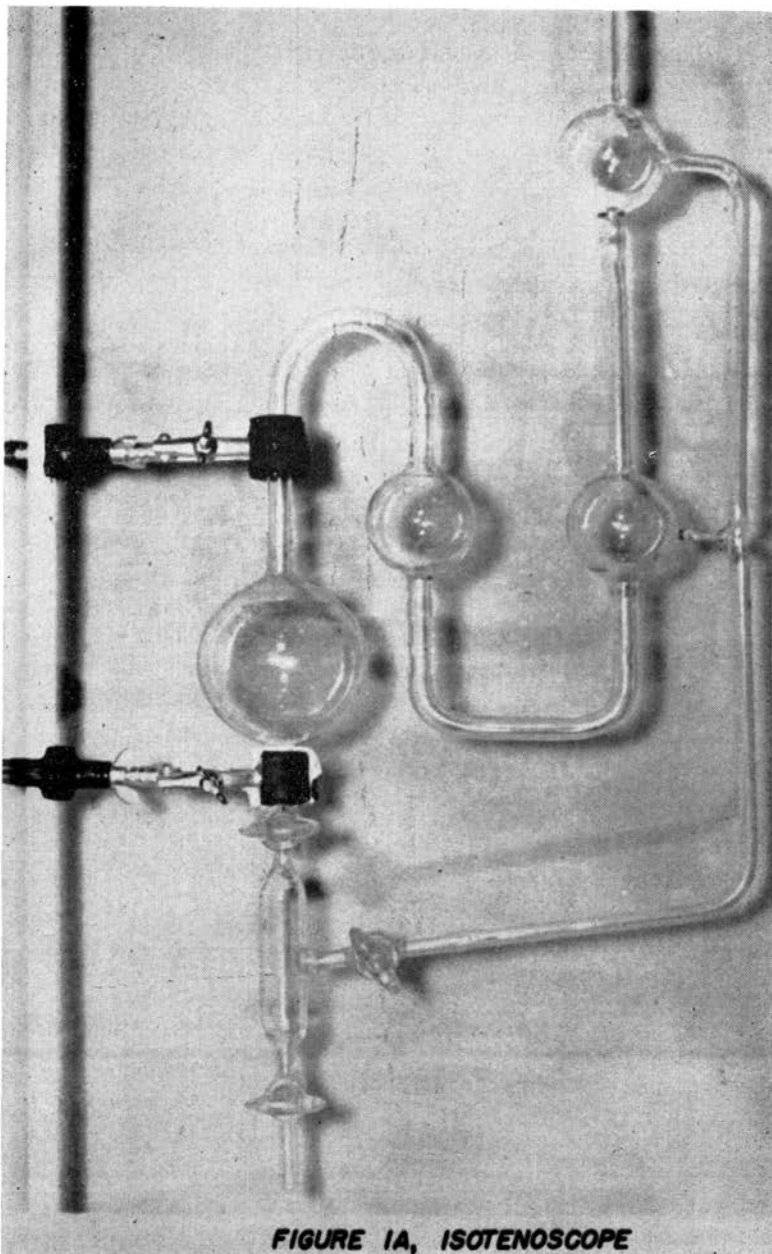


FIGURE 1A, ISOTENOSCOPE

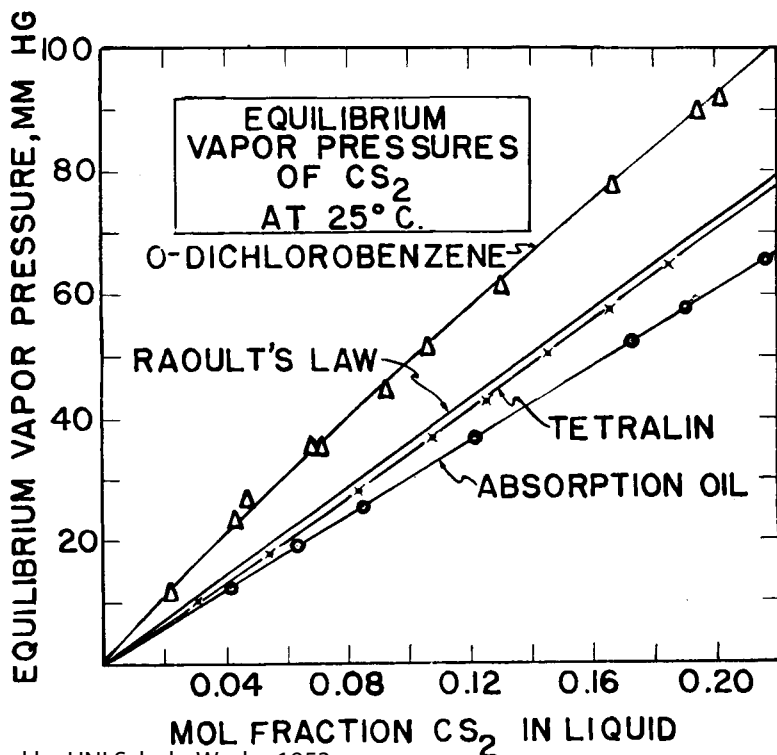
Carbon disulfide-solvent mixtures were analyzed by measuring the density in pycnometers, and reading the concentration from a graph of concentration *vs.* density.

Procedure

Carbon disulfide was added to the large bulb until it was about half full. Then the U-tube was filled to a level slightly below the bulbs. The assembly was placed on its side to permit the liquid in the U-tube to flow into the small bulbs, leaving a clear passage to the liquid in the large chamber. The system was then evacuated until the solution started to boil. At this point the apparatus was turned upright and placed in the constant temperature bath. Boiling was continued for 5 minutes to remove the air. The vent valve (V5) was then opened slightly to equalize the levels of liquid in the legs of the U-tube. After a period sufficient to insure attainment of equilibrium, the levels were equalized again, and the pressure read on the vacuum manometer. A sample was then removed through the sample trap and analyzed.

Results

The equilibrium data obtained in this manner at 25° C. are



shown in Tables 2, 3, and 4, and Figure 3. From the figure, it is seen that solutions of carbon disulfide in tetralin follow Raoult's Law rather closely, while those in o-dichlorobenzene show appreciable positive deviations. Solutions in absorption oil show negative deviations, and this behavior is not to be expected from theoretical

Table 2

Solutions in Absorption Oil

Equilibrium Vapor Pressure of Carbon Disulfide.

Concentration lbs. CS ₂ /lb. oil	Partial Pressure of CS ₂ ; mm. Hg.	Mol Fraction CS ₂
0.0155	12.2	0.0410
0.0247	19.2	0.0637
0.0337	25.8	0.0851
0.0503	37.0	0.1218
0.0756	52.8	0.1725
0.0850	57.8	0.1900
0.1001	65.6	0.2164

Table 3

Solutions In Tetralin

Equilibrium Vapor Pressure of Carbon Disulfide.

Concentration lbs. CS ₂ /lb. oil	Partial Pressure of CS ₂ ; mm. Hg.	Mol Fraction CS ₂
0.0187	10.2	0.0314
0.0329	18.0	0.0540
0.0519	28.4	0.0826
0.0692	37.0	0.1073
0.0824	42.9	0.1252
0.0979	50.7	0.1453
0.1144	57.9	0.1658
0.1303	64.9	0.1847

Table 4

Solutions in O-dichlorobenzene

Equilibrium Vapor Pressure of Carbon Disulfide.

Concentration lbs. CS ₂ /lb. oil	Partial Pressure of CS ₂ ; mm. Hg.	Mol Fraction CS ₂
0.0111	11.4	0.0209
0.0232	23.5	0.0429
0.0257	26.5	0.0472
0.0380	35.3	0.0684
0.0400	35.3	0.0717
0.0533	44.6	0.0933
0.0624	51.6	0.1075
0.0786	61.9	0.1318
0.1043	77.6	0.1676
0.1247	86.9	0.1941
0.2013	141.3	0.2013

considerations. This is probably due to the uncertainty in measuring the molecular weight of the oil, which gives only an approximation. The A.S.T.M. distillation used to estimate the molecular weight is accurate to $\pm 10\%$, and the correlation has the same degree of accuracy. The molecular weight thus has the possible deviation of $\pm 20\%$ and it is quite possible that the absorption oil solutions do follow Raoult's Law if the true molecular weight were known.

Summary

Three oils were chosen as solvents for carbon disulfide. The choice was based on the polarity, cost, vapor pressure, and heat of mixing of the solvents with carbon disulfide. The equilibrium vapor pressures of carbon disulfide above solutions in each of these solvents were measured with a modified isotenscope, and compared with those predicted by Raoult's Law.

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