that the pyridine/piperidine equilibrium may have been established at 400°C. At the higher hydrogen pressures the equilibrium is much more favorable for piperidine than at the 11 bars hydrogen pressure used in the present study. The product distributions shown in Figures 3 and 4 exhibit the same trends as the distributions reported by Sonnemans and Goudriaan, except for the downturn.

McIlvried (1971) studied the hydrodenitrogenation of pyridine at 315°C and pressures of 50 to 100 bars on a $NiCoMo/Al_2O_3$ catalyst. He did not analyze for piperidine in his products but he observed that the nitrogen content of the total product was about the same for a given set of reaction conditions starting with either pyridine or piperidine. In his case, the rate of hydrogenation of the pyridine ring was presumably rapid relative to subsequent steps, and at his higher pressure there was no thermodynamic limitation on the concentration of piperidine that could exist in equilibrium with pyridine. Here the rates of hydrogenation of pyridine to piperidine and of the hydrogenolysis step both appeared to affect the overall rate at the overall rate at the lower temperatures. At the higher temperatures the rate limiting step was solely hydrogenolysis of piperidine present in low concentration because of a thermodynamic limitation. The maximum in pyridine conversion at 375-400°C is caused by the decrease in the equilibrium concentration of piperidine with increased temperature being more important than the increase in the kinetic rate constant for piperidine cracking.

LITERATURE CITED

Cocchetto, J. F., "Thermodynamic Equilibria of Heterocyclic Nitrogen Compounds with Their Hydrogenated Derivatives," S.M. thesis, Mass. Inst. Technol., Cambridge (1974).

Goudriaan, F., "Hydrodenitrogenation of Pyridine," doctoral thesis, Twente Technical Institute, The Netherlands (1974).

Mayer, J. F., "Interactions between Hydrodesulfurization and Hydrodenitrogenation Reactions," Sc.D. thesis, Mass. Inst Technol., Cambridge (1974).

McIlvried, H. G., "Kinetics of the Hydrodenitrification of Pyridine," *Ind. Eng. Chem. Process Design Develop.*, **10**, 125 (1971).

Satterfield, C. N., Michael Modell, and J. F. Mayer, "Interactions between Catalytic Hydrodesulfurization of Thiophene and Hydrodenitrogenation of Pyridine," *AIChE J.* (in press).

Sonnemans, J., F. Goudriaan, and P. Mars, "The Hydrogenolysis of Pyridine on Molybdenum Oxide Containing Catalysts," Paper 76, Fifth Intl. Cong. on Catal., Palm Beach, Fla. (1972).

Sonnemans, J., G. H. Van der Berg and P. Mars, "The Mechanism of Pyridine Hydrogenolysis on Molybdenum-Containing Catalysts," II. "Hydrogenation of Pyridine to Piperidine." *J. Cat.* 31, 220 (1973).

Sonnemans, J., W. J. Neyens and P. Mars, "IV. The Conversion of Piperidine," *Ibid.*, 34, 230 (1974).

Stengler, W., J. Welker, and E. Leibnitz, *Freiberger Forchungsh.*, **329A** 51 (1964).

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A New Technique for Collecting Binary Vapor-Liquid Equilibrium Data without Measuring Composition: the Method of Intersecting Isochores

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The Burnett coupled isochoric *PVT* experiment possesses many advantages for determining volumetric properties. In this study, we suggest that it also provides an excellent vehicle for determining VLE data. Incorporating a magnetic densimeter into the apparatus encompasses a VLE experiment in which the phases are not sampled to determine composition. Material balances allow composition calculation; the Gibbs-Duhem equation is not necessary and thus remains available for consistency checks.

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SCOPE

Vapor-liquid equilibrium (VLE) data are fundamental, essential information required in chemical engineering practice. A vast literature indicates their importance but also makes it infeasible to list all workers making significant contributions. Recently, Wichterle and Kobayashi (1972) and Parrish and Hiza (1973) report very precise, conventional equipment. Fredenslund and Mollerup (1974) have a novel sampling system, while Smith et al. (1974) extend the total pressure method. Besserer and Robinson (1971) utilize refractive index in a unique experiment. Kidnay, Miller, and Hiza (1973) published a recent survey of VLE research.

The most vexing experimental problem in VLE studies is sampling the phases for composition analysis. Problems associated with sampling include obtaining representative samples, avoiding fractionation and adsorption in the sample lines and disturbing equilibrium by sampling. Chromatographic analysis is probably no better than 0.5% (accuracy).

With the current technique, we do not sample the phases; instead we measure the phase densities utilizing a magnetic densimeter. The experiment is an extension of the Burnett coupled isochoric *PVT* method. Simple material balances provide the phase compositions.

CONCLUSIONS AND SIGNIFICANCE

Sampling causes experimental difficulties when VLE data are collected. The desire to eliminate this source of error spurred development of various techniques for measuring VLE data without sampling. However, the alternatives to sampling introduced data reduction problems which restricted their use. Our technique substitutes measuring phase densities for sampling, an operation which is intrinsically more accurate.

We collected preliminary data on a prototype apparatus to demonstrate the feasibility of our technique. We chose the carbon dioxide/*n*-butane system because previous data are considered reliable by most users and because these data are easily compared with data collected by our method. These preliminary data indicate that the technique is a viable method for VLE determinations.

DESCRIPTION OF THE EXPERIMENT

Burnett (1936) proposed a remarkable apparatus for determining the equation of state of fluids measuring volume or mass directly. Today, the Burnett method ranks as one of the most precise techniques for determining *PVT* behavior. Recently, several investigations have demonstrated that the experiment possesses remarkable flexibility; Kramer and Miller (1957) used the technique to make as well as to study mixtures; Burnett (1963) introduced the Burnett coupled isochoric experiment and suggested using it in vapor-liquid equilibrium experiments; Pope, Chappelear, and Kobayashi (1972) introduced the isochoric coupled Burnett experiment and demonstrated its usefulness in collecting low-temperature data; Hall and Eubank (1972) used the Burnett coupled isochoric experiment to curtail adsorption errors; Hall and Eubank (1973, 1974) proposed an experiment with the Burnett apparatus for measuring directly interaction second-virial coefficients, excess volumes, and mixture compositions.

The Burnett coupled isochoric method provides the basic vehicle for the current experiment, but a magnetic densimeter is also necessary for determining saturated phase densities. The basic principle of the magnetic densimeter is to levitate a float in a magnetic field. The current required to produce the proper field can be made directly proportional to the density of the fluid containing the float. Papers describing magnetic densimeters include Hodgins and Beams (1971), Millero et al. (1972), and Haynes and Stewart (1971). These authors report precisions for their instruments approaching 0.0001% for liquid densities and 0.001% for vapor densities, with accuracy on the order of 0.1%. For our experiment the float or buoy is in the primary or isochoric volume V_A in Figure 1.

The experimental procedure consists of making a mixture with desired overall composition in the Burnett apparatus by using the mixing experiment described by Hall and Eubank (1974). The initial mixture must be single phase at a convenient temperature; the density should be recorded with the densimeter for comparison with Burnett determinations. An isochoric run then maps the isochore into the two-phase region. In the two-phase region, the magnetic densimeter provides values for the saturated vapor and liquid densities. (Care is necessary in these measurements because the liquid will tend to condense on the float and ruin vapor measurements. The effect is minimal in practice and can be reduced further by such measures as gold plating the float, designing the float to enhance runoff, and measuring the vapor density before that of the liquid.) The Burnett coupled isochoric run continues covering the *PVT* surface. The procedure is repeated for various overall compositions.

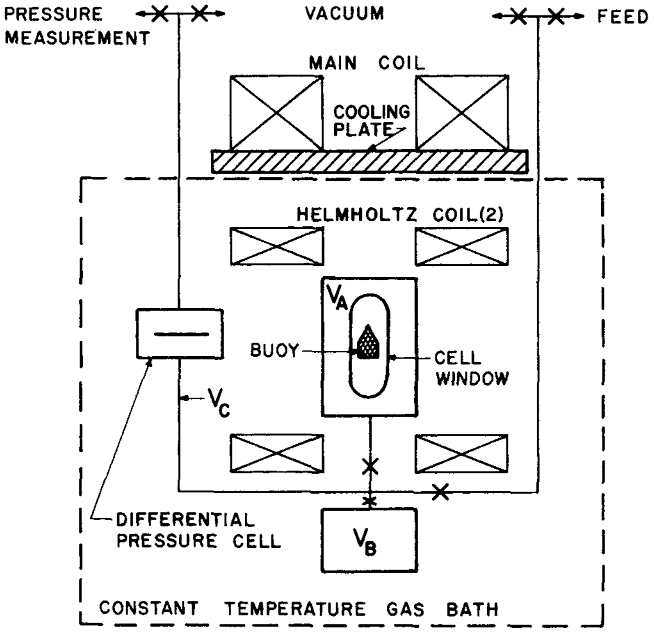

Fig. 1. Schematic diagram of the Burnett apparatus including magnetic densimeter.

ANALYSIS OF THE EXPERIMENT: METHOD OF INTERSECTING ISOCHORES

Figure 2 illustrates a typical run for some selected overall composition Z. The number of isotherms must be sufficient to establish the curvature of the isochores but need not accurately determine the dew and bubble point curves. Figure 3 demonstrates a unique feature of isochores on the two-phase region from different overall compositions Z_1 and Z_2; they usually intersect (unless Z_1 and Z_2 are widely different). For clarity, only one isochore is shown from each overall composition, but Burnett coupled isochoric runs on two overall compositions would produce multiple intersections. We call the analysis below the *method of intersecting isochores.*

Application of the phase rule to a two-phase, binary mixture provides two degrees of freedom:

$$f = c + 2 - p \tag{1}$$

At the points of intersection for different overall composition, T and P are identical, thus eliminating the degrees of freedom; the system is completely specified so compositions and phase densities are identical.

An overall material balance produces an expression for the volume fraction of vapor ϕ:

$$\phi = \frac{\rho_L - \rho_F}{\rho_L - \rho_V} \tag{2}$$

For all our equations either mass or mole units are correct. A component material balance provides

$$\rho_F Z = Y\phi\rho_V + X(1-\phi)\rho_L \tag{3}$$

In Equation (3), ρ_F, Z, ϕ, ρ_V, and ρ_L are all determined by direct measurement leaving Y and X, the phase compositions, as the unknowns. At the points of intersection, we can write two simultaneous equations in the unknowns Y and X:

$$(\rho_F Z)_1 = Y\phi_1\rho_V + X(1-\phi_1)\rho_L \tag{4a}$$

$$(\rho_F Z)_2 = Y\phi_2\rho_V + X(1-\phi_2)\rho_L \tag{4b}$$

The solution of these equations for Y and X is more expeditious if we observe the difference and the sum. Designating the difference by I and the sum by J, we obtain

$$I = \frac{\rho_L X - \rho_V Y}{\rho_L - \rho_V} = \frac{\rho_{F1}Z_1 - \rho_{F2}Z_2}{\rho_{F1} - \rho_{F2}} \tag{5}$$

$$J = \frac{\rho_V\rho_L(Y - X)}{\rho_L - \rho_V} = \rho_{F1}(Z_1 - I) = \rho_{F2}(Z_2 - I) \tag{6}$$

At a given temperature and pressure, I and J are invariants for various compositions. Combining Equations (5) and (6) we get

$$J = \rho_L(X - I) = \rho_V(Y - I) \tag{7}$$

Equation (7) provides the compositions conveniently, while Equation (6) establishes that the overall composition Z_i is a linear function of the overall volume ρ_{Fi}^{-1}.

EXPERIMENTAL VERIFICATION

Myerson (1974) reports construction of a prototype apparatus similar to Figure 1 and preliminary data for the carbon dioxide-*n*-butane system.* We chose to use the carbon dioxide-*n*-butane system because we can easily compare our data with those of Olds et al. (1949). In addition, Besserer and Robinson (1971) have checked these data on a newer apparatus. Our data are within 2% of the reported values which is the probable accuracy of Olds et al. (1949).

We wish to add that the prototype apparatus was a rough instrument by *PVT* standards, and the preliminary data are not representative of the quality possible with our technique. For the preliminary data, the measurements were within these limits: T measurement, 0.1 K; T control, 0.05 K; P measurement, 0.5 lb./sq.in.abs.; ρ_L calibration, 0.01%; ρ_V calibration, 1%. All these limits can be reduced by at least an order of magnitude in a precise apparatus. However, the preliminary data do demonstrate that the experiment is possible and, in fact, that a rough *PVT* apparatus can reproduce conventional VLE data within the accuracy of the latter.

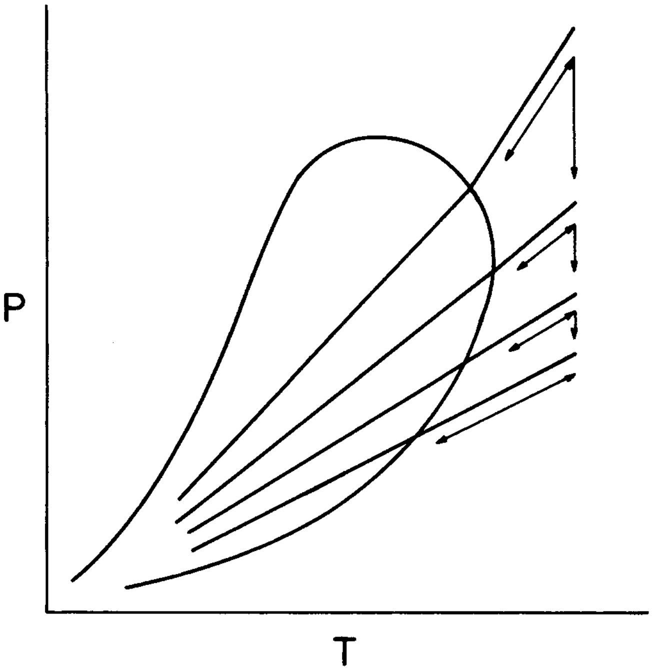

Fig. 2. Illustration of Burnett coupled isochoric experiment.

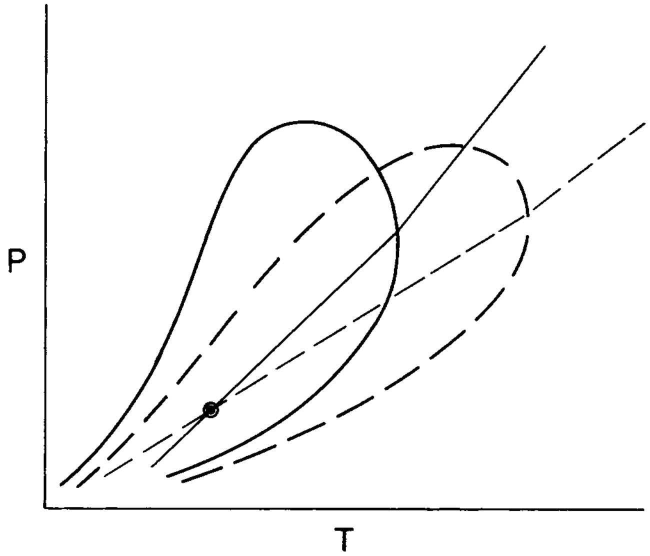

Fig. 3. Method of intersecting isochores.

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* Supplementary material has been deposited as Document No. 02643 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Ave. South, New York, NY 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.

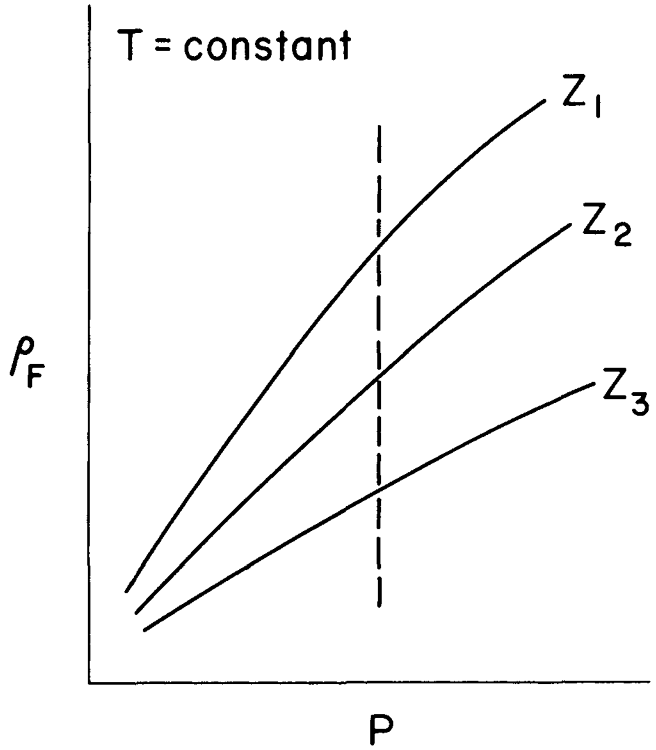

Fig. 4. Illustration of recommended data reduction.

DATA REDUCTION PROCEDURE

Proper data reduction increases the amount of information available from this experiment. Unlimited intersections result if, at a given temperature, we plot the overall density ρ_F vs. the observed two-phase pressure as a function of overall composition Z. Figure 4 illustrates this point. Note that any vertical line crossing two or more composition curves forms intersections as required by Equations (4*a*) and (4*b*). In addition, the saturated phase densities ρ_L and ρ_V should be plotted vs. pressure to facilitate obtaining these densities at the intersection conditions of Figure 4.

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NOTATION

c = number of components in the phase rule
f = degrees of freedom from phase rule
I = invariant formed from the difference between Equations (4*a*) and (4*b*)
J = invariant formed from the sum of Equations (4*a*) and (4*b*)
p = number of phases
P = pressure
T = temperature
V = volume
x = mole fraction of *n*-butane in liquid
X = mass fraction of *n*-butane in liquid
y = mole fraction of *n*-butane in vapor
Y = mass fraction of *n*-butane in vapor
z = mole fraction of *n*-butane in feed
Z = mass fraction of *n*-butane in feed
ρ = density
ϕ = volume fraction vapor

Subscripts

F = feed property
L = saturated liquid property
V = saturated vapor property
1 = component 1 (here *n*-butane)
2 = component 2 (here carbon dioxide)

LITERATURE CITED

Besserer, G. J., and D. B. Robinson, "A High Pressure, Autocollimating Refractometer for Determining Coexisting Liquid and Vapor Phase Densities," *Can. J. Chem. Engr.*, **49**, 651 (1971).

Burnett, E. S., "Compressibility Determinations without Volume Measurements," *J. Appl. Mech.*, **58**, A 136 (1936).

———., "Applications of the Burnett Method of Compressibility Determinations to Multiphase Fluid Mixtures," *U.S. Bu. M. Rept. Inv.*, **6267** (1963).

Fredenslund, A., and J. Mollerup, "Vapor-Liquid Equilibrium of the C_2H_6-CO_2 System," paper presented at 76th Natl. Meeting AIChE, Tulsa, Okla. (1974).

Hall, K. R., and P. T. Eubank, "Burnett-Isochoric Coupled Data with Application to Adsorbing Gases," *Physica*, **61**, 346 (1972).

———., "Experimental Technique for Direct Measurement of Interaction Second Virial Coefficients," *J. Chem. Phys.*, **59**, 709, 6691 (1973).

———., "Mixture Compositions and Excess Volumes from the Burnett Apparatus," *AIChE J.*, **20**, 815 (1974).

Haynes, W. M., and H. W. Stewart, "A Magnetic Densimeter for Low Temperatures and High Pressures," *Rev. Sci. Instr.*, **42**, 1142 (1971).

Hodgins, M. G., and J. W. Beams, "Magnetic Densimeter-Viscometer," *ibid.*, 1455.

Kidnay, A. J., M. J. Hiza, and R. C. Miller, "Vapor-Liquid Equilibria Research on Systems of Interest in Cryogenics," *Cryogenics*, **13**, 575 (1973).

Kramer, G. M., and J. F. Miller, "Compressibility of Gases III. The Second and Third Virial Coefficients of Mixtures of Helium and Nitrogen at 30°," *J. Phys. Chem.*, **61**, 785 (1957).

Millero, F. J., J. H. Knox, and R. T. Emmet, "A High Precision, Variable-Pressure Magnetic Float Densimeter," *J. Sol. Chem.*, **1**, 173 (1972).

Myerson, A. S., M.S. thesis, "Binary Vapor-Liquid Equilibrium Compositions Without Sampling of the Phases," Univ. Va., Charlottesville (1974). (Available from University Microfilms, Ann Arbor, Michigan)

Olds, R. H., H. H. Reamer, B. H. Sage, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems, The *n*-Butane-Carbon Dioxide System," *Ind. Eng. Chem.*, **41**, 475 (1949).

Parrish, W. R., and M. J. Hiza, "Liquid-Vapor Equilibria in the Nitrogen-Methane System Between 95 and 120 K," paper presented at the Cryogenic Engineering Conference, Atlanta, Ga. (1973).

Pope, G. A., P. S. Chappelear, and R. Kobayashi, "Analyses of Data Obtained by Isochorically Coupled Burnett Experiments," *Physica*, **57**, 127 (1972).

Smith, B. D., M. S. Klix, and T. J. Reynolds, "Fast Accurate Vapor-Liquid Equilibrium Data for Binaries by Total Pressure Measurement," paper presented at 78th Natl. Meeting AIChE, Salt Lake City, Utah (1974).

Wichterle, I., and R. Kobayashi, "Vapor-Liquid Equilibrium of the Methane-Propane System at Low Temperature and High Pressure," *J. Chem. Eng. Data*, **17**, 4 (1972).

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