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Thermodynamic Properties of a Non-Ideal He^3-He^4 Solution Model

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Deviations from ideality for He^3-He^4 solutions are calculated on the basis of a simple real solution model. Expressions for equilibrium total pressure are derived for situations with and without superfluid He^4. Effects of non-ideality on previously reported calculations of lambda-point dependence on He^3 concentration are examined, and an equation representing the lambda-points of concentrated as well as dilute He^3 solutions is given. The results are used in the comparison of various bases for treatment of the lambda-point shift. Assumption that the partial molal enthalpy of superfluid vanishes gives more satisfactory results than assumption of zero partial molal entropy of superfluid.

I. INTRODUCTION

THERMODYNAMIC treatment of ideal liquid solutions of He^3 and He^4 has been given recently by a number of investigators.[1-4] Previous workers have pointed out the dependence of theoretical results on assumption of solution ideality and have indicated the difficulty of obtaining any precise measure of ideality deviation from available measurements of solution properties. Systematic estimation of non-ideality corrections is, therefore, important for the understanding of real solution behavior. This paper considers the calculation of corrections for a simple real solution model and the comparison of model properties with those of the ideal and actual solutions.

II. CHEMICAL POTENTIALS

At temperatures for which there is no superfluid, solutions of He^3 and He^4 are two component mixtures. Interaction of these non-electrolytes gives rise to deviations from ideality conveniently described by the excess chemical potentials of the substances, that is, the differences between actual chemical potentials and values for ideal mixtures. A useful representation of the excess chemical potential of A in a two-component mixture, A and B, is $\mu_A{}^E=\sum_i k_i f_B{}^i$. The volume fraction of component B, f_B, is defined as

$$N_BV_B/(N_AV_A+N_BV_B) \quad \text{or} \quad x_B/(x_AV_A+x_BV_B),$$

where V_j is the molar volume of pure j and N_j is the number of moles of substance j.

Scatchard has considered[5] the results of non-electrolyte interaction and has shown that, for a simple solution model, $k_i=0$ for $i\neq 2$ and

$$k_2=V_A(a_{AA}{}^{\frac{1}{2}}-a_{BB}{}^{\frac{1}{2}})^2, \tag{1}$$

where $-a_{jj}$ is the energy of unit volume of pure liquid j minus that of the same quantity of perfect gas j at the same temperature. Using this model, one can express potentials of isotopic helium solutions as

$$\mu_3=\mu_3{}^0+RT\ln x_3+V_3af_4{}^2, \tag{2}$$

$$\mu_4=\mu_4{}^0+RT\ln x_4+V_4af_3{}^2, \tag{3}$$

where $a\equiv(a_{33}{}^{\frac{1}{2}}-a_{44}{}^{\frac{1}{2}})^2$. Detailed description of the solution model, derivation of Eq. (1), and extension of the treatment to mixtures with more than two components has been given by Scatchard.[6,7]

One of the chief recommendations for the above expression for the potentials is that it seems to combine reasonable approximation with simplicity of mathematical form. More complicated equations have been used but often the data are not precise enough to warrant the added terms.

The assumptions on which the derivation rests are listed in reference 7. The relations of these assumptions to the validity of the simple equation have been considered by many investigators. The assumption of temperature independence for the molecular distribution function and the related ideal entropy of mixing have been discussed critically for various deviations by Hildebrand and Wood,[8] Guggenheim,[9] Scatchard and Hamer,[10] and Hildebrand.[11] Kirkwood[12] has calculated the effect of sorting on the thermodynamic properties. Even when the temperature is such as to produce critical mixing, the correction for the excess free energy is only about five percent. For isotopic solutions this correction can be neglected.

In practice, use of a Flory-Huggins excess entropy of mixing instead of the zero value of the above development does not seem to be justified until the ratio of molar volumes becomes greater than 2 to 1; the ratio for He^3 and He^4 (about 1.4 to 1) makes the use of this correction inappropriate.

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Correction for nonzero volume change on mixing[7] is a multiplicative term in the excess free energy $1-\beta_0 a f_3 f_4/2$ where β_0 is the compressibility of the isolated components. Even though β for helium is very large compared with other liquids, the value to be subtracted from unity is of the order of 10^{-2}; in view of other uncertainties, the error arising from use of the zero volume change equation, that is, Eq. (1) can be neglected.

Use of the geometric mean of a_{33} and a_{44} as a rough approximation for a_{34}, which enables one to obtain the energy parameter for a mixture from the parameters of its components, has been discussed by Hildebrand and Wood[8] and by Hildebrand.[11]

On the basis of the above treatments, calculation of a gives a reasonable expression for chemical potential as a function of composition. The quantity a_{jj} is very nearly equal to the heat required to vaporize one cm³ of liquid j minus the corresponding external work. In the following calculations the experimental heats of vaporization were used and the perfect gas law was employed to obtain the gas volume portion of the external work. Calculated in this manner, a is 0.1005 cal/cm³. Densities and heats of vaporization used are those given by Keesom[13] for He⁴ and those given by Grilly, Hammel, and Sydoriak[14] for He³.

III. SOLUTION VAPOR PRESSURES

Conditions for liquid-vapor equilibrium include the equality of liquid and vapor chemical potentials. Equations (2) and (3) with $\mu_{il}{}^0(P_i{}^0, T)+\bar{V}_{il}(P-P_i{}^0)$ replacing $\mu_{il}{}^0(P, T)$ can be used for the liquid potentials, since the liquids can be taken as incompressible without very great error at the low pressures considered. The vapor potentials can be easily obtained if the equation of state of the gas mixture is known. One can use an expression stopping with terms in $1/V$ such as

$$PV=(N_3+N_4)RT[1+(N_3+N_4)B_y/V]$$

where $B_y=B_3y_3{}^2+2B_{34}y_3y_4+B_4y_4{}^2$; B_i is the second virial coefficient of the gas i, and y_i is the gas mole fraction.

Neither experimental nor quantum-mechanical (computed) values are available for B_{34}, but it seems reasonable that the value estimated from properties of the pure gases will be as good an approximation as the rest of the calculations. Various rules for obtaining mixture parameters have been reviewed by Beattie.[15] For the simple equation of state chosen, probably the best rule is the Lorentz approximation $B_{34}=(B_3{}^{\frac{1}{3}}+B_4{}^{\frac{1}{3}})^3/8$ which is obtained by averaging molecular diameters.

The chemical potentials of the gases i and j of a two-component system obeying the above equation of state are given by

$$\mu_{ig}(P,T)=\mu_{ig}{}^0(P_i^0,T)+RT\ln(py_i/P_i{}^0)+B_i(P-P_i{}^0)+r_i,$$

where $r_i=(2B_{ij}-B_i-B_j)(1-y_i)^2P$ and j refers to the other component. Equating potentials and remembering that the sum of y_3 and y_4 must be unity, one has for the total pressure

$$\begin{aligned}P=P_4{}^0x_4\exp\{[k_4f_3{}^2+(\bar{V}_{4l}-B_4)(P-P_4{}^0)-r_4]/RT\}\\ +P_4{}^0x_3\exp\{[k_3f_4{}^2+(\bar{V}_{3l}-B_3)\\ \times(P-P_3{}^0)-r_3]/RT\}.\quad(4)\end{aligned}$$

The y_i values obtained from a Dalton-Raoult computation are sufficiently close for calculation of the r_i since the r terms are small corrections. By successive approximations, P can then be obtained for any given liquid mole fraction from the temperature and properties of the pure gases and liquids.

Vapor pressures of the pure liquids (as functions of T) and liquid volumes are given in references 13 and 14; B as a function of temperature is available for both isotope three[16] and isotope four.[17] Experimental pressures for testing (4) are not available, but P is known to be greater than the ideal value. The signs of terms in the exponentials insure that the deviations calculated from (4) are in the right direction. It should be noted that (4) can hold below 2.19°K for a range dependent on x_3 since He³ depresses the lambda-point.

For temperatures less than the lambda-temperature, the treatment must be modified to include the influence of superfluid. Rice and Engel[18] have proposed corrections for the presence of superfluid. Adding these correction terms to the chemical potential expressions (2) and (3) multiplies the nonsuperfluid total pressure by corresponding corrections so that

$$\begin{aligned}\text{total pressure}=P_s(x_3+x_{4n})^{-1}\\ \times\exp\{S_\lambda[x_{4s}+\ln(1-x_{4s})]/R(r+1)\},\end{aligned}$$

where P_s is the right side of (4) with x_{4n} replacing x_4, S_λ is the entropy at the lambda-point, r is an empirical constant given in reference 18, n refers to normal fluid, and s refers to superfluid. It is important to note that the mole fractions used to evaluate P_s, as well as the correction factor, must be calculated from the total number of moles $N_3+N_{4n}+N_{4s}$. Rice and Engel[18] have indicated the use of the equality of normal and superfluid chemical potentials for calculation of x_{4n} and x_{4s} from the total amount of He⁴ and the total amount of He³ in a given sample. As it should, the expression for the total pressure reduces to P, the nonsuperfluid value, when $x_{4s}=0$.

IV. LAMBDA-POINTS OF THE SOLUTION MODEL

Thermodynamic investigation of the He³ composition effect on He³—He⁴ solution lambda-points, as described by Rice,[4] has involved the assumption of solution ideality. Investigation of the lambda-point-composition relation for the non-ideal model described above can

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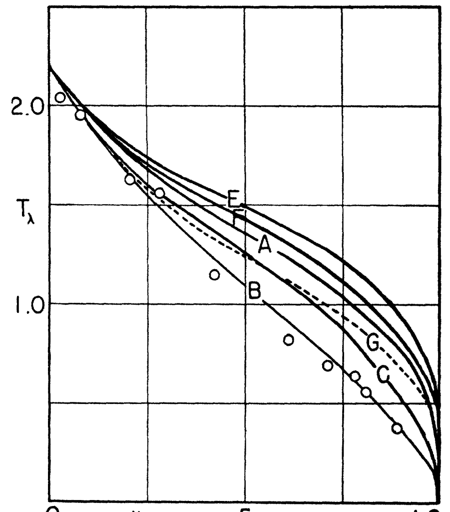

FIG. 1. Lambda-temperature *vs* He^3 mole fraction. Experimental points are circled.

point in some measure to the relative importance of the ideality assumption. The fundamental equation of Engel and Rice[3] in the two fluid lambda-point discussion is

$$-\bar{S}_{4s,\lambda}dT_\lambda = -\bar{S}_{4n,\lambda}dT_\lambda + (\partial\mu_{4n}/\partial x_3)_\lambda dx_3 \tag{5}$$

where the notation is the same as that of reference 3. Rearrangement of (5) gives the change of T_λ with composition as

$$dT_\lambda/dx_3 = (\partial\mu_{4n}/\partial x_3)_\lambda/(\bar{S}_{4n}-\bar{S}_{4s}). \tag{6}$$

Non-ideality effects for the solution model appear in the partial derivative in (6), and these effects are introduced explicitly by calculation of this quantity from (3). Equation (3) is appropriate since the mole fraction of superfluid is taken as zero along the lambda-curve. Noting that $x_3+x_4=1$, expressing f_3 in terms of mole fractions and volumes, and taking $\mu_{4n}{}^0$, V_3, V_4, and a as properties of the pure materials, one obtains by differentiation of (3)

$$\begin{aligned}(\partial\mu_{4n}/\partial x_3)_\lambda = & -RT_\lambda/(1-x_3) \\ & +2V_4{}^2V_3af_3/(x_3V_3+x_4V_4)^2 \\ = & -1.987T_\lambda/(1-x_3) \\ & +152.66x_3/(2.397+x_3)^3 \end{aligned} \tag{7}$$

if $V_3=38.86$ cm^3/mole, $V_4=27.42$ cm^3/mole, and $a=0.1005$ cal/cm^3.

With the information of (7) available, the problem of representing T_λ as a function of x_3 is reduced to that of representing the partial molal entropies as functions of T_λ and x_3. Since the solution model has as one of its basic features zero excess entropy, the concentration dependence is simple. The temperature dependence is more speculative, and each of the possibilities discussed by Engel and Rice[3] for the ideal solution is considered here.

There remains one further uncertainty concerning the superfluid term. Previous workers have shown that either $\bar{S}_{4s}=0$, or $\bar{H}_{4s}=0$ is a possibility. Assumption of the former and of solution ideality gives essentially the results of Gorter,[2] while the latter gives those of Rice.[4] Starting with either the Gorter or Rice case, one can distinguish subcases depending on the heat capacity behavior assumed.

Cases for which $\bar{S}_{4s}=0$

For the Gorter case, Eq. (6) yields the general result,

$$dT_\lambda/dx_3 = D/\bar{S}_{4n}, \tag{8}$$

where $D\equiv(\partial\mu_{4n}/\partial x_3)_\lambda$. If C_p is zero and, therefore, $\bar{S}_{4n}{}^0$ is temperature independent, $\bar{S}_{4n}=1.59-R\ln(1-x_3)$ where the experimental value at the normal lambda-point, 1.59 cal/deg/mole, has been used. Since D is known from (7), the equation can be integrated. The results appear as curve E in Fig. 1.

Assumption of a linear heat capacity will make $\bar{S}_{4n}{}^0$ equal to AT and $\bar{S}_{4n}=AT-R\ln(1-x_3)$. The constant A is 0.725 cal/deg^2/mole since $S_{4n}{}^0$ is 1.59 cal/deg/mole when T is 2.19°K. The results of this heat capacity assumption appear as curve F.

The third heat capacity subcase appears as curve A. Here the heat capacity is assumed to remain equal to its value of 2.2 cal/deg/mole at 2.19°K for a short interval and then decrease to zero according to a T cube relationship, so that there must be a separate discussion for each part of the C_p curve. The method of determination of the range for constant C_p and for AT^3 value of C_p is that given by Engel and Rice,[3] but the entropy and enthalpy data are those used by Rice.[4] As a result

$$C_p=2.2 \text{ cal/deg/mole}, \qquad 2.19°\text{K}\geqslant T\geqslant 1.48°\text{K},$$
$$C_p=0.679T^3 \text{ cal/deg/mole}, \qquad 1.48°\text{K}\geqslant T\geqslant 0°\text{K}.$$

For the upper portion of the curve

$$\bar{S}_{4n}=2.2\ln T-0.135-R\ln(1-x_3),$$

while for the lower part $\bar{S}_{4n}=0.2263T^3-R\ln(1-x_3)$. This modified cubic behavior seems to give the closest approximation to the experimental values for any of the $\bar{S}_{4s}=0$ cases.

Cases for which $\bar{H}_{4s}=0$

Engel and Rice,[3] in examining ideal solutions, assumed that $\bar{H}_{4s}$ vanishes, rather than $\bar{S}_{4s}$, and transformed (6) to read

$$dT_\lambda/dx_3 = DT_\lambda/\bar{H}_{4n,\lambda}. \tag{9}$$

The problem of determining the lambda-temperature shift, then, is that of expressing $\bar{H}_{4n}$ as a function of x_3 and T_λ.

Scatchard has calculated[7] for the model solution the heat of mixing, a quantity in general different from the excess free energy because of the volume change on mixing. Discarding compressibility terms, one has approximately $H^M=E_v{}^M+V^MT\alpha_0/\beta_0$ where α_0 is the coefficient of thermal expansion for the isolated components. Assuming that $\alpha_0=\alpha_4$, the value for He^4, and differentiating, one has $\bar{H}_{4n}=\bar{H}_{4n}{}^0+V_4af_3{}^2(1+\alpha_4T)$. For the very small values of T considered, α_4 is about 0.03 deg^{-1}. Thus it appears that, if one discards the thermal expansion term, $\bar{H}_{4n}=\bar{H}_{4n}{}^0+V_4af_3{}^2$, and the excess free energy and the enthalpy of mixing will, for the special circumstances considered, be alike. This treatment of the enthalpy is rather rough, and its best justification is perhaps the simplicity of the concentration dependence. Certainly the assumption of a zero heat of mixing is no bolder than the above. So both zero and nonzero heats of mixing are to be considered along with the three types of temperature behavior used in the previous section. There are, then, six subcases under the general case $\bar{H}_{45}=0$.

For the zero heat of mixing and zero heat capacity $\bar{H}_{4n}=2.95$ cal/mole, the experimental value for $\bar{H}_{4n}{}^0$ at the normal lambda-point. Integration of the T_λ equation for this value gives results shown as curve A; the points are not identical with those of the previous section presented as curve A, but are so close that a single graph is sufficient to represent both sets of results.

A linear C_p and zero heat of mixing produce $\bar{H}_{4n}=1.21+0.3625T_\lambda{}^2$. Integration of (9) for this set of assumptions yields the results appearing as curve C.

The modified cubic C_p and zero heat of mixing give $\bar{H}_{4n}=2.2T_\lambda-1.868$ between the normal lambda-point and 1.48°K and $\bar{H}_{4n}=0.1698T_\lambda{}^4+0.5736$ below 1.48°K. Curve B represents the lambda-temperatures obtained.

In order to modify the above enthalpies in accordance with the nonzero heat of mixing described, one has only to add to each expression for $\bar{H}_{4n}$ the term $V_4af_3{}^2$, that is, $2.76f_3{}^2$. The zero heat capacity assumption then will give curve F. The linear C_p will produce curve A, and the modified cubic results in curve G. Again it should be noted that the points for $C_p=0$ and $C_p=AT$ do not fall precisely on curves F and A, but they are so close that separate curves are not desirable in the figure.

Solution of the Differential Equations

Constants of integration appearing in solutions of the lambda-point shift equations can be determined from the condition that T_λ has its normal value, 2.19°K, when there is no He^3, that is, when x_3 is zero. Each of the differential equations was solved by numerical integration, T_λ being determined for $0\leqslant x_3\leqslant 1$ in steps of 0.02 in x_3. The values for curve (B), the closest to the experimental points, are represented empirically by

$$T_\lambda=2.19/[1-3.397\log_{10}(1-x_3)]+0.04175x_3+0.2195x_3{}^2-0.471x_3{}^3$$

for $0\leqslant x_3\leqslant 0.93$; the largest deviation of this equation from the integration values is 0.005°. For solutions more concentrated than 0.93, the deviations are too large for use of the equation and integration values are quoted here as 0.276°K for $x_3=0.94$ and 0.222°K for $x_3=0.96$, respectively.

V. COMPARISON OF MODEL AND EXPERIMENTAL BEHAVIOR

Precise measurement of equilibrium total pressure considered in Sec. III offers a means of determining the degree of success of the non-ideality theory without involving any of the speculations of Sec. IV. If one could obtain such pressures and vapor compositions, the actual values of the excess potentials could be found and could then be used in the solution of problems appearing in Sec. IV. As it is, one can but check a number of assumptions at once by examining the experimental T_λ *vs* x_3 curve. The direction of deviation from Raoult's law is known and the non-ideality model considered does offer agreement. So the lambda-point properties of the model mixture can be at least a general guide to the success of some superfluid property assumptions in the T_λ treatment.

For the model considered, better results are obtained for assumption of vanishing $\bar{H}_{4s}$ than for vanishing $\bar{S}_{4s}$. The entire group of $\bar{S}_{4s}$ curves (E, F, and A) lies a considerable distance to one side of the experimental curve, while the $\bar{H}_{4s}$ group in general lies much closer and provides one member (curve B) giving an excellent representation of the experimental points. Comparison of C_p models shows that, for any given situation, the modified cubic behavior gives better agreement than the linear. The assumption of temperature invariance for entropy and enthalpy leads to the greatest departure from agreement for any basic choice. This feature would seem a considerable improvement over the ideal treatment in which at least one of the $C_p=0$ curves lies very near the experimental values.

Within the group for which $\bar{H}_{4s}$ is zero, the results for vanishing mixing enthalpy of He^4 are better than for the composition dependent value (e.g., compare curves B and G). This fact is a reminder that (2) and (3) do not provide the whole picture of non-ideality. Finally, the properties of the simple model considered here seem to support the idea that, for the actual solution, the heat of mixing of He^3 and He^4 is very small, that $\bar{H}_{4s}=0$, and that the heat capacity of normal He^4 goes to zero at $T=0$°K in a manner similar to that of Engel and Rice's modified cubic relation.