the variation of free paths with velocity and the possibility of inelastic collisions.

A numerical integration of the Barbiere distribution of electrons in argon for $E/p=1$ was performed, using the free path data of Ramsauer and Kollath.[9] The result was $\langle cL\rangle/\langle L\rangle=4.4\times10^7$ cm/sec, a drastically smaller value than that given by Townsend and Bailey. A high probable error, possibly as high as 10%, should be assigned to this value because of the uncertainty in reading the Ramsauer and Barbiere values.

The resulting curve based on the above value is plotted as a dashed line in Fig. 8. The agreement between experiment and the modified Varney theory is seen to be much better, with close agreement at high $(E/p)_{34}$. It is believed that the disagreement at low $(E/p)_{34}$ can be explained by the use of Eq. (6). At low E/p values an appreciable number of electrons have free paths comparable with the 1-cm drift space used, even at pressures as high as 90 mm Hg.

The use of Eq. (6) is also called for at high values of E/p where inelastic collisions occur. In this case X is the mean distance to the first inelastic collision, and this value can be used to calculate an inelastic collision probability. Experimental evidence as well as Barbiere's theoretical calculations indicate that very small inelastic collision probabilities greatly alter the energy distribution of electrons in argon.

Actually a weighted average in computing $D/(vL)$ should be used for H_2 and N_2, but since the free path is relatively constant this is not necessary. It is only in argon, where the free path behaves almost like a delta function, that the weighted average is necessary.

In conclusion, the methods of back diffusion are capable of giving quantitative results in molecular gases, and can conceivably be used in place of the cross-diffusion techniques to give values of c and other parameters. Confirmation of the Theobald results under an extended range of all variables and the successful analysis of the discrepancies with the simple theory in the case of the rare gases give the present results considerable value for applied purposes. For such use Figs. 2, 3, and 4 are especially significant.

The author wishes to express his gratitude to Professor R. N. Varney, who proposed and directed this work, for his assistance and advice during the course of the work.

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[9] S. C. Brown, *Basic Data of Plasma Physics* (John Wiley & Sons, Inc., New York, 1959), p. 19.

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Osmotic Pressure of He^3 in Liquid He^4, with Proposals for a Refrigerator to Work below 1°K

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An experimental study has been carried out of the osmotic pressure of solutions of the isotope He^3 in liquid He^4 at low temperatures, between 0.8 and 1.2°K. A superleak, a tube packed with a fine powder, acted as a semipermeable membrane which allowed only the superfluid He^4 to pass. The conclusion from these experiments was that the measured osmotic pressures were in reasonable agreement with values expected from the thermodynamic relations with other equilibrium properties of the mixtures, notably their vapor pressures. Thermodynamic equilibrium therefore seemed to have been attained under the conditions of the experiments. The second half of this paper concerns a study of the cooling which must take place during the adiabatic dilution of He^3 by He^4. If the dilution is carried out at low temperatures where the solutions separate into two phases, the absorption of heat is estimated to be usefully large. After dilution the solution can be distilled, condensed and recirculated so as to make a continuously acting refrigerator. It should be possible to operate at temperatures of 0.1°K or below.

1. INTRODUCTION

THE object of this paper is to explore the feasibility of a new kind of refrigerator for operation below 1°K. The proposed method uses as the working substance a solution of He^3 in He^4; the cooling is produced by a process of adiabatic dilution and is followed by a distillation in order to reconcentrate the diluted solution and then recirculate it. Thus, the evaporation of the He^3 takes place in two stages—the dilution of the He^3 by He^4 followed by the evaporation of the dilute liquid. This, it is calculated, should allow very low temperature (below 0.1°K) to be reached.

At low temperatures where the entropy of liquid He^4 is very small, a solution of He^3 in He^4 can profitably be regarded as a one-component system consisting of He^3 alone with the He^4 merely altering the volume occupied by the He^3. When the liquid separates into two phases, these can be thought of as a quasi-liquid in equilibrium with a quasi-gas. When a He^3 solution is diluted, cooling can result partly from the external work done during the expansion of the solute "gas" but mostly from the heat of transition from the concentrated to the dilute phase. In these processes, the osmotic pressure of the solution plays the part of the pressure acting on a one-component system. We therefore thought it appropriate to begin this study by measuring the osmotic pressure of concentrated He^3 solutions. Fixed temperatures near 1°K were chosen where the results could be compared, through a thermodynamic relation, with vapor pressure measurements. These experiments and the conclusions drawn from them will now be described.

2. SUMMARY OF THERMODYNAMIC RELATIONS OF SOLUTIONS

We begin by stating several definitions and relations which will be used later. A full account of this subject has been given by Guggenheim.[1]

When a solution of solute B in solvent A communicates with the pure solvent through a semipermeable membrane permeable only to A, a pressure equal to the osmotic pressure of B in the solution must be applied to the solution in order to stop the flow of solvent into it. The thermodynamic relation between this osmotic pressure Π, the vapor pressure of $p_A{}^0$ of the pure solvent, the partial vapor pressure p_A of the solvent in the solution, and the partial molar volume V_A is

$$\Pi = (RT/V_A)\ln(p_A{}^0/p_A). \qquad (1)$$

The partial pressures of the components (for vapors obeying the perfect gas laws) are given by

$$p_A = (1-X_v)p, \qquad p_B = X_v p, \qquad (2)$$

where p is the total pressure, X_v is the molar fraction of the solute equal to $n_B/(n_A+n_B)$ where the n's denote the number of moles in the vapor. The partial molar liquid volumes V_A and V_B are most conveniently calculated from

$$V_A = V_m - X\partial V_m/\partial X, \qquad V_B = V_m + (1-X)\partial V_m/\partial X, \qquad (3)$$

where V_m is the total volume containing 6×10^{23} molecules, X the molar fraction in the liquid. For a mixture which exhibits no volume changes on mixing, V_A and V_B are simply equal to the molar volumes M_A/ρ_A, M_B/ρ_B, respectively. Analogous relations define the partial chemical potentials μ_A and μ_B.

If the vapor pressure is so high that deviations from the perfect gas laws become significant, the form of (1) can be retained by substituting fugacities p^* for pressures p, where, for example,

$$p_A{}^* = (1-X_v)p\ \exp\{(p/RT)[B_{AA} - X_v{}^2(B_{AA}-2B_{AB}+B_{BB})]\}, \qquad (4)$$

the B's denoting the appropriate virial coefficients.

A convenient standard of comparison for the behavior of real solutions is the *ideal* solution, in which the internal energy of a mass of A atoms is not altered by the substitution of a number of B atoms; that is the potential energy of an AB pair of atoms is the mean of those for AA and BB pairs. For such mixtures, assuming classical statistics,

$$p_A = (1-X)p_A{}^0, \qquad p_B = Xp_B{}^0, \qquad (5)$$

$$\mu_A = \mu_A{}^0 + RT\ln(1-X), \qquad \mu_B = \mu_B{}^0 + RT\ln X, \qquad (6)$$

where X is the concentration of B in the liquid. In the simplest case of an ideal solution where the vapors are ideal gases and the liquid molar volumes V_A and V_B are independent of temperature, it follows from (1) that the osmotic pressure should obey the law

$$\frac{\Pi V}{RT} = \left[\frac{V_B}{V_A} + \frac{1-X}{X}\right]\ln\left(\frac{1}{1-X}\right) = 1 + \sum_{n=1}^{\infty}\left(\frac{V_B}{V_A} - \frac{1}{n+1}\right)\frac{X^n}{n}, \qquad (7)$$

which for small concentrations X becomes $\Pi V = RT$. In these equations V is the volume of solution which contains 6×10^{23} atoms of solute B, that is

$$V = V_B + [(1-X)/X]V_A; \qquad (8)$$

V is therefore considerably bigger than V_B if the solution is dilute.

For any real solution which exhibits deviations from ideality, we may define the excess chemical potentials by the equations

$$\mu_A = \mu_A{}^0 + RT\ln(1-X) + \mu_A{}^E, \qquad \mu_B = \mu_B{}^0 + RT\ln X + \mu_B{}^E, \qquad (9)$$

so that

$$p_A = (1-X)p_A{}^0\exp(\mu_A{}^E/RT), \qquad p_B = Xp_B{}^0\exp(\mu_B{}^E/RT). \qquad (10)$$

A thermodynamic relation, the Gibbs-Duhem equation, exists between $\mu_A{}^E$ and $\mu_B{}^E$; in integrated form this reads

$$\mu_B{}^E = \mu_B{}^E(X=0) - \int_0^X \frac{1-X}{X}d\mu_A{}^E. \qquad (11)$$

One further simple model of a solution will be mentioned, namely, the *regular* solution of A in B. Here the assumption is that the potential energy of an AB pair of atoms is equal to the mean of those for AA and BB pairs plus a constant, usually written as $W/2$, which is assumed independent of concentration and tempera-

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[1] E. A. Guggenheim, *Mixtures* (Oxford University Press, New York, 1952).

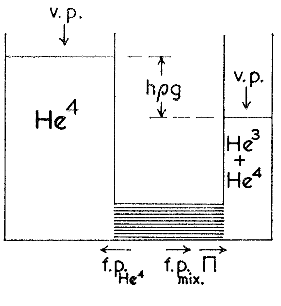

FIG. 1. Principle of method of measuring osmotic pressure of He^3 solutions. Π is osmotic pressure, f.p. is fountain pressure, and v.p. is vapor pressure.

ture. Such a mixture, obeying classical statistics, has excess chemical potentials given by

$$\mu_A{}^E = WX^2, \qquad \mu_B{}^E = W(1-X)^2. \tag{12}$$

For such a solution the (Π, X) isotherms take the form

$$\Pi V_A/RT = 1 + (\tfrac{1}{2} - W/RT)X + \tfrac{1}{3}X^2 + \cdots, \tag{13}$$

so that since V_A usually varies little with temperature a virial plot of this kind provides an easy method of measuring W. There is a point of inflexion on the isotherm $T_c = W/2R$ at $X = \frac{1}{2}$, analogous to the critical point of a vapor-gas system; below that temperature there is a separation into phases rich in A and B. A more refined treatment indicates that T_c is given by $W/RT_c = 2$ for large coordination numbers, 2.5 for small coordinations.

The formulas of the preceding paragraphs will subsequently be used with subscripts 4 and 3 in place of A and B and with X representing the concentration of He^3 in the solution.

3. APPARATUS

In principle, it is simple to measure the osmotic pressure of superfluid mixtures of He^3 and He^4. Firstly, it should be easy to construct an efficient semipermeable membrane—a superleak through which He^4 travels but He^3 does not. Secondly, the osmotic pressure can be opposed by a fountain pressure, by allowing the mixture to communicate through a superleak with a bath of pure He^4 at a higher temperature. This arrangement, which is shown in Fig. 1, has also been used by Wansink and Taconis.[2] The experimental procedure is to condense into a chamber a quantity of the He^3-He^4 mixture containing a known mass of He^3, at a known temperature; the temperature of the other bath is maintained at a known higher temperature; flow of superfluid through the superleak takes place one way or the other. In equilibrium the osmotic pressure of the solution is balanced by the difference between the fountain pressures of the solution and the outer bath (deduced from the entropy of pure He^4) with small corrections for the difference of hydrostatic heads of the liquids in the two baths, and for the difference of vapor pressures on the two sides.

The low-temperature parts of the apparatus actually used are shown in Fig. 2. The superleak was a german silver tube, 0.3-mm i.d. and 86 mm long, packed with a fine powder. The powder was introduced into the tube in small amounts, filling a length of the tube of the same order as its internal diameter, and then compressed by pressing on it with a fine wire carrying a small weight, the pressure being of the order of tons per square inch. In this way a total length of 50 mm was packed. The powder had a coefficient of thermal expansion roughly equal to that of german silver so that it did not crack away from the tube on cooling. Its performance as a superleak can be judged from the fact that the leak rate to helium gas at 4.2°K at a pressure near 1 atm was of the order of 10^{-3} cc NTP per h, whereas with superfluid He^4 the rate of rise or fall of the meniscus showed that the flow rate could be as high as the order of cubic centimeters per minute, being limited only by the rate of abstraction or evolution of heat at the ends. In practice however these large rates of superfluid flow were not used; precautions were taken to ensure that conditions close to temperature equilibrium were maintained at all times.

The liquid mixture was contained in a chamber 3.2-mm i.d., 59 mm long, joined to the superleak through a metal-glass seal. It was judged that the main cause of error might be temperature inhomogeneities in this chamber. To minimize these, the warmer helium bath entirely surrounded this chamber (it was called the outer helium bath), and the narrow filling tube leading to the chamber passed through an upper helium bath which was kept at a temperature near that of the chamber, so as to minimize the heat influx down this tube. But probably the most important precaution adopted was to place a copper wire inside the chamber, along its length. Its thermal conductivity was estimated

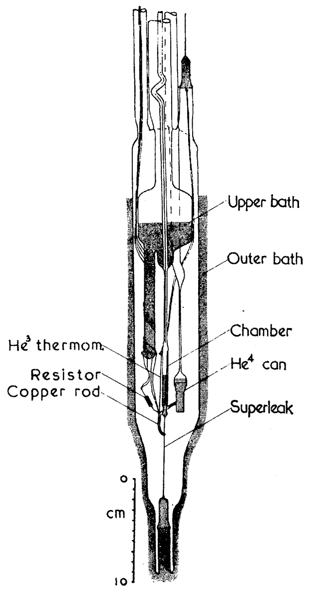

FIG. 2. Apparatus used to measure osmotic pressures.

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[2] D. H. N. Wansink and K. W. Taconis, Physica 23, 125 (1957).

to be sufficiently large to smooth out temperature differences along the length of the liquid in the chamber, in spite of the low thermal conductivity of this liquid.

To the metal seal at the top of the superleak was soldered a copper rod which carried a carbon resistance thermometer, whose leads were carefully bonded to the upper helium bath, and a He^3 vapor pressure thermometer (consisting of a german silver tube 0.3-mm i.d. with sufficient pressure of pure He^3 gas introduced at room temperature to produce the first drop of liquid at 1.2°K). These two thermometers served to measure the temperature at the bottom of the chamber containing the liquid. The vapor pressure of the liquid mixture itself and (at 1°K and above) the vapor pressure of the He^4 in the upper helium bath allowed the temperature at the top surface of the liquid to be measured.

The copper rod was also soldered to a small metal can of 2-cc capacity containing liquid He^4 which could be pumped through a constriction, thus cooling the chamber to quite a low temperature near 0.8°K—a technique often employed in adiabatic demagnetization crysotats. It was desired to be able to fill this can by condensation at 4.2°K; the constriction was therefore made just greater than 0.95-mm diam, so that gas trapped in the can during the filling could bubble through the constriction.

For maintaining the chamber at 1°K or above, the upper helium bath was pumped to the required temperature, when refluxing of the helium vapor could be relied upon to cool the solution. But for keeping the chamber at 0.8°K by pumping on the helium can while the upper bath was still at about 1°K, the fact that the solution was cooled from below (because the can was attached to the lower end of the chamber) meant that no concentration gradient could be produced in it.

The upper helium bath, the chamber and the helium can were all inside a space pumped to high vacuum and surrounded by the outer helium bath, which was of $2\frac{1}{2}$ liters capacity. A wick of woolen cloth covered the whole assembly so that experiments could be done even though the level of the outer liquid helium was very low. Heat influxes from above were reduced by a liquid air pocket which was kept automatically topped up; radiative heat input was minimized by covering the vacuum jacket and all its pumping tubes with colloidal graphite and enclosing them in aluminum foil, except for small viewing windows for the upper bath and chamber. Most of the length of the clear strips of the outer liquid-air Dewar was also covered up. The level of the liquid in the chamber was observed by dim light through small holes in these shields. Careful observations showed that the light had no appreciable effect on the temperature of the liquid mixture or the thermometers. The liquid helium in the outer Dewar was topped up every day and runs lasted for several days.

4. EXPERIMENTAL PROCEDURES

The volume of the chamber as a function of height above the metal seal was found once and for all by condensing known amounts of liquid He^4 into it.

At the beginning of each osmotic pressure experiment a known mass of mixture of known composition was distilled into the chamber. Most of this gas condensed, but a small amount remained at room temperature in the manometers and other dead volumes. It was assumed that the composition of this gas did not alter during an experiment even though that of the liquid in the chamber did change because of flow through the superleak. This was justified because the rate of gaseous diffusion through the long, narrow, filling tube was calculated to be very small, and also because samples of gas taken at low temperature from above the liquid at the end of the experiments confirmed the assumption. To calculate the concentration of He^3 in the liquid in the chamber from the position of the meniscus, an iterative method was used. As a first approximation, it was assumed that all the He^3 was condensed into the liquid. This yielded a rough value of the liquid concentration and hence of the concentration in the vapor phase. Knowing the volume of the vapor space in the chamber above the meniscus, a second approximation to the mass of He^3 in the liquid was found. The third and fourth approximations were determined in this way, using an electronic computer.

The experiments were carried out by measuring the temperatures of the upper bath and the helium can and the vapor pressure of the outer bath, noting the position of the meniscus in the chamber. Conditions were then held constant for some minutes to check that true equilibrium had been attained. A number of tests were made to show that hysteresis in these observations, with falling and rising temperatures, was small.

A. Calculation of Osmotic Pressures from Experimental Data

For most of our observations the osmotic pressures were between 30 and 50 cm Hg. Much the largest contribution to each of these came from the fountain pressure of the outer bath; the fountain pressure of the inner bath, the hydrostatic head and the vapor pressures always contributed only small corrections. Our most important readings for calculating the osmotic pressure values were therefore the vapor pressures of the outer bath. The majority of these were between 20 and 36 mm Hg, corresponding to temperatures between approximately 1.95 and 2.15°K, that is to just below the λ point.

It was realized that there exist quite large uncertainties in the known data for converting these vapor pressures into fountain pressures, and this made the analysis of the data subject to even larger uncertainties. This is because the excess potentials depend on small deviations from ideal behavior and are very sen-

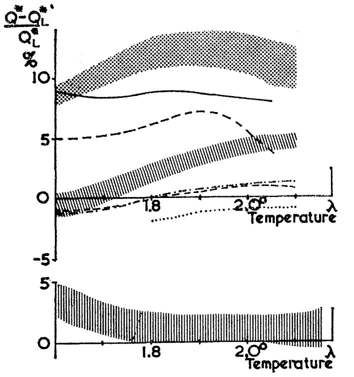

FIG. 3. Deviation, expressed as percentage, of heat of transport Q^* from value Q_L^* deduced from recalculated Leiden specific heat data. Upper diagram: existing measurements. Taken in order downwards, these are as follows. Shaded area: direct measurement of Q^* (reference 17). Full line: specific-heat measurements (reference 11). Dashed line and cross-hatched area: measurements of Q^* and dp/dT (references 16 and 4). Dash-dot line: measurement of dp/dT (reference 14). Dashed line and dotted line: specific-heat measurements (references 9 and 10). Lower diagram: present measurements deduced from Fig. 4.

sitive to small changes in the osmotic pressure; for example, a 3% change in the assumed fountain pressure of He^4 altered the calculated values of $\mu_4{}^E$ in the region of 1.0 and 1.2°K by 15%.

We were therefore led to analyze critically the known data for the fountain pressure of He^4, particularly in the region between 1.95°K and the λ point.

B. Existing Data for the Fountain Pressure of Pure He^4

The most straightforward method for calculating the fountain pressure is by integrating the entropy of liquid He^4:

$$P=\int_0^T \rho S dT, \tag{14}$$

along the saturated vapor pressure curve, where S is the entropy per gram, ρ the density, and T the temperature concerned. Entropy values are derived from specific heat measurements. [It should be noted that doubt was at one time cast on the validity of (14) at very low temperatures, below 0.7°K; it was thought that discrepancies between this equation and measured values of dP/dT were due to the phonon contribution to the specific heat. Recent recalculations by Bots and Gorter[3] of old experimental data confirm the validity of this relation, however.] P can also be derived from observations of the differential fountain pressure dP/dT [which by (14) is equal to ρS], and from the measurement of the heat of transport Q^* (which is equal to $T\rho S$). It is convenient for purposes of comparison to represent all these different kinds of measurement on a single diagram. Following Brewer and Edwards[4] we take the heat of transport as a convenient quantity, and we take the values of Q^* calculated from the Leiden specific heat data (discussed later[5]) as standard, denoted by Q_L^*. In Fig. 3 the % deviation from these Leiden values are plotted as functions of temperature. This diagram differs from that given by Brewer and Edwards in incorporating some recent data and in showing all values recalculated to the 1958 scale of temperature which, it is assumed, is the most reliable thermodynamically.

The specific heat data, despite earlier inconsistencies, are now fairly concordant. The most generally accepted data are those of Keesom and Miss Keesom[5] reinterpreted on the 1949 scale of temperature by Kramers, Wasscher, and Gorter[6] and on the 1958 scale by ter Harmsel and van Dijk.[7] Several sets of specific-heat data confirm these within 1%.[8–10]

However, there remains one set of data which do not conform to these, though *a priori* they should be just as reliable—namely, the measurements of Hercus and Wilks[11] which, when recalculated to the 1958 scale, are about 8–9% higher than the Leiden values in this region. Measurements of the velocity of second sound together with measurements of the ratio of the normal and superfluid densities (by oscillating disks or by Rayleigh disks) give no unequivocal decision against the Hercus and Wilks data,[11,12] nor do the precise measurements of Fairbank, Buckingham, and Kellers[13] at temperatures very close to the λ point.

Data deduced from direct measurements of dP/dT and of Q^* in less satisfactory general agreement, as can be seen from Fig. 3. One set of dP/dT data, by van den Meijdenberg, Taconis, Beenakker, and Wansink[14] recalculated to the 1958 scale[15] do agree quite well with the Leiden specific-heat data, but all the rest yield values of the entropy which are considerably greater than these—see the data of Kapitza[16] and Brewer and Edwards[4] who measured Q^* and dP/dT, and of Chandrasekhar and Mendelssohn[17] who measured Q^* only. It must be remarked that the interpretation of the Q^* measurements depends critically on the drawing of

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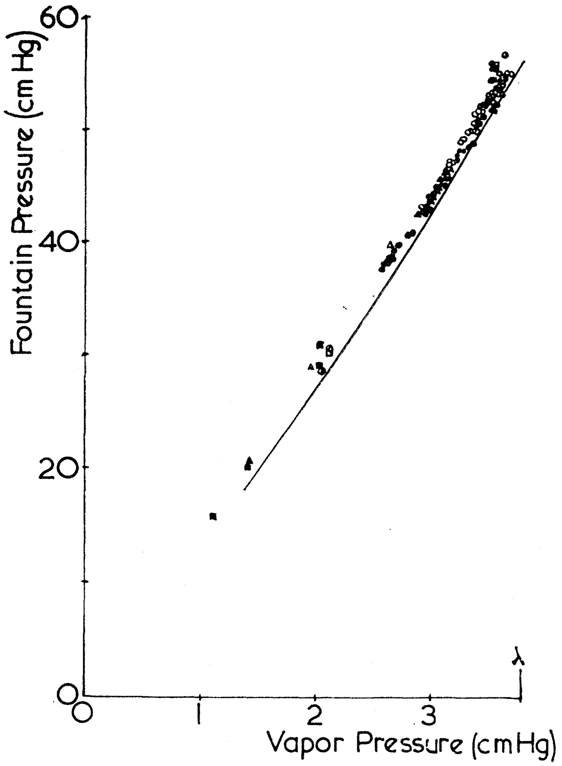

FIG. 4. Fountain pressure of pure He^4 as a function of vapor pressure. Continuous curve deduced from Leiden specific-heat measurements. Points deduced from present measurements of osmotic pressures together with vapor pressures of solutions. Different symbols indicate different runs. Solid points: He^3 solution near 1°K. Open points: solution near 1.2°K. Centered circles: solution near 1.4, 1.6, and 1.8°K.

tangents to experimental curves, which is a notoriously inaccurate process.

C. Our Values for the Fountain Pressure of He^4

Though there is fairly good agreement between the different methods of determining the heat of transport and hence the fountain pressure of He^4, the data above 1.6°K cannot be said to be settled to the accuracy desired by us. We have therefore proceeded as follows. We have *assumed* that the excess potentials deduced from vapor pressures at temperatures above 1.0°K are correct; we have also *assumed* that our own osmotic pressure measurements above 1°K are correct; from these data we have *deduced* the fountain pressures of pure He^4 as a function of outer bath temperature. In these calculations, the extensive tables of the excess thermodynamic functions deduced by Roberts and Swartz[18] from the vapor pressure measurements of Sydoriak and Roberts,[19] with entries every 0.1° of temperature above 1°K and at 10% intervals of concentration, allowed the excess functions to be interpolated accurately.

The results for the fountain pressure P are shown in Fig. 4. Of the points plotted, seven were quite isolated readings taken in the initial stages of various runs when the solution was at temperatures between 1.840 and 1.475°K. Of the rest, about half were taken with the inner bath temperatures between 1.150 and 1.231°K (mostly from runs on two different days when X varied from 6 to 26%, with a few isolated points taken from other runs) and the other half with the bath temperature between 0.975 and 1.017°K (again the majority from two different runs with X between 6 and 31%, and a few isolated points.) The self-consistence of this plot, with points taken under a wide variety of conditions, shows that there were no large systematic errors in the measurements. These fountain pressures were then compared with Leiden specific-heat data by integrating their entropies; this curve is also shown in Fig. 4. The agreement is satisfactory. It is difficult to transfer these data back to Fig. 3 because this necessitates differentiating a smooth curve drawn through our points, which is somewhat arbitrary. However, if this is done for the points above 1.9°K it seems that our values of S would differ from the Leiden ones by less than 2%; this is exhibited in the lower diagram in Fig. 3. In subsequent calculations we have used our own fountain pressures rather than those deduced from other data.

D. Our results near 1.2 and 1.0°K

In order to be able to interpolate our osmotic pressures to exactly 1.2 and 1.0°K, the following procedure was adopted. It was assumed that to a first approximation the solutions were regular. The excess chemical potentials were calculated from the readings near 1.2 and 1.0°K using (1) and (10), and plotted as functions of X^2. They lay on two distinct curved lines showing that the solution was not regular in that W varied both with temperature and concentration, but this variation was slow enough to permit interpolation. Simple algebraic formulas were deduced, expressing the trend of $\mu_4{}^E$ with temperature at constant X; these were then used to interpolate $\mu_4{}^E$ to exactly 1.2 and 1.0°K. The resulting points are shown in Fig. 5, together with the curves taken from the tables of Roberts and Swartz. The general agreement is necessarily good because of the method used in calculating the fountain pressures.

5. OUR RESULTS AT 0.8°K

The same method of interpolation and the same fountain pressure data were then used on a large number of points taken between 0.788 and 0.817°K to produce an isotherm at 0.8°K; this is also shown in Fig. 5. Of the large number of points in this isotherm, five had to be rejected. It was noticed during these observations

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[18] T. R. Roberts and B. K. Swartz, in *Helium Three*, edited by J. G. Daunt (Ohio University Press, Columbus, 1960), p. 158; and private communication.

[19] S. G. Sydoriak and T. R. Roberts, Phys. Rev. **118**, 901 (1960).

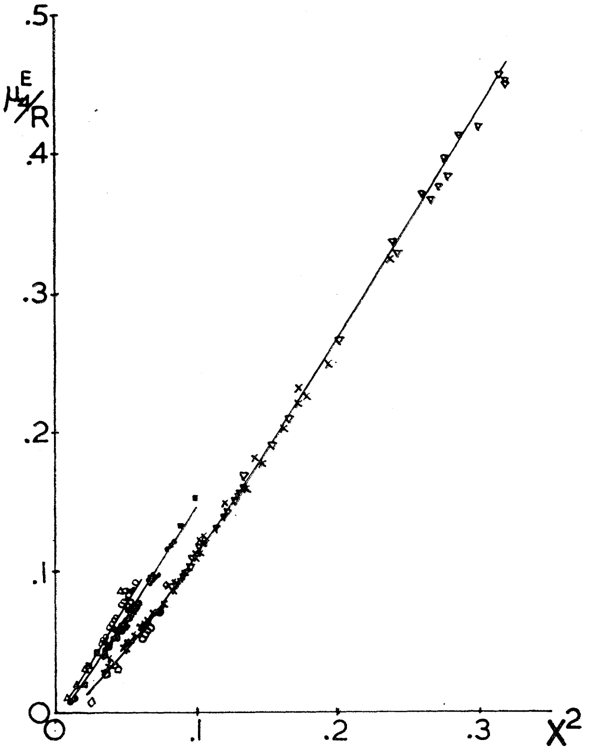

FIG. 5. Excess chemical potential as function of X^2 for three different isotherms. Reading downwards: 1.2, 1.0, and 0.8°K. Symbols for first two curves as in Fig. 4. Symbols for 0.8°K curve: crosses, experiment of 5.23.58; triangles, 5.24.58; diamonds, isolated points from earlier runs; circles, points with curved meniscus.

that the meniscus of the liquid in the capillary was strongly curved whereas normally it was quite flat. The corresponding points lie distinctly off the curve through the majority and they have been ignored in drawing the graph, though the phenomenon was never understood.

Below 1°K, Roberts and Swartz have not calculated the excess functions from the vapor pressure data of Sydoriak and Roberts. A direct comparison between these and our own excess functions is unfortunately difficult to make, since the calculation of vapor pressures depends on an accurate knowledge of μ_3^E near $X=0$, whereas our own method only measures μ_4^E at small X. We therefore combined our measurements with the vapor pressure data in order to find $\mu_3^E(X=0)$ by the following method. We substituted our values of the data of Fig. 5 and of the second column of Table I into the Gibbs-Duhem equation (11), and computed μ_3^E. The integration constant $\mu_3^E(X=0)$ was unknown, but using (10) we calculated the vapor pressure of the mixture and finally chose that value of the constant which gave the best fit with the vapor pressures up to our largest concentration of approximately 50%. The values of μ_3^E so derived are given in Table I. These figures now led directly to the concentrations of the two components in the gas phase [using (10) and (2) but with fugacities instead of pressures, making use of the known virial coefficients.[20]] We were now in a position to attempt a test of the thermodynamic consistency of these data for the vapor and gas phases—the Redlich and Kister test.[18] This states that at any temperature

$$\int_0^1 \ln(C_V/C_L)dX=\ln(p_3^0/p_4^0)+\frac{B_{33}+B_{44}-V_3^0-V_4^0}{2RT}(p_3^0-p_4^0), \quad (15)$$

where the C's (with subscripts denoting vapor and liquid phases) represent molar ratios defined by n_3/n_4 (where the n's denote numbers of moles) and equal to $X/(1-X)$. Using the He^3 vapor pressures of Sydoriak and Roberts,[21] the He^4 vapor pressures from the data used in the 1958 temperature scale,[22] the data of Kerr and Taylor[23] and Kerr[24] (extrapolated) for the densities of He^3 and He^4, respectively, and the known virial coefficients,[20] the right-hand side is equal to 5.284 at 0.8°K. Thus, the integral of $\ln(C_V/C_L)$ from $X=0$ to $X=100\%$ should be equal to this figure. Our readings only go up to $X=50\%$ so that a complete test is not possible, but inspection of the last column of Table I shows that the trend of the figures there is reasonable and of the type to be expected. It is therefore concluded that our data are acceptable. The major error in the value of all our excess potentials is likely to have arisen ultimately from the uncertainty in the absolute fountain pressures, and there is some arbitrariness in the way the graph of Fig. 5 is drawn through the scattered points. However, it is probable that the value of $\mu_3^E(X=0)$ is correct to about ±5%.

Osmotic pressures were finally deduced from these graphs using the equation

$$\Pi=-(RT/V_4)[(\mu_4^E/RT)+\ln(1-X)], \quad (16)$$

which uses (1) and (10). The partial molar volumes V_4 were computed, using (3), from Kerr's measurements of V_m as functions of X and T down to 1.2°K[25]; these

TABLE I. Excess chemical potentials and ratio of concentrations in vapor and liquid phases, deduced from data of Fig. 5 together with vapor pressure data. Temperature 0.8°K.

X	μ_4^E/R	μ_3^E/R	$\ln(C_V/C_L)$
0	0	1.227	6.966
0.1	0.006_4	1.112	6.862
0.2	0.035_4	0.953	6.623
0.3	0.101	0.757	6.293
0.4	0.207	0.560	5.914
0.5	0.347	0.389	5.525

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[20] J. E. Kilpatrick, W. E. Keller, E. F. Hammel, and N. Metropolis, Phys. Rev. **94**, 1103 (1954).

[21] S. G. Sydoriak and T. R. Roberts, Phys. Rev. **106**, 175 (1957).

[22] H. van Dijk and M. Durieux, Physica **24**, 920 (1958).

[23] E. C. Kerr and R. D. Taylor, in *Low-Temperature Physics*, edited by G. M. Graham and A. C. Hollis-Hallett (University of Toronto Press, Toronto, 1960), p. 605.

[24] E. C. Kerr, J. Chem. Phys. **26**, 571 (1957).

[25] E. C. Kerr, *Low-Temperature Physics and Chemistry* (University of Wisconsin Press, Madison, 1958), p. 158.

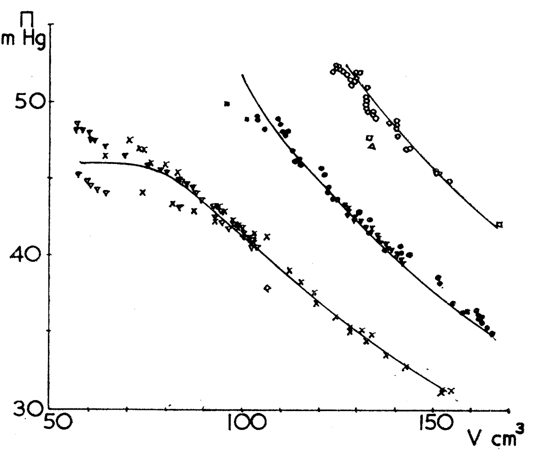

FIG. 6. Osmotic pressure deduced from curves of Fig. 5, as function of volume of solution containing 1 g mole of He^3. Reading downwards: 1.2, 1.0, and 0.8°K isotherms. Symbols as for Figs. 4 and 5.

figures for V_4 were then extrapolated down to 0.8°K with an estimated accuracy of $\frac{1}{2}\%$. The volume V of solution containing 1 mole of He^3 (as defined in (8), was also calculated from the same data, and the results plotted as (Π,V) isotherms in Fig. 6. The fact that the 0.8°K isotherm turns over horizontally at high concentrations does *not* depend critically on the way the curve is drawn through the scattered points in Fig. 5; several slightly different curves can reasonably be drawn through these points, but all of them give (Π,V) isotherms which turn over in the same way.

6. CONCLUSIONS FROM THE EXPERIMENTS

The conclusions from these experiments are that with this apparatus, conditions approximating the true equilibrium could be obtained in a few minutes, that quite large changes of He^3 concentration could be carried out reasonably reversibly and hence that osmotic pressures could be measured accurately to about $\pm 2\%$.

7. COOLING BY ADIABATIC DILUTION

The resemblance of Fig. 6 to the (p,V) isotherms of a condensible gas is striking. The difference in shape between the curves for 1 and 0.8°K—in particular the horizontal portion at low molar volumes—is obviously connected with the phase separation which is known to take place at temperatures below 0.87°K. Since liquid He^4 at low temperatures has almost no entropy whereas liquid He^3 still has a comparatively large entropy we can, to a good approximation, ignore the presence of the He^4 and regard any mixture as a *one-component system* consisting of only He^3 which can exist in two phases—a quasi-liquid phase and a quasi-gas phase with a "critical temperature" of 0.87°K. The "volume" of the "gas" or "liquid" is the total volume of the solution and the "pressure" is the osmotic pressure of the He^3. This approach is fertile in suggesting methods of refrigeration using the adiabatic dilution of He^3-He^4 mixtures.

The osmotic pressures are very large compared with vapor pressures—the only other pressures usually available for cooling—and the molar volumes are correspondingly smaller. For a 2% solution at 0.1°K, for example, the ratio Π/p can be calculated (from data to be given later) to be of the order of 10^{11}. The cooling resulting from the reversible adiabatic dilution of such a solution, analogous to the adiabatic expansion of a gas, should be useful.[26] But a dilution of a concentrated solution across the two-phase region, analogous to the adiabatic evaporation of a liquid, should absorb greater quantities of heat for a given throughput (change of volume) since the entropy change is of the order of R per mole. The rest of this paper is devoted to examining this proposal.

A. Methods of Dilution

In an adiabatic dilution, there exists the choice between two methods of mixing. In one process, the mixing takes place through a valve, via the irreversible mechanism of diffusion down a concentration gradient. The osmotic pressure is not manifest in any way, and the pressures on either side of the opening are equal. In the other process the diffusion of the solvent into the concentrated mixture takes place reversibly or irreversibly through a semipermeable membrane. Both processes are adiabatic, but it will be shown subsequently that the second process produces a greater cooling. It is also suitable as the basis for a continuously acting refrigerator.

B. Definitions

The heat of mixing H^E *per mole of solution* is defined by the equation

$$H(X,T)=XH(\mathrm{He}^3,T)+(1-X)H(\mathrm{He}^4,T)+H^E(X,T), \quad (17)$$

where H is an enthalpy, determined by integrating a specific heat at constant external pressure; usually the specific heat at saturated vapor pressure is measured and a small correction has to be applied. In what follows it is useful to refer all quantities to *1 mole of He*^{3}; thus H^E/X will be frequently used. H^E is always zero when $X=0$ and 1, and is a maximum at some intermediate concentration, but H^E/X at any temperature tends to a constant limit as X tends to zero; this is called the heat of dilution.

C. Constant-Pressure and Constant-Volume Systems

We consider some of the thermodynamic properties of a mixture of He^3 and He^4 in an open vessel *in com-*

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[26] H. London, *Proceedings of the International Conference on Low-Temperature Physics, Oxford* (Clarendon Laboratory, 1951), p. 157.

munication with pure He^4 at constant temperature through a superleak. The solution can draw pure He^4 through the superleak; the fountain pressure P of the He^4 in the external bath is equal to the sum of the fountain pressure of the He^4 in the solution plus its osmotic pressure Π. (In most of what follows we will in fact assume that the temperature of the solution is so low that P can be neglected compared with Π.) When changes are carried out in such a solution, it behaves like a constant-pressure system. By contrast, in the more usual experimental arrangement the mixture is in a closed vessel (and for simplicity it is assumed that the condensation of the vapor can be neglected); this behaves like a constant-volume system.

For very dilute solutions in this latter situation, the contribution of the He^3 to the specific heat is $\frac{3}{2}R$ per mole of solute (as suggested by Pomeranchuk[27] and approximately verified by de Bruyn Ouboter, Taconis, le Pair, and Beenakker[28]). However, in the "constant-pressure" system, very dilute solutions may be expected, by straight-forward arguments, to have a molar specific heat of $\frac{5}{2}R$.

In the same way we may consider the heat required to dilute a solution in the two-phase region from X_1 to X_2, the concentrations which are in equilibrium with one another at the temperature concerned. For the constant-volume case, corresponding to He^4 diffusing into the solution X_2 through a valve or pierced diaphragm, this is equal to $(H/X)_1-(H/X)_2$. But at constant pressure Π there is an additional contribution of $\Pi(V_1-V_2)$, where V_1 and V_2 are the volumes of solutions of concentrations X_1 and X_2 containing 1 mole of solute. The total quantity of heat in the second case is truly analogous to the latent heat of evaporation in a one-component system. It can be seen that when there is a superleak present the quantity H^E/X plays the role of an internal energy, although H^E is often called the excess enthalpy. It is true that for concentrated solutions which are not superfluid and which cannot exert their osmotic pressure across a superleak, the ΠdV term is absent. However, in a system in which the two phases are in equilibrium and in which the dilute phase is superfluid, the transfer of He^3 across the boundary is reversible and the increase of volume of the dilute phase can be effected by supplying He^4 through a superleak; therefore the ΠdV term must be included.

Finally, it is relevant to discuss a superfluid solution contained in a tube, along which is maintained a temperature gradient. The steady-state condition is that $(\Pi+P)$, the total pressure of the normal phase, should be the same everywhere. This condition holds even though no superleaks are present to act as manostats; it is analogous to the constancy of pressure throughout an ordinary gas in the presence of a temperature gradient. It is another way of expressing the heat flush phenomenon, in which the He^3 in a solution migrates towards the cooler end of a closed tube. If the tube is at such a low temperature that the fountain pressure is negligible while the osmotic pressure obeys the perfect gas laws, the ratio of concentrations at the two ends is in inverse ratio of their temperatures.

8. OSMOTIC ENTHALPY DIAGRAM

Any dilution process can usefully be represented by a family of curves of the relevant enthalpy against temperature at constant concentration. The mixing is represented by a horizontal line from initial to final concentration and the change of temperature can be read off. For the proposed dilution process the appropriate thermodynamic function must be of the type $H/X+\Pi V$; we can obtain a consistent representation for both superfluid and nonsuperfluid solutions by defining the *osmotic enthalpy* as

$$\mathcal{H}=H/X+\Pi(V-V_3^0)=H(\mathrm{He}^3,T)+H^E/X+\Pi(V-V_3^0), \quad (18)$$

where $V=V_m/X$ is the volume of a solution containing 1 g mole of He^3. This definition is very nearly correct for X approaching zero and unity, though near the λ-line at high temperatures it is not rigorous. It also includes the approximation that the fountain pressure of the solution can be neglected; this is true at low temperatures. We will first construct as much of the diagram of H/X against T as is possible from the available data, and thence construct the general shape of the diagram of the osmotic enthalpy against temperature. The design data of a practical refrigerator can be drawn from this.

A. Experimental Data Available

The enthalpy curve for $X=1$, the pure liquid, is easily constructed by integrating the C_{sat} curve which is known accurately from 0.75 down to 0.085°K.[29] Above 0.75°K, two formulas are quoted by Hammel,[30] namely, those of Roberts and Sydoriak[31] and of Osborne Abraham, and Weinstock[32] which agree quite closely. The probable errors at 0.75 and 1°K are both about $\pm 1\frac{1}{2}\%$.

Data for H^E have been presented both by Roberts and Swartz[18] for temperatures down to 1.05°K and by de Bruyn Ouboter, Taconis, le Pair, and Beenakker[28] down to 0.5°K. In the region above 1°K, where it is possible to compare the two sets of data, there is a serious discrepancy between them. It is thought that the method of treating the Leiden observations makes

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[27] I. J. Pomeranchuk, Soviet Phys.—JETP **19**, 42 (1949).

[28] R. de Bruyn Ouboter, K. W. Taconis, C. le Pair, and J. J. M. Beenakker, Physica **26**, 853 (1960).

[29] D. F. Brewer, J. G. Daunt, and A. K. Sreedhar, Phys. Rev. **115**, 836 (1959).

[30] E. F. Hammel, in *Progress in Low-Temperature Physics*, edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1955), Vol. I, p. 78

[31] T. R. Roberts and S. G. Sydoriak, Phys. Rev. **93**, 1418 (1954).

[32] D. W. Osborne, B. M. Abraham, and B. Weinstock, Phys. Rev. **94**, 202 (1954).

their published figures the more liable to error; their method is as follows. Their lowest accessible temperature was 0.39°K, where the equilibrium concentrations were 15 and 95.4%. At all temperatures down to 0.39° and at concentrations between the limits just mentioned, they measured a quantity H^{E*}, defined as the excess enthalpy with respect to solutions of concentrations 15 and 95.4%. The method of calculation was to integrate the measured specific heats round a rectangle in the (T,X) diagram, partly inside and partly outside the phase separation region, and within these limits of concentration was very accurate. However, the values of H^E with respect to 0% (or 100%) had to be found by extrapolation, and there is a good deal of latitude in this process. At 1.05°K, for example, H^{E*} was extrapolated to -0.274 and -0.107 cal/mole at 0 and 100%, respectively, so that according to this analysis H^E/X at $X=0$ is equal to 1.69 cal/mole. The tables of Roberts and Swartz give 2.24 cal/mole—a 25% discrepancy. However, the extrapolation of the H^{E*} data can be taken to -0.310 and -0.143 cal/mole, respectively, without doing any violence to the curve, and this brings the Leiden values of H^E into good agreement with the others over the whole range of concentration at this temperature. There is, therefore, no essential discrepancy between the two sets of observations. To recalculate H^E down to 0.5°K, the values at 1.05°K were taken from the tables of Roberts and Swartz, interpolated to the standard concentrations used in the Leiden experiments; at any concentration the difference between this value and the Leiden value was found and then added to the Leiden figures at all lower temperatures. In this way the curves from $X=0.15$ to $X=0.9$ in Fig. 7 were plotted down to 0.5°K. The experiment of Sommers, Keller, and Dash[33] who observed the change of temperature when He^3 was diluted to 8.6% by diffusion through a pierced membrane cannot be directly represented on this diagram, because of the influence of the condensing vapor in their setup.

B. Heat of Dilution at Absolute Zero

The available data are still not accurate enough to allow extrapolation to $X=0$, nor of course do they extend below 0.5°K. The only other datum which can be estimated with any precision is H/X for X tending to zero at absolute zero. Several methods of calculating this will now be described.

The first, and probably the most accurate, method is as follows. H/X for a 4.66% solution at 0.5°K can be found by combining the Los Alamos and Leiden data, as indicated above; this is the point R in Fig. 7. ($H^E=0.526$ cal/mole, H for pure He$^3=0.292$ cal/mole). It was found at Leiden that above 0.5°K the He^3 in solution contributed an almost constant amount 1.315 R to the specific heat at this concentration. This has to be compared with the theoretical prediction of Pomeranchuk,[21] that the dissolved He^3 would behave like a classical gas of specific heat $\frac{3}{2}R$ per mole. If we accept the experimental value, however, we have on cooling to absolute zero

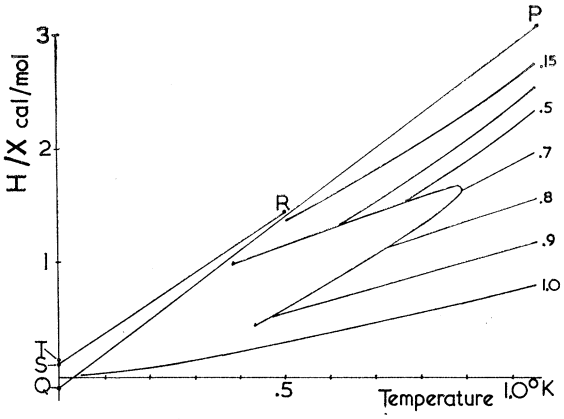

FIG. 7. Enthalpy per mole of He^3 as function of temperature for different concentrations. The curve for $X=0$ is not drawn. Q, S, and T are estimates of the heat of dilution at absolute zero.

$$H(X,0^0)/X=H(1,0.5^0)+H^E(X,0.5^0)/X-1.315\times0.5^0, \quad (19)$$

for $X=.0466$. This is represented by the line RS in Fig. 7 and H/X for X tending to zero at absolute zero is 0.114 cal/mole.

The second method is likely to be less accurate, but gives an indication of the probable error which is likely to exist in the estimates of the heat of dilution. The *infinitely* dilute solution can plausibly be expected to follow Pomeranchuk's model at 1.05°K. Therefore we can use the same equation with $X=0$ substituting $\frac{3}{2}R$ for 1.315R and 1.05°K for 0.5°K. This gives the line PQ in Fig. 7, where the enthalpy at P is equal to 2.242+0.795 cal/mole; the intercept is negative, -0.092 cal/mole.

The third method avoids the uncertainty in the enthalpy of the pure liquid but substitutes the comparable uncertainty of the latent heat of evaporation. The infinitely dilute liquid at 1.05°K can be evaporated to a dilute gas, in two stages—first concentrated to pure He^3, emitting H^E/X, and then evaporating the pure He^3 by absorbing the latent heat $L(1.05^0)$. The gas can then be irreversibly expanded to large volume, which does not involve any change in H if we neglect the Joule-Thomson effect. The dilute gas can then be cooled ($C_p=\frac{5}{2}R$) to absolute zero and condensed, emitting $L(0^0)$. When mixed to form a dilute solution, the heat of dilution $H(X,0^0)/X$ is emitted. Alternatively, the direct path from P to absolute zero could be followed. Hence, for X tending to zero:

$$H^E(X,1.05^0)/X-L(1.05^0)+\tfrac{5}{2}R\times1.05^0+L(0^0)-H(X,0^0)/X=\tfrac{3}{2}R\times1.05^0. \quad (20)$$

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[33] H. S. Sommers, Jr., W. E. Keller, and J. G. Dash, Phys. Rev. **92**, 1345 (1953).

The first term has the value 2.242 cal/mole, as mentioned previously.

From Kerr,[34] $L(1.05^0)=9.241\pm 0.015$ cal/mole, after allowing for possible errors in estimating the vapor density. The vapor pressure equation of Sydoriak and Roberts[21] which is thermodynamically reasonable at $T=0$ implies that $L(0^0)=5.032\pm 0.012$ cal/mole, allowing for uncertainties in the temperature scale. Hence the heat of dilution at $T=0$ is positive, 0.119 ± 0.019 cal/mole. This is represented by the point T in Fig. 7.

The significant thing established by these methods is that the heat of dilution at absolute zero is certainly a small quantity. There is some additional evidence that this conclusion is correct. Adopting the one-component analogy, we expect the (Π,T) curve for the equilibrium of the two phases at low concentrations to obey a vapor pressure equation. Since the molar specific heat of the concentrated phase is small compared with that of the dilute phase (see Fig. 7), this equation should be of the type

$$\ln\Pi=\tfrac{5}{2}\ln T-(L(0^0)/RT)+\mathrm{const}, \qquad (21)$$

or assuming that the dilute phase obeys the perfect gas laws the phase-separation line should show

$$X\propto T^{3/2}\exp(-L(0^0)/RT), \qquad (22)$$

where $L(0^0)$ can be identified with the heat of dilution at absolute zero. The available data[19] show no evidence of deviation from a $T^{3/2}$ law at low temperatures, however, confirming that this heat of dilution at absolute zero is small.

From the theoretical point of view it does not seem possible to predict even the sign of the heat of dilution at absolute zero. The third law of thermodynamics does not state that it must necessarily be positive, but merely that if it is negative the equilibrium concentration is finite at absolute zero.

Finally, therefore, we are left with the conclusion from the data that the heat of dilution at absolute zero lies within the range ±0.1 cal/mole, a positive value being rather more probable than a negative one.

In what follows we will use the working hypothesis that this heat of dilution is zero.

C. The $\mathcal{H}$ Diagram

With this assumption the $\mathcal{H}$ diagram can now be derived (Fig. 8). The $X=1$ curve is unchanged, the $X=0$ curve has gradient $\frac{5}{2}R$. Down to 0.8°K, the extra $\Pi(V-V_3^0)$ to be added to H/X can be derived from our osmotic pressure measurements. (For small concentrations this term is equal to RT, which accounts of course for the difference between the $\frac{3}{2}RT$ and the $\frac{5}{2}RT$ curves.) At lower temperatures the phase separation curve can be expected to fan out rapidly, since most of the extra RT occurs because of the volume change between the two phases.

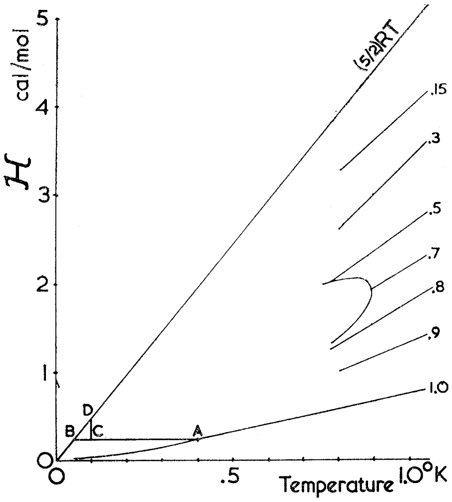

FIG. 8. Osmotic enthalpy per mole of He³ as function of temperature for different concentrations, assuming that the heat of dilution at absolute zero is zero.

9. PERFORMANCE OF A DILUTION REFRIGERATOR

The $\mathcal{H}$ diagram shows at once that it is advantageous to start the dilution from as low a temperature as possible. To take a numerical example, an initial temperature of 0.4°K, attainable with a conventional He^3 refrigerator, should allow a temperature below 0.05°K to be reached if there is no heat input. This process is represented by the line AB in Fig. 8.

If the temperature is to be held steady at a value higher than that just estimated, for example at 0.1°K, than the enthalpy of the fully diluted mixture is represented by the ordinate of the point D in Fig. 8, whereas the initial enthalpy is the ordinate of A. The amount of heat which can be absorbed per mole of He^3 circulated is therefore represented by CD (though the point C represents formally a mixture of the two phases in proportions determined by the position of C between the phase boundary lines, which are close to the $X=0$ and $X=1$ lines). With an initial temperature of 0.4°K, 0.28 cal should be dissipated per mole of He^3 circulated at 0.1°K.

10. SCHEMATIC DESIGNS OF DILUTION REFRIGERATORS

Two schemes are illustrated in Fig. 9 and 10. In each case the circuits can be divided into two parts (as indicated by the dotted lines), namely, the cryostat C, in which the concentrated mixture is diluted to reach a low temperature, and the rest of the circuit above the temperature of the cryostat of which the main component is the still S, in which the dilute solution is reconcentrated by a single-stage distillation and later recirculated. The thermodynamic arguments developed so far apply to the cryostat and the principles underlying this part of the apparatus can be considered to be fairly well understood. As to the rest of the circuit,

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[34] E. C. Kerr, Phys. Rev. **96**, 551 (1954).

where transport phenomena are relevant, there is sufficient latitude in the design to accommodate uncertainties concerning these quantities.

A. The Cryostat

In the cryostat C the concentrated solution (which enters at a "high" temperature) is diluted across the two phase region, that is to such a concentration that at the "low" temperature all the concentrated phase is just converted into the dilute phase with which it is in equilibrium. We estimate this concentration using the fact, mentioned previously, that the phase boundary is expected to show X proportional to $T^{3/2}$ at low concentrations and low temperatures. At 0.39°K the boundary is at $X=0.15$; we therefore extrapolate to 0.02 at 0.1°K, for example; the osmotic pressure of this solution is calculated to be about 4.2 mm Hg (the correction for nonideality being somewhat uncertain because of the difficulty of estimating $\mu_4{}^E$ from vapor pressures).

The one-component analog for the dilution process is the flash evaporation (at constant enthalpy) of a liquid at high pressure and temperature to produce saturated vapor at low temperatures and pressure. The cooling takes place at the interface between the two phases, as in a liquid which evaporates only at the surface. As the thermal conductivity of both phases is low, the thermal load must be brought into good thermal contact with the phase boundary. The "liquid" phase has a smaller density than the "gas" phase and therefore lies above it; the usual arrangement in the evaporator of an ordinary refrigerator is turned upside down.

B. Methods of Recirculation

The low-temperature distillation of very dilute mixtures can yield remarkably highly concentrated distillates. For example, a reconcentration from 0.25% to well over 90%, probably about 95%, should be possible in a single-stage distillation at 0.65°K. This concentration is however likely to be reduced because of creep of He^4 up the sides of the still and subsequent evaporation. This effect can be limited to a few percent by designing for a sufficiently large throughput of He^3 (of the order of 10^{-4} mole/sec) and by introducing a constriction in the tube above the level of the liquid.

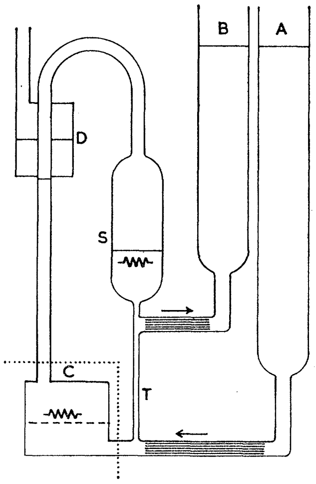

FIG. 9. Schematic diagram of dilution refrigerator. Dotted line separates cryostat *C* from recirculating mechanism. Dashed line in cryostat represents phase boundary, with concentrated He^3 solution on top. T is narrow capillary to flush dilute He^3 into still S. D is condenser. He^4 circulates from bath A through superleak, through T and out again through another superleak into bath B at higher temperature.

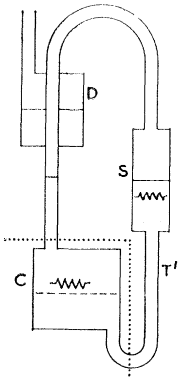

FIG. 10. Schematic diagram of dilution refrigerator. Cryostat C is like that in Fig. 9, but flow of dilute He^3 into still S is through wide tube T′ and is nonturbulent. Motive force pulling He^3 round is pumping action exerted by condenser D.

In both the circuits illustrated in Figs. 9 and 10, the concentrated vapor from the still is condensed in an inner tube in D (which may be a conventional He^3 bath), whose temperature determines the inlet temperature to the cryostat *C*. The two arrangements differ in the method of bringing the dilute liquid from cryostat C to still S. In Fig. 9 the dilute He^3 from C is flushed up through a narrow capillary T so dimensioned that the velocity of a stream of He^4 flowing through it exceeds its critical value (10–20 cm/sec); the flow is turbulent and the He^3 is flushed along with the He^4. Thus the concentration at the top of the capillary should be equal to that in the cryostat in spite of the temperature difference. The He^4 used in the flushing process enters the capillary T through a superleak from a He^4 bath A and goes out at the top through another superleak into another He^4 bath B at a higher temperature than A. If X_c is the concentration in the cryostat, the throughput of He^4 has to be a factor $1/X_c$ times as great as that of the He^3, and the design of the superleaks is likely to set the ultimate limit on the refrigerating capacity of the system.

The concentration in the still itself can be higher or lower than that at the top of the capillary, depending on the rate of evaporation caused by the heater in the still. If for example the rate of evaporation in the still is too low, He^3 will accumulate till a steady state is reached in which the He^3 evaporates at the same rate at which it is supplied. The higher the concentration in the still, the easier is the reconcentration. However, for practical reasons it should not be too great—it should not exceed 0.4% if the still is held at about 0.65°K, for example. This is because the osmotic pressure there would then correspond to a column of He^3 of about 50 cm and the vertical height of the liquid in the condensing limb must be able to drive the dilute He^3 against this pressure. Fortunately, as already mentioned, this is a concentration and a temperature at which effective evaporation and reconcentration by single-stage distillation is possible. The flushing method is therefore particularly appropriate for use with low cryostat temperatures, below 0.1°K for example; the concentration of the dilute phase is very low, but it is possible to enrich the solution to the figure given above prior to evaporation.

In the transport from cryostat to still in Fig. 9 the vortices in the turbulent He^4 in the capillary T are expected to act like the jet of a diffusion pump and the two He^4 baths A and B are like manostats. However in the simpler arrangement of Fig. 10 there is no pressure gradient between cryostat and still and therefore no need for the "pump". The dilute phase moves slowly through the wide tube T' under quasi-equilibrium conditions under the normal phase pressure only, and Π_s is nearly equal to Π_c. Thus, X_s is much less than X_c (since $X_cT_c=X_sT_s$ approximately) and the reconcentration is made more difficult. However, for the figures assumed ($T_c=0.1$°K, $X_c=2\%$ and $T_s=0.65$°K), the concentration in the still would still be equal to over 0.25% and the vapor concentration would be about 95%. Equating partial pressures of He^3 in still and condenser (0.015 mm),[19] the condenser must be maintained at 0.374°K, which is a reasonable figure. To summarize, the following data are self-consistent and reasonable for the arrangement of Fig. 10: in the cryostat a 2% solution at 0.1°K with $\Pi=4.2$ mm Hg, in the still a 0.25% solution at 0.65°K with $\Pi=3.86$ mm Hg, $P=0.34$ mm Hg and a partial vapor pressure of 0.015 mm Hg, and in the condenser a concentration of about 95% at 0.374°K.

A third quite different arrangement[35] (not illustrated) makes use of the fact that the difference of enthalpy of dilute He^3 between 0.1 and 0.6°K (about 1.5 cal/mole) is considerably greater than the enthalpy of pure (or even 95%) He^3 at 1°K. It is therefore possible to dispense with the He^3 condensing bath D. This can be done by bringing the vapor from the still up to room temperature, recompressing it by a diffusion pump, and condensing it in a He^4 bath at 1°K. A heat exchanger has to be employed between this liquid and the dilute solution between the cryostat and the still. It may be noted that in order to produce the same throughput of He^3 round the refrigerating circuit, the size of pump necessary to circulate the concentrated distillate in this arrangement is practically the same as that needed on the pure He^3 in the condenser D of Fig. 9 or 10. At the same time the design problem posed by the need for good heat transfer through the condensed D is replaced by that of the exchanger leading to the cryostat—a problem which is simplified by the smallness of the heat load there. This arrangement has the further advantage that the concentrated He^3 entering the cryostat can be precooled to an even lower temperature than that attainable with an ordinary He^3 bath, thus making it possible that an even lower temperature might be reached than with the other arrangements illustrated.

C. Refrigerating Capacities

We will finally make rough estimates of the refrigerating capacities of this system and of the arrangement of Fig. 10 (but not of Fig. 9 because the efficiency of large superleaks is difficult to estimate). In these circuits the speed of the pump just mentioned can be reasonably taken to be of the order of 10^{-4} mole/sec. This refers to a typical 9-in. diffusion-ejector combination for He^3 at the pressure of the still, 15μ. When taken in conjunction with the data deduced from the osmotic enthalpy diagram, the refrigeration load is determined.

However, the heat conducted into the cryostat from higher temperatures must be included in this load. The most important heat leak is likely to be that from the still. This is because the tube connecting cryostat to still contains almost pure He^4—98% He^4 at the bottom, 99.75% at the top—and the tube must be sufficiently wide for the flow to be nonturbulent. We therefore first estimate the dimensions of tube to accommodate the flow and then estimate the heat conduction down it.

The viscosity of the solution can be estimated from the measurements of Staas and Taconis,[36] extrapolated below 1°K using a gas-kinetic model, since Sandiford and Fairbank[37] have shown that He^3-He^3 collisions are dominant in limiting the mean free path. From this, the viscosity is calculated to be between 10^{-4} and 10^{-5} P in the range considered. A flow of 10^{-4} mole/sec at 0.25% concentration means a liquid flow of the order of 1 cc/sec and if the linear velocity must not exceed 10 cm/sec (to avoid turbulence in the He^4) the area of cross section of the tube must be at least 0.1 cm^2. It follows that the flow will be streamline. Further, applying Poiseuille's formula, the osmotic pressure differential will be very small for any tube of reasonable length, compared with the absolute value of 4.2 mm Hg.

Next we estimate the thermal conductivity of the mixture. Sandiford and Fairbank[37] have shown that the phonon mean free path is limited by collisions with He^3 atoms and varies as $T^{-3.5}$. For Rayleigh scattering however a T^{-4} variation would be expected and we will adopt this for extrapolation to lower temperatures. Fitting their observations numerically gives $l=1.15\times10^{-6}/XT^4$ cm for the mean free path and this may certainly be assumed to be an upper limit. Writing the thermal conductivity

$$k=\tfrac{1}{3}cC_4\rho l,$$

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[35] It was suggested by Professor H. E. Hall.

[36] F. A. Staas and K. W. Taconis, in *Low-Temperature Physics*, edited by G. M. Graham and A. C. Hollis-Hallett (University of Toronto Press, Toronto, 1960), p. 650.

[37] D. J. Sandiford and H. A. Fairbank, in *Low-Temperature Physics*, edited by G. M. Graham and A. C. Hollis-Hallett (University of Toronto Press, Toronto, 1960), p. 641.

where c is the velocity of sound through liquid He^4, taken as 2.4×10^4 cm/sec, C_4 the phonon specific heat of He^4, $0.0235T^3$ J/g deg, and ρ its density, then the conductivity must be approximately $3\times10^{-5}/XT$ W cm^{-1} deg^{-1}. In the tube concerned XT is constant and equal to 2×10^{-3}, so the heat conducted into the cryostat from the still for a 1° temperature difference would be $1.5\times10^{-3}/L$ W for a tube of length L cm. However this is opposed by the bulk flow of the cold liquid out of the cryostat into the still. For a 1° temperature difference this heat flow would be $\frac{5}{2}R$ cal/mole multiplied by 10^{-4} mole/sec, that is, 2.1×10^{-3} W. Thus the length L of the tube is determined by the fact that $1.5\times10^{-3}/L$ W must be small compared with this—which is easily satisfied.

We are left with the conclusion that the problem of dimensioning the tube from cryostat to still should not be difficult and should allow a throughput of 10^{-4} mole/sec with only a small heat leak into the cryostat. Combining this with the datum that 0.28 cal/mole of He^3 is available for refrigeration at 0.1°K (assuming the heat of dilution at 0°K to be zero), we see that a total of 1180 erg/sec should be absorbed at that temperature. If H/X at $T=0$ is in fact $+0.1$ cal/mole, the lowest temperature attainable from the same condenser temperature should be in the region of 0.022°K and the load at 0.1°K should be 1600 erg/sec. If H/X has its least favorable value of -0.1 cal/mole, the figures become very uncertain but may lie in the region of 0.065°K and 760 erg/sec at 0.1°K. Compared with existing refrigerators these are very useful characteristics. Neither the conventional He^3 evaporator nor the magnetic refrigerator seems capable of operating far below 0.2°K, even with no heat input. The dilution refrigerator therefore seems to be worthy of further study.

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