An attempt was made to find a break in the curve indicative of the existence of this compound. As stated before, the wagon-pipet method could not be applied. Accordingly, the cooling-curve method was employed, but the data obtained, while indicating a very slight break in this region, were not sufficiently accurate to prove this conclusively.

Summary

Complete solubility data were obtained for trinitrotoluene in 11 solvents frequently used. A summary is given in the foregoing table showing the values at 5° intervals. In the course of the work it was necessary to use different methods depending upon the nature of the solvent and the relative solubility.

Acknowledgments.—Mr. A. C. Fieldner, Superintendent, and R. E. Hall, Physical Chemist, of the Bureau of Mines at Pittsburgh, gave many suggestions in overcoming difficulties and approved the methods and procedure followed. The work was done under the observation of Professor A. Lowy of the University of Pittsburgh and accepted by the University as the junior author's thesis for the degree of Master of Science.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

AN IMPROVED OPTICAL LEVER MANOMETER

BY EMMETT K. CARVER

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In considering some measurements on the adsorption of toluene vapor by plane glass surfaces, as described in the paper immediately following, it was found that none of the manometers described in the literature was entirely suitable. The McLeod gage is inaccurate with easily condensable vapors. The hot wire manometer[1] is hardly sensitive enough. The thermionic pressure gage[2] would decompose the toluene. The use of the Knudsen gage[3] offered many difficulties. The Rayleigh manometer[4] and the optical lever manometer of Shrader and Ryder[5] appeared to be the only ones that could be used. After some experimentation, the optical lever manometer was selected.

This manometer as previously described is essentially a U-tube mercury manometer. Floating on one of the mercury surfaces is a glass ball, which is attached to a mirror pivoted on 2 knife edges in such a way that

[1] Pirani, *Verh. I. Deut. Phys. Ges.*, **4**, 686 (1906).

[2] Buckley, *Proc. Nat. Acad. Sci.*, **2**, 683 (1916).

[3] Knudsen, *Ann. Physik*, **32**, 809 (1910).

[4] Rayleigh, *Phil. Trans.*, **196A**, 905 (1901).

[5] Shrader and Ryder, *Phys. Rev.*, **13**, 321 (1919).

as the mercury rises it tilts the mirror. A beam of light reflected from the mirror to a scale some distance away magnifies its motion to almost any desired extent.

The factors limiting the accuracy of this instrument appeared to be: (1) clinging of the mercury to the walls of the tube, (2) irregular wetting of the glass float by the mercury, (3) shifts of the zero point due to the knife edges slipping in their slots, (4) imperfections in the optical system, (5) vibrations of the mercury surface, causing the spot of light to oscillate, (6) a rise or fall of the mercury due to temperature changes.

The irregular clinging of the mercury column is considered by Shrader and Ryder to be the chief cause of error. They reduced it by tapping the tube with a vibrator before each reading, and by making the mercury

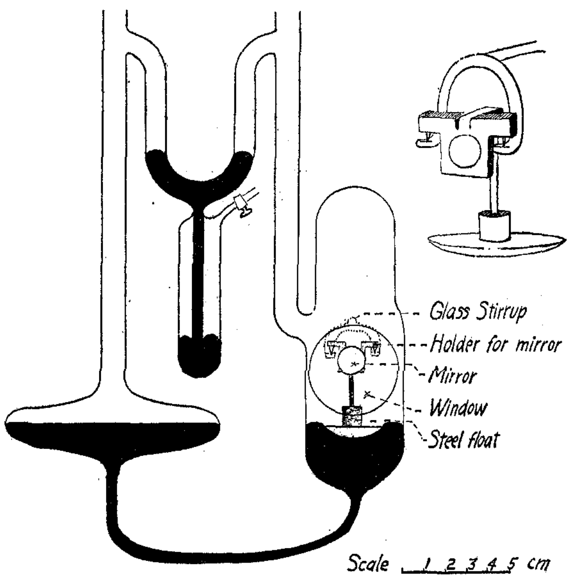

Fig. 1.—Improved optical lever manometer, with perspective view of the moving parts.

surfaces large. As the effect of this clinging can be considered as an irregular capillary depression of the center of the mercury column, it can readily be seen that if the tube be made wide enough the capillary depression will become negligible, and so its variations may be disregarded. The maximum possible capillary depressions for mercury in tubes of various diameters, calculated from Rayleigh's tables,[6] are for 20, 24, 31 and 35 mm. tubes, 0.026, 0.010, 0.0015 and 0.00059 mm., respectively. It will thus be seen that with a tube 35 mm. in diameter there could not possibly be a depression greater than 0.0006 mm., and that if this varied by 16%,

[6] Lord Rayleigh, *Proc. Roy. Soc.*, 92A, 184 (1915).

the error would be about 0.0001 mm. In order to allow for possible effects of the float, a tube of 44 mm. diameter was used.

To obviate the irregular wetting of the float by the mercury, it was made as shown in Fig. 1, of steel of such dimensions that it floated with the base almost submerged, and the mercury in contact all around it and up to the sharp knife edge at the circumference.

To avoid the shifting of the knife edges in the slots, they were replaced by needle points of hardened steel, one of which rested in a pit, and the other in a slot. When the parts were accurately made, the points would always come back to the same resting places if jarred loose. At first, steel was used for the pit and slot, but later glass was found to be more satisfactory. The pit was made by pressing a carefully sharpened steel punch into glass barely softened by heat. The slot was made in the same way, using a sharp knife instead of a punch.

The steel float carried a needle point of hardened steel which fitted into a conical pit drilled into the lever arm of the holder for the mirror. This pit at first presented considerable difficulty. Ordinary methods of drilling left it rounded at the vertex, and so gave the needle point opportunity to shift its position, but it was found that by drilling this rounded portion with a small sized, jeweler's pivot drill, and then punching it with a carefully sharpened steel punch, a pit of the required accuracy could be made. When the parts were well made, all the needle points would reseat themselves to within 0.0001 mm.

Variations in temperature were controlled by placing the manometer in a thermostat with an optical-glass window. The stirrer was shut off just before a reading was taken.

The vibrations of the mercury column proved to be the most serious difficulty. Minute ripples on the surface of the mercury, too small to be observed directly, caused the spot of light to vibrate over a distance of several centimeters. They were practically as great during the night as during the day. Placing the apparatus on a concrete pillar not connected with the rest of the building did not overcome the difficulty. The surface movements seemed to be due to horizontal vibrations of the earth itself. The difficulty was avoided by placing the whole apparatus on a heavy soapstone table which was suspended by 6 steel rods from a rigid bracket fastened to the concrete pillar. When the system was thus suspended, the vibrations practically ceased, and the shadow of the cross wire could be located to within 0.2 mm. on the scale, which corresponded to about 0.0001 mm. change in pressure.

To prevent distortion of the beam of light, Shrader and Ryder cemented a window of optical glass into their manometer. As any cement we could use might absorb toluene vapors, a window of ground and polished Pyrex glass was fused in place. By heating the whole to a point just below softening and melting the edges together with an oxygen-fed flame, this could be done with almost no warping of the glass.

A convex mirror with a 2-meter focal distance was used. As silver was attacked by the mercury vapors, and as any protective coating might absorb the vapors being studied, a platinum film was spattered on by placing the disk of glass under a platinum cathode in a vacuum discharge tube. This made a brilliant and satisfactory mirror.

Light from a tungsten lamp was concentrated on this and was reflected to a target on a scale at the other end of the room (about 6 meters away). The scale could be moved with a screw so that a horizontal line could be brought into coincidence with the image of a cross wire, making the reading of the manometer easier and more accurate.

The manometer was calibrated by accurately measuring the dimensions of the moving part with a micrometer microscope, by measuring the diameters of the 2 mercury surfaces with calipers, and by measuring the distance from the mirror to the scale with a steel tape.[7] The volumes of the various parts of the apparatus were measured by filling them with water from a buret.

To test the calibration, a known volume of hydrogen was admitted to one side of the manometer and the change in pressure read. This was compared with the change in pressure calculated from the gas law. The following is the result of one such series.

Pressure change obs. Mm.	Pressure change calc. Mm.	Error Mm.
0.1491	0.1487	−0.0004
0.1350	0.1346	−0.0004
0.1210	0.1213	+0.0003
0.0942	0.0944	+0.0002
0.0880	0.0878	−0.0002
0.0796	0.0795	−0.0001

The agreement is within the accuracy of the readings.

At first the manometer was solidly mounted in plaster of Paris in an

[7] The horizontal distance from the line between the needle points to the vertex of the socket was 4.41 mm. The distance from the mirror to the scale was 6193 mm. Therefore, 1 mm. rise of the shadow would correspond to $\frac{4.41}{2 \times 6193} = .0003560$ mm. fall of the float.

The area of the wide part of the manometer was 7305 sq. mm.; that of the small part 1227 sq. mm. As the mercury rises and falls inversely as the areas, a total difference in level of 1 mm. would mean a change of $\frac{7305}{1227 + 7305} = 0.857$ mm. Therefore, 1 mm. movement of the spot of light corresponds to $\frac{0.000356}{0.857}$ mm. change in pressure. This is true only for a pressure change so small that the difference between the sine and the tangent of the angle through which the mirror rotates is negligible. With the apparatus used, this difference would not be negligible with pressure changes greater than about 0.2 mm.

iron frame, but this binder cracked the glass, wrecking the whole apparatus. By putting a thin layer of litharge and glycerin between the plaster and the glass, the cracking was prevented.

The manometer was filled with mercury under a vacuum. A funnel with a long capillary tip was sealed into one side of the manometer. A ground-glass plug kept the mercury from running in while the manometer was being baked out and evacuated with a mercury diffusion pump. When the evacuation was completed the plug was lifted and the mercury allowed to run in. By cracking off the dome (see Fig. 1) the float and mirror were lowered into place with wires.

As is the case with nearly every instrument which is pushed to the limits of its sensibility, this manometer is somewhat difficult to work with. The zero point would sometimes shift, due to some unknown cause. At one time a steady shift was traced to a slow warping of the wooden brackets which supported the swinging table. When the brackets were covered with aluminum leaf and varnished, the shift stopped. By carefully watching the apparatus and discarding readings when the shifts took place good results were obtained.

Thanks are due to Drs. Shrader and Ryder for suggestions regarding the manometer, and to Professor T. W. Richards for invaluable help. The work was done with the aid of a fellowship from the National Research Council.

Summary

The sensitivity of the optical lever manometer of Shrader and Ryder has by a few changes been increased to about 0.0001 mm., with an accuracy of about 0.0002 mm. of mercury.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE ADSORPTION OF TOLUENE VAPOR ON PLANE GLASS SURFACES

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The data on the adsorption of vapors, although they ought to furnish information of a decisive character regarding the nature of the intermolecular forces, are so complicated by unknown factors that it is difficult to draw trustworthy conclusions from them.

The important question of the thickness of the adsorbed layer is as yet not definitely settled. Most of the experimental work tends to show that this layer is many molecules deep, but Langmuir[1] points out that all such

[1] Langmuir, THIS JOURNAL, 40, 1361 (1918).