A MULTIPURPOSE PHASE EQUILIBRIUM APPARATUS TO STUDY MIXTURES OF CRYOGENIC FLUIDS: APPLICATION TO ARGON–METHANE

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INTRODUCTION

With the increased use of cryogenics in both technical and theoretical applications, there is an increased requirement for reliable phase equilibrium and related thermodynamic data for cryogenic fluids and their mixtures. For this reason a new apparatus has been constructed which is capable of providing phase equilibrium data of sufficient accuracy for the derivation of meaningful thermodynamic properties of fluid mixtures.

In the past, separate experimental systems were employed for liquid–vapor and solid–vapor studies primarily to gain simplicity and reliability at the expense of flexibility. Based on the experience gained in those experimental studies, the apparatus described herein was designed to incorporate the best features of each of the earlier systems as well as to include the additional capability of detecting the solid–liquid phase change, to provide improved control and detection of experimental parameters, and to improve the refrigeration efficiency at lower temperatures.

This multipurpose apparatus includes both single-pass and recirculation flow options, temperature measurement with either a platinum or germanium resistance thermometer, and phase composition determination by chromatographic or continuous analysis. Thus it is possible to study equilibrium $P$, $T$, and $x$ properties in the liquid–vapor and solid–vapor regions and along the three phase loci from 10 to 150°K up to 200 atm. From these measurements, one may derive such properties as excess free energies of mixing, excess entropies of mixing, excess enthalpies of mixing, interaction virial coefficients, heats of vaporization, and heats of fusion.

APPARATUS

The arrangement of the cryostat and equilibrium cell is shown in Fig. 1. The equilibrium cell was constructed from electrolytic tough pitch copper and was designed to operate in the range of 10 to 150°K at pressures up to 200 atm (20.265

A Multipurpose Phase Equilibrium Apparatus

Fig. 1. Phase equilibrium apparatus.

The cell is 17.8 cm long and 7.62 cm in diameter. The closure is a compression seal which employs an indium-coated, copper-asbestos gasket. The inner space, 6.35 cm in length and 2.54 cm in diameter, contains in the upper end four equilibrium trays and in its lower end a stainless-steel-sheathed chromel vs constantan differential thermocouple referenced to an external point on the upper end of the cell.

The 0.64 cm spacing between equilibrium trays is packed with copper wool, and the transfer area provided by the trays has been designed to allow study of solid-vapor phase equilibrium in a wide variety of systems. Two additional stainless steel capillary tubes, not shown in Fig. 1, are used to support the cell from the top plate.

Refrigeration is provided by injection of refrigerant liquid, from a reservoir (1400 cm$^3$) below the cell, through a heat exchanger soldered to a skirt on the base of the cell. The resulting refrigerant gas passes through an annular space on the cell, exits at the upper end, and is used to cool a light copper radiation shield. The gas then may be passed through a heat exchanger to cool the gas entering the equilibrium cell, or it may be vented directly to the throttle valve which regulates the refrigeration rate.

A 60-Ω heater, on the upper end of the cell, is used for temperature control and another 200-Ω heater, at the lower end, is used to balance out any temperature gradient which may be detected by an external copper vs gold-cobalt differential thermocouple. The temperature is controlled by providing sufficient refrigeration for spontaneous cooling, while feeding back the amplified unbalance from the temperature-measuring potentiometer to a dc power regulator which operates the control heater. The power regulator is similar to the one described by Goodwin [1]. Using