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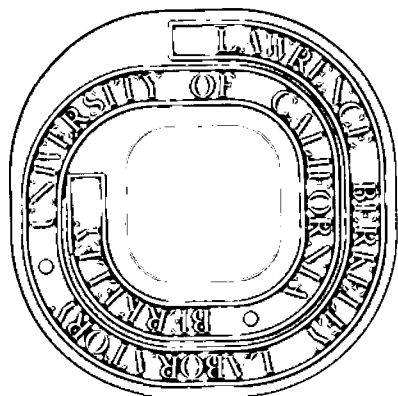
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## Diphenyl Ether, A Versatile Substance for Laboratory Demonstrations

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During the assembly of a diphenyl ether (DPE) drop calorimeter<sup>(6)</sup> recently I had the opportunity of observing the remarkable properties of this substance. Especially the purification and manipulation of this substance permitted me to perform the experiments described below, which I find extremely suited for educational purposes in freshman general chemistry, physical chemistry, and even in solid chemistry curricula.

The experiments are easy to prepare, little time consuming both in preparing and in performing them; they are reliable, cheap, and what is perhaps more interesting they show in a clear and striking way the magnitude of the phenomena under study.

The properties exhibited by this substance, both in solid and liquid phases, are almost superlatives. Both phases are in equilibrium at room temperature at 26.9°C. The liquid phase has a great tendency to supercool, 5° to 10°, depending upon purity. Liquid DPE at 22°C can remain liquid for long periods of time; a sample in our laboratory has remained liquid for more than two months.

Melting produces a total expansion which is nearly three times the contraction exhibited by the melting of ordinary ice. This property and

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the nearness of the melting point to the reference standard temperature, 25°C, are the principal reasons for substituting ice by DPE in isothermal Bunsen type calorimeters. (6, 4, 7, 3)

The liquid is an excellent solvent for air, although actual data for gas solubilities seem to be lacking. Liquid DPE has a noticeable optical dispersion power and is a poor heat conductor: upon heating or cooling the convection currents are easily seen.

DPE has an intense geranium odor. It boils at 259°C and forms explosive mixtures with air because of a rather high vapor pressure. It is very soluble in diethyl ether, benzene, toluene, and alcohol, in decreasing order. Care must be taken to avoid contact of DPE with the skin and particularly the eyes.

Purification. For any of the following experiments a rather pure product is needed. A rapid method of purification will now be described.

Because of the enormous expansion during melting, solid DPE is carefully melted by directing a stream of warm air to the upper part of the original container. Once the first layer is melted, the rest of the solid is free to move, and total melting is obtained by immersion of the container in warm water at 35° - 40°C. The liquid is then transferred to a tall form beaker and allowed to cool to room temperature before starting fractional crystallization. The beaker is placed in a stand that holds a gas trap, such as those used in vacuum lines with liquid nitrogen in the outside. The gas trap is connected by means of a glass T-joint to both warm and cool water with stopcocks, to enable the temperature control. When cool water flows in,

the trap acts as a cold finger refrigerator, to be used for the crystallization by immersing it in the liquid DPE. As mentioned before DPE tends to supercool and starting nuclei for the crystallization is difficult. It is easy to seed the cold finger by crushing with it some DPE crystals, obtained by cooling a small drop of DPE with dry ice. Some tiny crystals stick on the round bottom and serve as seeds when immersed. Then the crystallization starts immediately and the crystals grow as a uniform mantle at the surface of the cold finger. (This gives an excellent opportunity for seeing how crystals and dendrytes grow and ramify, because as is obvious the mantle grows only when the total immersed surface is covered with crystals.)

For a 23 mm diameter cold finger, with tap water at 15° - 18°C, a 1 cm thick mantle will be formed in 30-45 minutes, depending on the depth of liquid in the beaker the total amount of DPE per batch. This is the reason for using a tall form beaker. It is not recommended to try to obtain a thicker mantle because, as said before, DPE is poor heat conductor. Then the cold finger is lifted up and the liquid DPE allowed to drop into the beaker. By turning off the cool water and switching on warm water, the mantle is slipped from the cold finger into a beaker as a hollow round bottom cylinder. Switching back to cool water and touching these crystals, one is ready with new seeds for the next crystallization batch. It is convenient after adding more liquid DPE to warm the whole batch to avoid the growing of crystals that will bridge the growing mantle with the walls of the beaker if the liquid becomes too cool. One must be careful to protect the new crystals from dust.

As the crystallization proceeds the liquid becomes more impure and gets a green tinge. It is recommended to operate with a given amount of DPE each time, control the crystallization by weighing the initial amount, and stop when 25 to 30% of DPE remains as liquid. Repeat two more times for a very pure product. To maintain a uniform rate of production one must use at the end a tall beaker of small capacity in order to have a convenient depth. Operate under a good hood and use safety glasses.

If the original product is too impure it is better to distill under vacuum with an electric heating mantle, in the usual way, but proceeding carefully because of the air dissolved. (See below Nucleation from the liquid phase and gas dissolved.)

Supercooling. As the DPE becomes pure, the supercooling appears. With room temperatures of the order of 20°- 25°C, even the first fractions obtained will remain liquid for one day or more, if they are protected from dust. Pure DPE super cooled to 15°- 18°C, in a clean container can be shocked several times before it crystallizes, if it ever does.

Crystal growth. Prepare a tube, 10-15 mm diameter and closed at one end, bend the open end at 40°-50° with the horizontal, and leave 20-25 cm from bottom to the bend. Fill up to the bend with DPE, super cool 10°-15°, and hold horizontally for observation. Apply a piece of dry ice at one extreme, or seed by touching the surface of DPE with a glass rod holding some crystals. The crystallization starts immediately. Under such conditions a crystal growth rate of approximately 18 cm/min has been observed.

Dendrites growth. Repeat by cooling only to 20° - 23°C. The rate is now lower but still can be followed with the naked eye to observe how the dendrites ramify. Trapping a drop of liquid and crystals will permit better observation with a microscope.

Nucleation from the liquid and gas dissolved; degassing upon solidification.

Fill two thirds of a round bottom flask with liquid DPE and connect it to a vacuum line; protect the diffusion pump with a cold trap. Seal the neck of the flask to the line to avoid contamination by vacuum greases. (DPE is a solvent of them, even silicone grease, Apiezon, etc.) Supercool the DPE 15°C and connect to vacuum before turning off the cooling water. Use a water bath.

Start the nucleation by using a piece of dry ice. Be careful. Both nucleation and degassing start simultaneously. The starting nuclei grow rapidly to small crystals that are broken by the stream of gas; these broken crystals will be projected into the mass of liquid and onto the walls where they will eventually stick, and more gas will be released where the crystals stick and more crystals are broken and projected. The entire mass of liquid gives the impression of boiling vigorously. If necessary, turn off the vacuum until degassing decreases and then carefully open again to the pumps. The entire mass can be solidified under vacuum by adding ice water to the water bath, allowing the level to increase gradually so as not to trap gas in the interior. To degassify the DPE completely it is necessary to melt the mass again under vacuum. During the melting some gas will be released but stops when no more solid remains. Melting must be done carefully: some ice



water is removed and a stream of warm air directed to the upper part of the flask while the ice water is removed. We have done this by simply using an electrically heated simmer pot. The flask was of 3 liters capacity and the pressure before the start of degassing was  $10^{-4}$  mm of Hg. A second degassing was still observable but neither the crystal growth nor the degassing is so striking as the first one. A third degassing produces only some sporadic tiny bubbles. Admitting air over the liquid DPE will return it to the initial condition.

Nucleation from the gas phase. Use the same vacuum line as above but with an empty flask sealed near the first one containing liquid DPE. Be careful in cleaning all glass tubing and flask. Control the glass blowing work by using a trap for moisture and grease; a simple  $\text{CaCl}_2$  and glass wool bulb is enough. After degassing thoroughly as before, heat under vacuum to  $35^\circ$ -  $40^\circ\text{C}$ , or even  $50^\circ\text{C}$ , while applying a piece of dry ice in the empty flask. As soon as nuclei are formed remove the dry ice and stop heating. Let stand after turning off the vacuum pumps. The crystal will grow glassy like, giving the appearance of a single crystal.

Zone refining. Zone levelling. Use a 10 mm diameter glass tube and fill up to 25 cm with a saturated DPE solution of Alizarin Red S, prepared at  $35^\circ$ -  $40^\circ\text{C}$ ; supercool and solidify by seeding. (We used Alizarin Red S from Allied Chemicals because it was available in the laboratory; the reader is encouraged to use methyl orange or other dye-substance at hand.) Fix the tube vertically in a stand. The furnace was a 25 mm long aluminum tube made from a rod, 30 mm in diameter and machining it to have a 7 mm long

central hole just fitting in the tube. The remaining aluminum was cut in order to have a 2 mm wall. In this form only a small length of DPE is melted. We used a simple Lab-jack to displace the furnace all along the tube. If a more automated outfit is desired, the reader is referred to several proposed zone refining procedures at low temperature. (2,5,8,9,10) The passes must be done in a downward direction because of the expansion upon melting.

Start melting then the upper part and stop when a 1 cm height ring of liquid is obtained. Freeze it with dry ice. Continue the downward travel only when a ring of DPE is frozen completely to the center. Care must be taken to ensure the solidification of the liquid, not only in order to perform the zone refining but also to avoid cracking the glass tube by the expansion upon melting. We recommend the use of a tap water cooler in tandem with the furnace. By either method the formation of a ring of excess alizarin in the lower part of the liquid ring will be observed after 3 to 4 cm travel. A second pass gives a solid with a pale yellow color and a second ring of alizarin travels to the bottom.

For zone levelling, proceed as before and when the pure DPE is solid, add the desired colorant by means of a glass tube that fits closely into the 10 mm diameter tube to avoid having the colorant stick on the walls. Be careful in observing the directions given for the first portion melted.

Diffusion in the solid phase. It will be observed that after a zone refining travel the alizarin gathers at the bottom of the tube as a dark brown zone and tends to diffuse upwards as may be seen by the intense yellow color. As this observation takes several days it is better to start

as follows. Solidify a small amount of alizarin solution in the bottom of a test tube as mentioned. Cover with 2-3 mm of pure DPE liquid and solidify it again. Then add more pure DPE liquid and solidify. Keep at room temperature, 22°- 24°C, and observe after a week how much diffusion has occurred.

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#### Literature Cited

- (1) Cases, J. C. , submitted to J. of Chem. Eng. Data, May, 1972.
- (2) Christian, J. D. , J. Chem. Educ. 33, 32 (1956). A Chem. Educ. Tested Demonstration, J. Chem. Educ. 40, A-409 (1963).
- (3) Davies, J. V. , Pritchard, H. O, J. Chem. Thermodynamics 4, 9-22 (1972).
- (4) Giguere, P. A. , Morissette, B. G. , Olmos, A. W. , Can. J. Chem. 33, 657-64 (1955).
- (5) Hinton, J. F. , McIntyre, J. M. , and Amis, E. S. , J. Chem. Educ. 45, 116-7 (1968).
- (6) Hultgren, R. R. , Newcomb, P. , Orr, R. L. , Warner, L. , Phys. Chem. Metallic Solns. Natl. Phys. Lab. Symp. No. 9, 1, Paper 1H, H. M. S. O. London, 1959.
- (7) Jessup, R. S. , J. Res. Natl. Bur. Stand. 55, 317-22 (1955).
- (8) Knypl, E. T. , and Zielenski, K. , J. Chem. Educ. 40, 352 (1963).

- (9) Lippert, I. S. , and Ritter, J. E. , Jr. , J. Chem. Educ. 46, 650-2 (1969).
- (10) Zief, M. , Ruch, H. , and Schramm, Ch. H. , J. Chem. Educ. 40, 351-2 (1963).

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