F–1

SOLID–VAPOR EQUILIBRIUM IN THE SYSTEM
HELIUM–METHANE

M. J. Hiza and A. J. Kidnay

Cryogenics Division—Institute for Materials Research
Boulder, Colorado

INTRODUCTION

The present investigation is part of a program to provide accurate, low-temperature, phase-equilibria data for binary systems of both technical and theoretical importance. It was pointed out in a previous paper [1] that, particularly in the solid–vapor region, there was a deficiency of data for several systems of interest, specifically, the hydrogen and helium light-hydrocarbon systems. In that paper data were presented for the entire solid–vapor region of the hydrogen-methane system up to 150 atm.

The purpose of the present investigation was to determine the gas-phase compositions in equilibrium with the solid phase in the helium-methane system from the triple-point temperature of methane down to as low a temperature as possible consistent with quantitative-analysis limitations of the hydrogen flame-ionization technique. The pressure range selected extends up to 140 atm.

The regions for which data are available for the helium-methane system are shown in Fig. 1, where melting and vapor pressure curves and the critical points (C.P.) for the pure components were taken from appropriate literature sources [2–5]. Kharakhorin [6] obtained data in the liquid–vapor region (B in Fig. 1) at 91.1°K from 5.40 to 69.75 atm, at 111.5°K from 4.85 to 154.7 atm, at 137.0°K from 12.10 to 152.7 atm, and at 150.3°K from 22.80 to 167.3 atm pressure. Gonikberg and Fastovskii [7] report only liquid phase compositions (C in Fig. 1) at 90.3°K from 29.0 to 156.8 atm and at 106.0°K from 25.2 to 154.8 atm pressure. No references were found containing data in the solid–vapor region for this system.

With such limited data available, the helium-methane system is inadequately investigated in the liquid–vapor region, as well as having been devoid of data in the solid–vapor region. It was decided to measure the gas phase compositions in the liquid–vapor region at 91.00°K and in the solid–vapor region at the same integral temperatures as in the previous investigation of the hydrogen–methane system. Thus a direct comparison can be made with the other data for the helium–methane system as well as with the data for the hydrogen–methane system.

The regions experimentally covered in this investigation are also shown as A in Fig. 1. The gas phase data extend from 91.00°K down to 55.00°K and generally up to 140 atm pressure.

EXPERIMENTAL

The apparatus and subsequent modifications, used to determine the equilibrium gas phase compositions for the helium–methane system, were described in detail in previous papers [1,8].

K. D. Timmerhaus (ed.), Advances in Cryogenic Engineering
© Springer Science+Business Media New York 1966
A single-pass flow technique was used in which the heavy component is evaporated into a pure light-component stream. Grade-A helium gas was fed from a gas cylinder through a high-pressure regulating valve and a silica-gel adsorption purifier maintained at 76°C. The pure gas was then cooled to the desired experimental temperature by heat exchange with the effluent equilibrium gas and refrigerant and passed through the equilibrium cell containing solid methane on five uniformly spaced trays. The equilibrium mixture was warmed to room temperature and reduced to low pressure with a high-purity PRV to allow low-pressure flow control and continuous analysis with a hydrogen flame-ionization detector.

At the start of each series of runs a calculated amount of commercial grade methane of 99.65% purity was fed through the discharge line and condensed in the equilibrium cell at 100°C with atmospheric pressure helium in the system. Pure helium gas flow was then started in the normal direction at 5 atm pressure or lower, and the cell was cooled slowly to a temperature just below the methane triple point, usually to 87.00°C, thus freezing the methane in place. The system was run for several hours at this temperature. The cryostat was then filled with liquid nitrogen to a point near the top of the equilibrium cell and maintained at this level for two days with continuous low-pressure helium gas flow at approximately 30 STP cc/min. During the entire time, the cell discharge line was maintained at a temperature 10° to 30° warmer than the cell with an electric heater. This technique required a minimum of attention to the apparatus during the time the residual methane was being removed from the cell discharge line and provided a good method for retaining the solid methane in the cell for periods of time required to measure several isotherms.

The desired operating temperature was subsequently established and gas phase compositions were measured along the isotherm, generally from low to high pressure, requiring approximately one hour per point. Some of the isotherms were measured from both low to high and high to low pressure with no detectable difference in results. From