

Calorimetric Determination of the Isothermal Effect of Pressure on the Enthalpy of Methane and Two Methane-Propane Mixtures

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By using an isothermal throttling calorimeter, built for recirculating vapor operation, the effects of pressure on the enthalpy of methane and two methane-propane (93.9 and 86.2% methane) mixtures were measured. Pure methane was run at 150°F. and the two mixtures were studied at 90, 150, and 200°F. The pressures for these experiments were 500, 1,000, 1,500, and 2,000 lb./sq.in.abs.

The resulting data were compared with similar data from other sources for these same systems and conditions. Agreement is good with enthalpy values obtained from both experimental volumetric and Joule-Thomson data.

Prediction methods for the isothermal pressure effect on the enthalpy are compared with these data. These methods demonstrate the reliability of the Redlich-Kwong and Benedict-Webb-Rubin equations and Pitzer's corresponding states correlation for calculating isothermal enthalpy changes for these systems and conditions.

For both pure substances and mixtures, the change of enthalpy with temperature can be accurately calculated at zero pressure, where enthalpies are additive for mixture components. Enthalpies, and other properties of the ideal gas state, have been selected and compiled elsewhere (1).

Isothermal changes in enthalpy with pressure for constant composition systems (pure components or mixtures) can be computed by an equation of state or derived from compressibility factor compilations. The development and testing of such predictive methods are important problems in the technical data area.

In a previous experimental investigation of the isothermal effect of pressure on the enthalpy of hydrocarbon mixtures, an isothermal throttling calorimeter was built and operated on the propane-benzene system (16, 17). For the investigations described in this paper (4), the previously built apparatus was modified and used to study the methane-propane system.

EXPERIMENTAL APPARATUS AND PROCEDURE

The equipment we used is a modification of that constructed by Yarborough (16). The details of its design and operation are described elsewhere (16, 17). The calorimeter portion of the equipment used in this study is identical to Yarborough's; only the peripheral apparatus has been changed. Thus, only the modifications will be described.

The equipment was originally designed for liquid-phase feed to the equipment, once-through operation, and effluent collection by condensation. For the present study, each of these features proved impractical, and modifications were made to yield the apparatus shown schematically in Figure 1.

The first modification was to arrange for continuous recycle operation by installation of a closed loop employing two stages of compression, 1 and 2. Long line-out times required to reach steady state operation (with subsequently high gas consumption) led to abandonment of once-through operations and the adoption of the recycle operation.

The second modification of the apparatus was a change in method of flow rate measurement. Existing facilities for condensing the calorimeter effluent proved inadequate for the

methane-propane system. Thus, the condensation method of flow rate determination was replaced by the equipment to the right of the solenoid valve, 14. After steady state conditions were reached in recycle operation, flow was diverted to high pressure aluminum bombs immersed in liquid nitrogen, 16, and makeup gas was supplied above the surge tank, 15. By using the valve directly above the high pressure bombs, the calorimeter effluent pressure was adjusted to approximately 1 atm. Valve 14 was then actuated to divert flow into originally evacuated glass collection bombs, 19.

Flow into this collection system was continued for a measured time, until the calorimeter effluent pressure returned to the initial pressure as indicated by manometer, 12. Flow was then returned to the aluminum bombs. From the known pressure, 21, and temperature, 18, of the gas in the calibrated volume of the sample system, the mass of gas was calculated by using the known low pressure volumetric behavior of the gas. The mass and flow time served to establish flow rate.

The calorimeter effluent temperature and pressure during flow measurements differed from the values for which the energy measurements were made. During line-out on recycle operations, the low capacity of the compressor system required that the intake pressure to the first stage compressor be as high as 50 lb./sq. in. (for the 2,000 lb./sq. in. runs). Thus, during line-out, the calorimeter outlet pressure was as high as 50 lb./sq.in. During flow measurement, however, this pressure was reduced to less than 1 atm. If, as was believed, critical flow conditions existed at the capillary outlet at the higher pressure, this outlet pressure difference caused no change in flow rate through the capillary. Also, experimental data indicated that the temperature change accompanying the pressure change was small; and its effect on flow rate was negligible. A pressure regulating valve at the outlet of the calorimeter would have permitted operating at a uniform pressure, but a suitable regulating valve could not be found. Flow measurements would have been simplified and operations made easier with such a regulating valve and/or larger compressors.

A third modification of the equipment involved relocation of thermocouples used to measure the gas inlet and outlet temperatures. These thermocouples were removed from thermal wells and sealed directly in the fluid stream in an effort to reduce the time lag in response to changes in energy input to the calorimeter.