

DISCUSSION

J. E. S. Venart²

Drs. Bishnoi and Robinson provide an interesting and valuable discussion of the available methods of determining absolute and relative values of enthalpy change and specific heat. It is perhaps unfortunate that the title does not adequately reflect the fact that the determined thermal property is to be the heat capacity ratio. Nevertheless, the description and testing of instruments capable of high precision is especially relevant to present day industry whose evaluation and design methods employ large data banks of sometimes questionable and outdated data. With the increased scale of present day and projected operations, the importance of more accurate thermodynamic and transport property data does not need any justification—it is by means of such data that competent plant evaluation and design are carried out.

Accurate utilization of the method requires choosing small pressure and temperature drops through the exchanger under conditions of both heating and cooling such that for heating [2]

$$\frac{C_p}{C_{p0}} = - \frac{T_4 - T_3 + \mu_0(p_3 - p_4)}{T_2 - T_1 + \mu(p_1 - p_2)} + \frac{q}{C_{p0}[T_2 - T_1 + \mu(p_1 - p_2)]} \quad (4)$$

Equations (2) and (3) of the paper immediately follow provided the variations in μ , C_p , and C_{p0} can be assumed linear. This later assumption not only restricts measurements to small pressure and temperature drops but also to single phase behavior remote from the phase boundaries.

In the calorimeter construction it is most important to prevent thermal exchange between the inlets of both the high and low pressure streams prior to measurement since the maximum temperature difference exists at these points. The nonsymmetry of the two extrapolated $\Delta T_0/\Delta T$ curves about unity at a pressure equal to that of the low pressure stream will be an indicator of any such errors—their agreement to within ± 0.5 percent is gratifying. It would however have been very useful to utilize various stream temperature differences to obtain several mean curves for one mean temperature so as to critically examine the reproducibility and randomness of the behavior.

In summary, this paper provides the description of method and performance of an exceptionally precise instrument for the determination of heat capacity ratios.

Authors' Closure

The points made by Dr. Venart in his discussion are well taken. His comments concerning the linear variation in μ , C_p , and C_{p0} are the basis for our choosing small pressure and temperature drops. We did not use various stream temperature differences to obtain several mean curves for one mean temperature because we did not feel justified in spending the excessive time required to do so in view of the very small error obtained when the $\Delta T_0/\Delta T$ curves were extrapolated to zero pressure.

² Department of Mechanical Engineering, The University of Calgary, Calgary, Alberta, Canada.

18 Gilliland, E. R., and Lukes, R. V., "Effect of Pressure on the Enthalpy of Benzene," *Industrial and Engineering Chemistry*, Vol. 32, 1940, pp. 957-962.

19 Yarborough, L., and Edmister, W. C., "Calorimetric Determination of the Isothermal Pressure Effect on the Enthalpy of Propane-Benzene System," *American Institute of Chemical Engineers Journal*, Vol. 11, No. 3, 1965, pp. 492-497.

20 Collins, S. C., and Keyes, F. G., "Note on the Year's Progress in the Precise Measurement of the Effects of Intermolecular Potential in Gases," *Journal of Physical Chemistry*, Vol. 43, No. 1, 1939, pp. 5-14.

21 Mather, A. E., "The Direct Determination of the Enthalpy of Fluids Under Pressure," PhD thesis, University of Michigan, 1967.

22 Ishkin, I. P. and Kaganer, M. G., "An Investigation of the Thermodynamical Properties of Air and Nitrogen at High Pressures and Low Temperatures," *Soviet Physics Technical Physics*, Vol. 1, 1957, pp. 2255-2271.

23 Andersen, J. R., "Some New Values of the Second Enthalpy Coefficient for Dry Air," *TRANS. ASME*, Vol. 72, 1950, pp. 759-765.

24 Joule, J. P. and Thomson, W., "On the Thermal Effect of Fluids in Motion," *Philosophical Transactions of the Royal Society (London)*, Vol. 143, 1853, pp. 357-366.

25 Reamer, H. H., Richter, G. N., Dewitt, W. M., and Sage, B. H., "Apparatus for the Experimental Study of the Thermodynamic Properties of Water," *TRANS. ASME*, Vol. 80, 1958, pp. 1004-1008.

26 Potter, J. H., "The Joule-Thomson Effect in Superheated Steam," *Journal of Engineering for Industry*, *TRANS. ASME*, Series B., Vol. 9, No. 2, May 1970, pp. 257-262.

27 Johnston, H. L., "An Apparatus for Measuring Joule-Thomson Effects in Gases by Direct Expansion Through a Valve," *Journal of American Chemical Society*, Vol. 68, 1946, pp. 2362-2366.

28 Koeppe, W., "Der Integrale Thomson-Joule-Effekt von Wasserstoff bei tiefen Temperaturen und Drücken bis zu 120 atü," *Kältetechnik*, Vol. 8, 1956, pp. 275-279.

29 Stockett, A. L., and Wenzel, L. A., "Joule-Thomson Effects for Nitrogen-Ethane Mixtures," *American Institute of Chemical Engineers Journal*, Vol. 10, No. 4, 1964, pp. 557-561.

30 Rowlinson, J. S., *Liquids and Liquid Mixtures*, Butterworth's, London, 1st, ed; 1959, p. 131.

31 Beenakker, J. J. M., and Coremans, J. M. J., "Some Considerations on the Determination of Thermodynamic Quantities of Gaseous Mixtures," in "Progress in International Research on Thermodynamic and Transport Properties," Papers presented at the second Symposium on Thermophysical Properties, Jan. 24-26, 1962, ASME, Academic Press, New York, pp. 3-4.

32 Lee, J. I., and Mather, A. E., "The Excess Enthalpy of Gaseous Mixtures of Nitrogen and Carbon Dioxide," *Journal of Chemical Thermodynamics*, Vol. 2, 1970, pp. 881-895.

33 McCracken, P. G., "Enthalpies of Mixtures of Methanol, Benzene, and Hexane," PhD thesis, Purdue University, 1956.

34 Nelson, J. M., Holcomb, D. E., "Thermodynamic Properties of Ternary Hydrocarbon Mixtures," *Chemical Engineering Progress Symposium Series*, Vol. 49, No. 7, 1953, pp. 93-106.

35 Macriss, R. A., "Liquid and Vapor Phase Enthalpy of Monomethylamine," *Journal of Chemical and Engineering Data*, Vol. 12, No. 1, 1967, pp. 28-33.

36 Callendar, H. L., "On Variation of the Specific Heat of Water With Experiments by a New Method," *Proceedings of the Royal Society (London)*, Series A, Vol. 86, 1912, pp. 254-257.

37 Callendar, H. L., "On the Variation of the Specific Heat of Water, with Experiments by a New Method," *Philosophical Transactions of the Royal Society (London)*, Series A., Vol. 212, 1913, pp. 1-32.

38 Romberg, A., "The Ratio of the Calorie at 73° to That at 20°," *Proceedings American Academy of Arts and Sciences*, Vol. 57, 1922, pp. 377-387.

39 Jacobsen, J. A., and Barieau, R. E., "Experimental Determination of the Enthalpy of Helium-Nitrogen Mixture at Room Temperature and up to 300 Atmospheres, by a New Method," Paper presented at the A.C.S., I.&E.C. division symposium on Enthalpy of Mixtures, February 22-27, 1970, Houston, Texas.

40 Bishnoi, P. R., "Experimental Heat Capacities of Carbon Dioxide-Methane Mixtures, and the Correlation of Volumetric and Thermal Properties," PhD thesis, University of Alberta, 1970.

41 Lapidus, L., *Digital Computation for Chemical Engineers*, McGraw-Hill, Toronto, 1962, Chapter 7, p. 335.

42 Wood, R. E., "Thermodynamic Properties of He, N₂, and He-N₂ Mixtures From 240° to 950°R for Pressures Between 14.696 and 3000 Psia," U. S. Bureau of Mines Report of Investigation, 7190 1968.

43 Lunbeck, R. J., Michels, A., and Wolkers, G. J., "Thermodynamic Properties of Nitrogen as Functions of Pressure and Temperature Between 0 and 6000 Atmospheres and -125° and +150°C," *Applied Science Research*, Section A, Vol. 3, 1953, pp. 197-210.