

Heat and Entropy of Mixing of  $\text{He}^3$  and  $\text{He}^4$  on the Basis of the Two-Fluid Theory of  $\text{He}^4$ †

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Recent data on the heat and entropy of mixing of  $\text{He}^3$  and  $\text{He}^4$  are treated by use of the two-fluid theory of  $\text{He}^4$  together with Taconis' hypothesis that the  $\text{He}^3$  dissolves only in normal fluid. Solution of  $\text{He}^3$  causes normal fluid to be formed due to osmotic effects. It is assumed that the heat of mixing is a measure of the amount of normal fluid formed. It is then possible roughly to calculate the entropy of mixing of  $\text{He}^3$  and  $\text{He}^4$ , taking into account entropy of mixing of  $\text{He}^3$  and normal  $\text{He}^4$ , intrinsic entropy of the normal  $\text{He}^4$  formed, and the entropy of mixing of normal and superfluid. This gives reasonable agreement with experiment. It is also shown that the theory indicates reasonably good fulfillment of the condition for internal equilibrium between normal and superfluid.

RECENTLY Sommers, Keller, and Dash<sup>1</sup> have measured the heat of mixing of  $\text{He}^3$  with  $\text{He}^4$  to form an 8.6 percent solution of  $\text{He}^3$  in  $\text{He}^4$  at 1.02°K. The integral heat of mixing was found to be about 0.17 cal absorbed per mole of solution, and the entropy of mixing times the temperature was 0.06 cal per mole less than would be expected from an ideal classical solution. Heats of mixing can of course be calculated from any well defined theory of mixing of  $\text{He}^3$  and  $\text{He}^4$ , and Nanda<sup>2</sup> has recently given a tabulation of results obtained from several such theories. He has pointed out that valuable information on the mechanism of mixing might be obtained from data over a range of temperatures. Though such data are not at present available, it is to be noted that Sommers, Keller, and Dash actually provided two items, the heat and entropy of mixing, and together they can give more information than the heat of mixing alone at a single temperature.

We should like to consider these data from a rough mechanistic point of view, based upon a theory of helium II around 1°K which we have recently developed.<sup>3</sup> This theory involves a rather literal interpretation of the two-fluid hypothesis, the superfluid and the normal fluid (the latter being in the form of rotons when the temperature is near 1°K) being separated in ordinary space and having an entropy of mixing. This lends itself very readily, as may be seen, to the application of the Taconis<sup>4</sup> hypothesis which states that  $\text{He}^3$  dissolves only in the normal-fluid part of  $\text{He}^4$ . This hypothesis we shall assume to be true, and from it the positive heat of mixing can be understood in a qualitative way. Addition of  $\text{He}^3$  to  $\text{He}^4$  produces osmotic forces which cause more normal fluid to be formed,<sup>5</sup> thus requiring absorption of heat.<sup>6</sup> We shall, in fact,

try the very rough assumption that *all* the heat absorbed is due to the formation of more normal fluid, and that this normal fluid requires the same amount of energy (which we take from reference 3 to be 2.5 cal per mole of normal fluid around 1°K) as when it is formed in pure  $\text{He}^4$ . This may seem especially questionable when the normal fluid is in the form of rotons, and when the total amount of normal fluid does not exceed the amount of  $\text{He}^3$ ; nevertheless it seems to be the most sensible first approximation. On this basis, the heat of mixing found by Sommers, Keller, and Dash means that the presence of 0.086 mole of  $\text{He}^3$  in a solution containing a total of 1 mole induces the formation of  $0.17/2.5=0.068$  mole of normal fluid at 1.02°K. The original amount of normal fluid at this temperature is negligible. Thus, by the Taconis hypothesis, the mole fractions within the rotons are  $x_{3r}=0.56$  and  $x_{4r}=0.44$ .

Actually the amount of normal fluid formed should be calculated on the basis of a definite theory of mixing by setting the chemical potential of normal fluid in a mixture equal to that of superfluid. This requires somewhat involved considerations, however, and we shall first proceed to estimate the entropy of mixture based on the above estimate of the amount of normal fluid formed, and shall later attempt to check the equality of the chemical potentials.

In reference 3 we supposed that the normal fluid consisted of rotons containing about 8 atoms each. We shall continue to make the rough assumption that normal fluid consists of rotons of 8 atoms each, but will suppose that these may be partly  $\text{He}^4$  and partly  $\text{He}^3$ . The entropy of mixing  $S_{mr}$  of  $\text{He}^4$  and  $\text{He}^3$  within the rotons times the temperature will be

$$TS_{mr} = -RTx_{3r} \ln x_{3r} - RTx_{4r} \ln x_{4r} \quad (1)$$

per mole of rotons. Within the rotons there will be  $x_r=0.154$  moles of material per mole of total fluid.

times the temperature is 0.11 cal per mole less than that for ideal classical gases. Since the total volume is assumed to remain constant in the mixing process, the effect of the mixing in this ideal gas theory is a mutual dilution, which pulls the Bose gas molecules into higher-energy levels (i.e., changes superfluid to normal fluid, wherein the ideal gas theory resembles the one we are considering here) and allows the Fermi gas molecules to sink into lower levels, a partially but not completely compensating effect.

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<sup>1</sup> Sommers, Keller, and Dash, *Phys. Rev.* **92**, 1345 (1953).

<sup>2</sup> V. S. Nanda, *Phys. Rev.* **94**, 241 (1954).

<sup>3</sup> O. K. Rice, preceding paper [*Phys. Rev.* **96**, 1460 (1954)].

<sup>4</sup> Taconis, Beenakker, Nier, and Aldrich, *Phys. Rev.* **75**, 1966 (1949).

<sup>5</sup> O. K. Rice, *Phys. Rev.* **77**, 142 (1950).

<sup>6</sup> L. Goldstein, *Phys. Rev.* **95**, 869 (1954), has just published results for the heat and entropy of mixing of ideal Bose and Fermi gases. For thermodynamic variables corresponding to the experiment of Sommers, Keller, and Dash the heat of mixing thus obtained is 0.1 cal absorbed per mole of mixture, and the entropy

We thus have for the entropy of mixing within rotons

$$x_r TS_{mr} = 0.214 \text{ cal/mole.}$$

We next consider the entropy of mixing of rotons and superfluid. This is given by Eq. (1) of the cited paper,<sup>3</sup> and we assume this is unchanged. We shall use this equation in the form it takes when the number of rotons is small compared to the number of superfluid atoms, namely,

$$S_{mrs} = nk + nk \ln(N'/n). \quad (2)$$

Here  $k$  is the Boltzmann constant,  $n$  is the number of rotons, and  $N'$  is the total of atoms not in rotons. In this case  $N = N' + nq$  (where  $q$  is the number of atoms per roton, taken here as 8) is equal to Avogadro's number. Actually, it is hardly justified in the case under consideration to suppose that the roton concentration is small, and there are even likely to be some complications arising from coalescence of rotons. We know so little about how to handle this situation, however, that it seems just as well to get a rough estimate by the use of Eq. (2).

Assuming  $q=8$ , and recalling that in the case considered there are 0.154 mole in the rotons per mole of material, we see that  $n = (0.154/8)N$  and  $N'/n = 8(0.846/0.154)$ . Hence for one mole of solution,

$$TS_{mrs} = 0.186 \text{ cal/mole.}$$

Finally we have to consider the entropy  $S_{4r}$  of the He<sup>4</sup> in the rotons formed on solution of He<sup>3</sup>. By Eq. (2) of reference 3 this was  $k \ln m$  in pure He<sup>4</sup>,  $m$  being the degeneracy of the roton excitation. This means an entropy of  $(k/q) \ln m$  per atom. The number of He<sup>4</sup> atoms per roton in the present case is  $x_{4r}q$  and the total number of rotons is  $n$ . We therefore have

$$S_{4r} = nx_{4r}k \ln m, \quad (3)$$

and using  $n = (0.154/8)N$ , recalling that  $x_{4r} = 0.44$ , and taking  $m = 9.3$  from reference 3, we have

$$TS_{4r} = 0.038 \text{ cal/mole.}$$

Adding together the contributions we obtain for the total entropy of mixing per mole of solution,

$$TS_m = x_r TS_{mr} + TS_{mrs} + TS_{4r} = 0.44 \text{ cal/mole.}$$

For a classical ideal fluid we would have

$$TS_m = -RTx_3 \ln x_3 - RTx_4 \ln x_4,$$

where, in this case,  $x_3 = 0.086$  and  $x_4 = 0.914$ . This is equal to 0.60. It is seen that our calculated value is 0.16 cal/mole less than the ideal energy of mixing times the temperature, while according to the Sommers, Keller, and Dash the observed entropy of mixing times  $T$  is 0.06 less than the ideal entropy. In view of the rather rough approximations made, it appears that we have achieved a reasonably good correlation of the entropy of mixing with the heat of mixing. It should be noted that the experimental data were also rough.

We now turn to the question of the equality of the chemical potential of the superfluid with that of the normal part of He<sup>4</sup>, namely the part in the rotons. The chemical potential of the superfluid is equal to  $-T\bar{S}_s$ , where  $\bar{S}_s$  is the partial molal entropy of superfluid, the enthalpy of superfluid being taken as zero. By Eqs. (11) and (6) of reference 3, we see that  $\bar{S}_s$  is roughly equal to  $(n/N)R$ , which is very small. Hence, we must essentially have

$$\bar{H}_n = T\bar{S}_n, \quad (4)$$

for the normal fluid.  $\bar{H}_n$  is approximately 2.5 cal per mole. In calculating  $\bar{S}_n$  we consider what happens when a small amount of normal fluid, say,  $dn_r$  atoms, is added to the rotons. In the first place we note that it mixes with the He<sup>3</sup> and the partial molal entropy of mixing is  $-R \ln x_{4r}$ . Secondly, the partial molal entropy arising from intrinsic entropy is  $(R/q) \ln m$ . Finally, there is a change in the number of rotons given by  $dn = dn_r/q$ , and there will be a contribution from the entropy of mixing equal to  $q^{-1} \partial S_{mrs} / \partial n$  per molecule. Thus this contribution to the partial molal entropy is  $(R/q) \ln(N'/n)$ , and we may write

$$T\bar{S}_n = -RT \ln x_{4r} + (RT/q) \ln m + (RT/q) \ln(N'/n) = 3.2.$$

Again, considering the roughness of the calculation, this would seem to balance  $\bar{H}_n$  fairly well. Within the limits of the approximations involved, we may be said, then, to have a reasonable explanation for the heat mixing of He<sup>3</sup> and He<sup>4</sup> at 1.02°K, and the attendant change of entropy.