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THE SOLUBILITY OF HYDROGEN IN NON-POLAR SOLVENTS

Marshall Wayne Cook

Thesis

January 14, 1954

Berkeley, California

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THE SOLUBILITY OF HYDROGEN IN NON-POLAR SOLVENTS

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January 14, 1954

ABSTRACT

The solubility of hydrogen has been measured in eight non-polar solvents. These measurements have been made in the temperature range from -30° to 50° C. and at pressures in the vicinity of one atmosphere. The solvents investigated were n-heptane, n-octane, 2, 2, 4-trimethylpentane, toluene, benzene, carbon disulfide, carbon tetrachloride, and n-perfluoro heptane. The data taken on these systems have been used to test the solubility theory of Hildebrand.

From a survey of the literature it was apparent that previous methods for measuring gas solubilities could not meet the specifications for accuracy and reproducibility required in this work, namely, ±0.05%. Accordingly, the criteria for obtaining accurate reproducible data have been established, and an apparatus and a technique have been developed which fulfill these criteria.

Data other than the solubility of hydrogen have been taken. These results will be found in a forthcoming University of California Radiation Laboratory Report.

This work was performed under the auspices of the U. S. Atomic Energy Commission.

THE SOLUBILITY OF HYDROGEN IN NON-POLAR SOLVENTS

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January 14, 1954

I. INTRODUCTION

The solubility of gases in liquids has been studied by many investigators. The published experimental data of these investigators show wide discrepancies not only between workers but also within the work of any single investigator.

In the present work it was required to obtain solubility data for hydrogen in various solvents to an accuracy of ±0.05%. At the inception of the work, it was clear that previously reported apparatus and techniques were not sufficient to meet this requirement; however, it was not clear in what particulars they were faulty. Accordingly, the factors influencing the accuracy of the data were investigated separately and an apparatus was designed such that the composite effect of these factors would not impair the data within the desired accuracy.

The solubility of hydrogen has been measured in several non-polar solvents in the temperature range from -30° to 50° C. and in the vicinity of one atmosphere pressure. The solubility theory of Hildebrand[9] has been tested with these data in order to determine how closely the solubility of hydrogen may be predicted.

Data on other systems have also been taken. These data are at present classified and contained in a forthcoming University of California Radiation Laboratory report.

II. CRITERIA FOR EVALUATION OF SOLUBILITY DETERMINATIONS

In the measurement of gas solubilities, there is a basic sequence of operations and measurements to be made and a set of conditions to be met regardless of the techniques or the apparatus employed. There are essentially two criteria to be met in order to obtain accurate reproducible data. These criteria are that the experimental measurements be made with an accuracy consistent with the desired accuracy of the data, and that the announced conditions under which these measurements are made have been fulfilled. These measurements and conditions are the following:

1. The pressure, volume and temperature of the gas charged to the dissolution vessel,
2. The partial pressure, volume and temperature of the undissolved gas (here temperature becomes increasingly important as one deals with solvents of high vapor pressure),
3. The degree of purity of the solvent with respect to previously dissolved gases,
4. The degree of attainment of equilibrium,
5. The temperature and the temperature control,
6. The solvent volume or mass,
7. Contamination of the gas during the charging process.

The above list neglects the purity of the solvents and gases employed since impurities in the materials used have little effect on the reproducibility of the data taken by any single investigator, and it is that reproducibility with which we are primarily concerned since this will demonstrate the effectiveness of the apparatus and techniques.

III. DISCUSSION OF PREVIOUS WORK

There have been such a large number of previous investigators in the field of gas solubility measurement that only a few of these workers will be discussed. These few have been selected either because of their prominence or because they have made measurements which we have repeated during this work. A most adequate summary of the data taken up to 1950 is given by Seidell.[20, 21]

All of these investigations, including our own, have used the principles established by Bunsen[2] who in 1855 determined the solubility of several gases in water. These principles are that the initial and residual gases are measured volumetrically, that the pressures of these gases are measured, that provision be made to hasten the attainment of equilibrium by shaking the dissolution vessel, that equilibrium is established when no further solution rate of gas is observed, that the solvent quantity is determined either volumetrically or gravimetrically, and that the solvent must be thoroughly degassed before the gas and solvent are contacted. To accomplish these purposes a wide variety of apparatus is described in the literature, but this variety is largely the result of variation in technique made possible by technological advances in laboratory equipment. Real originality is lacking in apparatus design. For example, Horiuti[11] and Lannung[14] both used apparatus suggested by van Antropoff[1] who modified the apparatus of Estreicher.[3] In turn, Estreicher improved the apparatus of Timofejew[25] which was originally suggested by Ostwald.

The use of a previous investigator's apparatus is certainly not objectionable in itself. However, the data reported in the literature indicate that the apparatus and techniques used do not yield accurate data. There is a marked divergence among solubility values determined by different investigators on the same system. Furthermore, in cases where a worker has reported values obtained from duplicate runs, the low degree of reproducibility seems inordinate. Hildebrand[9] points out several gross discrepancies between values obtained by different investigators. In the work of Lannung[14] disagreements between duplicate determinations were frequently as great as 2% and sometimes greater than 5%. Furthermore, if values determined by different investigators are within 5 to 10% of one another, the agreement is considered to be reasonable.

Such differences as these cannot be justified when one considers the accuracy with which the variables involved can be measured. For example, with minimal care, one can make volumetric measurements to 0.1%; an error of 1% in pressure would involve a reading discrepancy of almost a centimeter; referring to the temperature coefficient of hydrogen solubility, an error of 1° C. would yield an error of less than 0.6%. A further consideration is that the care used in purification and handling of solvents and gases as described by most investigators would seem to rule out discrepancies in the data on account of impurities. Solvent impurity errors should not be overlooked, however. Kretschmer[13] finds, for example, that the solubilities of nitrogen and oxygen are about 20% less in 95% ethanol than

in absolute ethanol.

If the purity of materials is satisfactory and the measurements of temperature, volume, and pressure are sufficiently accurate, the discrepancies in the solubility values must result from other sources of error. These errors, which are the result of faulty technique, can be one or more of the following:

1. Failure to reach equilibrium,
2. Failure to degas the solvent completely,
3. Failure to ascertain the true amount of gas dissolved,
4. Failure to ensure that the transfer of gas from a primary container to the apparatus does not involve air contamination.

If all of these techniques have been properly administered, the results should be reproducible to a degree consistent with the accuracy of the directly observable variables, i.e., with the a priori accuracy. Non-agreement of successive values resulting from faulty technique cannot be analyzed to determine which of the four techniques is at fault after the experiments have been completed. Experiments must therefore be designed to demonstrate separately the reproducibility attainable with each of the above techniques in order to determine which of these must be improved.

Many variations in the measurement of gas quantities are noted in the literature. Lannung[14] measured both the initial and residual gas saturated with solvent; Horiuti[11] measured the initial and residual gas dry except for that gas actually in the solvent bulb; van Antropoff[1] measured the initial gas dry and the residual gas

saturated;* Bunsen[2] measured the initial gas dry and the residual gas saturated.

The measurement of a solvent-saturated gas is inherently inaccurate because saturation occurs by diffusion which is a relatively slow process, especially when it must occur through a long slender tube. Also, temperature variations can cause semi-irreversible condensations. Finally, P-V-T data are seldom available for systems of this type, especially to the accuracy required, and therefore the true amount of gas, i.e., moles, cannot be calculated. In general, to ensure complete saturation of a gas, it must be in intimate contact with the solvent, and this condition is difficult to meet in, for example, a gas burette. In our investigation of this measurement, carried out in an apparatus similar to Lannung's,[14] it was found that the volume of gas increased slowly with time at any given temperature indicating incomplete saturation of the gas. Furthermore, when the same gas charge was measured at successively lower temperature levels, the apparent quantity of gas, in moles, appeared to increase, and this would certainly follow since the solvent partial pressure would become less important at lower temperatures. It is therefore recommended that wherever possible, gas quantities be determined on dry, i.e., solvent-free, gas.

That degassing of the solvent must be complete to within the desired accuracy of the determination is obvious. To isolate this

*In this case, the residual gas was almost certainly not saturated because of the long diffusion path imposed by a glass coil connecting the gas burette to the solvent bulb.

technique for individual attention would be tedious and somewhat impractical. In this case, then, the ultimate criterion is simply whether the results of successive experiments are in satisfactory agreement, when other sources of error have been eliminated. In addition, two secondary criteria for the determination of the completeness of degassing have been used in this work, and although these criteria are not absolute in character, they have been shown to be satisfactory tests of degassing by the reproducibility of the final data. These criteria are described in a later section.

Previous workers have also employed secondary criteria for completeness of degassing of the solvent. Timofejew[25] mentioned that when the solvent was completely degassed, shaking of the solvent container produced a "metallischen Klang". This was the earliest mention of the phenomenon and almost without exception, Timofejew's successors have used this criterion. Unfortunately, no one has determined the threshold gas concentration at which these metallic sounds occur.

In addition to the "metallischen Klang", Lannung[14] condensed the vapor in his solvent vessel by confining the degassed solvent between mercury and observing whether a bubble of gas remained in the system. We have found this test to be reliable for the reproducibility desired, namely, ±0.05%.

The relatively slow rate of solution of a gas in a liquid imposes a serious problem in determining the equilibrium point of a solubility determination. This point has apparently been overlooked by previous workers. Hildebrand[8] has mentioned the problem of super-saturation in gas solubility measurements, but from

observations made in the present work it is believed that this is rather a manifestation of the very slow rates of gas solution or evolution even at appreciable displacements from equilibrium.

The criterion universally used for determination of the equilibrium point has been that no further dissolution of gas was apparent between successive shaking periods of relatively short duration, e.g., one to ten minutes. The technique of upsetting the apparently equilibrated system by changing the pressure and then observing whether dissolution or evolution takes place has not previously been used. By this method, equilibrium can be approached from both sides, a technique frequently used in physical chemical experiments. Furthermore, this method allows one to determine how closely equilibrium can be approached in a given apparatus and in a given gas-solvent system. From our observations, gas solubility rates in many cases can be slow enough to cause errors of 1% or more in the determination of the equilibrium point by the classical method. It was for this reason that in the present apparatus a separate residual gas burette was included (see Fig. 1). This burette is of high enough sensitivity to allow the determination of the equilibrium point to an accuracy of about 0.01%. (This problem is discussed in more detail in section V-F.)

A last point of criticism concerns the manner in which many of the previous investigators have charged gas to their apparatus. This method involves dipping a U-shaped capillary tube, one end of which is free, the other end attached to the solubility apparatus, into a mercury vessel so that the open end enters a gas container

inverted over mercury. Gas is then admitted to the apparatus through the U tube and mercury is allowed to follow in order to seal off the system. If the solubility apparatus is so designed that this U tube is held permanently with the free end in the gas container (cf. Horiuti[11]), then this procedure is quite acceptable. However, if this U tube must be dipped into the gas container for every solubility determination, considerable air contamination can result, possibly from air bubbles clinging to the tube in question. This latter arrangement was used by Lannung[14], von Antropoff,[1] Gjalbaek,[5] Estreicher,[3] and others. Results of tests made on a system of this type showed that the amount of air entering the system in this manner can be of the order of 1%.

Bunsen,[2] one of the earliest investigators of gas solubilities, used an original apparatus which was less subject to the above mentioned errors than many of the more complex designs used by recent workers. He measured the initial gas dry. The residual gas, in intimate contact with the solvent, was undoubtedly saturated. Although his apparatus was volumetrically insensitive, it was an ingenious design (it contained no stopcocks) considering the lack of technology at the time.

Some hydrogen data of the previous investigators are discussed in a later section.

IV. APPARATUS AND PROCEDURE

A. Materials Used

The hydrogen was obtained from the Mathiesen Chemical Corporation. Its purity, as determined by mass spectrographic

analysis, was 99.75% hydrogen, the balance consisting primarily of nitrogen. This nitrogen content required that a small but pertinent correction of the data be made. This correction is outlined in Appendix D and it has been applied to all of the data reported.

All of the solvents were distilled and a center portion of the distillate was selected which exhibited a boiling range of less than 0.1° C. The solvents used were n-heptane, n-octane, 2, 2, 4-trimethylpentane, benzene, toluene, carbon tetrachloride, carbon disulfide, and n-perfluoro heptane. The n-heptane and the 2, 2, 4-trimethylpentane were Phillips 99^{+} mole %, the n-octane was obtained from the Eastman Kodak Company, the benzene, toluene, carbon tetrachloride, and the carbon disulfide were Baker and Adamson's Reagent grade. The carbon disulfide was stored in the dark after distillation. The n-perfluoro heptane was on hand in the laboratory storeroom and is of unknown origin.

Table 1 compares some measured physical properties of the above solvents with literature values of those properties.

All of the literature values listed in Table 1 except those for n-perfluoro heptane are taken from Timmerman's compilation of data.[24] The n-perfluoro heptane values are reported by Fowler[4] and Grosse.[7] The "observed boiling points" are simply those temperatures read during the distillation of the solvents with a partial immersion thermometer calibrated in 1° divisions. This temperature has been corrected to 760 mm. pressure, but no stem correction has been applied. The refractive indices were measured

Table 1

Solvent Properties, Observed and Literature Values

Solvent	Boiling point (°C.)		Density (at 25° C.)		Refractive index (14.6° C.)	
	obs.	lit.	obs.	lit.	obs.	lit.
n-heptane	98.3	98.424	0.6795	0.6795	1.3900	1.3902
n-octane	125.5	125.665	0.6988	0.6988	1.3999	1.3999
2, 2, 4-trimethylpentane	99.2	99.238	0.6879	0.6878	1.3938	1.3942
n-perfluoro heptane	82.5	82.47	1.7203	1.7190	1.267	1.265
benzene	80.0	80.10	0.8733	0.8737	1.5037	1.5045
toluene	110.5	110.61	0.8612	0.8622	1.4987	1.5000
carbon tetrachloride	76.8	76.75	1.5847	1.5843	1.4630	1.4632
carbon disulfide	46.5	46.26	1.2558	1.2558	1.6314	1.6323

Table 1 (Cont.)

Vapor Pressures,[b] mm. Hg

Solvent	0° C. obs.	0° C. lit.	25° C. obs.	25° C. lit.	35° C. obs.	35° C. lit.	Ref. No.
n-heptane	11.3	11.13	45.5_5	45.43	73.4_5	73.65	(26)
n-octane	2.7	2.9	13.9	13.8	24.0	24.0	(24)
2, 2, 4-trimethylpentane	12.8_5	12.99	49.0	49.36	77.9_5	78.25	(26)
n-perfluoro heptane	19.1	21.2	76.1_5	80.1	122.6	128.5	(4)
benzene	45.4[a]	45.47[a]	95.0	95.01	147.6_5	148.15	(26)
toluene	6.6	6.75	28.3	28.40	46.5	46.7	(17, 26)
carbon tetrachloride	33.1	33.1	113.9	112.8	173.9	169.5	(24)
carbon disulfide	126.85	126.5	360.95	359.0	197.7[a]	196.8[a]	(24)

[a] 10° C.

[b] Literature values were obtained by fitting the available data to the equation $\log p = C + A/B + T$.

with an Abbe refractometer, and the densities were measured with pycnometers of 5 cc. capacity.

The vapor pressures were measured in the temperature range from 0° to 35° C. in order to demonstrate solvent purity and to obtain vapor pressures for calculation of the solubility values from the solvents actually used. These measurements were made in an apparatus designed during the present work which is described in Appendix F.

Ballard's triple-distilled mercury was used in these determinations. Before re-use of the mercury, air was bubbled through it for about two hours to remove solvents and to oxidize base metals. It was then passed through a pin hole in a filter paper. This latter process removed all visible solid material.

B. Apparatus

The solubility apparatus is shown in Figs. 1, 2, and 3, and the auxiliary equipment is shown in Figs. 4 through 16. As shown in Fig. 2, there were two solubility apparatus in this work. Each was fastened to a separate steel mounting plate with "3-M" Bedding Compound, an adhesive product of the Minnesota Mining and Manufacturing Company which sets into a rubber-like substance. Each apparatus is provided with its own millimeter scale which is fastened securely to the steel mounting plate with machine screws. Each mounting plate is fixed semi-permanently to the shaking mechanism (Fig. 4) in such a manner as to allow levelling of the apparatus.

As shown in Fig. 4, the shaking mechanism is designed to allow a variation in the frequency of shaking by changing gears,

while the amplitude of shaking may be changed by adjusting a variable eccentric. A frequency of about 170 minute^{-1} and an amplitude of about 3/8 of an inch were employed in all of the experiments. It will be noted that the shaking mechanism also provides a horizontal motion which is intended to avoid pressure disturbances due to vertical accelerations during the periods of shaking.

The air thermostat consists of a chamber in which the experiments are conducted and through which air is circulated upwards to a blower which is external to this chamber. The air then passes downward through a cooler and a heater and finally returns to the thermostatted chamber (see Fig. 6). The inlet to outlet temperature difference in this chamber was about 0.1^{o} C. while operating at -30^{o} C. At the same time, the temperature difference over the length of the solvent bulb was less than 0.01^{o} C.

During the solubility determinations all levels were sighted with a cathetometer telescope and referred to the above mentioned millimeter scales. The cathetometer was used to avoid parallax errors.

This apparatus was designed specifically to measure hydrogen solubilities. A few modifications as set forth in section V-K would adapt this design for use with a wide range of systems.

Barometric pressures were read on a Fortin type U. S. Signal Corps barometer, and tabulated corrections provided by the manufacturer were made for temperature and local gravity.

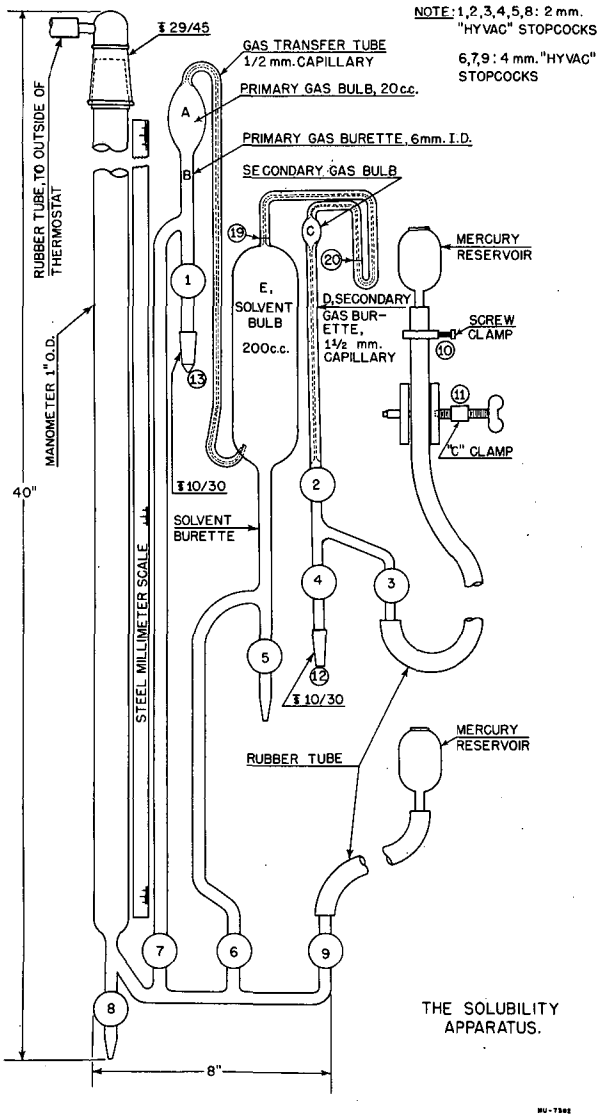


Fig. 1. The solubility apparatus.

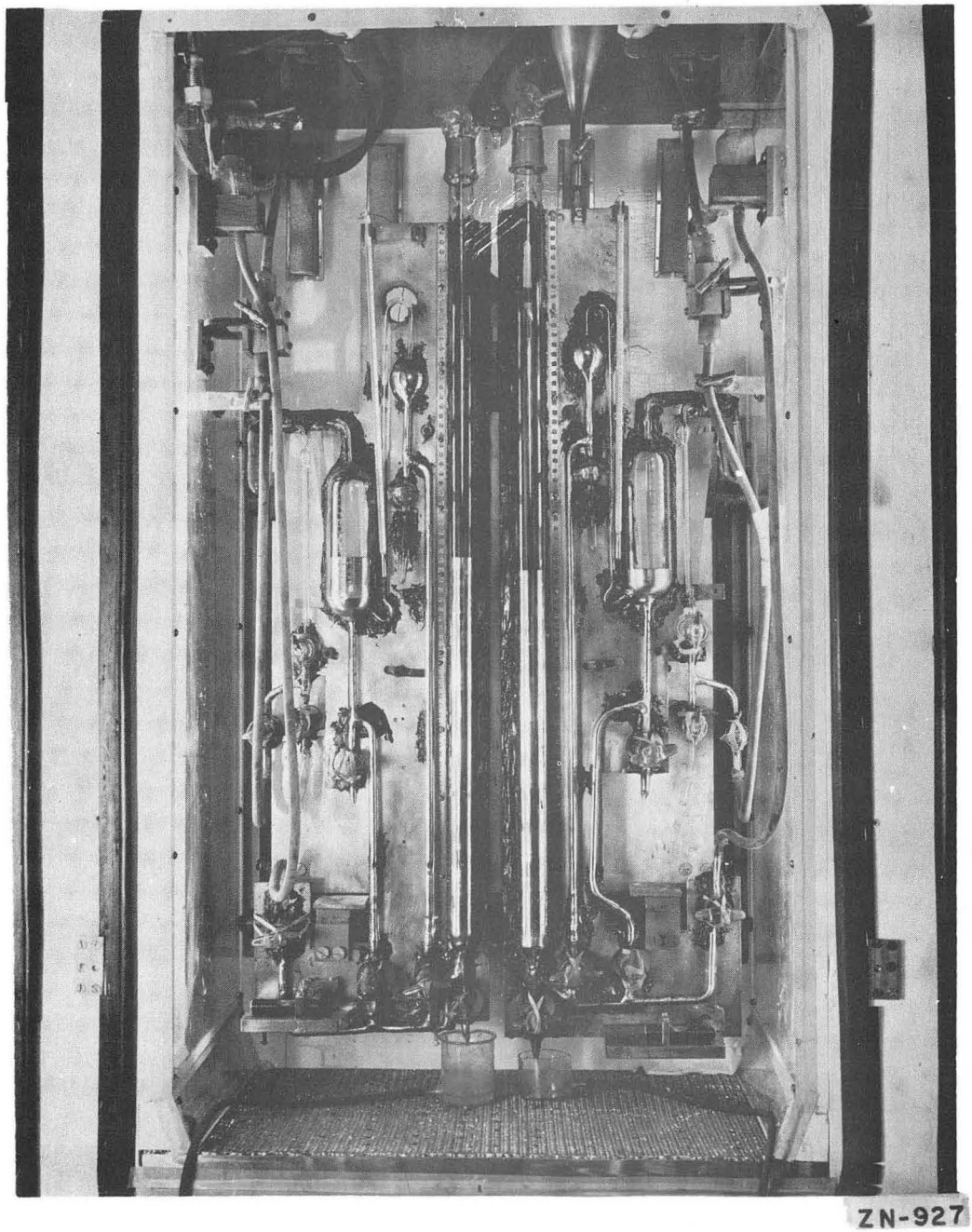


Fig. 2. Both solubility apparatus in place.

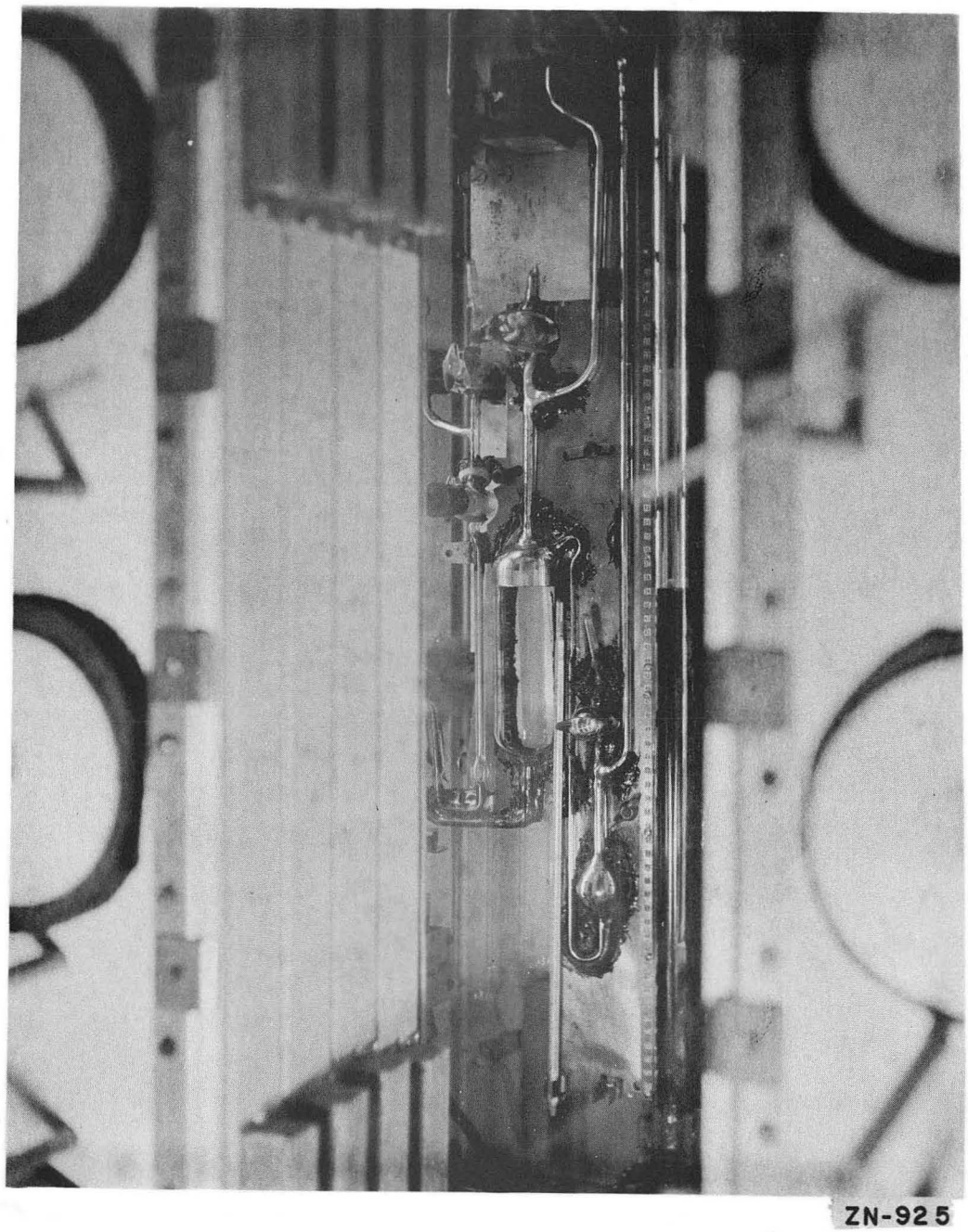
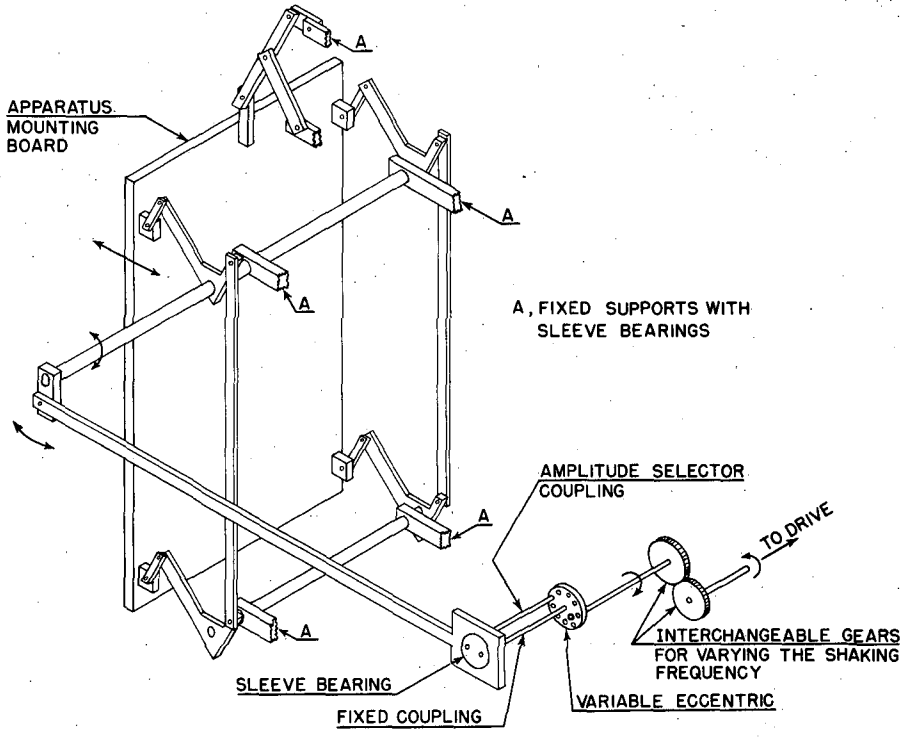


Fig. 3. A view of the apparatus through the thermostat window.



SCHEMATIC DIAGRAM OF THE SHAKER MECHANISM.

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Fig. 4. Schematic diagram of the shaker mechanism.

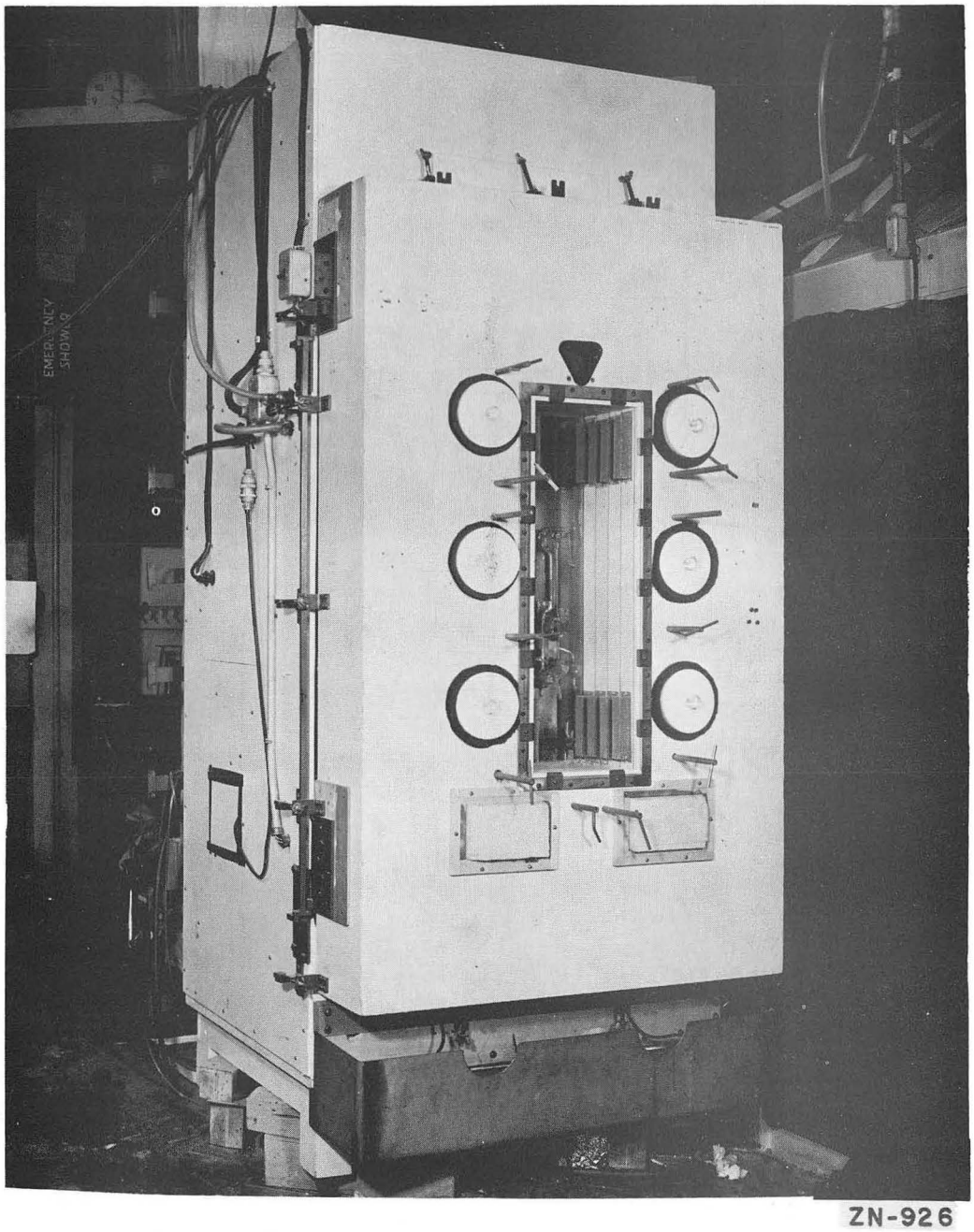

Fig. 5. The air-bath thermostat.

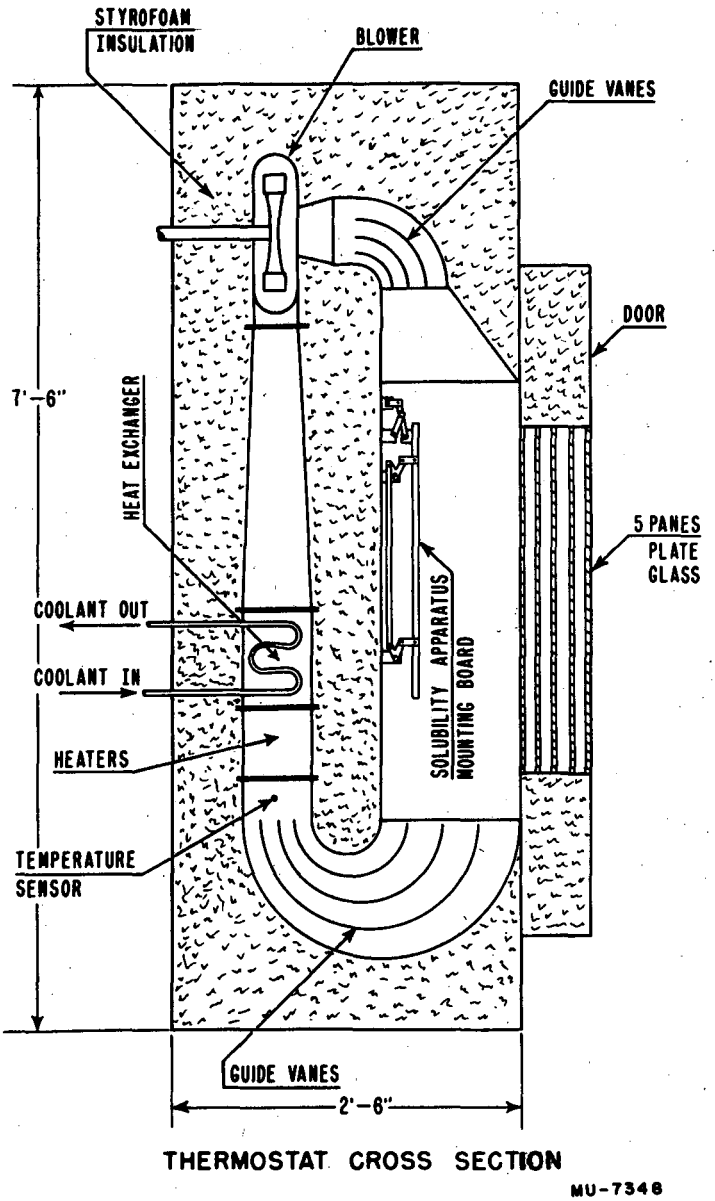

Fig. 6. Thermostat cross section.

The solvent densities were measured with pycnometers of 5 cc. capacity.

Temperatures from -10° to 50° C. were determined with thermometers calibrated in 0.1° divisions and certified by the National Bureau of Standards. Between -30° and -10° C. an A. P. I. aniline point thermometer calibrated in 0.2° divisions was used. In the whole temperature range, nine iron constantan thermocouples distributed throughout the thermostat were used in conjunction with a Leeds and Northrup "K-2" potentiometer to determine temperature gradients within the thermostat. The thermocouples were calibrated at the dry ice point by the method of Scott,[19] and also at the sodium sulfate point (32.38° C.).

C. Procedure

Volumetric calibration was performed by weighing mercury displaced from pertinent sections of the apparatus as shown in Fig. 1. Check calibrations were made at both 25° and 35° C. In order to exclude air bubbles during this procedure, the section being calibrated was evacuated to about 10 microns before filling it with mercury. Referring to Fig. 1, the parts calibrated in this manner are the gas bulbs, A and C, the gas burettes, B and D, the solvent bulb, E, from point 19 down to and including the solvent burette. The secondary gas burette and bulb were calibrated by attaching a delivery tip fused to a 10/30 T joint which mates with the tip and point 12. This part was calibrated from 19 down to stopcock 2. Throughout the calibration all readings were made by sighting the pertinent levels with a cathetometer. The cathetometer telescope

was then rotated in order to refer these readings to the steel scale attached to the apparatus mounting board.

The temperature coefficient of volumetric expansion found from the calibrations made at 25^{o} and 35^{o} was 1.1×10^{-5} degrees^{-1}. This agrees well with the value of 1.09×10^{-5} reported for pyrex glass in the Corning Glass Catalogue.

The approximate capacities of the various parts of the apparatus are:

Solvent bulb	200 cc.
Primary gas bulb	22 cc.
Secondary gas bulb	1 cc.
Solvent burette	0.1 cc./cm.
Primary gas burette	0.25 cc./cm.
Secondary gas burette	0.015 cc./cm.

Solubility determinations are carried out in the following manner. The gas bulb and solvent bulb sections are filled with mercury by a process of evacuation described above. Stopcocks 2 and 4 are thoroughly degreased and then rinsed at least three times with the solvent to be charged to the apparatus. This rinsing is done by connecting a clean hypodermic syringe full of solvent to point 12 by means of a tygon tube.

A funnel fused to a female 10/30 ℑ joint is then attached to point 12. Solvent flows into the solvent bulb by means of the attached funnel, and displaces the mercury which is allowed to flow into the manometer. Vacuum is applied to the manometer as necessary.

When the desired amount of solvent has been admitted to the solvent bulb, air is allowed to follow so that about an inch of vapor space is provided above the solvent for boiling. The secondary gas burette is then dried by evacuation, and stopcocks 2 and 4 are greased lightly with Dow Corning high vacuum stopcock lubricant.* With only stopcocks 2 and 4 open, the solvent is degassed by evacuation through 12 which is connected to a vacuum system with a rubber tube. The evaporated solvent is condensed in a liquid nitrogen trap (see Fig. 7.).

By means of an infrared heat lamp, heat is applied to the solvent to induce boiling and to the secondary burette section to ensure that all of the solvent passing through stopcocks 2 and 4 is in the vapor state so that dissolution and removal of the lubricant will be prevented.

After degassing is complete, as indicated by a vacuum thermocouple gauge (see section V-D), mercury is admitted to the system through stopcock 3, 4 first having been closed, until the secondary burette system is filled. Stopcock 6 is then opened

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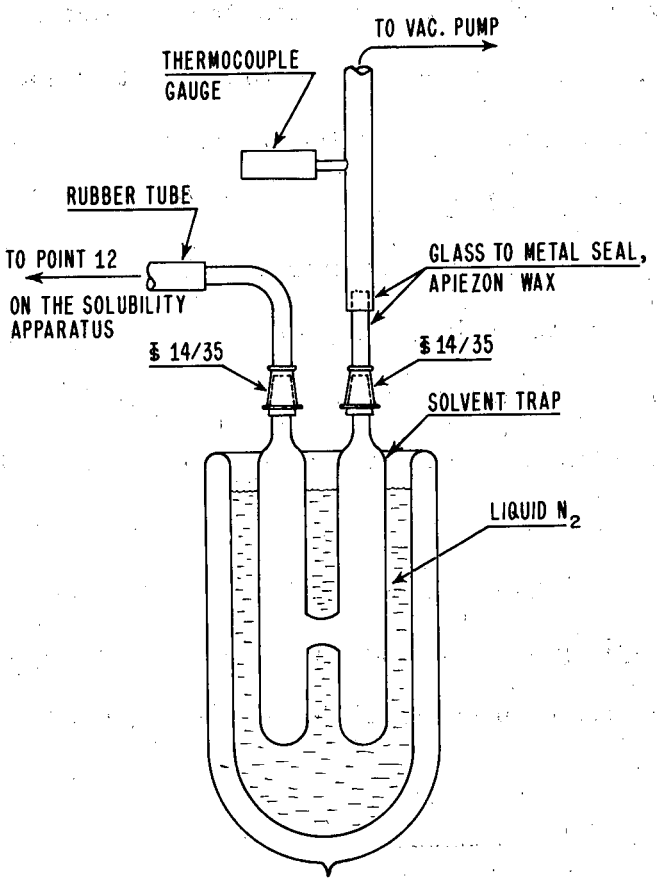
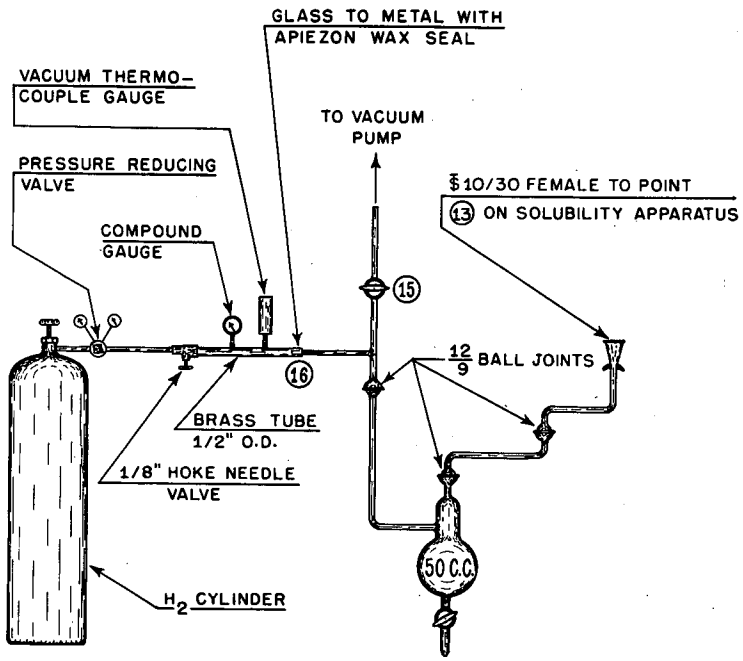
*This was found to be the only satisfactory lubricant for the temperature range under investigation. It allows manipulation of stopcocks at temperatures less than -40° C. and is still sufficiently viscous at 50° C. for vacuum work. Only stopcocks 2, 4, 8, and 9 were greased with this lubricant since these are the only stopcocks used at the lower temperatures. "Lubriseal" high vacuum compound, distributed by Central Scientific Company, was used in the remaining stopcocks.



AUXILIARY DEGASSING APPARATUS

MU-7349

Fig. 7. Auxiliary degassing apparatus.



GAS CHARGING SYSTEM.

MU-7350

Fig. 8. Gas charging system.

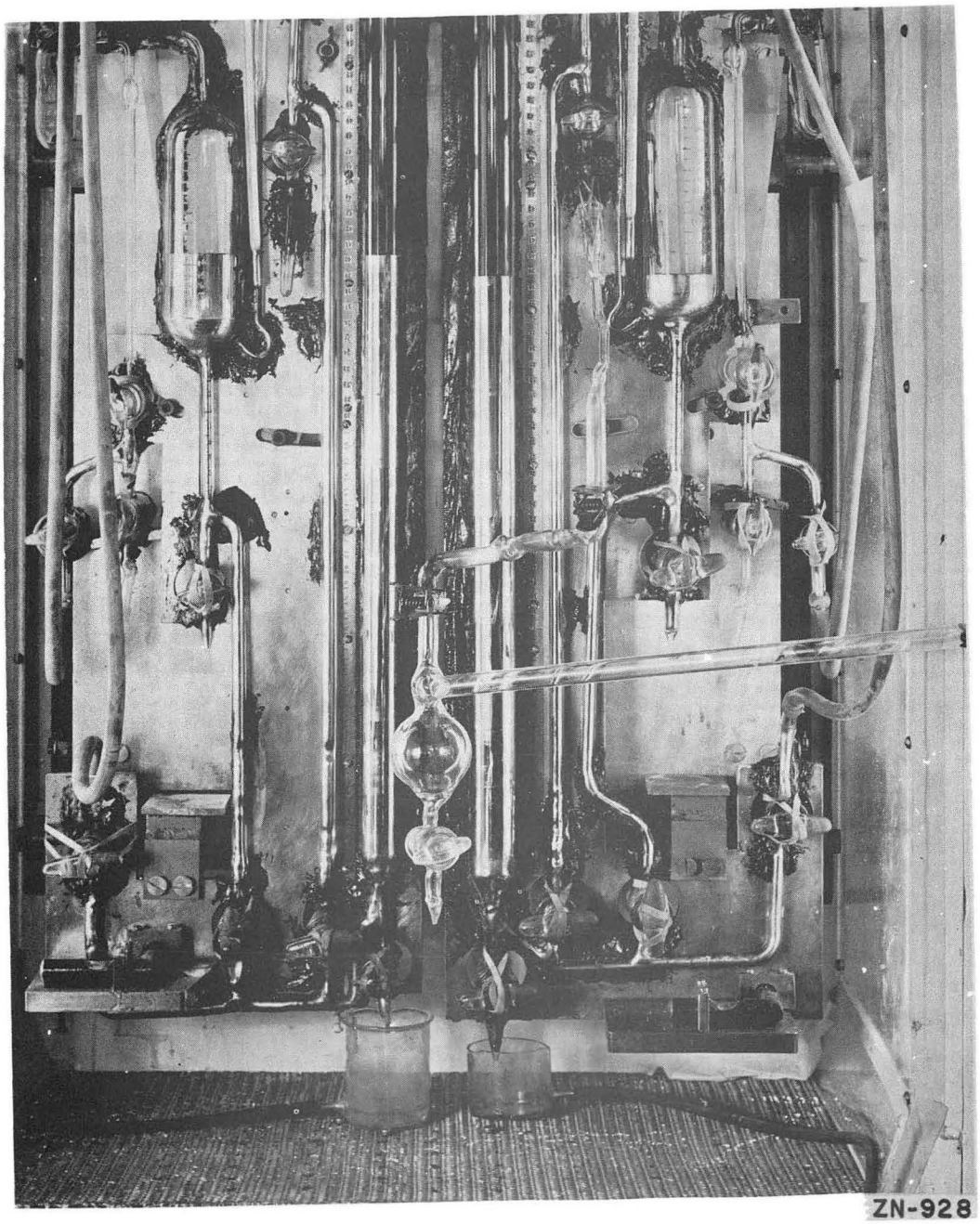


Fig. 9. The solubility apparatus with the gas charging system in place.

to allow mercury to flow into the solvent bulb. At this point, if a gas bubble remains in the solvent bulb, the degassing process is resumed. In the degassing process it was found that from 10 to 20% of the solvent was evaporated, that the amount of solvent required to be evaporated is increased as the rate of boiling increases, and that the time required for degassing was about one to two hours.

After the solvent has been confined between mercury as described above, all stopcocks are closed except 2 and 6, which are left open to allow expansion or contraction of the confined solvent and mercury.

The gas charging system is then put in place and evacuated. (See Figs. 8 and 9.) This system is tested for tightness by closing stopcock 15 and observing the rate of rise of pressure on a thermocouple vacuum gauge. A rate of less than 5 microns per minute was considered satisfactory. The system was then purged four times with hydrogen, and the system was pumped down to at least 10 microns between each purge. At this point stopcock 16 is closed, the charging system is evacuated, and stopcock 1 is opened after closing stopcock 6. The mercury in the "primary gas bulb" flows out through stopcock 1 leaving a Toricellian vacuum in the gas bulb.

At this point care was taken to see that the mercury leg in the capillary between the gas bulb and the solvent bulb was sufficient to overcome the vapor pressure of the solvent; in some cases chilling of the solvent was necessary. Then, by closing 15 and opening 16, gas is admitted to the gas bulb through needle

valve 17 until the approximate desired pressure is read on the compound gauge. Mercury is then admitted to the gas bulb through 7, and 1 is closed. The charging system is then retested for tightness as described above before acceptance of the gas charged.

When the gas and solvent have been placed in the apparatus, stopcocks 6 and 7 are opened, and the manometer level is adjusted so that the mercury level in the gas burette is in a readable position. The gas charging system is removed, and the thermostat is closed and brought to 25° C. Temperature equilibrium is indicated by observing that no change in the mercury level in the gas transfer capillary occurs when stopcock 6 is closed for a period of two or three minutes (i.e., the solvent bult and its contents furnish a very sensitive thermometer). Temperature equilibrium was generally attained in from two to three hours. Appendix E indicates how this time can be shortened by means of a time-temperature schedule.

When temperature equilibrium has been established, the mercury levels in the gas burette, the gas transfer capillary, and the manometer are read on the scale with a cathetometer. A barometer reading is also made. Two sets of readings are made at one manometer setting, and then the pressure is changed by about two centimeters and one or two more sets of readings are made. These check determinations serve to indicate whether temperature equilibrium has been attained and whether the stopcock bore connecting the gas bulb to the manometer is free of lubricant. From these readings and the volumetric calibrations of the apparatus, the quantity of gas in moles is calculated. For this

calculation, the molal volume of hydrogen is taken to be 24,481 cc. at 25° and one atmosphere.[27] The ideal gas laws are assumed in correcting for the difference in pressure from one atmosphere. The determination of the initial quantity of gas is continued until concordant results are obtained which correspond to ±0.1 mm. of mercury pressure.

It has been found that a change in pressure of about one to two centimeters in the gas pressure, as described above, can cause adiabatic heating or cooling sufficient to require at least half an hour for temperature equilibrium to be re-attained.

After a satisfactory value of the gas quantity has been determined, the gas is passed into the solvent bulb by first closing 7, opening 6, and applying vacuum to 14. Then by closing 6, after releasing the vacuum, and opening 7, a part of the gas flows into the solvent bulb. This procedure is repeated until all of the gas has been pushed into the solvent bulb at which point the gas delivery tip in the solvent bulb is exposed to the solvent by suitably applying vacuum to 14. Then, after closing 6 and releasing the vacuum, 7 is barely opened to push the last bubble of gas, if any, into the solvent bulb.

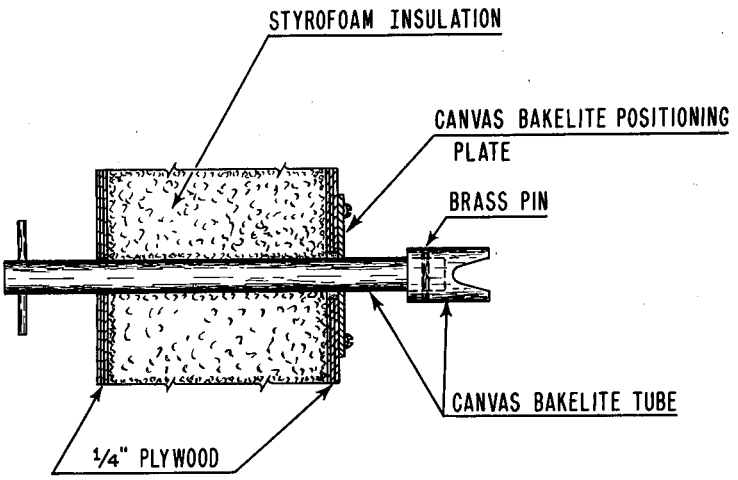
With stopcock 6 open, dissolution of the gas in the solvent is begun by starting the shaker mechanism. This initial dissolution was generally hastened by applying about 10 p.s.i.g. to the manometer through 14.

From this point, all manipulations are carried out remotely in order to avoid temperature upsets caused by placing one's hands in the thermostat. Stopcocks 2, 8, and 9 and clamps 10 and 11 are

operated by a device shown in Fig. 10.

When a residual gas bubble of a size suitable for measuring (about 1 cc.) remains, the bubble is pulled into the secondary gas bulb and burette. This transfer is done by opening stopcock 2 and releasing the pressure on the rubber tube with "C" clamp 10. When the solvent is at point 19, the mercury level in the burette is read and the gas is pushed back into the solvent bulb. Shaking is resumed for a measured period of time and the reading process is repeated. The manometer is then adjusted in a direction to oppose the observed change in the burette reading, and this process is continued until the equilibrium pressure is found to within about one or two millimeters.

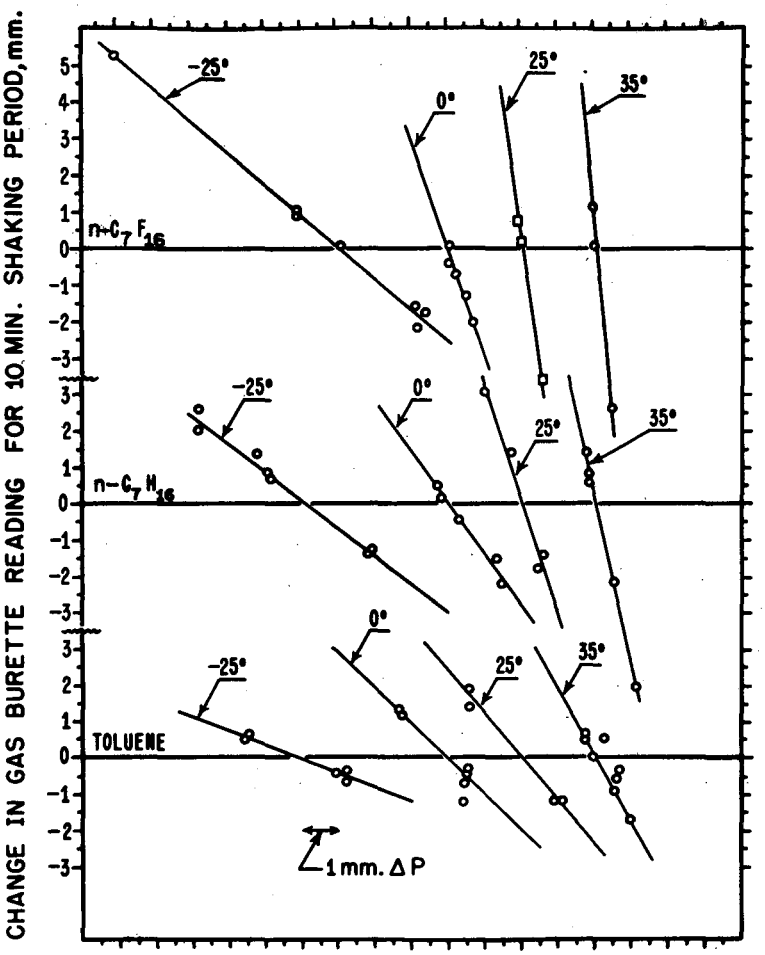
The final equilibrium pressure is determined by measuring the change in the burette reading for a given period of shaking (usually 10 to 20 minutes). Duplicate determinations of this change in reading are made for two or more pressures such that the gas dissolves at the higher pressure and evolves at the lower pressure. Depending on the solution rate, the difference in these two pressures was from 0.5 to 5.0 mm. The equilibrium pressure was then determined by drawing a straight line between the values of these differences plotted versus the manometer readings which have been corrected to a base barometric pressure. An example of this plot is given in Fig. 11. The validity of this procedure and the restrictions involved are discussed in Appendix B. For each burette reading, a corresponding barometric pressure is determined, and while the gas is in the solvent bulb the levels of the mercury in the manometer,



A SECTION OF THE THERMOSTAT DOOR SHOWING THE REMOTE STOPCOK MANIPULATOR.

MU-7351

Fig. 10. A section of the thermostat door showing the remote stopcock manipulator.



RELATIVE RATES OF SOLUTION vs PRESSURE SETTING, FOR DETERMINATION OF THE EQUILIBRIUM PRESSURE (SEE TEXT)

MU-7382

Fig. 11. Relative rates of solution versus pressure setting.

the mercury in the solvent bulb, and the solvent-gas interface are read.

This process is then repeated for the other desired temperatures, after which the solvent volume is determined at 35° C.* by opening stopcocks 2 and 4 to the atmosphere, closing stopcocks 3, 6, and 7, and pulling the mercury out of the secondary gas burette system by means of a syringe and rubber tube attached to 12. After making suitable adjustments in the manometer mercury level, stopcock 6 is opened, and the solvent level is pulled up to 19, again with the aid of a syringe. With stopcocks 6 and 7 both closed, the mercury in the solvent bulb is drained into a tared bottle and weighed. The volume of the solvent is determined by the difference between the solvent bulb volume and the volume of the mercury just drained.

The solubility in gram moles/gram, atm. is then calculated from the initial and final quantities of gas, the pressure measurements, and the vapor pressure of the solvent. A detailed sample calculation is given in Appendix A.

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*Manipulations made during the determination of the solvent volume require that one's hands be placed in the thermostat. Since 35° C. is quite near to body temperature, less temperature upset is likely to occur at this temperature than, for example, at 25° C. No change in the thermometer readings was observed during these manipulations.

V. DISCUSSION OF THE APPARATUS AND PROCEDURE

A. General Design Considerations

The criteria for obtaining reproducible, accurate gas solubility data have been enumerated in a previous section. The apparatus shown in Fig. 1 has been designed to fulfill these criteria.

The initial gas measuring system (the primary gas bulb and burette) allows the gas to be measured in a dry state, i.e., free of solvent. The amount of initial gas can therefore be calculated from P-V-T data which are generally available. The volume of the gas bulb is fixed approximately by the volume of the solvent bulb since the apparatus was designed primarily for the measurement of hydrogen solubility. With the gas bulb volume a known value, the burette diameter was specified so that the most accurate value of the PV product could be obtained; i.e., the uncertainty introduced by capillary corrections required in a burette of small diameter were balanced against the volume uncertainties sustained in a burette of large diameter.

The initial gas measuring system is placed at a level sufficiently higher than the solvent bulb so that evacuation of the gas bulb can be carried out in the gas charging process without causing vaporization of the previously degassed solvent.

After accurate measurement of the gas charged to the apparatus was provided for, it seemed desirable to transfer that gas quantitatively to the solvent bulb. This provision is met by the capillary tube connecting the top of the primary gas bulb to the solvent bulb. The end of this tube is a delivery tip drawn out to about 0.2 mm. i.d. to prevent gas bubbles from remaining in the

delivery tube. It will also be noted that the gas contacts no stopcocks while being transferred; this provision prevents contamination and/or absorption of the gas, as well as loss of the gas as bubbles which fail to pass through a stopcock.

In order to preserve the accuracy obtained in the measurement of the initial gas, it was desirable to dissolve most of it. The residual gas will be saturated with solvent, and as well as the previously discussed errors which are likely in the measurement of a solvent saturated gas, a large residual volume would lead to the decrease in accuracy accompanying the subtraction of two large numbers to find the amount of gas actually dissolved. On the other hand, as the amount of residual gas decreases, the area of the gas solvent interface also decreases; therefore the rate of solution of the gas decreases and makes the determination of the equilibrium point more difficult. Here again a compromise was made and the residual gas volume was set at 1 cc. which is about 5% of the initial gas charged. The uncertainty in the amount of residual gas as calculated from the law of additive pressures is therefore decreased by a factor of about 0.05. Furthermore, the top of the solvent bulb was specified to have very little curvature so that the small quantity of residual gas presents a relatively large area for dissolution.

From work done prior to this design, the problem of the slow rate of gas dissolution was recognized and provided for by a sensitive capillary burette of about 1.5 mm. i.d. Measurements in this burette allow the detection of very small changes in the

volume of the residual gas; hence, by observing these changes with pressure settings in the vicinity of the equilibrium value, the equilibrium point may be determined well within the desired accuracy.

Measurement of the residual gas volume entails upsetting the pressure of the system, i.e., as the gas is pulled over into the secondary gas bulb and burette, it is displaced by mercury flowing into the solvent bulb from the manometer. To minimize this change in pressure, a manometer of about 2 centimeters i.d. was specified. Even so, this measurement entails a pressure change of about 3 mm., but since the solvent gas interface is at that time in a capillary, the rate of solution is negligible. This has been shown to be the case experimentally.

The specification that 95% of the gas charged should be dissolved imposes the disadvantage on the apparatus that the value of the solubility must be known at least approximately before charging the apparatus. To offset this disadvantage, the manometer was made sufficiently long to allow a range of pressures from 0.5 to 1.5 atmospheres.

The design of the apparatus finally employed was the result of testing and rejecting a series of five designs. The criterion for acceptance was that the data should be reproducible to at least ±0.05%, and the sixth design exhibited this reproducibility. In all such tests the system used was hydrogen-n-heptane. Other solvents were not used until the problem of reproducibility had been overcome. The seventh design (Fig. 1) was simply an improved version of the sixth design affording somewhat more accuracy and considerably greater ease in manipulation. The first apparatus tested was the

design of Lannung,[14] specifically, the apparatus used by Gjaldbaek.[5] For comparison, the following data are presented to exhibit reproducibility of our final design.

Table 2

Solubility of Hydrogen in n-heptane at 35° C., gram moles/gram atm.

App. No. 1[a]		App. No. 6		App. No. 7-R		App. No. 7-L	
Run No.	Sol.	Run No.	Sol.	Run No.	Sol.	Run No.	Sol.
1	7.34×10^{-6}	24	7.281	44	7.282	46	7.281
4	7.40	25	7.278				
6	7.14	26	7.281				
		30	7.274				
		42	7.276				

[a] Gjaldbaek's apparatus.

B. Measurement of the Gas Charged and Dissolved

It is commonly considered that the two mercury legs in an open manometer of constant inside diameter will come to the same height, the capillary correction cancelling out. That this is not necessarily the fact is both observable experimentally and calculable from data on capillary corrections for mercury in glass.[10] The capillarity correction is a function not only of the tube diameter, but also of the meniscus height. In a clean 4 mm. i.d. glass U tube, the author observed differences in the height of mercury therein as great as 2 mm., while if the menisci heights were measured and corrected for, this difference disappeared. Since it is often difficult to read the height of a meniscus accurately a pressure

determination can be made most accurately by simply using a large diameter manometer, in which case the corrections are small. However, if one leg of the manometer is also a burette in which a gas volume is being measured, it is apparent that increasing the diameter of the manometer leg will decrease the accuracy to which the gas volume can be measured. In order to measure a given quantity of gas to the best accuracy, an optimum tube diameter is indicated such that the percentage accuracy of the volume is equal to the percentage accuracy of the pressure. In the present case a gas volume of about 20 cc. was measured at approximately atmospheric pressure. If an error of 0.1 mm. in the gas burette reading is assumed, Table 3 gives pressure and volume errors. As indicated by the values in Table 3, a gas burette diameter of approximately 6 mm. was chosen.

Table 3

Errors in Pressure and Volume for Measurement of 20 cc. of Gas at 1 Atmosphere as Related to Burette Diameter. A Reading Error of 0.1 mm. Is Assumed.

Burette diameter mm.	Vol. error cc.	% Vol. error	Press. error mm.	Cap. corr. error mm.	% P error	PV error
4	0.0012	0.006	-0.1	-0.2	0.040	0.046
5	0.0019	0.0095	-0.1	-0.15	0.035	0.044
6	0.0028	0.014	-0.1	-0.10	0.026	0.040
7	0.0037	0.018	-0.1	-0.07	0.022	0.040
8	0.0049	0.024	-0.1	-0.05	0.020	0.044

Experimentally, check determinations on the quantity of initial gas charged checked with no difficulty to better than 0.05% between two pressure settings as described under "Procedure". Table 4 furnishes three examples of this reproducibility for the determination of the quantity of initial gas.

Inasmuch as the apparatus is designed so that about 95% of the gas charged is finally dissolved, the amount of gas dissolved is automatically known to a fair accuracy. In addition, the volume of residual gas was measured to a high accuracy in a capillary burette.

Table 4

Examples of the Reproducibility Obtained in the Determination of the Quantity of Initial Gas

Run No.	Total pressure, mm.	Moles of gas x 10^4
51-42-V	475.8_5	5.473_2
"	475.8	5.472_6
"	465.2	5.472_7
53-44-V	569.1	7.022_6
"	563.3	7.022_2
50-41-V	431.2	5.334_9
"	425.4	5.334_7

In determining the moles of gas remaining from the measured volume there is an inaccuracy in the computation since a volume of gas saturated with a vapor is measured and PVT data for the mixture are unavailable. However, this possible error must be quite small since such a small quantity of gas remains undissolved and the law

of additive pressures is sufficiently accurate for this purpose. Complete saturation of the residual gas is assured in our apparatus because all of this gas is in intimate contact with the solvent.

C. The Pressure of the Experiment

As shown in a previous section, the amount of gas dissolved is known at least to ±0.05%, while the equilibrium total pressure is determined in most cases to well within ±0.2 mm., which for a total pressure of 760 mm. is approximately ±0.025%. The question may then be asked as to whether the total pressure minus the vapor pressure of the solvent truly gives the partial pressure of the gas in the vapor phase. It is believed that such is the case inasmuch as the solubilities obtained are calculated per atmosphere of the gas partial pressure, and identical results within the desired accuracy are obtained in the case of n-heptane where the hydrogen partial pressure was varied from about 500 mm. to 850 mm. The slight deviations in the calculated solubility show no correlation with the pressure level of the experiment; that the law of additive pressures holds (and incidentally that Henry's Law holds) is also illustrated by the data on perfluoro heptane for which a series of four experiments was run in two pieces of our apparatus. These results are given in Table 5. Here, p_g is the partial pressure of hydrogen.

Table 5

The Solubility of H_2 in n-C_7F_{16} at Various Partial Pressures of H_2

Run No.	App. No.	25° C. $\bar{p}_g$, mm.	25° C. Solubility gram moles/ gram, atm.	35° C. $\bar{p}_g$, mm.	35° C. Solubility gram moles/ gram, atm.
47	7-R	688.0	3.612	649.7	3.850
31	6	811.4	3.611	758.2	3.852
32	6	638.9	3.613	601.5	3.848
33	6	591.0	3.611	555.9	3.850

D. Solvent Degassing

The degassing process of the solvent is one step in the procedure which cannot be designed for, the only good criterion for sufficient degassing being a high precision in results between various solubility determinations on successive quantities of the same solvent. The Ramsay-Rayleigh equation[16] for batch binary distillation predicts that as little as 0.1% of the solvent being evaporated should suffice to reduce the gas content of the solvent by several thousandfold, but this equation presumes equilibrium between gas and liquid which is probably not attained in the present case. However, two other criteria for complete outgassing have been found which have withstood the test of reproducibility for the solubility data.

The first of these criteria is a dynamic test based on the observation of a vacuum thermocouple gauge* located in the vacuum

*Manufactured by the National Research Corporation.

system beyond the liquid nitrogen trap and ahead of the vacuum pump (see Fig. 7). As the degassing of the solvent proceeds, the vacuum gauge reading falls slowly from >1000 microns to about 5 microns, the base pressure of the pump. This observation is made while the solvent is boiling vigorously. This indicates that negligible non-condensable gases are being driven off. Then, as a precaution, at least as much more solvent as has already been evaporated is boiled away before stopping the outgassing procedure.

The second criterion consists of the appearance of no gas bubble in the solvent bulb as the outgassed solvent is cushioned between mercury prior to the gas charging operation. This test is quite sensitive in that gas bubbles much smaller than 0.001 cc. can be readily detected and this is the amount of gas which occupied about 30 cc. of volume prior to compression. These gas bubbles persist for periods of several minutes because solution rates are quite slow.

E. Gas Charging

As previously mentioned, the method of charging gas to the apparatus from a vessel inverted over mercury by means of a U tube dipped under the mercury and into that vessel was found to be unsatisfactory. This method has been studied with a gas sampling vessel designed to duplicate the conditions under which gas was charged to the apparatus. The results of these tests as obtained by mass spectrographic analyses show that air contamination of the order of 1% can result from this procedure. It is hypothesized that air contamination is incurred by air bubbles which cling to the U tube as it passes from the air through the mercury and into the gas

reservoir.

Another series of tests was carried out on the present gas charging system which is shown in Figs. 8 and 9. These tests were made in accordance with the purging and evacuation method used in filling the apparatus, and mass spectrographic analyses showed that no measurable air contamination occurred. It is assumed, therefore, that the transferring of gas from the gas cylinder to the apparatus does not result in air contamination.

F. Determination of Equilibrium

Previous investigators have used as a criterion for equilibrium no apparent dissolution within periods of time of the order of 10 minutes. At least for the case of hydrogen, this criterion could lead to errors of the order of 1% at 35° and much greater errors at lower temperatures. Calculation of these errors is given in Appendix C. It is believed that this error in finding the true equilibrium point along with incomplete degassing of the solvent and measurement of large "saturated" gas volumes comprise the major reasons for lack of consistent data by previous workers.

A large error in the determination of the equilibrium point can be sustained if the same vessel is used for the determination of the amounts of both the initial and residual gas. Although a burette allowing an accuracy of 0.1% is sufficient to determine the amount of gas dissolved to the desired accuracy, it does not allow sufficient precision for detecting the extremely small rates of solution in the vicinity of equilibrium. The author discovered this phenomenon by running an apparatus of Lannung's[14] design for a

period of about 12 hours, during which time the rate of solution appeared to be essentially constant. This observation indicated that in this period of time the amount of gas dissolved was insufficient to alter the concentration of dissolved gas appreciably. If, on the other hand, two readings had been made at about a one hour interval, the difference in the readings would not have been detectable within the accuracy of the apparatus.

This rate of solution is, of course, a function of interfacial area and the shaking intensity, as well as of the gas and solvent involved. However, insofar as can be determined, the shaking intensity and interfacial area employed here do not vary a great deal from those reported in the literature.

To provide an accurate determination of the equilibrium point, a system for measuring the residual gas (a 1 cc. gas bulb with a 1.5 mm. capillary burette) has been designed to give a precision enabling the detection of a change in residual gas volume as small as 0.00015 cc. which amounts to a change of about 0.0005%. This precision is required only to detect the rate of solution, while the volume of residual gas is known to an absurd accuracy.

The equilibrium point is then determined, as described in section V-F, by plotting the difference between burette readings made before and after shaking periods of from 5 to 20 minutes, depending on the rate. This procedure is repeated at some other pressure setting so that the two measured differences are of a different sign, the two different values are plotted versus the manometer setting and the equilibrium pressure is determined by

interpolation to the manometer setting where the solution rate is zero. As shown in Fig. 7, this point can be easily determined to within 0.1 to 0.2 mm., which is well within the required ±0.05% accuracy required. The validity of this linear interpolation is discussed in Appendix B along with the necessary restrictions.

One point concerning measuring of consistent solution rates (or differences) is that the solution rate when not shaking the apparatus is appreciable although considerably smaller than with shaking. In the several instances measured, this solubility rate while the apparatus is at rest was about 1/3 to 1/10 of that during agitation. It can therefore be concluded that to obtain consistent rates, one must adopt a consistent manipulative procedure which is carried out in detail for each set of readings. For example, the author adopted the procedure of measuring the manometer heights just after moving the gas from the burette to the solvent bulb, then the apparatus was shaken for a period, generally 10 minutes to within ±3 seconds, after which the gas was transferred into the burette system as rapidly as possible. Once in the burette, the rate of solution was found to be completely negligible in spite of the slight pressure upset (3 to 4 mm.) required to make this transfer. It might be pointed out again here that the reason for the large diameter manometer was not only to avoid capillary correction, but also to minimize the pressure change on the gas as it is transferred into the measuring system from the solvent bulb.

G. The Solvent Volume

The solvent bulb, as shown in Fig. 1, is actually a pipette, the upper tube of which is a 1.5 mm. capillary and the lower tube a 4 mm. capillary previously calibrated by mercury displacement. Check calibrations of the solvent bulb were well within ±0.004 cc. which represents a volume inaccuracy of ±0.0005%. This checks well with the fact that the solvent burette had a volume of 0.0009 cc. per 0.1 mm., and that 0.1 mm. would be approximately the reading error likely to be made. The actual determination of solvent volume--the draining and weighing of mercury and finding the solvent volume by difference--would of course be less accurate percentagewise since the solvent occupied only a fraction of the bulb (usually 150 cc. of solvent in the 210 cc. bulb). But even so, the accuracy is beyond that required for ultimate reproducibility of ±0.05%.

A consideration of temperature control is also pertinent in obtaining accurate values of the quantity of solvent. Temperature control and how it affects this determination as well as the other variables is discussed in the next section.

H. Temperature and Temperature Control

A first approach to specifying the temperature control requirements for gas solubility determinations would consist of examining the temperature coefficient of solubility, and with this coefficient and the accuracy desired in the final results, calculating the allowable temperature fluctuations. For example, in the case of the system hydrogen-n-heptane, the solubility changes

approximately 0.05% per 0.1° C., hence a temperature fluctuation of ±0.05° C. would seem tolerable.

On the other hand, each of the operations, e.g., the initial gas measurement, solvent volume measurement, and equilibrium determination, is affected by the temperature and each must be considered separately and the temperature specifications set according to the most stringent requirements thus found.

In the determination of the moles of gas charged to the apparatus a PV product is measured. The PV product for hydrogen at one atmosphere and various temperatures is known.[16] Across small temperature changes, changes of the order of the uncertainty in the measured temperature, the compressibility factor would be constant, and the number of moles and the PV product would be directly proportional to the temperature. Hence, a discrepancy of ±0.0005(298) = ± 0.15° C. would be tolerable in order to obtain the gas quantity to ±0.05%.

For the determination of the solvent volume using n-heptane as an example, the fractional change in the density is 0.124% per °C. This leads to a temperature specification of about ±0.2° C. in order that the solvent mass may be determined to ±0.05%.

The temperature specification for the solubility variable is considerably more complex than that outlined in the first paragraph of this section. The experimentally observable variable as the temperature is arbitrarily changed is the change in total pressure of the system. Temperature control affects the accuracy of this measurement in two ways. The first of these is "temperature offset",

or the static temperature difference between the gas-solvent system and the temperature reading. The second consists of temperature fluctuations.

The allowable temperature offset depends both on the system and the temperature level of the experiment. It is determined by four factors:

1. The temperature coefficient of the solvent vapor pressure,
2. The temperature coefficient of solubility, or more exactly, the change in the equilibrium partial pressure of the dissolved gas with temperature at an approximately constant concentration,
3. The temperature level of the experiment, and
4. The pressure level of the experiment.

The first of these factors will of course increase in importance, as the temperature level of the experiment increases, while it will become less important percentagewise as the pressure level increases.

In any single experiment the observed variable is the equilibrium total pressure, which is a function of temperature. If the observed total pressure is correct with respect to the actual temperature of the system, but the observed temperature of the experiment is in error, then the vapor pressure used in calculation of the data will be in error with respect to the actual temperature of the system. The vapor pressure used, however, will be correct for the observed temperature and it may equally well be said that the observed total pressure was in error. Hence the calculated partial pressure of the gas will be wrong only by the error in the observed

total pressure. This error in partial pressure will result in an error in solubility since the solubility is calculated as gram moles of gas dissolved per atmosphere partial pressure of gas in the vapor phase. The residual gas and hence the concentration of dissolved gas in the liquid will also be in error, but due to the small quantity of residual gas, this error will be negligible.

The temperature coefficient of solubility tends to counteract the effect of the vapor pressure coefficient in the case of hydrogen, i.e., the solubility of hydrogen per atmosphere of partial pressure increases with temperature. The observed total pressure is the sum of the partial pressure of the gas and the solvent vapor pressure. In any experiment the partial pressure of hydrogen at equilibrium will decrease as temperature increases. Conversely, the vapor pressure of solvent increases. These effects tend to cancel and can result in no change in the total pressure with temperature. If the total pressure is thus independent of temperature, no error will be made in the calculated solubility. Since the effects will not cancel exactly, an error will generally be made, but its magnitude will be less than that indicated by the temperature coefficient of solubility alone.

In general, at low temperatures the temperature coefficient of solubility will largely determine the allowable temperature offset, while at higher temperatures the temperature coefficient of solvent vapor pressure will control. To obtain the allowable temperature offset, the following expressions are proposed:

$$P = p_g + p_s, \qquad (1)$$

where P = the total pressure,

p_g = the partial pressure of the gas,

p_s = the partial pressure of the solvent.

Differentiating with respect to temperature we have

$$\frac{dP}{dT} = \frac{\partial p_g}{\partial T} + \frac{\partial p_s}{\partial T} \tag{2}$$

and the fractional change in total pressure with respect to p_g is

$$\frac{dP}{p_g dT} = \frac{1}{p_g}\left(\frac{\partial p_g}{\partial T} + \frac{\partial p_s}{\partial T}\right). \tag{3}$$

This equation implies a constant concentration of gas in the solvent phase. This assumption fits our systems well since the amount of undissolved gas is small. Then, at a given temperature

$$p_g = \frac{c}{S}, \tag{4}$$

where S is the solubility, gram mole/gram, atm., and c is a concentration defining the liquid phase, gram moles gas/grams solvent.

Differentiating,

$$\frac{\partial p_g}{\partial T} = \frac{c\partial\frac{1}{S}}{\partial T} = -\frac{c}{S^2}\frac{\partial S}{\partial T},$$

and

$$\frac{1}{p_g}\frac{\partial p_g}{\partial T} = -\frac{1}{S}\frac{\partial S}{\partial T}, \tag{5}$$

and Eq. (3) becomes

$$\frac{1}{p_g}\frac{dP}{dT} = \frac{1}{p_g}\frac{\partial p_s}{\partial T} - \frac{1}{S}\frac{\partial S}{\partial T}. \tag{6}$$

Since the desired accuracies are high, the allowable temperature offsets will be small, and with the exception of the

region where the vapor pressure and solubility coefficients are equal, we may write:

$$\frac{1}{p_g}\frac{\Delta P}{\Delta T} = \frac{1}{p_g}\frac{\partial p_s}{\partial T} - \frac{1}{S}\frac{\partial S}{\partial T}. \tag{7}$$

Since we desire an accuracy of ±0.05%,

$$\frac{\Delta P}{p_g} = 0.005.$$

Therefore ΔT becomes the allowable temperature offset.

$$\Delta T \cong \frac{0.0005}{\frac{1}{p_g}\frac{\partial p_s}{\partial T} - \frac{1}{S}\frac{\partial S}{\partial T}}. \tag{8}$$

This equation has been evaluated for the two systems, hydrogen-n-heptane and hydrogen-carbon disulfide. The results are given in the following table. It will be noted that n-heptane exhibits a very large allowable temperature offset in the vicinity of 35° C. where the two above coefficients all but cancel one another. This explains why data taken in a previous thermostat, in which temperature control was poor, agree so well at 35° C. while larger discrepancies were found at 10° C.

The thermostat was designed to operate at -35° C. with only about 0.1° C. temperature rise from bottom to top in the thermostatted region, which would correspond to a temperature variation of less than 0.01° C. in the vicinity of the solvent bulb (assuming a linear gradient). The temperature offset specifications derived from Eq. (8) have thus been met.

Table 6

Allowable Temperature Offsets at Various Temperatures in the Systems H_2-n-C_7H_{16} and H_2-CS_2

Solvent	Temp. °C.	$\frac{1}{S}\frac{\partial S}{\partial T} \times 10^3$	$\frac{1}{p_g}\frac{\partial p_g}{\partial T} \times 10^3$	ΔT, °C.
n-C_7H_{16}	50	5.4	8.6	0.16
"	35	5.6	4.5	0.42
"	25	5.8	2.6	0.15
"	0	6.35	1.05	0.092
"	-25	7.4	0.26	0.074
CS_2	35	8.8	21.5	0.039
"	25	9.1	17.0	0.063
"	0	10.0	7.8	0.16
"	-25	11.3	2.2	0.055

It might be pointed out that an excellent starting point for testing an apparatus is with solvents such as n-heptane or isooctane which are readily available at high purity and need no special care insofar as they are non-hygroscopic. When the initial test is at such a temperature that the denominator in Eq. (8) is approximately zero, the apparatus can be evaluated almost independently of temperature control.

The above considerations are somewhat misleading, because the real meaning of Eq. (8) is that a temperature difference of ΔT between the solvent and the temperature read can be tolerated to the extent that it will cause only about 0.05% error in the calculated results. On the other hand, there is still another error

which stems from temperature fluctuations and which can in some cases be even more serious than the errors outlined above. As pointed out in the previous section on procedure, the equilibrium point is determined by measuring solution rates at two pressures between which lies the equilibrium pressure at which the rate of solution is zero. This rate is observed as a volume change which is caused only by evolving or dissolving of the gas if the temperature is perfectly steady. If, however, the temperature changes, a volume change will also be caused by evaporation or condensation of the solvent. One can synthesize a case in which these two phenomena could cancel each other and hence lead to a pseudo equlibrium point. Fortunately, our apparatus follows the air temperature rapidly enough (see Appendix E) compared with a typical 10 minute shaking period, that a change in temperature appears as a grossly erratic rate when several rates are determined at the same pressure. Hence, whether these rates are reproducible is a good indication of whether the temperature of the system is varying. To show the magnitude of this error, consider benzene at 35° C. where $dp_s/dT \cong 6.4$ mm. per $^{\circ}$C. and assume that the total pressure is 760 mm. Since the manometer has a large diameter (approximately 2 cm.), the vapor and gas above the solvent very nearly constitute a constant pressure system. Therefore, as the vapor pressure increases 0.64 mm. (a temperature increase of 0.1° C.), the volume will increase by about $(0.64/760)1.2 \cong 10^{-3}$ cc., since the total volume is about 1.2 cc. This corresponds to a reading on the gas burette of about 0.7 mm. which is a relatively

large discrepancy when compared with the rates observed (see Fig. 11). Furthermore, this value would be increased to about 1 mm. when the simple gas expansion due to heating is considered.

That little difficulty was encountered in obtaining consistent solution rates tends to show that temperatures were indeed steady to the degree required.

I. The Air-Bath Thermostat

In the determination of precise physical data, the use of an air-bath thermostat is generally avoided in favor of a liquid-bath thermostat. The air-bath thermostat is inherently unstable because of its very small heat capacity, and this results in sizable differences in temperature for even relatively small heat leak rates. At the beginning of this work both of these types of thermostats were considered. The air-bath thermostat appeared to offer advantages in the manipulation of our rather large apparatus. Since these advantages seemed to outweigh the possibility of temperature instability, an air-bath thermostat was designed and constructed. Another factor which influenced this choice was that the proposed investigations required operation at frequently changed temperature levels, and only relatively small heating and cooling facilities are required for making these changes in an air-bath thermostat.

For this work the temperature requirements were that a maximum inlet to outlet (see Fig. 6) temperature difference of 0.1° C. would be allowable, while the change in temperature with time at any point in the thermostat should not exceed 0.03° C.

These specifications were derived from considerations presented in the preceding section. The range in temperature was -30° to 50° C.

A schematic drawing of the thermostat used is shown in Fig. 6. The air flows from an air conditioning system past the temperature sensor and into the thermostatted region. From this region the air is recirculated to the air conditioning system by means of a centrifugal blower. The whole apparatus is insulated with a minimum of 8 inches of Styrofoam (expanded polystyrene manufactured by the Dow Chemical Company). The blower has a capacity of 200 c.f.m., each of the two heaters have maximum capacities of 300 watts, and the cooler (or heat exchanger) along with the refrigeration system (see Figs. 12 and 13) was designed to have a maximum capacity of 1500 Btu/hr. for operation at -35° C.

The temperature control system, which is shown schematically in Fig. 14, is designed around a commercial temperature controller which consists of a nickel resistance thermometer in a bridge and amplifier circuit. This instrument gives an on-off response sensitive to about 0.001° C. as claimed by the manufacturer.* The signal from the controller turns one of the heaters on and off. The voltage to this heater is manually adjusted with a variable transformer. The voltage to the other heater which is on continuously is automatically set by a reversible motor coupled to another variable transformer. Accordingly, this motor drives in such a way that at

*Technical Equipment Company, Emeryville, California

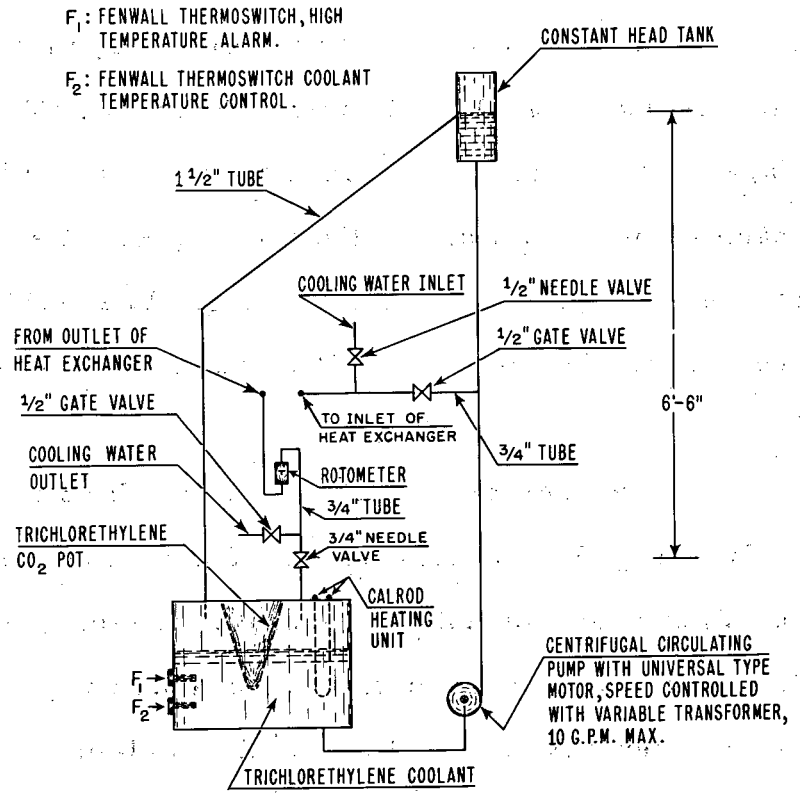


Fig. 12. Refrigeration system, schematic.

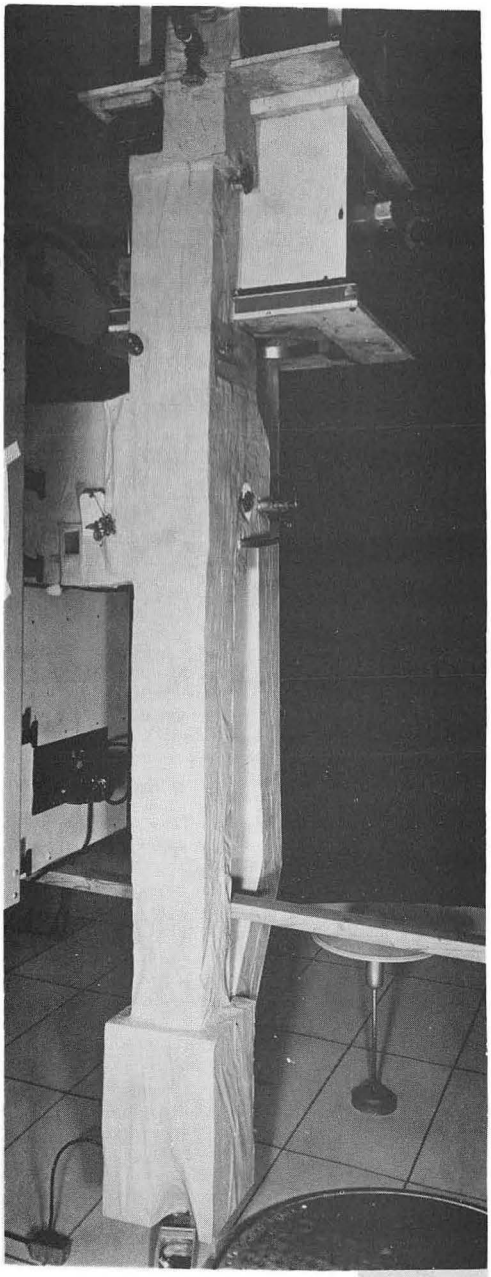
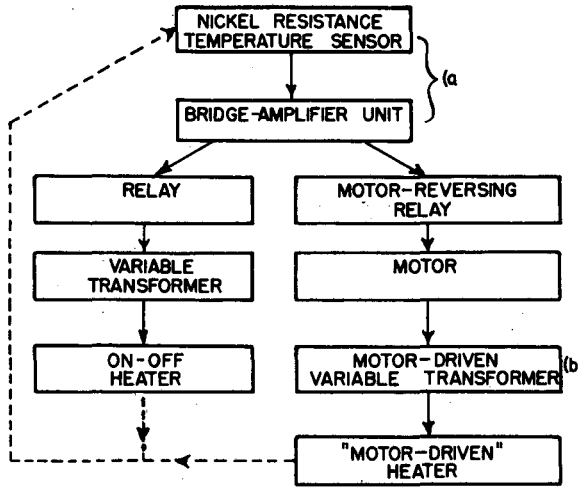


Fig. 13. The refrigeration system.



a) "Electronotherm", made by Technical Equipment Co., Emeryville, Calif.
b) "on" signal increases the voltage 3 v/min.

SCHEMATIC DIAGRAM OF THE TEMPERATURE CONTROL SYSTEM

MU-7354

Fig. 14. Schematic diagram of the temperature control system.

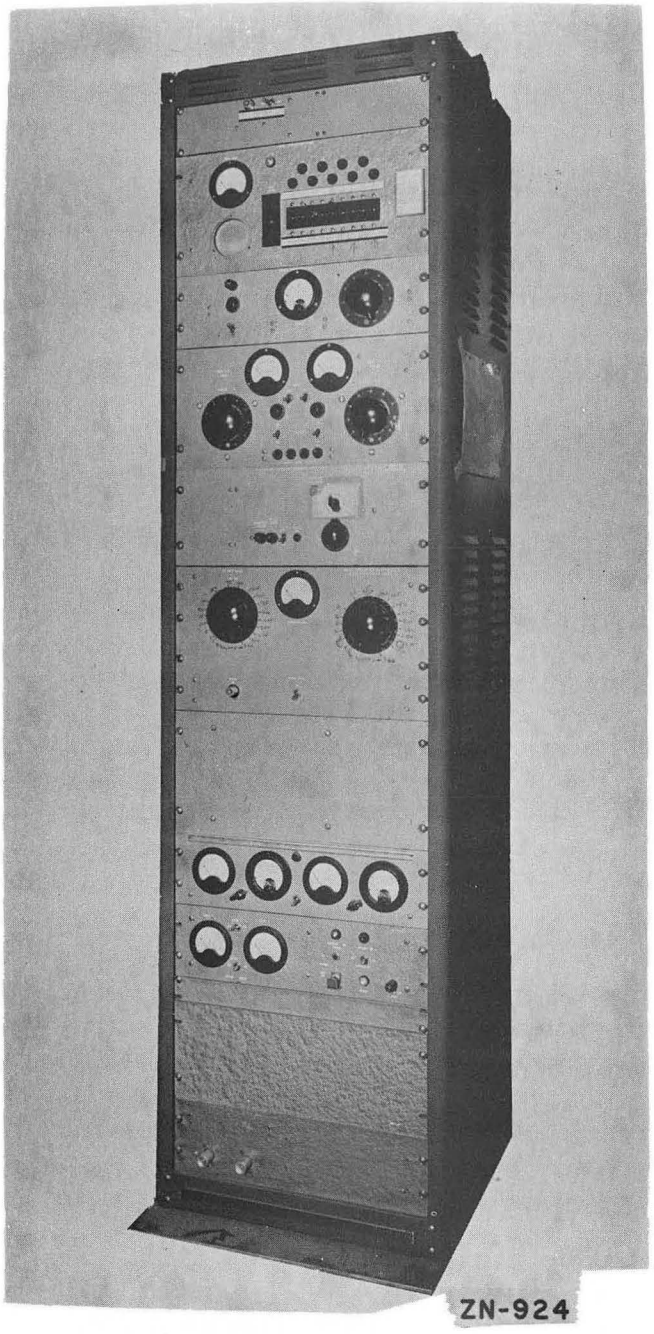


Fig. 15. The thermostat control panel.

steady state the "on" and "off" times are equal. The driving speed of this motor is about 3 volts/minute and the coupling between the motor and transformer has sufficient lost motion that no voltage change occurs at steady state.

The functional parts of the thermostat are arranged to make the best possible use of the temperature controller. To avoid time lags in controller response, the temperature sensor is placed close to the heaters which are actuated by the controller. The large heat capacity of the inlet duct tends to smooth temperature cycling caused by the on-off heater. The blower and the heat exchanger are placed ahead of the heaters so that variations in the air temperature caused by unstable blower operation or changes in coolant temperature will be compensated before these effects can be "seen" by the solubility apparatus.

In order that temperature upsets due to placing the hands in the thermostat might be prevented, all manipulations were done remotely by means of a mechanism shown in Fig. 10.

It was necessary to provide lighting in the thermostat so that the various readings could be made. Fluorescent lights were chosen because of their high efficiency. These lights were installed as shown in Fig. 16. This installation provides that most of the heat output of the lights is carried away by a stream of room temperature air, and this air also maintains the lights at room temperature below which the light output of fluorescent lights becomes progressively smaller. The lights are further insulated from the thermostat by a vacuum jacket, a dead air

space, and two air spaces through which "thermostat air" is circulated. It was found that the lights had no measurable effect on the temperature in the thermostat.

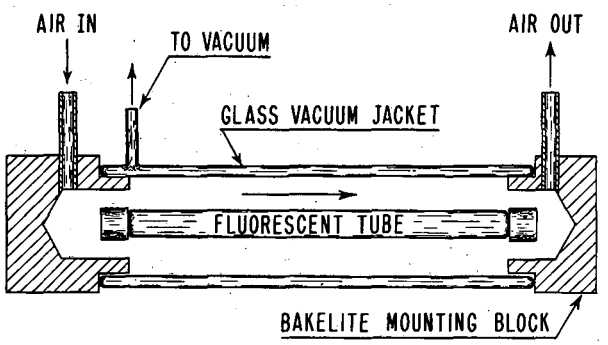
Tests of this thermostat showed it to be satisfactory to well within the desired temperature specifications.

J. Shaker Mechanism

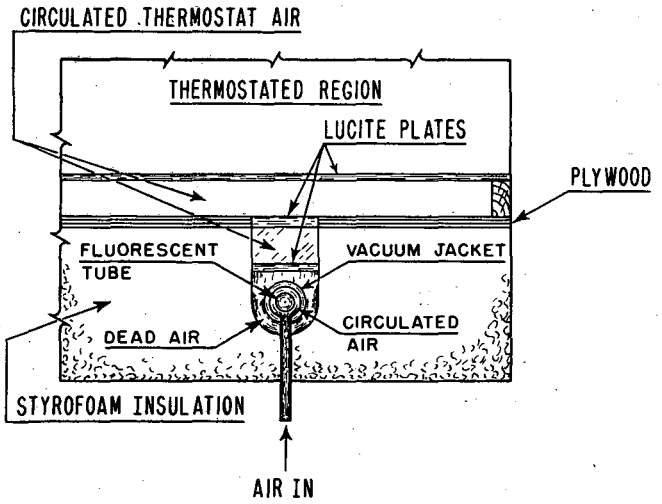
The shaker mechanism to which our apparatus No. 7 was mounted (see Fig. 4), imparted a horizontal motion to within the accuracy of the cathetometer reading, 0.05 mm., with the shaker in motion. Our thought in this regard was to avoid vertical accelerations insofar as they might upset the pressure in the system. Apparatus No. 6, on the other hand, was rocked somewhat like a pendulum. Inasmuch as the data from both pieces of apparatus agree, it is deduced that small vertical components of velocity do not alter the average pressure.

K. Other Features of the Apparatus and Suggested Modifications

Ternary data can be taken with the apparatus as shown in Fig. 1. Although only binary data were taken in this work, the apparatus was designed for eventual investigation of the simultaneous solubility determination of two gases. For this determination a binary gas mixture of known composition is charged to the apparatus as described in section IV-C. The procedure is much the same as for the previously outlined determination of a single gas, except that the equilibrium pressure is set as closely as possible.



VENTILATED LIGHT
(SCHEMATIC)



PLACEMENT AND HEAT SHIELDING
OF LIGHTS.

MU-7355

Fig. 16. Placement and heat shielding of the ventilated lights.

After equilibrium has been established, the residual gas volume is carefully measured, and then the solvent level is pulled from 19 (see Fig. 1) to 20. The U capillary tube in the secondary gas system is then immersed in a small dewar of liquid nitrogen in order to freeze the solvent in that vicinity. In this manner the gas and liquid phases are separated by a vacuum tight barrier of frozen solvent and the gas sample may be placed in a gas sample bottle by means of a Toepler pump through 12, and the gas ratios measured by mass spectroscopy. Since the amount of gas in the liquid phases is known, this ratio, along with the solvent vapor pressure, will give the partial pressures of each and hence the amounts of each gas in both gas and liquid phases. Hence the solubilities of each gas can be calculated.

Concerning the phase barrier of frozen solvent mentioned above, this technique was tried and found satisfactory against vacuum, provided that the frozen solvent is backed up by liquid solvent which presumably enters the interstices left between the crystals of solvent upon freezing, it too freezing to form an impervious barrier.

One suggested modification for future pieces of apparatus which would make it a more versatile apparatus would be to include a series of graduated bulbs and burettes instead of the single primary gas bulb and burette. This series could be started with a small bulb of about 2 cc. for measuring such solubilities as helium in water, and ended with a large bulb bringing the total volume to about 150 cc. in order to measure such solubilities as ethane in

hexane. The intermediate burettes should, of course, be designed according to the procedure in section V-B in order to obtain optimum values of the PV product.

Another modification, which was used successfully in our apparatus No. 6, is the incorporation of a platinum resistance heater in the solvent bulb to aid in degassing the solvent. The heater consisted of a loose coil of 10 cm. of 0.020 in. diameter platinum wire spot welded to two tungsten electrodes which entered the solvent bulb at a level about 1 cm. above the gas inlet, the seals being pyrex to tungsten. About 5 volts A.C. was used to energize the heater. This system was found to be a definite aid to degassing because it not only furnished a heat source for boiling, but also completely eliminated bumping and provided smooth boiling and rapid outgassing.

VI. PRESENTATION AND DISCUSSION OF THE RESULTS

The complete tabulation of hydrogen solubility data is given in Table 8, as well as a tabulation of values taken from a smoothed curve. The data are plotted in Figs. 16 and 17. The smoothed data favor the experiments done in the thermostat previously described and with apparatus No. 7; the thermostat used for the experiments done in apparatus No. 6 did not allow the required temperature control, especially at temperatures other than 25° or 35° C.

There are a large number of data on hydrogen-n-heptane because this system was used exclusively in the development of the apparatus and technique. Of the seven runs reported, the maximum

deviation found was ±0.055%; while for the two runs carried out in the previously described thermostat, one in apparatus 7-L and one in apparatus 7-R, the deviations are less than ±0.02%.

For n-perfluoro heptane, one run was made in apparatus 7 while three runs were made in apparatus 6. With the exception of the data at 50° C., which were taken in the first thermostat in which the temperature control was poor, these four runs agree to within ±0.05%. Of the two toluene runs made in apparatus 7, agreement is better than ±0.03%.

The benzene runs made in apparatus 6 may be discounted, not only on the basis of poor temperature control as previously mentioned, but also on the basis that the solvent was reagent grade benzene used without further treatment. However, the benzene used for run 48 in apparatus 7 was carefully purified by distillation. Even so, the deviations among these three runs are only ±0.08% at 25° and ±0.18% at 35° C.

The data on the other solvents are from single runs. The least accurate of these would probably be for carbon disulfide in which case the initial gas was measured at 250 mm. pressure since the low solubility of hydrogen in carbon disulfide requires that the quantity of gas charged be small. Also, the relatively high vapor pressure of carbon disulfide requires that the temperature be very closely controlled.

In Tables 7 and 8, the listed temperatures are exact to the previously stated precision of reading the thermometers; namely, ±0.01° from -10° to 50° and ±0.02° from -30° to -10°. All of the

Table 7

Solubility of Hydrogen

10^6 x Gram Moles/Gram Solvent, Atm. Partial Pressure

(Complete Data Summary)

Solvent	Run number	Apparatus number	t., °C.	Solubility
n-heptane	44	7-R	-30	4.7
	46	7-L	-25	4.976
	44	7-R	-10	5.513
	46	7-L	0	5.894
	44	7-R	10	6.281
	30	6	12.1	6.354
	42	6	15	6.465
	30	6	25	6.866
	42	6	25	6.871
	44	7-R	25	6.874
	46	7-L	25	6.871
	24	6	35	7.281
	25	6	35	7.278
	26	6	35	7.281
	30	6	35	7.274
	42	6	35	7.276
	44	7-R	35	7.282
	46	7-L	35	7.281
	42	6	45	7.70
	30	6	50	7.91

Table 7 (Cont.)

Solvent	Run number	Apparatus number	t., °C.	Solubility
n-perfluoro heptane	47	7-R	-25	2.589
	47	7-R	0	3.077
	31	6	12.1	3.333
	33	6	12.1	3.334
	31	6	25	3.613
	32	6	25	3.616
	33	6	25	3.615
	47	7-R	25	3.614
	31	6	35	3.853
	32	6	35	3.849
	33	6	35	3.849
	47	7-R	35	3.850
	32	6	50	4.29
	33	6	50	4.30
benzene	48	7-L	10	2.884
	37	6	15.1	3.030
	38	6	15.1	3.024
	37	6	25	3.306
	38	6	25	3.301
	48	7-L	25	3.303
	37	6	35	3.595
	38	6	35	3.582
	48	7-L	35	3.596
	37	6	45	3.89
	38	6	45	3.88

Table 7 (Cont.)

Solvent	Run number	Apparatus number	t., °C.	Solubility
toluene	50	7-R	-15	2.507
	50	7-R	0	2.844
	49	7-R	25	3.438
	50	7-R	25	3.436
	49	7-R	35	3.685
	50	7-R	35	3.685
2, 2, 4-trimethyl pentane	51	7-R	-25	5.080
	51	7-R	0	5.937
	51	7-R	25	6.845
	51	7-R	35	7.234
n-octane	53	7-R	-25	4.331
	53	7-R	0	5.139
	53	7-R	25	5.984
	53	7-R	35	6.343
CCl_4	52	7-R	0	1.688
	52	7-R	25	2.078
	52	7-R	35	2.245
CS_2	54	7-R	-25	1.270
	54	7-R	0	1.656
	54	7-R	25	2.101

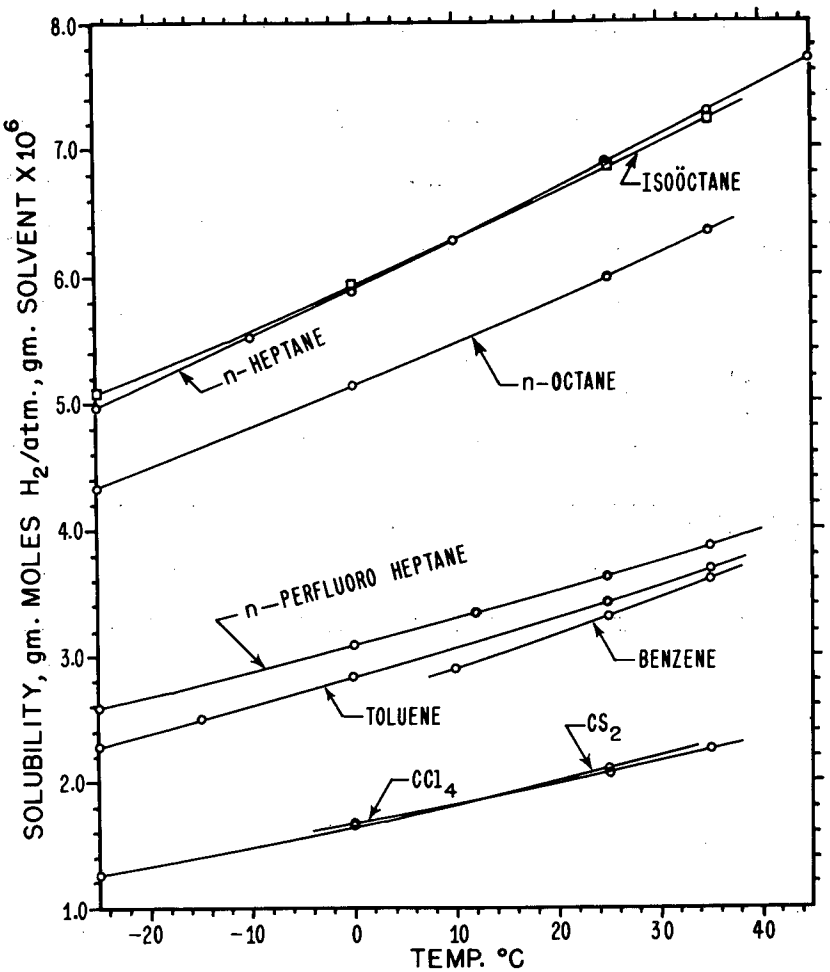


Fig. 17. The solubility of hydrogen in various non-polar solvents.

Table 8

Solubility of Hydrogen

10^6 x Gram Moles/Gram Solvent, Atm. Partial Pressure

(Recommended Values from Smoothed Curves)

Solvent	-25° C.	-15° C.	0° C.	10° C.	25° C.	35° C.
n-heptane	4.976	-----	5.894	6.281	6.873	7.281
n-perfluoro heptane	2.589	-----	3.077	-----	3.614	3.850
toluene	2.284	2.505	2.841	-----	3.433	3.682
benzene	-----	-----	-----	2.884	3.303	3.596
n-octane	4.331	-----	5.139	-----	5.984	6.342
2, 2, 4-tri-methyl pentane	5.081	-----	5.942	-----	6.845	7.234
CCl_4	-----	-----	1.688	-----	2.078	2.245
CS_2	1.270	-----	1.656	-----	2.101	-----

data have been corrected for the 0.25% nitrogen impurity which the hydrogen contained. This correction is outlined in Appendix D.

The basis for reporting the data; namely, gram moles of gas/gram solvent, atm. partial pressure, seems to the author a more logical value than either of the more conventional Bunsen or Ostwald coefficients, especially from the standpoint of engineering calculations. The solubility, S, as reported can be readily converted to the mole fraction, X, to the Bunsen coefficient, β, or to the Ostwald coefficient, γ, by the following formulas:

$$X = \frac{SM_s}{1 + SM_s},$$

$$\beta = SV_o\rho_t,$$

$$\gamma = SV_t\rho_t.$$

Here, V_t is the molal volume of the gas, cc./gram mole, at t^o C., ρ_t is the density of the solvent at t^o C., gram/cc., M_s is the molecular weight of the solvent, β is the volume of gas reduced to S.T.P. dissolved per unit volume of solvent when the partial pressure of the gas is 760 mm., and γ is the ratio of concentrations of the gas in the liquid and vapor phases, respectively.

The previous hydrogen solubility data which we have repeated are plotted along with our data in Figs. 18 through 21. Of these data, Just's,[12] taken in 1901 with the apparatus of Timofejew,[25] seem to be the most in error. His benzene and toluene data are about 7% higher than ours, while his carbon disulfide values are about one-half of those we have found. In addition to the possible errors mentioned previously, it is quite possible that he had difficulty in securing pure gases and solvents.

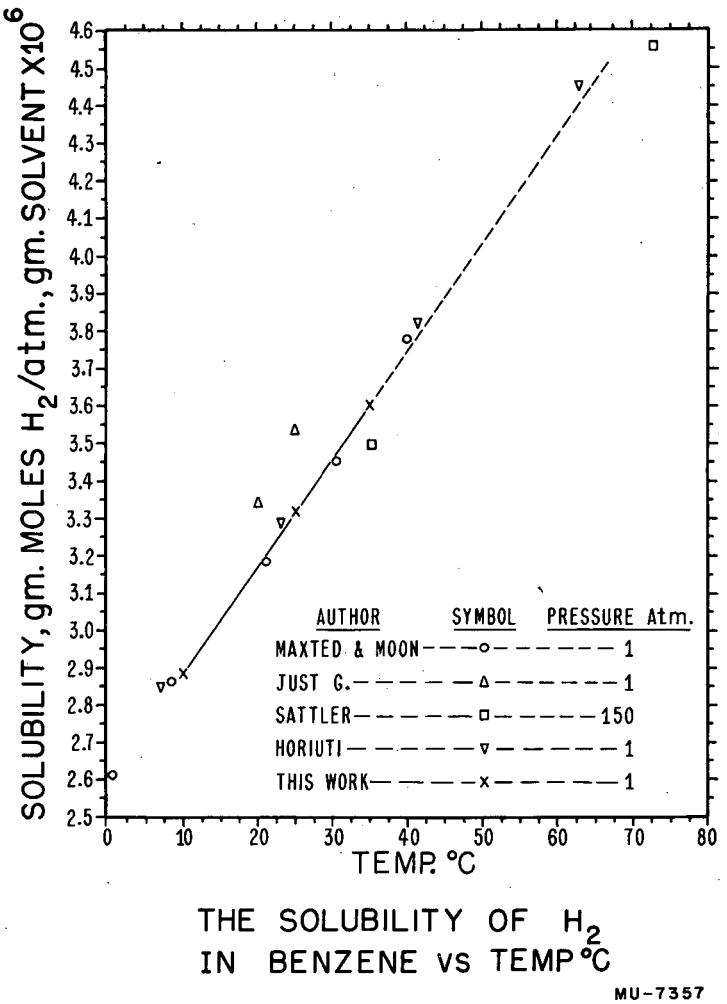


Fig. 18. The solubility of hydrogen in benzene.

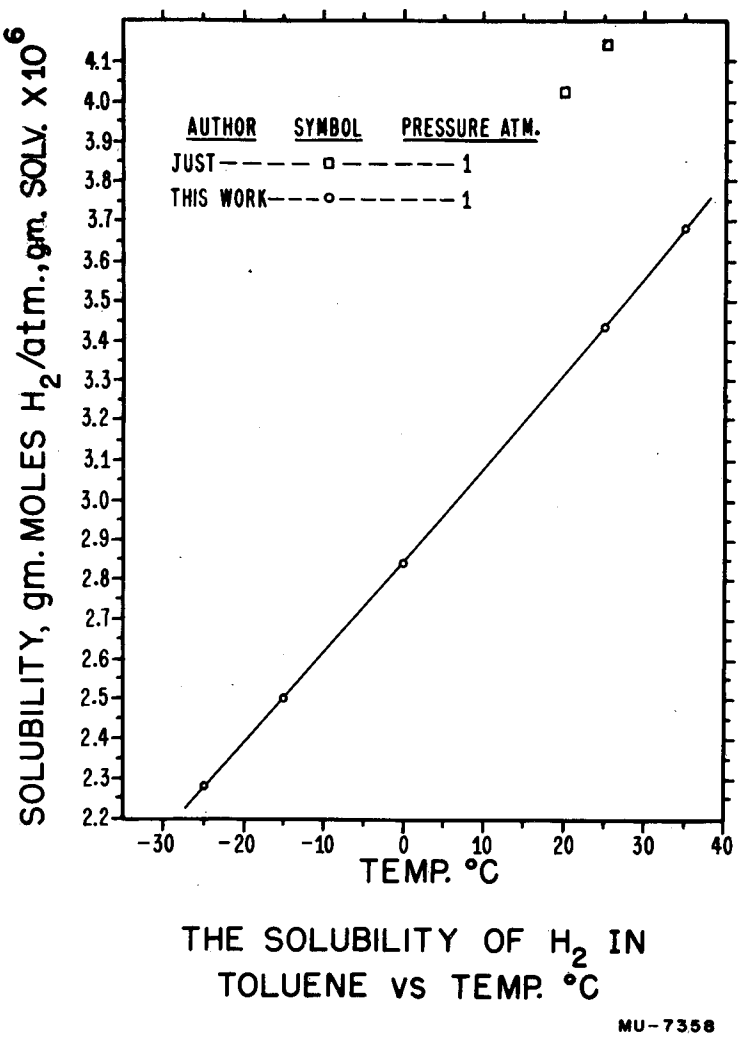


Fig. 19. The solubility of hydrogen in toluene.

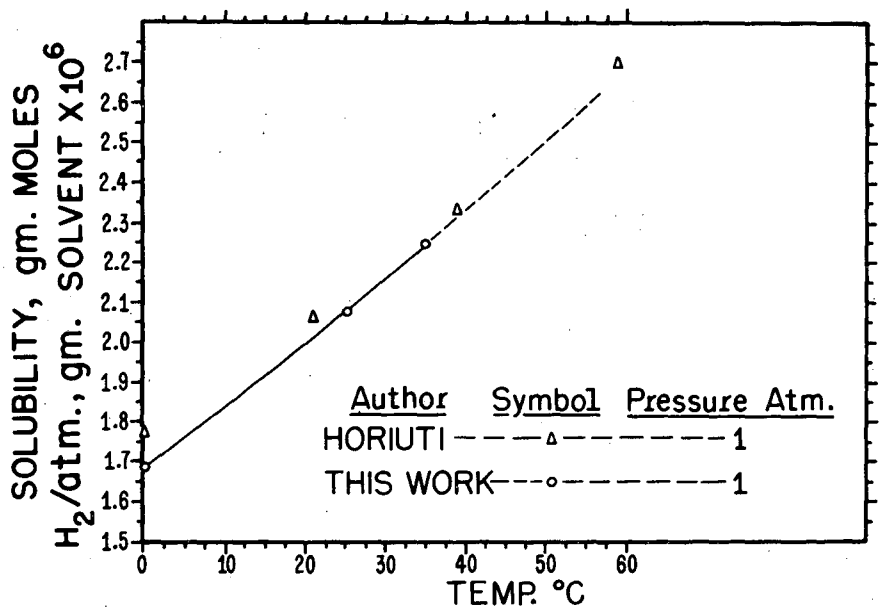


Fig. 20. The solubility of hydrogen in carbon tetrachloride.

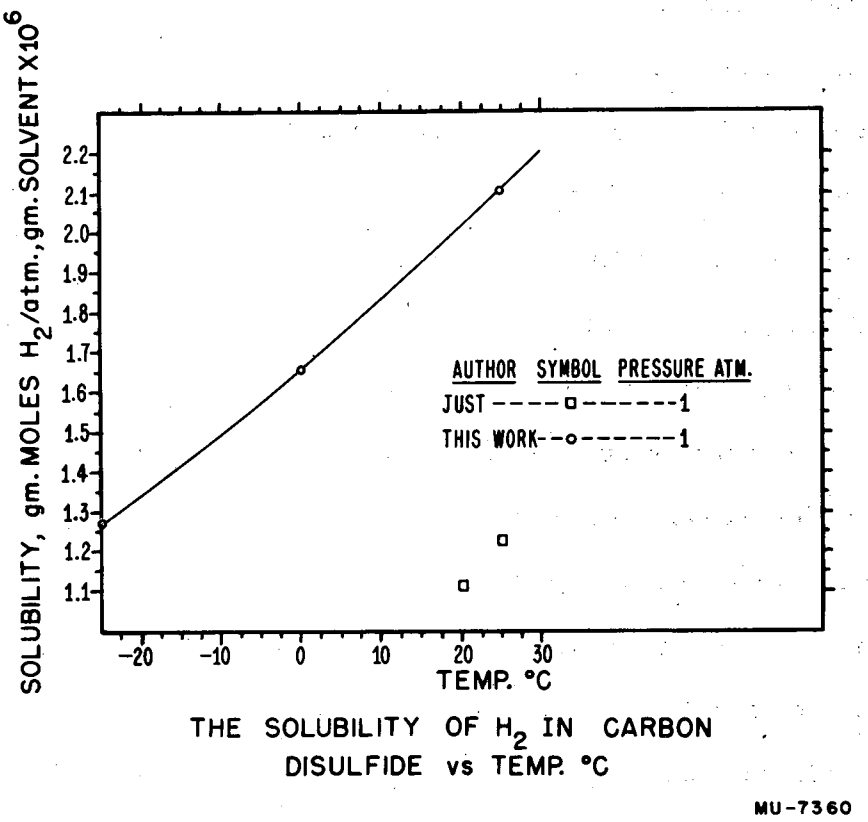


Fig. 21. The solubility of hydrogen in carbon disulfide.

The data of both Horiuti[11] and of Maxted and Moon[15] are within 1% of our results for benzene and carbon tetrachloride. Horiuti's data are somewhat higher than ours. This discrepancy can be explained on the basis that his solvent was at a somewhat higher temperature than his thermostat. He used a magnetic stirrer consisting of a solenoid in close proximity to his solvent bulb and a glass-enclosed iron impellor within his solvent bulb which was caused to rise and fall by interruptions in the coil current. The hysteresis losses of this impellor and the heat produced by the coil could readily account for this hypothesized temperature error. His data, nonetheless, have been carefully taken and we believe them to be generally reliable to better than 1%. In addition, his apparatus has the advantage that data may be taken at very low temperatures limited only by the freezing point of the solvent, whereas in our apparatus the lower temperature limit is fixed by the freezing point of mercury. Although it does possess the possibility of a temperature error, his apparatus provides adequate stirring and a large interfacial area between the gas and the solvent so that with care, equilibrium can be attained.

The apparatus of Maxted and Moon[15] is seen upon careful comparison to be an adaptation of von Antropoff's apparatus[1] and it also incorporates some of the advantages of Horiuti's apparatus. Their data for hydrogen in benzene appear to be quite acceptable except that the value which they give at 0.5° C. is unexplained (the freezing point of benzene is about 5.5° C.). Their procedure involved a rather tedious process of breaking the solvent bulb from

the system, degassing the solvent therein, and then fusing the bulb back into the system. This procedure was followed for each point determined, i.e., for each temperature. Their procedure for determining the "zero" burette reading by allowing the gas to enter the vapor space in the solvent bulb and then "quickly reading the gas burette before any gas dissolves" would tend to make their results somewhat low if any gas did dissolve. That their results are somewhat lower than ours may be explained on this basis.

The other data shown in Fig. 18 are high pressure determinations so that the methods used and possible Henry's Law deviations make these results not strictly comparable to ours.

VII. AN APPLICATION OF GAS SOLUBILITY THEORY

A. Hildebrand's Solubility Theory

The theories relating to the solubilities of non-electrolytes are presented by Hildebrand.[9] In particular, he relates the solubility of a gas in a liquid to the gas and liquid properties by the following equation:

$$\ln \frac{f_g}{f^o_g} = \ln \phi_g + \phi_\ell \left(1 - \frac{V_g}{V_\ell}\right) + \frac{\phi_\ell^2 V_g (\delta_\ell - \delta_g)^2}{RT},$$

where,

f = fugacity

f^o = standard state fugacity

ϕ = volume fraction

V = molal volume, cc.

δ = solubility parameter, $(\text{cal./cc.})^{1/2}$

g, ℓ refer to the gas and liquid, respectively.

Hildebrand identifies f^o with the vapor pressure of the gas extrapolated by means of a log p vs. 1/T plot beyond the critical point to the temperature of the experiment. The model taken for an ideal solution is therefore Raoult's Law and the standard state is the hypothetical liquefied gas.

Equation (1) applies to non-associated, non-polar systems. As such, deviations from Raoult's Law result from the heat and entropy of mixing. The term, $\ln\phi_g$, is the correction for the ideal entropy of mixing. The term containing $(1 - V_\ell/V_g)$ is an entropy correction to account for the disparity between the solvent and solute molal volumes. The last term is a partial molal energy of mixing (for the solute) which Hildebrand has shown to be approximately equal to the heat of mixing.

B. Empirical Treatment of Hildebrand's Equation

In the present work, it was desirable to be able to extend the present data to other systems. In using Eq. (1) for this purpose, the values of f^o, V_g, and δ_g must be evaluated. To determine f^o, it is identified with the pseudo vapor pressure of the gas, as described above, but in the case of hydrogen, the extrapolation required can introduce a large uncertainty in the value so obtained. The term V_g, which is also implicit in the ϕ terms, is, strictly speaking, a partial molal volume. Also, V_g has been shown to be a function of the solvent,[6] and since the determination of V_g for each solvent would be nearly as difficult as the solubility determination itself, the initial purpose of data prediction would be defeated. Finally, the solubility parameter, δ_g, is generally determined empirically from solubility determinations.

Of the two solvent properties, δ_ℓ can readily be calculated from the latent heat (see Appendix G), while V_s can be calculated from the density because the solvent molal volume will not differ appreciably from the partial molal volume in the dilute solutions encountered.

Since there is considerable uncertainty in the evaluation of f^o and δ_g, and since the determination of V_g is time consuming, all three of these values have been treated as empirical constants. That is, assuming Eq. (1) to be a correct functional relationship between the gas and solvent properties, f^o, δ_g and V_g have been calculated by a simultaneous solution of (1) having substituted the solubility and the respective solvent properties of three systems into that equation. This calculation is valid insofar as the calculation of f^o is concerned since this term is virtually independent of system. On the other hand, V_g, and hence δ_g, are dependent to some extent on the systems chosen for this calculation. Consequently all three of these "parameters" will be, in a sense, average values.

For this calculation the systems were chosen to include a wide range in the values of δ_ℓ and V_ℓ which was intended to make the calculation more sensitive. The solvents used were n-perfluoro heptane, n-heptane, and toluene. These solvents exhibit respectively solubility parameters of 5.98, 7.43, and 8.91, and molal volumes of 225.6, 147.5, and 107.0 at 25° C. The values at other temperatures will be found in Appendix G. The results of this calculation are given in Table 9.

Table 9

Calculated Values of δ, V and f^o for Hydrogen

t °C.	δ, $(cal./cc.)^{1/2}$	V, cc./mole	f^o, atm.
-25	5.10_4	29.1_5	2680
0	4.46_0	26.0_7	2482
25	3.69_7	23.2_0	2305
35	3.34_0	22.1_0	2235

Since the calculated values are parameters, they do not necessarily have real significance. It will be noted, for example, that δ_g decreases as the temperature increases. Such is the case for liquid δ's, but the percentagewise change in δ_g with temperature seems rather large.

The decrease in f^o with increasing temperature seems contrary to the hypothesized standard state, since this value will increase with temperature if obtained by the method of extrapolation described above. This unexpected result may be accounted for, however, since f^o is the factor which largely determines the solubility of hydrogen, and hydrogen exhibits a marked increase in solubility with temperature.

With the values of δ_g, V_g, and f_g^o given in Table 9, the solubility of hydrogen has been calculated for the other five solvents investigated. The results of this calculation are compared with the experimental solubilities in Table 10. The deviations between the observed and calculated values are large compared with the accuracy desired; namely, ±0.05%. These deviations are not, however, as severe as those reported from a somewhat similar calculation* by

*Gjaldbaek used an extrapolated vapor pressure for f^o and an average value from measured partial molal volumes for V_g.

Table 10.

Calculated and Observed Solubilities of Hydrogen
Mole Fraction x 10^4

Solvent	t° C.	$X_{calc.}$	$X_{obs.}$	$\log X_{mf} + 4$	% diff.
iso-C_8H_{18}*	-25	6.678	5.801		15.1
	0	7.753	6.782		14.3
	25	8.911	7.812	0.847	14.1
	35	9.398	8.256		13.8
n-C_8H_{18}	-25	5.301	4.945		7.2
	0	6.247	5.867		6.5
	25	7.264	6.830	0.813	6.4
	35	7.672	7.239		6.0
CCl_4	0	2.747	2.596		5.8
	25	3.326	3.196	0.503	4.1
	35	3.564	3.453		3.2
benzene	25	2.489	2.579	0.404	-3.5
	35	2.704	2.808		-3.7
CS_2	-25	0.785	0.967		-18.7
	0	1.012	1.261	0.101	-19.6
	25	1.320	1.600		-17.5

*2, 2, 4-trimethylpentane.

Gjaldbaek[5] for the solubility of nitrogen. These deviations bear out Hildebrand's[9] observation that when a gas solubility is desired to better than 10%, it must be measured.

VIII. SUMMARY AND CONCLUSIONS

The criteria for obtaining reproducible accurate gas solubility data have been discussed and an apparatus and procedure which fulfills these criteria have been developed.

The solubility of hydrogen has been measured in eight non-polar solvents at temperatures ranging from -30° to 50° C. and at approximately one atmosphere pressure.

The solubility theory of Hildebrand has been applied to these data and qualitative agreement with the theory has been found.

IX. ACKNOWLEDGMENT

The author wishes to thank Professor D. N. Hanson for his assistance in developing the solubility apparatus and for his sustained encouragement during the course of this work. Thanks are also expressed to J. L. Fick for his technical assistance, and to G. Unger for his patience in constructing and revising the several pieces of solubility apparatus during the developmental stages of this work.

X. NOMENCLATURE

A, B, C = constants

c = concentration, gm. moles/gm.

C_p = heat capacity, cal/^{o} C.

f = fugacity

f^{o} = standard state fugacity

H = Henry's law constant

ΔH_v = heat of vaporization, cal/mole

k = rate constant, time^{-1}

m = moles of gas in a vapor phase

M = moles of gas in a liquid phase

M_s = molecular weight of a solvent

n = any integer

p_g = partial pressure of a gas, mm.

p_s = vapor pressure of a solvent, mm.

P = total pressure, or a manometer reading, mm.

P^{o} = a datum total pressure

P_e = the total pressure or manometer reading at equilibrium

q = heat flow, calories

R = gas constant, 1.986 cal./mole, ^{o}K.

S = solubility, gm. moles gas/gm. solvent, atm.

t = temperature, ^{o}C.

t_a = air temperature (in the thermostat)

T = temperature, ^{o}K.

T_c = critical temperature, ^{o}K.

U = overall heat transfer coefficient, cal./Δt^{o}C.

X. Nomenclature (Cont.)

V, Vm = molal volume, cc.

X = mole fraction, liquid phase

Y = mole fraction, vapor phase

Z = overall or system mole fraction

α = relative volatility

β = Bunsen coefficient of gas solubility, volume of gas at S.T.P. dissolved per cc. of solvent at the temperature of the experiment when p_g = 760 mm.

γ = Ostwald coefficient of gas solubility, the ratio of gas concentrations in respectively the liquid and vapor phases

δ = solubility parameter, $(\text{cal./cc.})^{1/2}$

Δ = difference operator, or a difference in a gas burette reading before and after a stipulated period of dissolution

ρ = density, gm./cc.

θ = time

ϕ = volume fraction

XI. APPENDIX

A. Example Gas Solubility Calculation

Run No. 51: Solubility of H_2 in 2, 2, 4-trimethyl pentane at 25° C.

I. Initial moles of gas

1) temperature	25.00° C.
2) molal volume of H_2 at 1 atm.	24,481 cc.
3) gas volume	21,406 cc.
4) barometric pressure (corrected for temperature and gravity)	737.85 mm. Hg
5) ΔP in manometric system (corrected for temperature and gravity)	-262.0 mm. Hg
6) gas pressure, 4) + 5)	475.85 mm. Hg
7) moles gas charged: 6) · 3)/2) · 760 =	5.473×10^{-4} moles

II. Residual moles of gas

8) residual gas volume	1.2578 cc.
9) temperature	25.00° C.
10) barometric pressure, (corrected for temperature and gravity)	737.0 mm. Hg
11) ΔP in manometric system (mercury + solvent legs)	-138.0 mm. Hg
12) vapor pressure of the solvent	49.0 mm. Hg
13) residual gas partial pressure: 10) + 11) - 12)	550.0 mm. Hg
14) residual moles gas: 13) · 8)/2) · 760 =	37.2×10^{-6} moles

III. Moles gas dissolved

15) 7) - 14) =	5.101×10^{-4} moles

IV. Weight of solvent

16) volume of solvent at 35° C.	150.806 cc.
17) density of solvent at 35° C.	0.67825 gm./cc.
18) weight of solvent	102.284 gm.

V. Solubility

19) barometric pressure, corrected	737.0 mm. Hg
20) ΔP in manometric system, corrected (mercury + solvent legs)	-135.0 mm. Hg
21) vapor pressure of solvent	49.0 mm. Hg
22) gas partial pressure, 19) + 20) -21) =	553.0 mm. Hg
23) solubility: 15) · 760/18) · 22) =	6.854×10^{-6} moles H_2/gm. solvent atm.
24) correction for N_2 impurity: 0.9987 · 23) =	6.845×10^{-6}

B. Validity of the Method Used in the Determination of Equilibrium Pressure

As described in the section on procedure, the equilibrium point is determined by plotting the change in the secondary burette reading (see Fig. 1) for a given period of shaking versus the manometer reading, and then by a linear interpolation, the equilibrium value of the manometer is determined. In short, the solution rate is plotted versus the pressure setting and the point of zero rate is found by interpolation. At least two rate determinations are made at each of two pressures which are chosen such that the gas evolves at the lower pressure and dissolves at the higher pressure.

The question arises as to the validity of linear interpolation for obtaining an equilibrium value of the pressure to better than ±0.05%.

Except at the lower temperatures, these rates are measured at pressures on both sides of the equilibrium pressure with a total variation in pressure of 0.5 to 2.0 mm. Hence there is little doubt that the equilibrium pressure can be established to within 0.5 mm. which would meet our accuracy specifications if the gas partial pressure is greater than 500 mm. Rates of solution are slow at the lower temperatures and the total variation in pressure may be as high as 5.0 mm. in order to obtain significant changes in the burette readings within a reasonable time. In any case, it is pertinent to establish the validity of the method adopted for finding the equilibrium point.

The pressure changes made in order to observe rates of solution on the one hand and rates of evolution on the other are small compared to one atmosphere. Therefore, the number of moles of gas dissolved per unit change in the burette reading may be considered the same at the two pressure extremes, i.e., the maximum pressure change is less than 1%, whereas the volume of gas dissolved generally corresponds to a burette reading change of less than 3.0 mm., which is known to about 3%. We can therefore say that the rate is proportional to the change in burette reading.

The law for gas dissolution may be written as:

$$-\Delta = k(P-P_e), \qquad (1)$$

where Δ is the change in the burette reading for a given period of shaking (negative for gas dissolution), P is the pressure at which Δ is determined, P_e is the equilibrium pressure corresponding to the amount of gas in solution at the time Δ is determined, and k is a rate constant. (P and P_e can also be considered as manometer readings since the quantity $P-P_e$ is independent of the datum pressure. These two definitions are used interchangeably.)

Strictly speaking, Eq. (1) should be in differential form since P_e changes as gas dissolves such that $P_e = Hx + p_s$, where x is the concentration of the gas in solution, H is a Henry's law constant, and p_s is the vapor pressure of the solvent. For any single determination of Δ, however, the amount of gas dissolved is small enough that an average value of P_e is valid. In spite of the fact that the differential equation is easily solvable, it is preferable to be able to plot experimentally determinable values directly, which at once

exhibit whether the equilibrium pressure is sufficiently well known or at what other pressures succeeding values of Δ should be taken.

The possible error in the determination of P_e by the above simple method lies, then, in the variation of P_e as gas dissolves. Consider a case where some divergence might be expected between the true P_e and the P_e determined by plotting Δ versus P.

Assume that Δ = 3.0 mm. and the total pressure is approximately 760 mm. In this case, P_e will be changed by approximately 0.15 mm. in pressure, that is, with the apparatus used in this work. As far as obtaining consistent values of Δ is concerned, this change in pressure would become serious as P approached P_e; therefore consider the case where $P-P_e$ is initially 1.0 mm. The next value of Δ, i.e., Δ_2 determined at the same manometer setting, accordingly will be about 15% less than Δ_1, while Δ_3 will be approximately 25% less than Δ_1, etc. However, if Δ_1 and Δ_2 are in reasonable agreement, the pressure is then changed so that Δ's of the opposite sign will be obtained, and therefore the errors in P_e will tend to cancel one another.

It might be pointed out here that waiting for equilibrium to obtain is generally impractical, not only from the standpoint of time consumption, but also because the barometric pressure is seldom dependably steady over long periods of time.

For the most exact work, P_e may be continuously corrected for changes due to gas dissolution. When Eq. (1) is rewritten in terms of some arbitrary initial conditions,

$$-\Delta = k(P^o - P_e^o) + k\Sigma\Delta P - k\Sigma\Delta P_e, \qquad (2)$$

where P^o is the initial or base manometer reading and P_e^o is the equilibrium value of the manometer reading corresponding to P^o and the amount of gas dissolved at the time P^o is determined. The algebraic summation of changes in the manometer setting is $\Sigma\Delta P$ and it also includes barometric pressure changes, while $\Sigma\Delta P_e$ is the algebraic summation of the changes in P_e due to gas dissolution or evolution. For example, increases in the barometric or manometric pressures would constitute positive ΔP's to be added to P^o, while the total change in P_e, i.e., $\sum_o^n \Delta P_e$, would be positive for net gas dissolved and proportional to $-(\Delta_n/2 + \sum_o^{n-1} \Delta)$ for the nth Δ determined.

This calculation process has been carried out for Run 44 in which Δ per mm. pressure change was about 4.5 mm. for a 10-minute shaking period. The Δ's observed were 2.2, 1.2, 0.9, -5.9, -5.5, and 1.75 mm. in that order. By plotting these values against the manometer reading corrected to a base barometric pressure, P_e was found to be 34.525 cm. by linear interpolation to $\Delta = 0$. For the above more complex process, Δ was plotted against $(\Sigma\Delta P - \Sigma\Delta P_e)$ and at $\Delta = 0$, P_e^o was calculated from the relation, $P_e^o = P^o - \Sigma\Delta P + \Sigma\Delta P_e$, from which P_e was found to be 34.53 cm. The added labor involved in this case is, therefore, by no means justified even though the plot obtained is more nearly linear.

In summary, then, the equilibrium value of the manometer reading, P_e, may be obtained accurately by simply plotting Δ, the change in the burette reading for a given period of shaking, versus

P, the manometric setting corrected for barometric pressure changes. This accuracy is maintained as long as the values of Δ are about 3.0 mm. or smaller; i.e., about 0.005 cc. out of 20 cc. of gas dissolved, and so long as plus and minus values of Δ are used in order to average out the discrepancy in P_e. In cases where rates are slower and larger values of $P-P_e$ are imposed to give readings in a reasonable time, the linearity of a simple Δ vs. P plot will be improved since the percentage change of $P-P_e$, and hence in Δ, is much less for a given amount of gas dissolving.

C. Rates of Solution and the Determination of Equilibrium

As stated in section V-F, one of the major errors in the determination of gas solubility data can be the lack of a suitable criterion for equilibrium. The purpose of this section is to show quantitatively how previous investigators may have failed to reach equilibrium and to present the rates of solution of hydrogen encountered in this work.

In most cases, previous workers have used burettes permitting an accuracy sufficient to determine gas volumes to about 0.1%, whereas in the cases where they have reported duplicate determinations, deviations of 1% and more are very common.

Consider the case of hydrogen dissolved in n-heptane. The rate which we observed at 35° C. with a shaking amplitude of about 3/8 of an inch and a frequency of about 170 $min.^{-1}$ was about 1.8×10^{-8} moles/min., mm. ΔP, or in terms of volume, about 0.00056 cc./min., mm. ΔP. This was one of the fastest

rates observed. As a percentagewise increase in the gas dissolved, this amounts to about 0.0028%/min., mm. ΔP. Most investigators state that equilibrium is attained in about one hour. Assume that after one hour a hydrogen-n-heptane system is within 1% of equilibrium, i.e., if the discrepancy from equilibrium is stated as a pressure difference, ΔP would equal approximately 7 mm. Let the system be equilibrated by shaking for another 10 minutes. This period seems reasonable for a total equilibration time of 1 hour. In this case, the amount of gas dissolved will be about 0.2% which could easily be mistaken for an error in burette reading; furthermore, rates ten times less than the one used for this example have been observed during runs at -25° C. It is concluded, then, that errors of the order of 1% are quite possible by using the classical method of no apparent further dissolution as a criterion for equilibrium.

The above considerations point to the need for a dual gas measuring system, the first part designed to measure the initial gas to the desired accuracy of the experiment, the second being designed with sufficient sensitivity to determine the equilibrium point accurately. In the present apparatus, the residual gas burette is sensitive to changes in volume as small as 0.00015 cc. for a reading of 0.1 mm., whereas the initial or primary gas burette is sensitive only to about 0.0025 cc. for a similar reading. The following table gives the rates observed in our more recent determinations. In general, the rate of solution was found to increase as temperature increases and as the solubility per cc. of solvent increases.

Table 11

Rates of Hydrogen Solution in Apparatus 7

(Percent increase in the gas dissolved per minute of shaking, per mm. pressure difference, $P-P_e \times 10^4$)

Solvent	-25° C.	-15°	0°	10°	25°	35°
$n\text{-}C_7H_{16}$	1.1	--	2.0	--	2.3	3.0
$n\text{-}C_7F_{16}$	1.0	--	2.0	--	4.4	4.8
$n\text{-}C_8H_{18}$	0.3	--	0.8	--	1.5	1.6
$iso\text{-}C_8H_{18}$*	1.0	--	1.4	--	2.8	3.5
CCl_4	--	--	0.7	--	1.4	1.7
CS_2	1.2	--	1.3	--	3.0	--
benzene	--	--	--	1.2	1.8	2.0
toluene	--	0.8	1.5	--	1.6	1.9

*2, 2, 4-trimethyl pentane

D. Correction of the Solubility Data for the Nitrogen Impurity in the Hydrogen

Inasmuch as the hydrogen used in this work contained 0.25% N_2, the only appreciable impurity, the question arises as to what effect this impurity will have on the data and how the impurity can be corrected for.

The equations used for this correction are:

$$\alpha_{H_2 - N_2} = \frac{Y_{H_2} X_{N_2}}{Y_{N_2} X_{H_2}} = \frac{(1 - Y_{N_2}) X_{N_2}}{Y_{N_2}(1 - X_{N_2})}, \qquad (1)$$

$$(M + m)Z_{N_2} = MX_{N_2} + mY_{N_2}. \qquad (2)$$

Equation (1) is a defining equation for the relative volatility, α, and Eq. (2) is a simple material balance on nitrogen. Here,

Y_{N_2} = mole fraction of N_2 in the vapor phase,

X_{N_2} = mole fraction of N_2 in the liquid phase,

Z_{N_2} = mole fraction of N_2 in the gas charged to the apparatus,

M = moles of gas dissolved,

m = moles of gas in the vapor phase.

All of these quantities are on a solvent free basis. Of these quantities, Z is known by analysis, M and m are determined at the time of the solubility determination, and α can be obtained from solubility data. It might be pointed out that since the amount of nitrogen present is small, the correction will also be small and hence the correction need not be known too accurately.

The calculation involves assuming a value of X_{N_2} and solving for Y_{N_2} in Eq. (2), then a substitution of X_{N_2} and Y_{N_2} into (1) is made to see if these values give the correct value for α. The process is repeated until Eqs. (1) and (2) are both satisfied.

With the corrected values of X_{N_2} and Y_{N_2}, X_{H_2} and Y_{H_2} are calculated respectively from $X_{H_2} = 1 - X_{N_2}$ and $Y_{H_2} = 1 - Y_{N_2}$. These values give respectively the fraction of dissolved gas and undissolved gas which is hydrogen. Also, Y_{H_2} is the fraction of the gas partial pressure which is due to hydrogen. The solubility has previously been calculated by assuming that both of these fractions are unity. This first calculation can be corrected, therefore, by multiplying this first value of the solubility by X_{H_2}/Y_{N_2}, since the solubility is expressed in moles of gas dissolved per atmosphere of gas partial pressure.

For the value of α, we have used binary solubility data and assumed Henry's Law which leads to:

$$\alpha_{H_2\text{-}N_2} = \frac{S_{N_2}}{S_{H_2}}, \tag{3}$$

since $Y_{H_2} = Y_{N_2}$, if the solubilities are reported on the basis of 1 atmosphere partial pressure. From the data available on nitrogen and hydrogen,[20, 21] and with our uncorrected hydrogen data, α values were calculated in ten solvents, and α was found in all cases to lie between 1.8 and 2.2. A value of 2.0 was used in all of our corrections.

Inspection of Eq. (2) shows that if most of the gas is dissolved, that is, M>>m, then $X_{N_2} \cong Z_{N_2}$. In our determinations this is the case since approximately 95% of the gas was dissolved during any given determination. Furthermore, X_{H_2} and Y_{H_2} are not sufficiently different from each other to influence the accuracy of the correction. These two approximations applied to Eq. (1) lead to:

$$Y_{N_2} = \frac{Z_{N_2}}{\alpha'}. \tag{4}$$

Two examples are presented which represent tests of Eq. (4). These two cases represent extremes in the data taken, the first being for n-heptane where the ratio m/M was about the minimum encountered and the second for toluene where that ratio was about the maximum encountered.

Solubility Correction Factors for the Nitrogen Impurity

Solvent	$M \times 10^4$	$m \times 10^4$	$(Y/X)_{H_2}$ Eqs. 1, 2	$(Y/X)_{H_2}$ Eq. 3
n-heptane, Run 44	6.374	0.375	0.9987	0.9987
toluene, Run 49	4.312	0.787	0.9986	0.9987

From these results, it is evident that utilizing a correction factor of 0.9987 is sufficiently accurate in order to sustain an error of less than ±0.05%.

E. Considerations of Unsteady State Heat Transfer to the Apparatus

It is exceedingly important to know how the solubility apparatus, and in particular the solvent bulb and its contents (see Fig. 1) respond to external temperature changes. For example, if the temperature of the solvent is offset from the desired point by 0.1° C., it is pertinent to know how long a time must elapse, after changing the air temperature by that amount, until the solvent reaches the new temperature. Also, it is desirable to know how to attain temperature equilibrium in a short time. Both of these questions can be answered if the heat transfer characteristics of the solvent bulb and its contents can be determined.

Consider the solvent bulb and its contents with a heat capacity C_p, and a temperature t_s. Let the external air temperature be t_a. Let t_a be constant and let the bulb have a heat transfer coefficient, U, in calories per °C. of temperature difference between the air and the solvent. Assume that perfect mixing takes place in the bulb, i.e., t_s is uniform throughout the bulb. The rate of heat transfer can then

be expressed as

$$\frac{dq}{d\theta} = U(t_a - t_s), \tag{1}$$

where q is the heat transferred and θ is time. Also $dq = C_p dt_s$, which leads to

$$\frac{dt_s}{d\theta} = \frac{U}{C_p}(t_a - t_s). \tag{2}$$

Integration of Eq. (2) gives

$$\frac{t_a - t_s}{t_a - t_s^{\,o}} = e^{-\frac{U\theta}{C_p}}, \tag{3}$$

where $t_s^{\,o}$ is the value of t_s at $\theta = 0$.

Unfortunately, t_s cannot be measured in our apparatus but it is possible to measure a rate which is proportional to $dt_s/d\theta$.

Hence by rearranging Eq. (3) and differentiating with respect to θ, it can be shown that:

$$\log_e \frac{dt_s}{d\theta} = -\frac{U\theta}{C_p} + \text{const.} \tag{4}$$

Therefore, any rate proportional to $dt_s/d\theta$ plotted as its logarithm versus time will exhibit linearity and what might be called a temperature half-time is obtained from the slope. This is the time which is required to halve the difference, $t_a - t_s$, while t_a is held constant.

The actual rate measured to determine this half-time is the rate of rise of mercury in the capillary gas transfer tube when stopcock 6 is closed (see Fig. 1) during the temperature equilibration period preceding measurement of the initial gas charged. This

rate is proportional to the temperature rate of rise insofar as the coefficients of expansion of mercury and the solvent in the solvent bulb are constant. An example of such a rate plot is shown in Fig. 22. From this curve the temperature half-time is about 10 minutes. This half-time will, of course, vary as the contents of the bulb vary from run to run thus varying C_p, the heat capacity.

As to the usefulness of this value, let us consider that the apparatus and thermostat are at 25.10° C. and it is desired to bring them both to 25.00° ±0.01° C. If the thermostat temperature is changed to 25.00° C. it would take more than 30 minutes to bring t_s to the desired temperature. When the temperature half-time is known, however, t_a can be set at 24.90° for 10 minutes and then brought to 25.00° at which time there would be reasonable assurance of having attained the desired temperature.

F. Vapor Pressure Apparatus

Incidental to the solubility of hydrogen measurements, the vapor pressures of all of the solvents used have been measured. These measurements were made not only as a criterion for purity but also in order to obtain vapor pressures measured under approximately the same conditions employed in the solubility determinations and to have vapor pressures of the actual solvents employed regardless of any slight impurities.

Initially, these measurements were made in an isoteniscope,[22] but since agreement of the results was not satisfactory, it was decided to use the apparatus shown in Figs. 23 and 24, which by

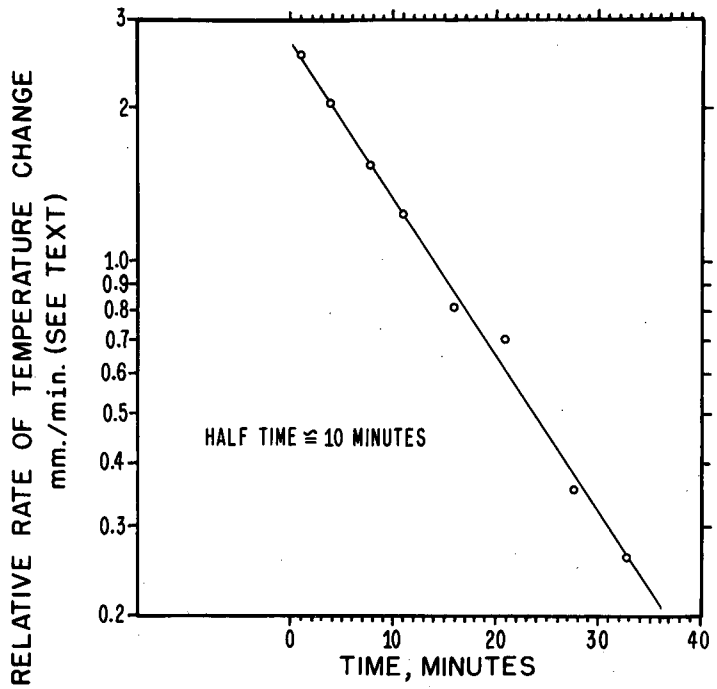


Fig. 22. **Temp**erature half-time determination.

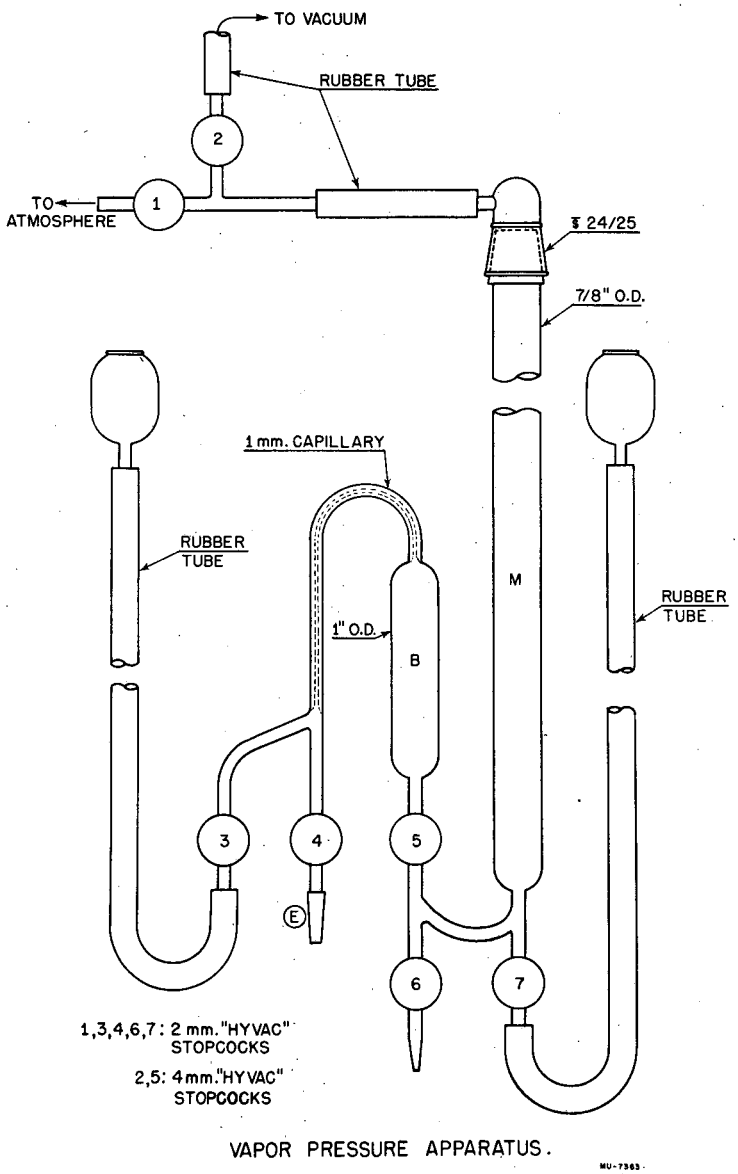


Fig. 23. The vapor pressure apparatus.

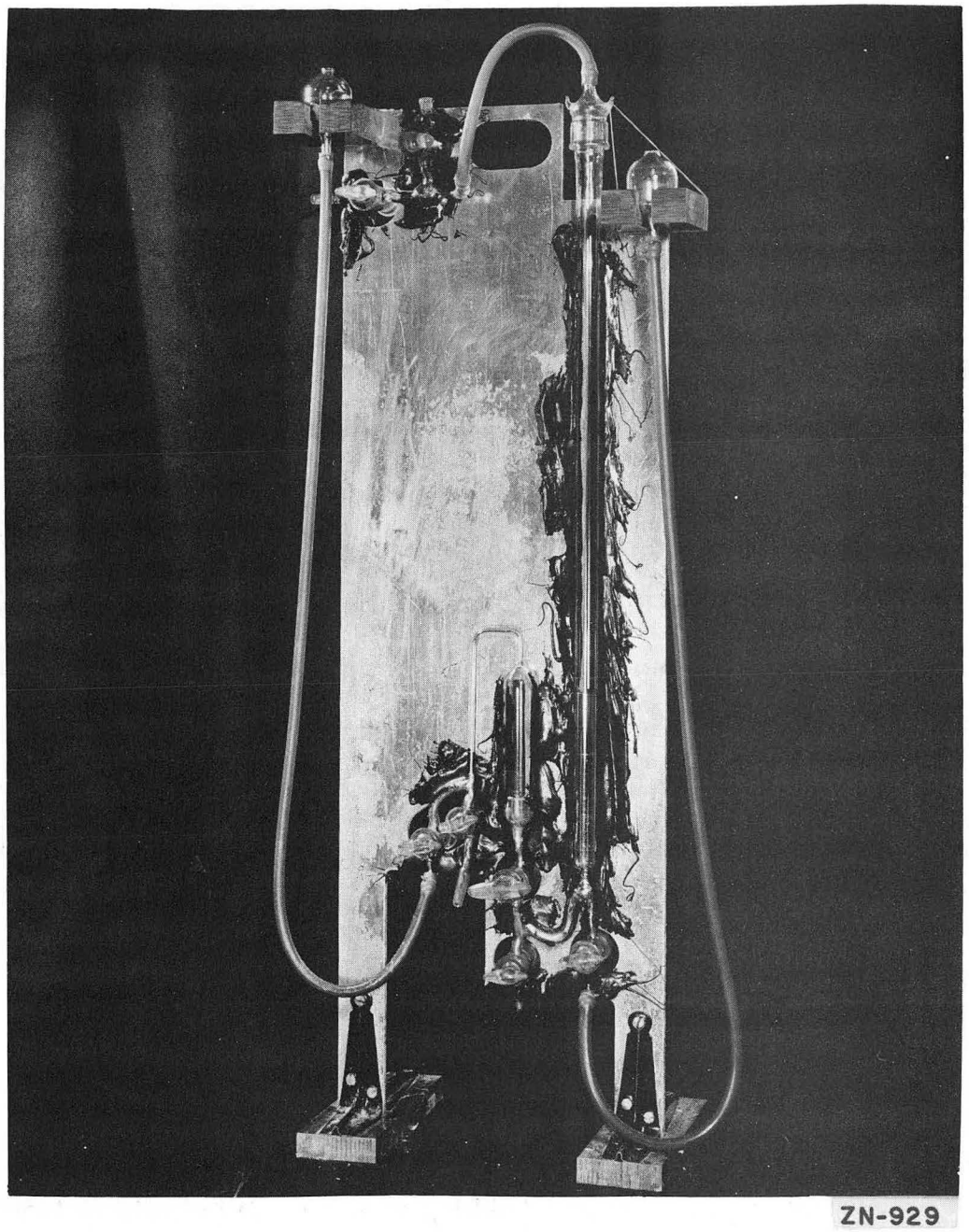


Fig. 24. A photograph of the vapor pressure apparatus

comparison with Fig. 1, is simply a repetition of the solubility apparatus with the provision for measuring gas volumes deleted. The apparatus is cemented to an aluminum plate with "3M" bedding compound, and the plate is fitted with angle braces so that the apparatus will stand erect.

To determine a vapor pressure, this apparatus is first thoroughly cleaned with chromic acid and after rinsing and drying, the solvent bulb B, and the system connecting it to the manometer M, are filled with mercury. All stopcocks except 4 have previously been lubricated. Solvent is placed in solvent bulb B by dipping the standard taper E into a beaker of the solvent and then applying vacuum to the manometer M with stopcock 5 open. When sufficient solvent has been added (generally about 25 cc.), air is allowed to pass into the solvent bulb B to provide a relatively large vapor space for boiling during the degassing procedure. Stopcock 5 is then closed and stopcock 4 is dried and lubricated.

The solvent is then degassed by applying vacuum to E through a liquid nitrogen trap--essentially that system shown in Fig. 7. The solvent is warmed by an infrared heat lamp to induce boiling and degassing is carried out according to the criteria set forth in section V-D.

When degassing is complete, mercury is let into the system through stopcock 3 until the capillary is full, and then through 5. At this point, if no gas bubble persists,, degassing is considered to be complete. Otherwise, the degassing procedure is repeated.

The mercury level in the manometer M is adjusted so that solvent and mercury levels in the solvent bulb will remain in the solvent bulb B when vacuum is applied to the manometer M in order to vaporize the solvent. This adjustment is made according to the expected vapor pressure. With only stopcock 5 open, the apparatus is immersed in a water bath thermostat and vacuum is applied to the manometer M through stopcock 2. In the cases of the less volatile solvents, it was occasionally necessary to shake the apparatus firmly in order to initiate vaporization.

When temperature equilibrium was reached, and when the pressure in the manometer had fallen to 10 microns or less, which required from 10 to 20 minutes, the heights of mercury in the solvent bulb and manometer and the height of solvent in the solvent bulb are read with a cathetometer. These readings are made at about 10-minute intervals until consistent results are obtained. Three sets of readings were found to be ample.

From the above measurements, the vapor pressure can be calculated directly by correcting the difference in the mercury levels in B and M for temperature and gravity and then subtracting the solvent leg as mercury at 0° C. from this difference.

The data obtained from this apparatus were found to be easily reproducible to 0.1 mm.; while for one case of incomplete degassing, the readings drifted slowly with time in the direction of an apparent high vapor pressure. This drift, or rather the lack of it, is then a further criterion for completeness of degassing.

The results obtained from this apparatus are given in Table 11. These data agree with previous work except for CCl_4 and n-C_7F_{16}. It is therefore suspected that the CCl_4 contained some impurity. On the other hand, only one literature reference[4] has been made to the vapor pressure of n-C_7F_{16}. It is possible that the n-C_7F_{16} which we used was not pure since it was of uncertain origin.

This apparatus overcomes some of the manipulative disadvantages of the isoteniscope and as well, the a priori accuracy of the present apparatus is somewhat improved. For example, the need for a careful adjustment of the external pressure with the isoteniscope is completely avoided. As well, proven criteria for degassing can be used in our apparatus, whereas the only criterion for the isoteniscope is that of consistent results after successive degassing. Another consideration is that only three readings need be made in our apparatus, one of which--the solvent level--is relatively incapable of affecting the accuracy insofar as errors in reading are concerned, that is, if a reading error of 0.1 mm. is assumed for all readings, this error in the solvent level would be equivalent to about 0.01 mm. of mercury. On the other hand, it is necessary to make two manometer readings for the isoteniscope and two readings (including the initial adjustment) on the barometer, and further errors in capillarity for the barometer could effectively give a third error. Therefore, if each reading can be assigned a possible error of 0.1 mm., the two pieces may be compared on the basis of a maximum error of 0.5 mm. for the isoteniscope against 0.2 mm. for the apparatus used in this work.

Our apparatus is also very well adapted to determine the vapor pressure when only very small quantities of solvent are available. For the isoteniscope degassing is generally carried out two or more times at each temperature to insure complete degassing. With our apparatus, degassing is complete and assured because there is no way in which gas may enter the apparatus. As a result, only a single degassing need be carried out for the complete determination of vapor pressure at a series of temperatures.

G. Calculation of the Solvent Solubility Parameters

In all cases except for n-perfluoro heptane, δ, the solubility parameter, was calculated from calorimetrically determined heats of vaporization[24] from the relation suggested by Hildebrand.[9]

$$\delta = \frac{(\Delta H_v - RT)^{1/2}}{Vm}, \qquad (1)$$

where,

δ = solubility parameter, $(\text{cal./cc.})^{1/2}$,

ΔH_v = heat of vaporization, cal./mole,

R = gas constant, cal./mole, ^{o}K.,

T = temperature, ^{o}K.,

Vm = solvent - molal volume.

In order to obtain values of ΔH_v at the desired temperatures; that is, -25°, 0°, 25°, and 35° C., the available ΔH_v values were plotted as $\log_{10}\Delta H_v$ vs. $T_c - T$, where T_c is the critical temperature. This plot gives curves which do not vary a great deal from linearity, hence the process of extrapolation and interpolation is fairly accurate.

Values of δ for the solvents used are given in Table 12 along with the heats of vaporization and the molal values used in the calculation.

In the case of n-perfluoro heptane, δ's were determined in the following manner from the vapor pressure data taken during this work. The vapor pressure data were fitted to the equation

$$\log_{10} p_s = C + \frac{A}{B + t}, \tag{2}$$

where p_s is the vapor pressure in mm. of mercury and t is the temperature, ^{o}C. The values of the constants were found to be $A = -1256._1$, $B = 216.4_9$, and $C = 7.083_1$. By combining the Clausius-Clapeyron equation,

$$\frac{d \ln p_s}{dT} = \frac{\Delta H_v}{RT^2}, \tag{3}$$

with the differential form of (2),

$$\frac{d \ln p_s}{dT} = 2.303 \frac{-A}{(B + t)^2},$$

an expression is obtained for ΔH_v as a function of temperature,

$$\Delta H_v = \frac{RT^2}{2.303} \left(\frac{-A}{(B + t)^2}\right), \tag{4}$$

but the heats of vaporization calculated in this manner for all of the solvents used were found to be about 1% higher at 25^{o} C. than the calorimetric values. Hence, for n-perfluoro heptane, the value of ΔH_v at 25^{o} calculated from Eq. (4) was reduced by 1% and placed on the previously mentioned ΔH_v vs. $T_c - T$ plot, the slope being estimated by inspection.

In summary, the values of δ given in the following table are probably accurate to 0.1% for all solvents except n-C_7F_{16} in which case the uncertainty may be as large as ±1%.

Table 12

Heats of Vaporization, Molal Volumes, and Solubility Parameters of the Solvents Investigated

Solvent	Temp. °C.	ΔH_v cal./mole	Vm cc./mole	δ (cal./mole)$^{1/2}$
$n\text{-}C_7H_{16}$	35	8610	149.28	7.318
	25	8735	147.46	7.430
	0	9043	143.10	7.701
	-25	9326	139.35	7.969
toluene	35	8970	108.11	8.786
	25	4079	106.98	8.906
	0	9328	104.21	9.177
	-25	9563	101.80	9.439
$n\text{-}C_7F_{16}$	35	8511	229.25	5.869
	25	8675	225.58	5.984
	0	9057	217.39	6.256
	-25	4419	209.17	6.530
$n\text{-}C_8H_{18}$	35	9790	165.60	7.445
	25	9914	163.71	7.546
	0	10225	159.28	7.797
	-25	10502	155.04	8.035
$i\text{-}C_8H_{18}$ *	35	8283	168.37	6.750
	25	8395	166.30	6.850
	0	8662	161.67	7.087
	-25	8906	157.28	7.314

*2, 2, 4-trimethyl pentane

Table 12 (Cont.)

Solvent	Temp. °C.	ΔH_v cal./mole	Vm cc./mole	δ $(cal./mole)^{1/2}$
CS_2	35	6512	61.40	9.803
	25	6604	60.67	9.954
	0	6802	58.96	10.303
	-25	6966	57.34	10.535
CCl_4	35	7645	98.34	8.457
	25	7755	97.14	8.587
	0	8009	94.34	8.897
benzene	35	7963	90.55	9.004
	25	8090	89.44	9.150
	10	8257	87.82	9.360

XII. BIBLIOGRAPHY

1. A. von Antropoff, Z. Elektrochem., 25, 269 (1919).
2. R. Bunsen, Ann. Chem., 93, 1 (1855).
3. T. Estreicher, Z. physik. Chem., 31, 176 (1899).
4. R. Fowler, et al., Ind. Eng. Chem., 39, 375 (1947).
5. J. Gjaldbaek and J. Hildebrand, J. Am. Chem. Soc., 71, 3147 (1949).
6. Ibid., 72, 1077 (1950).
7. A. Grosse and G. Cady, Ind. Eng. Chem., 39, 367 (1947).
8. J. H. Hildebrand, Private communication.
9. J. H. Hildebrand and R. L. Scott, "The Solubility of Non-Electrolytes," 3rd Edition, Reinhold Publishing Corp., New York, 1950.
10. C. Hodgman, "Handbook of Chemistry and Physics," 30th Edition, Chemical Rubber Publishing Co., Cleveland, 1946.
11. J. Horiuti, Sci. Papers Inst. Phys. Chem. Research (Tokyo), 17, 125 (1931-32).
12. G. Just, Z. physik. Chem., 37, 342 (1901).
13. C. B. Kretschmer, et. al., Ind. Eng. Chem., 38, 506 (1946).
14. A. Lannung, J. Am. Chem. Soc., 52, 68 (1930).
15. E. G. Maxted and C. H. Moon, Trans. Faraday Soc., 32, 769 (1936).
16. J. H. Perry, "Chemical Engineers Handbook," 3rd Edition, McGraw-Hill Book Company, Inc., New York, 1950.
17. K. Pitzer and D. Scott, J. Am. Chem. Soc., 65, 803 (1943).
18. H. Sattler, Z. tech. Phys., 21, 410 (1940).

Bibliography (Cont.)

19. R. Scott, J. Research Nat'l Bur. Standards, 25, 459 (1940).

20. A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, 3rd Edition, D. Van Nostrand Co., Inc., New York, 1940.

21. A. Seidell and W. F. Linke, "Solubilities of Inorganic and Metal Organic Compounds," Supplement to 3rd Edition, D. Van Nostrand and Co., Inc., 1952.

22. A. Smith and A. Menzies, J. Am. Chem. Soc., 32, 1412 (1910).

23. C. Smyth and E. Engel, J. Am. Chem. Soc., 51, 2646 (1929).

24. J. Timmermans, "Physical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, 1950.

25. W. Timofejew, Z. physik. Chem., 6, 141 (1890).

26. C. Willingham, et. al., J. Research Nat'l Bur. Standards, 35, 219 (1945).

27. H. Wooley, et. al., Ibid., 41, 379 (1948).