

expect detailed experiments as a function of field as well as temperature on substances used in the lower stages. However, when improved technique permits such investigations, the general considerations given above will apply. Heat flow will always be necessary at the upper temperature of each demagnetization stage. If it is impracticable to make the heat flow in a reversible manner, the problem can still be solved if equilibrium values of the magnetic properties can be observed by taking a sufficient time.

In the case of single stage demagnetizations, an experimenter who has a solenoid magnet available has little reason for not making measurements in a field. The measuring equipment for making such observations is certainly not more complicated or expensive than that required in connection with heat introduction and associated magnetic observation in initial fields. Moreover, fluxmeter and bridge measurements can be made with great rapidity compared with those associated with heat input.

PHYSICAL REVIEW

VOLUME 92, NUMBER 6

DECEMBER 15, 1953

Heat of Mixing of He³ in He⁴†

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(Received August 10, 1953)

The integral heat of mixing for an 8.6 percent solution of He³ in He⁴ at 1.0°K, measured by an adiabatic free-expansion process, is 0.17 cal/mol of solution. Combined with the free energy of mixing, obtained from vapor pressure data, this shows that at this temperature the bulk of the excess free energy of mixing is due to the heat of mixing.

WE have demonstrated the existence of a large positive heat of mixing of He³ in He⁴ by adiabatically mixing the two liquids and observing the drop in temperature. A schematic diagram of the apparatus is shown in Fig. 1. Measured amounts of the two liquids were condensed in the two liquid cells at 1.02°K. The click seals on top and bottom of the He³ cell (inner cell) were broken by lowering a fine tungsten wire, and the temperature of the mixture measured by recording the pressure on an He³ vapor pressure thermometer inserted in the He⁴ sample. From the variation of thermometer pressure with time, Fig. 2, a minimum temperature of 0.78°K¹ was deduced. Measurement of the masses in the vapor phase showed the only process which could give a net absorption of energy on breaking the click seals was the mixing of the two liquids.

A semiquantitative measurement of the value of the heat of mixing in terms of the latent heat of vaporization of the He³ was made by conducting the adiabatic mixing in an essentially isothermal manner. During the mixing process, the vapor pressure of the He³ above the pure liquid drops to its partial pressure over the resulting solution; if the correct mass of He³ is in the vapor phase at the start, the heat released by the condensation will just cancel the heat absorbed by the mixing of the liquids. Figure 3 gives a plot of the vapor pressures against time for this experiment, in which the apparatus for the first run has been modified by en-

larging the vapor space above the liquid He³. The upper curve, the pressure on the He³ thermometer against time, shows that the liquid temperature dropped from 1.060 to 1.018°K in the first minute following mixing and then rose to its final value of 1.044 in another twenty minutes. (The final temperature is lower than the initial temperature because of a decrease of film flow on mixing.) From measurements of the pressure over the sample, shown in the lower graph, we see that by two minutes mixing is essentially complete, for after that the sample has the same warm-up rate as the He³ thermometer.

Treating the mixing as an adiabatic constant volume process, one derives the following expression for the

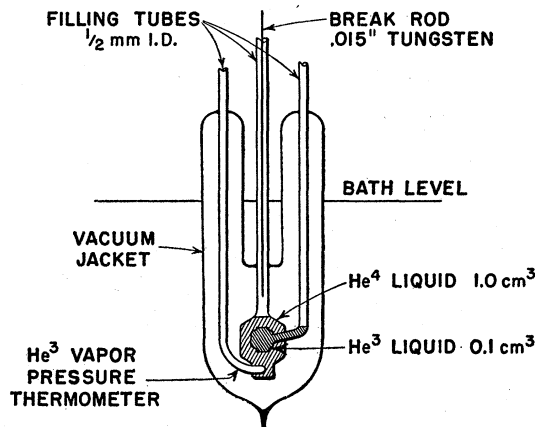


FIG. 1. He³-He⁴ sample cell.

† This paper is based on work performed under University of California contract with the U. S. Atomic Energy Commission.

¹ Abraham, Osborne, and Weinstock, *Phys. Rev.* **80**, 366 (1950); extrapolation of Eq. (4).

integral heat of mixing per mole,

$$\Delta H_m \equiv x\Delta\bar{H}_3 + (1-x)\Delta\bar{H}_4 = \frac{1}{m_3 + m_4} [\Delta m_3^v (L_3 - RT)].$$

Here x is the mole fraction of He^3 in the liquid, $\Delta\bar{H}_3$ and $\Delta\bar{H}_4$ are the partial molal heats of mixing, m_3 and m_4 the number of moles of the liquid, Δm_3^v the moles of He^3 condensing, and $(L_3 - RT)$ the latent heat of vaporization per mole for a free expansion. All second-order terms, involving change of mass of He^4 in the vapor, change in temperature, or change in liquid volume, have been dropped. Δm_3^v was determined from PVT measurements on the He^3 cell and filling line before the click seal was broken and on the filling line

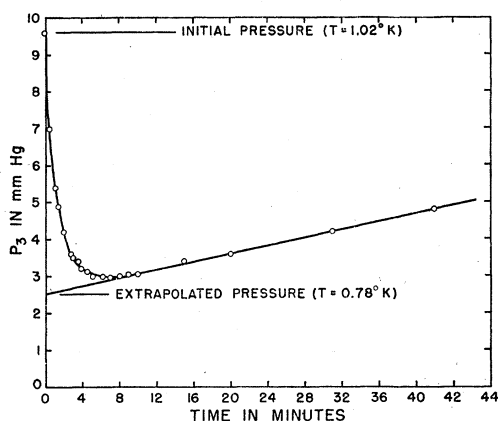


FIG. 2. Adiabatic mixing of He^3 - He^4 .

to the He^4 cell. A small correction was made for the volume occupied by the liquid He^3 . From the change in He^3 pressure on expansion, we then deduced the mass of He^3 condensing.

The experimental values are $(m_3 + m_4) = 2.02 \times 10^{-2}$ mole, $\Delta m_3^v = 4.8 \times 10^{-4}$ mole, and $(L_3 - RT) = 7.3$ cal/mole.¹ This gives an integral heat of mixing of 0.17

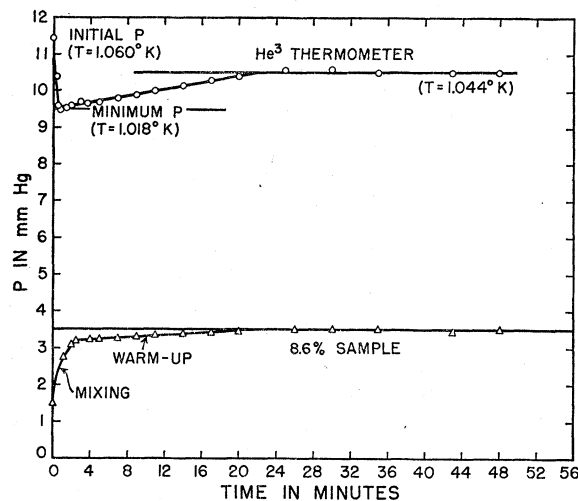


FIG. 3. Quasi-isothermal mixing of He^3 - He^4 .

cal/mole for an 8.6-percent solution of He^3 at 1.02°K. We have no way of estimating the accuracy of the result, but feel it is a lower limit because the principal source of error is due to the warm gas entering the cell during the initial drop in pressure of the He^3 line and thermometer. Such a discontinuous heat leak, whose presence would not be reflected in the warmup curves, would render our measured value for the heat of mixing too small.

From an extrapolation of the vapor pressure of dilute solutions of He^3 in He^4 to 1.0°K, the departure of the molal free energy of mixing from that for an ideal classical solution (from $RT[x \ln x + (1-x) \ln(1-x)]$) can be deduced. This turns out to be about 0.23 cal/mole for an 8.6 percent solution at 1.02°K; combined with our heat of mixing, this shows that the departure of the molal entropy of mixing from ideality is about -0.06 cal/mole, or -10 percent of the ideal mixing entropy.

² H. S. Sommers, Jr., Phys. Rev. **88**, 113 (1952).