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## On the Thermodynamics of Solutions. IV. The Determination of Liquid-Vapor Equilibria by Measuring the Total Pressure<sup>1,2</sup>

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It has been repeatedly noticed<sup>3</sup> that the knowledge of the total pressure over a binary solution as a function of the composition of the liquid at constant temperature is sufficient for a complete description of the liquid-vapor equilibrium at this temperature. In other words, the activity coefficients can be derived, in principle, from the total pressure without knowledge of the composition of the vapor. In spite of this considerable advantage, the method has not been used very often. One reason is obvious, namely, the difficulty of the calculation. Indeed, none of the various calculation methods appears to be satisfactory. Another reason may have been the suspicion that small experimental errors may entail unduly large errors in the resulting activity coefficients. This question appears to deserve a careful examination.

The present paper is restricted to a special case of some practical importance. The efficiency of distillation columns containing a large number of plates is frequently investigated by means of binary solutions of closely boiling hydrocarbons. The relative volatility of the binary system must be known with a fairly high accuracy since in a column of  $n$  plates the error in the resulting efficiency is  $n$  times the relative error in the relative volatility. A sufficiently accurate analysis of the liquid and the vapor presents, in general, serious difficulties since the properties of closely boiling hydrocarbons are not sufficiently different. The advantage of the measurement of the total pressure therefore is important. At the same time, convenient calculation methods can be developed for these systems which deviate only slightly from perfect solutions.

### Experimental

To obtain the full advantage of the method, one has to observe two conditions: (a) The composition of the liquid should be obtained by weighing the components. Accordingly the vapor space over the boiling liquid should be small so that the correction for the change of composition by vaporization is negligible or small. (b) Especially for systems of closely boiling components, a differential method is preferable in which the vapor pressure of a solution is directly compared with the vapor pressure of one component boiling at the same temperature. The temperature difference between the two boilers is measured by means of a thermocouple, which requires less vapor space than a resistance thermometer.

The vapor pressure of the component used for reference

(1) Presented at the Symposium on Thermodynamics and Molecular Structure of Solutions, 114th National Meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, Portland, Oregon, September 13 and 14, 1948.

(2) Previous papers of this series: *Ind. Eng. Chem.*, **40**, 341, 345 (1948); *J. Chem. Phys.*, **15**, 849 (1947).

(3) See, for instance, R. M. Levy, *Ind. Eng. Chem.*, **33**, 928 (1941).

and the pressure difference between the two boilers are determined by means of a mercury manometer. Capillary depression is eliminated by the use of 20 mm. tubing. The boiling temperature of the reference substance is calculated from the vapor pressure.

Between the manometer legs and the boilers are buffer bulbs (2 liters), Dry Ice traps and short condensers. The manometer and the buffer bulbs are enclosed in an air thermostat. The connecting lines between the manometer and the condensers are filled with nitrogen, the amount of which is precisely controlled by means of needle valves in side lines leading to a nitrogen tank and a vacuum pump. Pressure fluctuations are avoided by maintaining a steady flow rate of the cooling liquid (water or acetone cooled by means of Dry Ice) in the condensers.

The Cottrell boilers (Fig. 1) are enclosed in silvered vacuum jackets *j*. The kettle is heated by a coil fitting in the cylindrical space *h*. The thermocouple is introduced into the well *w*. The liquid thrown up to the well by the Cottrell pump returns through the line *r* and mixes there with the reflux from the condenser *c* so that there is practically no holdup of condensed vapor. After the measurement the boiler is drained through the tube *d*. The boilers are charged each with 85 ml. of liquid. The vapor space up to the level of condensation amounts to 185 ml. The heaters are arranged in series and operate at 60 watts each. The resistances of the heaters are made equal within 1%.

The desired boiling temperature is obtained by adjusting the amount of nitrogen in the connecting lines between manometer and boilers. The temperature difference is easily maintained below 0.02° and measured within 0.001°. Only a crude calibration of the thermocouple is therefore required, easily obtained by letting the same pure substance boil in the two boilers at different pressures.

The filling hole is in the connecting line above the Dry Ice-trap so that any contact between vapor and glass stopper is avoided. The solutions, however, are filled into the boiler through a glass tube extending through the trap so that the vapor cannot be carried into the manometer lines.

The purity of the components must be checked by comparing the difference of their vapor pressures with adopted values. Small impurities are harmless if the consistency of the results is maintained by a suitable correction.

The errors introduced by the determination of the pressures and the temperature difference and by weighing influence the total pressure (at about one atmosphere) only by a few thousandths of one per cent. The change of concentration by vaporization into the vapor space is of the

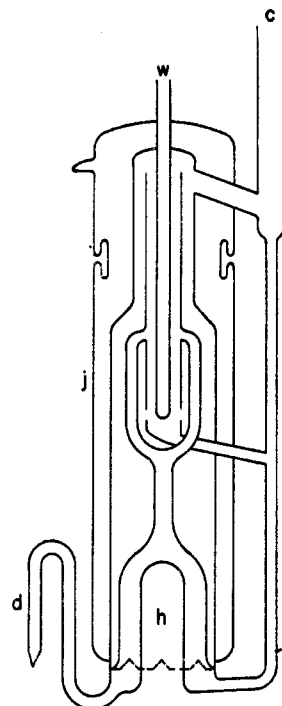


Fig. 1.—Boiler.

same order of magnitude for closely boiling systems. The main error, especially for low boiling mixtures, appears to be due to vaporization during the preparation of the solution. The possible error during the filling of *n*- and isopentane into the weighing flask was estimated and a correction of one half its amount was applied. The maximum correction corresponded to 0.025% in the total pressure. Altogether, errors of a few hundredths of one per cent. are to be expected.

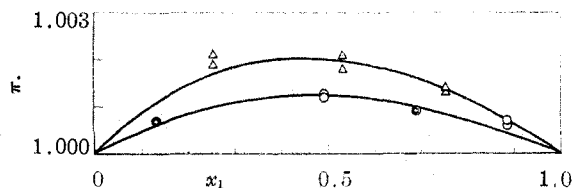


Fig. 2.—Ethylbenzene-*o*-xylene,  $\Delta$ ,  $B = 0.0035$ ; *m*-xylene-*o*-xylene,  $\circ$ ,  $B = 0.0021$ .

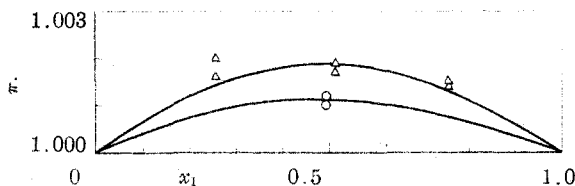


Fig. 3.—Ethylbenzene-*p*-xylene,  $\Delta$ ,  $B = 0.0031$ ; *p*-xylene-*o*-xylene,  $\circ$ ,  $B = 0.0019$ .

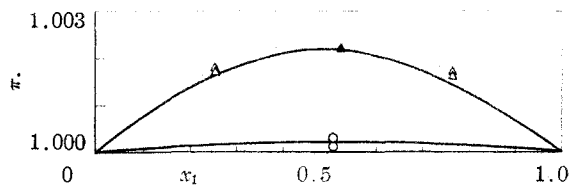


Fig. 4.—Ethylbenzene-*m*-xylene,  $\Delta$ ,  $B = 0.0036$ ; *p*-xylene-*m*-xylene,  $\circ$ ,  $B = 0.0003$ .

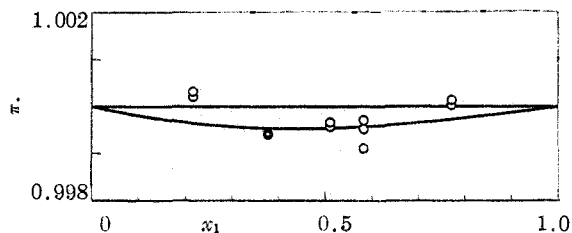


Fig. 5.—Isopentane-*n*-pentane,  $B = -0.0008$ .

### Results

The results obtained at approximately atmospheric pressure are shown in Figs. 2 to 5. The ordinate is the ratio

$$\pi = P/(x_1P_1 + x_2P_2) \quad (1)$$

( $x_1$  and  $x_2$  are the mole fractions of the liquid). The functions  $P_1$  and  $P_2$  are sufficiently approximated<sup>4</sup> for the present purpose by

$$\ln P_i/p_i^\circ = (V_1 - \beta_i)(P - p_i^\circ)/RT \quad (2)$$

(4) Cf. M. Benedict, C. A. Johnson, E. Solomon and L. C. Rubin, *Trans. Am. Inst. Chem. Engrs.*, **41**, 371 (1945). In other cases better approximations may be required, which will be discussed in the next paper of this series and in a paper by J. A. Beattie (*Chem. Revs.*, 1949).

( $p_i^\circ$  vapor pressure,  $V_1$  molal volume of the liquid,  $\beta_i$  second virial coefficient). Since

$$x_1\gamma_1P_1 = y_1P \quad (3)$$

( $\gamma_1$  activity coefficient), the total pressure is

$$P = x_1\gamma_1P_1 + x_2\gamma_2P_2 \quad (4)$$

The calculation of the activity coefficients presents no difficulty if, as in the present case, the approximation

$$\log \gamma_1 = Bx_2^2, \quad \log \gamma_2 = Bx_1^2 \quad (5)$$

is sufficient. In this case we calculate the function  $\pi$  of eqn. (1) for a few suitably chosen values of  $B$  according to (1), (4) and (5), draw the corresponding curves in a diagram containing the experimental points and find the best value of  $B$  by interpolation. This method has the advantage that the influence of experimental errors on the result is immediately seen.

The diagram furnishes a direct indication if the approximation (5) is insufficient and a second term of a Margules series is to be added. In this case the experimental points are consistently above the closest fitting curve in one part of the diagram and consistently below in the other part. The graphical method can be extended to this case without serious difficulty.

For small values of  $B$  an even simpler method can be used. Equation (5) is approximated by

$$\gamma_1 - 1 = 2.303 Bx_2^2, \quad \gamma_2 - 1 = 2.303 Bx_1^2 \quad (6)$$

so that

$$\pi = 1 + 2.303 Bx_1x_2(x_1P_2 + x_2P_1)/(x_1P_1 + x_2P_2) \quad (7)$$

This approximation is sufficient for  $P_1/P_2 = 1$  if  $B < 2.1 (d\pi)^{1/2}$  and for  $P_1/P_2 = \infty$  if  $B < 0.6 (d\pi)^{1/2}$  where  $d\pi$  is the permissible error in  $\pi$ .

The figures contain the curves representing the adopted values of  $B$ . The vapor pressures of Rosini and his co-workers<sup>5</sup> were used for the calculations. The second virial coefficients were calculated from Berthelot's equation. The values of  $B$  may be in error by a few units of the fourth decimal place, corresponding to a maximum error of 0.1% in the relative volatility.

In measurements of this type, the correction for the imperfection of the vapor (Eqn. 2) may be important even at atmospheric pressure. In the system iso- and *n*-pentane the value of  $B$  would be  $-0.0023$  without the appropriate correction instead of  $-0.0008$ .

**Acknowledgment.**—The authors are indebted to Mr. L. T. Carleton for valuable advice regarding the construction of the apparatus.

### Summary

Small deviations from the perfect solution are conveniently and accurately determined by measurement of the total pressure. The experimental procedure is described. Results are given for the six binary systems formed by the three xylenes

(5) American Petroleum Institute, Research Project 44 at the National Bureau of Standards, "Selected Values of Properties of Hydrocarbons," Tables No. 1k and 5k (June 30, 1944).

and ethylbenzene and for isopentane-*n*-pentane. The method is useful for systems to be used for determining the efficiency of distillation columns.

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## Physical Properties of Some Organic Insect Repellents<sup>1</sup>

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Under the Insecticide and Insect Control Research and Development Program carried out for the Department of National Defense, a large number of organic compounds were prepared and tested for their insect repellent effectiveness. It was thought that a critical study of the physical properties of some successful repellents might be of value in determining whether or not a correlation existed between repellent effectiveness and certain physical characteristics. However, the data required to make such a study were not available. We, therefore, were asked to provide certain physical data for a large number of compounds. The results which we have obtained up to the present are recorded in Table I.

### Experimental

**Purification of Materials.**—About 25 to 30 ml. of starting material (all that was available) was vacuum distilled. A Vigreux column, 1 cm. diameter and 15 cm. long, provided with a chromel heating jacket, was used for all distillations except for isobutyric acid,  $\alpha$ -hydroxy-, phenethyl ester and *dl*-malic acid, dibutyl ester. The middle fraction (50–60%) was collected under the conditions given in Table I.

**Refractive Indices.**—Measurements were made using an Abbe refractometer with temperature control. Check results agreeing to 0.0001 unit were obtained. The refractometer was calibrated against water (obs., 1.3325; lit., 1.3325) and with a test plate (obs. 1.5185; manufacturer's value for plate, 1.5185).

**Boiling Points.**—The boiling points were determined by a micro method.<sup>2</sup> The average of five to ten readings for each compound was always within 0.4° of the extreme readings. All boiling points were corrected to 760 mm. Based on the results for the reference materials listed in Table II and on the behavior of the test materials which did not decompose, we estimate the boiling points in Table I to be within 0.3°.

**General Information for Remaining Measurements.**—Due to the limited amounts of material available for the tests, it was necessary to design apparatus whose total volume was not over 2 cc. This necessitated the use of capillary tubing wherever possible. Such apparatus was usually cleaned with acetone, water, potassium chromate-sulfuric acid cleaning solution, water and distilled water. The apparatus was then dried with a current of clean dry air for about an hour while it was kept in the oven at about 45°.

Material was usually introduced into measuring apparatus by suction. All possible precautions to avoid picking up moisture in the course of an experiment were taken.

All thermostats (except the one used for refractive index measurements) were maintained at 35 ± 0.02°.

All thermometers were calibrated against thermometers previously calibrated by the Bureau of Standards.

After the test material was introduced into a measuring apparatus, the unit was allowed to come to temperature equilibrium in a minimum period of fifteen minutes.

**Density.**—Ostwald-Sprengel type pycnometers, volume about 1 ml., were used. Check weighings, agreeing to 0.1 mg., were made on a pycnometer and its contents. The precision is estimated to be 0.01%.

**Viscosity.**—Ostwald viscosimeters, volume between marks was 0.7 to 1.0 ml., were used. Five viscosimeters (small bore capillary) were calibrated with water, while one viscosimeter (large bore capillary) was calibrated with phthalimide, *N*-*s*-butyl-, after its viscosity was determined. The large bore viscosimeter was used for compounds whose viscosity was greater than 180 millipoises. The times of efflux on check runs agreed to 0.2%. Considering reproducibility and agreement with the value for benzene, we consider the results in Table I to be accurate to at least 0.2%.

**Solubility.**—The method discussed by Sobotka and Kahn<sup>3</sup> was used. The test material is added drop by drop from a calibrated, water-jacketed, 1-ml. microburet, to a definite amount of water contained in a thermostated, glass-stoppered flask, until the end-point is reached (corresponding to the saturation of the water by the test material). Sudan IV was used as the indicator. From the density and volume of the material used, its solubility in grams per 100 ml. of water is calculated. The results, given in Table I, are based on duplicate runs.

A test run made on diethyl succinate gave a value of 1.73 g./100 ml. of water compared to a value of 1.78 g./100 ml. of water obtained by saponification with subsequent titration of a saturated solution of diethyl succinate in water. Benzyl alcohol, *p*-methoxy-, gave a solubility of 3.83 g./100 ml. of water compared to a value of 3.84 g./100 ml. of water obtained from a refractive index calibration curve.

**Surface Tension.**—In the first part of this work, measurements were made by the capillary tube method. The radius of each of six different tubes was determined using both benzene and water as standards. The results for each tube agreed to 0.5%. Heights of liquid in the tube and in the reservoir were measured with a cathetometer reading to 0.1 mm. A duplicate run was made on each material using a different capillary. The reproducibility of data and the agreement with the ring method used on phthalic acid, dimethyl ester and phthalimide, *N*-*s*-butyl-, indicate that the results given in Table I are within 1% in all cases and within 0.5% in the majority of cases (*i. e.*, those values not designated by the letter R).

Difficulty was experienced in getting equilibrium heights by the capillary tube method in the case of some of the compounds. In those cases, the surface tensions were measured by the ring method, using a Cenco du Notuy precision direct tensiometer. The test liquid was placed in a weighing bottle surrounded by a jacket through which the bath water was circulated. The average of eight readings was used in each case to get the approxi-

(1) This research was carried out with funds provided by the U. S. Quartermaster Corps.

(2) Shriner and Fuson, "Identification of Organic Compounds," 2nd edition, John Wiley and Sons, New York, N. Y., p. 93.

(3) Sobotka and Kahn, *THIS JOURNAL*, **53**, 2935 (1931).