

# A METHOD FOR DETERMINING CRITICAL CONSTANTS AND ITS APPLICATION TO DIPHENYL ( $C_6H_5 \cdot C_6H_5$ )

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## ABSTRACT

A relatively simple method, leading to an evaluation of the critical constants characteristic of a substance as well as the liquid and saturated vapor densities with varying temperatures is described. The method is employed in the case of diphenyl ( $C_6H_5 \cdot C_6H_5$ ) giving values of the critical pressure, temperature and density, of 31,400 mm Hg.,  $528^\circ C$  and .343 gms/cm<sup>3</sup> respectively.

A knowledge of the critical constants of a substance as well as the liquid and saturated vapor densities, is of considerable importance since these quantities may appear directly or indirectly in the mathematical function representing relationships between liquid and gaseous states of the substance. Further they may often be employed to calculate other physical constants more difficult to obtain experimentally.

Many classical researches<sup>1</sup> have been carried out to determine some or all of these constants for certain substances but in most cases the apparatus has been exceedingly complicated and for accurate results required considerable care in manipulation such as maintaining the substance at constant temperature during a definite compression at very high pressures.

The method herein described is able to give directly the critical temperature and critical volume or density as well as liquid and vapor densities at all temperatures, and combined with the results of another experiment is able to give the critical pressure. It leads to results of considerable accuracy and may be carried out so simply that it is deemed to be worthy of description. The substance chosen for investigation was diphenyl ( $C_6H_5 \cdot C_6H_5$ ) supplied by the Federal Phosphorus Company, Birmingham, Alabama.

## APPARATUS

Three thick walled pyrex glass tubes about 30 cm long and 5 mm in diameter, sealed at one end, were carefully calibrated as to volume by filling to various levels with mercury and weighing. The liquid levels were read by a cathetometer reading to hundredths of a mm movable

<sup>1</sup> Ansdell, Proc. Roy. Soc. 30, 117; 1880. Cailletet and Mathias, Jour. de Phys. 5, 549; 1886. Cailletet and Colardeau, Comptes Rendus, 112, 563; 1891. Amagat, Comptes Rendus, 114, 1093; 1892.

along a vertical scale. The results for each tube were arranged graphically so that the volume of liquid corresponding to any length column could be read off directly. The three tubes were now filled with different calculated amounts of diphenyl, evacuated and sealed. The amounts of substance used were determined by the results of a preliminary experiment to determine the approximate critical density. Tube *A* was then filled with such an amount that at the critical temperature its density would be slightly under the critical density while tube *C* would have a density slightly greater than the critical density and tube *B* as nearly as possible equal to the critical density.

The three tubes were now mounted close together in grooves in a copper block and the whole suspended in a cylindrical electrical furnace wound to give uniform temperature distribution. The furnace was made by winding chromel resistance wire on a pyrex glass tube and insulating with asbestos sheet except for a narrow space along one side, which was left for observation of the tubes within, by the cathetometer telescope. The copper block was used to insure equitemperature conditions throughout the length of the tube and the temperature was measured by several thermocouples placed in various positions. Fig. 1 shows a sectional view of the tubes in place in the furnace.

#### MANIPULATION

The temperature was adjusted to any desired value and when it became constant, observations were made with the cathetometer upon the meniscus level, bottom and top reference points for each tube. These readings could then be expressed in terms of vapor and liquid volumes for each tube, giving three simultaneous equations, involving the two unknowns, liquid density ( $\rho_L$ ) and vapor density ( $\rho_V$ ) thus

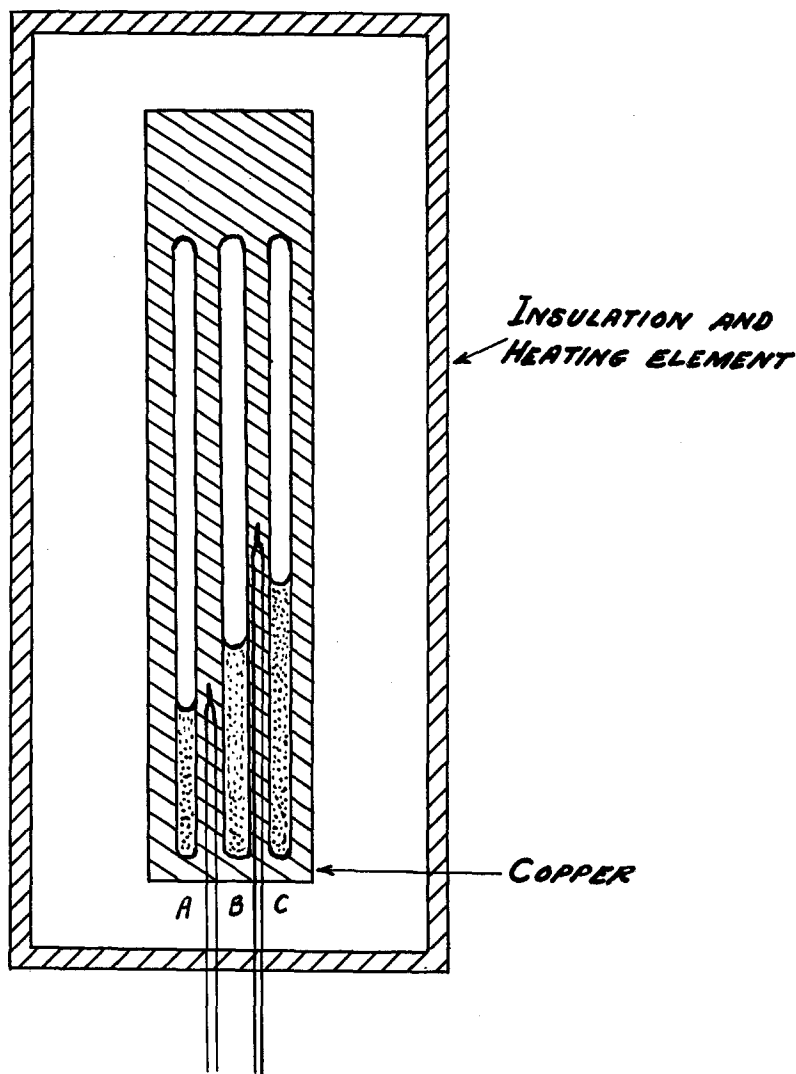
$$\rho_L V_L^A + \rho_V V_V^A = M^A$$

$$\rho_V V_L^B + \rho_V V_V^B = M^B$$

etc. where  $M^A$ ,  $M^B$  . . . represent the known masses in tubes *A*, *B*, . . .

The solution of these equations may most easily be carried out graphically as shown in Fig. 2. Each equation is represented by a straight line whose end points are the imaginary densities  $\rho_V$  if  $\rho_L$  be regarded zero and  $\rho_V$  regarding  $\rho_L$  as zero, the intersection giving the real solution  $\rho_L$  and  $\rho_V$  at the temperature employed. In favorable cases the intersections for the three pairs of equations come remarkably close to a definite point. For less favorable cases they form a triangle in which the coordinates of the center of area give average densities. This process may be

repeated at successively higher temperatures giving as many points as desired when the results are represented on a density-temperature curve.



### THERMOCOUPLES

FIG. 1. Sectional view of furnace with tubes in place.

To determine the critical temperature the tubes are observed as the temperature is slowly increased until the meniscus in each disappears. That in *A* or *C* disappears first, the former at the bottom of the tube

and the latter at the top, while if  $B$  has the proper amount of substance the meniscus will disappear at the center of the tube at a temperature greater than that for  $A$  or  $C$ . The temperature difference for the varying amounts is not great as may be seen by the flatness of the curve at the critical point in Fig. 3, so that the critical temperature may be expressed

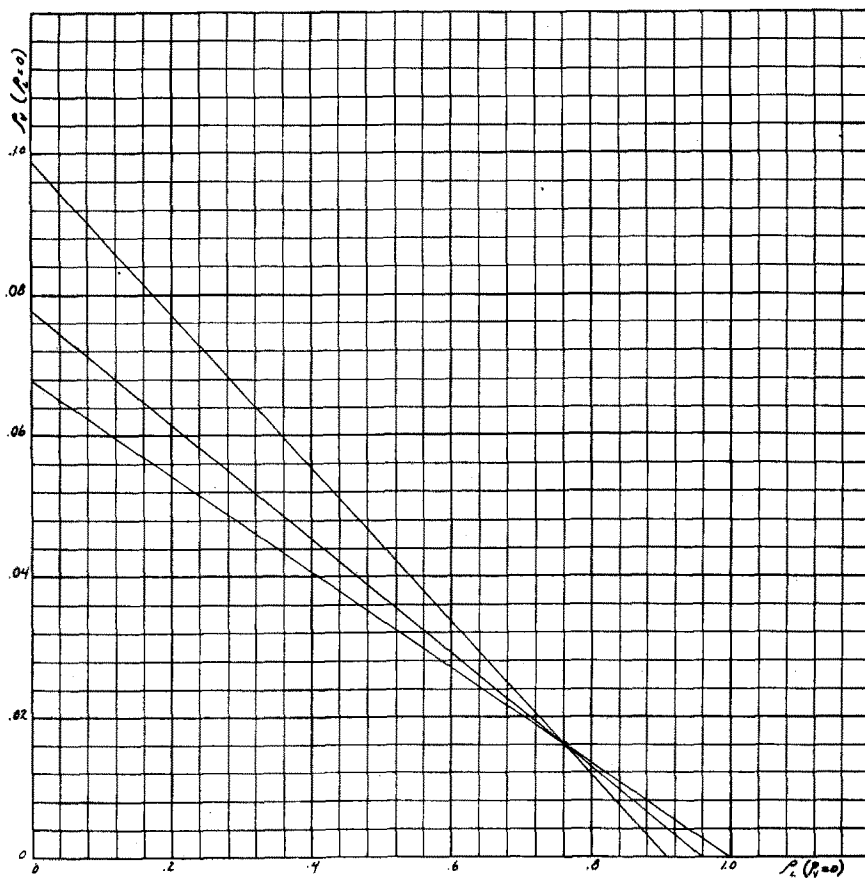


FIG. 2. Graphical solution of density equations.

with much greater accuracy than the critical volume. Observations were made both on heating and cooling through the critical point. The critical pressure may be obtained from a vapor pressure-temperature curve using the vapor pressure at the critical temperature. However, this may be found without actually using pressures in the neighborhood of the critical pressure. If the results at relatively low pressures be plot-

ted on a log P-log  $T$  chart, almost a straight line is obtained which may be extrapolated with safety through the critical temperature.

### RESULTS

For the diphenyl under investigation, which might have contained slight traces of impurities, the following physical constants were ob-

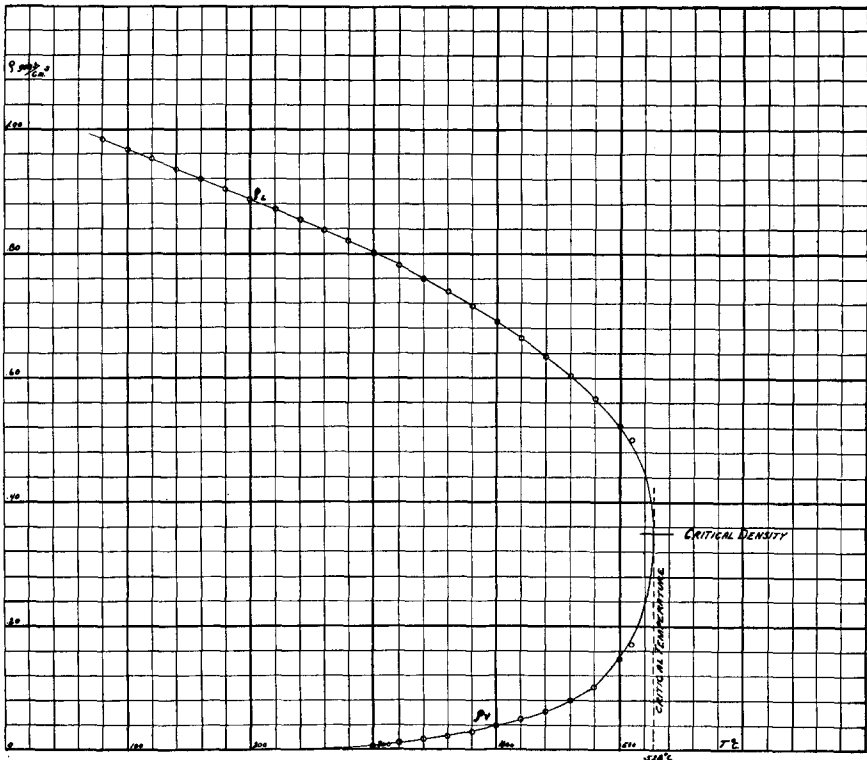


FIG. 3. Critical temperature and density of diphenyl ( $C_6H_6$ )<sub>2</sub>.

served: melting point  $70.4^\circ C$ , critical pressure 31,400 mm of Hg, critical temperature  $528^\circ C$ , critical density .343 gms/cm.<sup>3</sup> The collected density-temperature relationships for liquid and vapor states are shown in Fig. 3. From the liquid density-temperature curve the coefficient of volume expansion of the liquid at low temperatures ( $100^\circ$ – $150^\circ$ ) is found to be about .00080 per deg. centigrade.

While, as demonstrated, this method is relatively simple and convenient in the case of many substances, some materials at high tempera-

tures attack the glass so that it cannot always be employed. Care must be exercised to insure that the glass will withstand the pressures developed.

This opportunity is taken to express appreciation to Mr. J. E. Hill and Mr. W. P. Ewalt for the many observations taken by them in the development of the method.