

for extrapolation to lower temperatures. For extrapolation to high temperatures the value of the volume residual was assumed to be constant and the slopes of the isobars were taken as zero.

The uncertainty in the volume residuals for ethane appears to be somewhat larger than those for methane at low pressures, but are probably less than 2 parts in 1000. At higher pressures, data of equally reliable investigators are not available for comparison and an estimate of uncertainty cannot be made. However, from studies of Beattie's measurements on other compounds, it is safe to assume an uncertainty of less than 1 part in 1000 for the volume residuals at higher pressures.

UNCERTAINTIES IN FINAL VALUES TABULATED

The uncertainty in the value for free energy, $F - F_{\text{ideal}}$ and $F - F^\circ$, is equal to the integral of the uncertainty in the volume residual with respect to pressure. For methane and ethane the upper limit of this uncertainty in the regions where experimental P - V - T data are available is of the order of magnitude of 1.0 cal. per gram-mole at 50 atm., 2.0 cal. per gram-mole at 100 atm., 5.5 cal. per gram-mole at 500 atm., and 8.0 cal. per gram-mole at 1000 atm. These uncertainties are somewhat larger in the extrapolated regions of low and high temperatures.

It is impossible to estimate the uncertainty in the value of entropy, because the temperature coefficient of an uncertainty is involved. Considering methane alone for the time being, it can be seen in Figure 1 that while the volume residuals of selected data differ markedly from those of Olds, Reamer, Sage, and Lacey, the slopes of the volume residual isobars are in fair agreement. There is a strong temptation to estimate a very small uncertainty in the temperature coefficient of the volume residual and a correspondingly small uncertainty in the entropy functions. On the other hand, if the curves of Figure 4 were selected as the most reliable data, a very slight change in the steep slope of the low temperature isotherms could result in a considerable change in the slope of the isobars. As no estimate of uncertainty of the entropy residual can be made by an analysis of the volume residuals, it will suffice to place an upper limit on the possible magnitude of the uncertainty.

A rough estimate of the upper bound of the uncertainty in the isobaric slope can be taken as twice the uncertainty of the volume residual divided by the temperature interval over which the isobar is monotonic. For methane and ethane the upper bound on the possible uncertainty in the entropy functions, $S - S_{\text{ideal}}$ and $S - S^\circ$ is approximately 0.01 the uncertainty in the free energy functions.

The heat content or enthalpy may be considered as combinations of the free energy and entropy according to Equations 15 and 23. Therefore the upper limit on the uncertainty in the enthalpy may be taken as the uncertainty in the free energy function plus the uncertainty in the entropy multiplied by the absolute temperature.

By suitable mathematics it can be shown that the uncertainty in the activity coefficient is less than 0.5 the uncertainty in the free energy function divided by the absolute temperature.

For compounds other than methane and ethane, the

estimates of uncertainty will not be the same as those given here. Each compound must be analyzed separately. However, the method of analysis will be similar to that used for methane and ethane.

LITERATURE CITED

- (1) American Petroleum Research Project 44, Petroleum Research Laboratory, Carnegie Institute of Technology, "Selected Values of Properties of Hydrocarbon and Related Compounds."
- (2) Beattie, J. A., Hadlock, C., Poffenberger, N. J., *Chem. Phys.* **3**, 93 (1935).
- (3) Beattie, J. A., Su, G.-J., Simard, G. L., *J. Am. Chem. Soc.* **61**, 924 (1939).
- (4) *Ibid.*, p. 926.
- (5) Benedict, Manson, Webb, G. B., Rubin, L. C., *J. Chem. Phys.* **8**, 334 (1940).
- (6) Burrell, G. A., Jones, G. W., U. S. Bur. Mines, Rept. Invest. **2276** (1921).
- (7) Canjar, L. N., Rossini, F. D., "Work of American Petroleum Institute Research Project 44 on P - V - T Properties," Conference on Thermodynamic and Transport Properties of Fluids, sponsored jointly by British Institute of Mechanical Engineers and International Union of Pure and Applied Chemistry, London, England, July, 1957.
- (8) Cardoso, E., *J. chim. phys.* **13**, 312 (1915).
- (9) Cohen, A., 650 Program 9.6.002 IBM Corp., New York 22, N. Y.
- (10) Keyes, F. G., Burks, A. G., *J. Am. Chem. Soc.* **49**, 1403 (1927).
- (11) Kvalnes, H. M., Gaddy, V. L., *Ibid.*, **53**, 394 (1931).
- (12) Leduc, M. A., *Compt. rend.* **155**, 206 (1912).
- (13) Lewis, G. N., Randall, M., "Thermodynamics and Free Energy of Chemical Substances," McGraw-Hill, New York, 1923.
- (14) Michels, A., Nederbragt, G. W., *Physica* **2**, 1000 (1935).
- (15) *Ibid.*, **2**, 569 (1936).
- (16) Michels, A., Van Straaten, W., Dawson, J., *Ibid.*, **20**, 17 (1954).
- (17) Olds, R. H., Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.* **35**, 922 (1943).
- (18) Rossini, F. D., "Chemical Thermodynamics," Wiley, New York, 1950.
- (19) Rossini, F. D., Lyman, A. L., *Proc. Am. Petrol. Inst.* **34**, 67 (1954).
- (20) Sage, B. H., Webster, D. C., Lacey, W. N., *Ind. Eng. Chem.* **29**, 658 (1937).

Received June 6, 1957. Accepted January 13, 1958.

Investigation performed under the American Petroleum Institute Research Project 44. The report on the IBM 650 program may be obtained by writing to: George Wu, Applied Programming-650, International Business Machines Corp.-WHQ, 590 Madison Ave., New York 22, N. Y., for the 650 Program 9.6.002 on the calculation of P - V - T properties as used in the work of the American Petroleum Institute Research Project 44, Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

CORRECTION

Vapor Pressure and Viscosity of Solutions in the Calcium Oxide-Phosphoric Oxide-Water System at 25° C.

In the article "Vapor Pressure and Viscosity of Solutions in the Calcium Oxide-Phosphoric Oxide-Water System at 25° C." [E. O. Huffman, J. D. Fleming, A. J. Smith, *Ind. Eng. Chem., Chem. Eng. Data Series* **3**, No. 1, 17 (1958)] on page 18 in the second paragraph under Results, the figure for uncertainty in the density should be 0.0004 gram per ml.