Revised thermodynamic relations for λ transitions in mixtures III. The saturated vapour of solutions of ^{3}He in liquid ^{4}He below their λ temperatures

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Abstract. On the basis of the discussion in I of the possibility of obtaining Pippard's relations involving the dependence of a λ temperature on the composition of mixtures, together with standard relations for liquid–vapour equilibria generally, comparisons are made between the behaviour of the specific heat of solutions of ^{3}He in liquid ^{4}He and (a) the change in the composition of the saturated vapour as the λ temperature is approached, and (b) the change in the slope of the vapour pressure curve as the λ temperature is approached.

1. Introduction

Since the first pioneering attempt by Stout (1948 and 1949) to apply the thermodynamic theory of λ transitions to mixtures of liquid ^{4}He and ^{3}He, many further investigations based on the hypothesis of a second order transition (in Ehrenfest's sense) have been carried out and applied to experimental data (De Boer and Gorter 1950, 1952, Esel'son *et al* 1950, Esel'son *et al* 1958, De Bruyn Ouboter *et al* 1959, Roberts and Swartz 1960, De Bruyn Ouboter and Beenakker 1961, Sanikidze 1962, Le Pair *et al* 1962, Le Pair *et al* 1965). These investigations have presented and applied various relations between postulated discontinuities in the specific heat and consequent discontinuities in such properties as (a) the slopes $\partial p/\partial T$ of freezing and boiling curves for a liquid mixture of given composition, (b) the dependence of the composition of the saturated vapour on temperature, and (c) the slope of the boundary of the miscibility gap at the point of its intersection with the λ curve. A review has been given by Taconis and De Bruyn Ouboter (1964).

Some graphical comparisons (cf I) will be presented here in which corresponding accounts are based on the hypothesis that there are no (finite) discontinuities. This more realistic assumption was considered briefly by Sanikidze (1962).

2. Change in the composition of the saturated vapour as the λ temperature is approached

Consider a liquid mixture of fixed composition. If the vapour behaves approximately as a classical ideal gas, having a density much less than that of the liquid, then as the temperature varies the partial pressures of the two species vary according to the

generalized Clapeyron–Clausius equations

$$RT^2\left(\frac{\partial \ln p_3}{\partial T}\right)_{x_3^l} \simeq H_3^{0g} - \tilde{H}_3^l$$

$$RT^2\left(\frac{\partial \ln p_4}{\partial T}\right)_{x_3^l} \simeq H_4^{0g} - \tilde{H}_4^l$$

where the subscripts 3 and 4 denote respectively ^3He and ^4He, the superscripts g and 1 the vapour and liquid phases, ^{0} a pure substance, and the tilde a partial molar quantity. (x denotes a mole fraction, and H enthalpy.) From these two equations, it follows that

$$RT^2\left(\frac{\partial \ln(p_3/p_4)}{\partial T}\right)_{x_3^l} \simeq H_3^{0g} - H_4^{0g} - \tilde{H}_3^l + \tilde{H}_4^l.$$

By a certain choice of the zeros of the H, the right hand side can be reduced to $-(\tilde{H}_3^l - \tilde{H}_4^l)$ and then the expression becomes

$$R\left(\frac{\partial \ln(p_3/p_4)}{\partial(1/T)}\right)_{x_3^l} \simeq \tilde{H}_3^l - \tilde{H}_4^l.$$

Therefore, in the 'ideal' approximation prescribed, the left hand side (trivially obtainable from the slope of a graph of the logarithm of the molar ratio in the saturated vapour, plotted against the reciprocal of the absolute temperature) may be utilized in any comparison requiring values of $\tilde{H}_3^l - \tilde{H}_4^l$.

Now under comparison (i) of I, it is to be examined how closely, for various temperatures in the vicinity of a λ transition, $\tilde{H}_3^l - \tilde{H}_4^l$ approximates to

$$\text{constant} + \left(-\frac{\partial T_\lambda}{\partial x_3^l}\right)_p C_p^l$$

(where C_p^l will approximate to the measured C_{sat}^l for liquid in contact with its saturated vapour). Thus values of

$$R\left(\frac{\partial \ln(p_3/p_4)}{\partial(1/T)}\right)_{x_3^l}$$

for various temperatures, at a fixed composition, are to be plotted against the corresponding values of C_{sat}^l, and the plot is to be examined for linearity, and its slope compared with $(-\partial T_\lambda/\partial x_3^l)_p$ (or rather with $-dT_{\lambda sat}/dx_3^l$).

Values used for the composition of the saturated vapour have been taken from the experimental results of Sommers (1952) and Wansink *et al* (1956). The data of Esel'son and Berezniak (1956) gave much more scatter in the plots of $\ln(p_3/p_4)$ against $1/T$, and were used no further. These data have previously been recognized as less reliable than the others: De Bruyn Ouboter *et al* (1959) concluded that they failed to satisfy a thermodynamic test for consistency (the test of Redlich and Kister (1948) and Coulson and Herington (1948); in fact only an *approximate* test), while Sreedhar and Daunt (1960) and especially Sydoriak and Roberts (1960) have commented on sources of error in the experiments.

Values of C_{sat}^l were taken from the measurements of Dokoupil *et al* (1954), Dokoupil *et al* (1959), and De Bruyn Ouboter *et al* (1960).

The plots (figure 1) exhibit satisfactory linearity. For the more dilute solutions of ^{3}He, the slopes (1·5 K for $x_3^1 = 0.01$, and 1·4 K for $x_3^1 = 0.025$) are in good agreement with the experimental value of $-dT_{\lambda sat}/dx_3^1$. For less dilute solutions, however, the slopes are decidedly smaller (0·9 K for $x_3^1 = 0.0466$, and 0·8 K for $x_3^1 = 0.094$), and disagree with the experimental value of $-dT_{\lambda sat}/dx_3^1$.
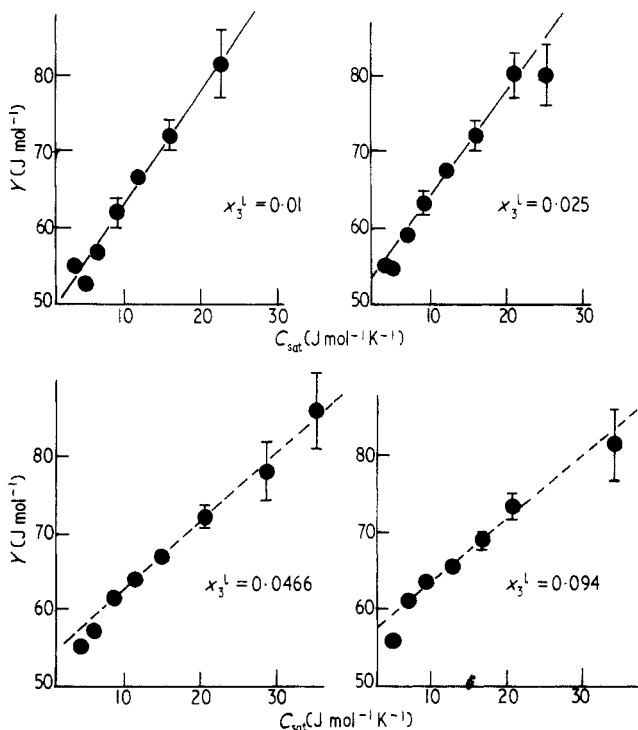

Figure 1. Plots based on the change in the composition of the saturated vapour as the λ temperature is approached.

Ordinate: $Y \equiv R\left(\dfrac{\partial \ln(p_3/p_4)}{\partial(1/T)}\right)_{x_3^1}$

Points over a range of temperature from 1·4 K upwards.

Such a situation, with agreement only for the more dilute solutions, was envisaged in I as likely to arise when a peak in the specific heat becomes markedly lower with change of composition (cf figures 2 and 3 of I), and for mixtures of ^{4}He with ^{3}He the peak certainly becomes markedly lower as the proportion of ^{3}He increases (Dokoupil *et al* 1959, De Bruyn Ouboter *et al* 1960). The argument given by Rice (1967) indeed indicates that for mixtures C_p will be expected to become infinite (at the most) at isolated points of the xT plane, and not along a curve therein.

3. Change in the slope of the vapour pressure curve as the λ temperature is approached

For a liquid mixture of fixed composition, if the vapour behaves approximately as a classical ideal gas with a density much less than that of the liquid, then, according to

the generalized Clapeyron–Clausius equations written in § 2, the total pressure of the saturated vapour varies with temperature according to the equation

$$\left(\frac{\partial p_{sat}}{\partial T}\right)_{x_3^l} = \left(\frac{\partial}{\partial T}\right)_{x_3^l}(p_3 + p_4) \simeq p_3\frac{H_3^{0g} - \tilde{H}_3^l}{RT^2} + p_4\frac{H_4^{0g} - \tilde{H}_4^l}{RT^2}.$$

By choosing zeros of the H as above, this reduces to

$$\frac{(p_3 + p_4)(H_4^{0g} - \tilde{H}_4^l) - p_3(\tilde{H}_3^l - \tilde{H}_4^l)}{RT^2}$$

giving

$$RT^2\left(\frac{\partial \ln p_{sat}}{\partial T}\right)_{x_3^l} \simeq H_4^{0g} - \tilde{H}_4^l - x_3^g(\tilde{H}_3^l - \tilde{H}_4^l)$$

$$= (H_4^{0g} - H_4^{01}) - x_3^g(\tilde{H}_3^l - \tilde{H}_4^l) - (\tilde{H}_4^l - H_4^{01}).$$

Here, the first term on the right hand side approximates to $RT^2 d \ln p_4^0/dT$ (where p_4^0 is the saturated vapour pressure of pure ^4He); while in the third term, by use of the Gibbs–Duhem equation for the $\tilde{H}$

$$x_3^l \, d\tilde{H}_3^l + x_4^l \, d\tilde{H}_4^l \simeq 0 \qquad \text{for constant } T$$

$\tilde{H}_4^l$ can be seen to be approximately equal to

$$H_4^{01} - \int_{x_3^l = 0}^{x_3^l} x_3^l \, d(\tilde{H}_3^l - \tilde{H}_4^l)$$

(the integral being taken along an isothermal path).

It follows, on taking the first term over to the left hand side and reversing the signs of both sides, that:

$$-RT^2\left(\frac{\partial \ln(p_{sat}/p_4^0)}{\partial T}\right)_{x_3^l} \simeq x_3^g(\tilde{H}_3^l - \tilde{H}_4^l) - \int_{x_3^l = 0}^{x_3^l} x_3^l \, d(\tilde{H}_3^l - \tilde{H}_4^l)$$

or

$$Z \equiv \frac{1}{x_3^g}R\left(\frac{\partial \ln(p_{sat}/p_4^0)}{\partial(1/T)}\right)_{x_3^l} \simeq (\tilde{H}_3^l - \tilde{H}_4^l) - \frac{1}{x_3^g}\int_{x_3^l = 0}^{x_3^l} x_3^l \, d(\tilde{H}_3^l - \tilde{H}_4^l).$$

Now, as before, under comparison (i) of I, it is to be considered how nearly $\tilde{H}_3^l - \tilde{H}_4^l$ may be replaced by

$$\text{constant} + \left(-\frac{\partial T_\lambda}{\partial x_3^l}\right)_P C_p^l$$

(or by a similar expression in terms of C_{sat}^l).

Therefore, values of the left hand side Z (trivially obtainable from the quotient of x_3^g into the slope of a graph of $\ln(p_{sat}/p_4^0)$ against the reciprocal of the absolute temperature) are to be compared with

$$\text{constant} + \left(-\frac{dT_{\lambda sat}}{dx_3^l}\right)C_{sat}^l - \frac{1}{x_3^g}\int_{x_3^l = 0}^{x_3^l} x_3^l\left(-\frac{dT_{\lambda sat}}{dx_3^l}\right)dC_{sat}^l$$

which is to be equated to

$$\text{constant} + \left(-\frac{dT_{\lambda\text{sat}}}{dx_3^l} \right) \left\{ C_{\text{sat}}^l - \frac{x_3^l}{x_3^g} \left(C_{\text{sat}}^l - \frac{1}{x_3^l} \int_0^{x_3^l} C_{\text{sat}}^l \, dx_3^l \right) \right\}.$$

The left hand side Z, then, is to be plotted against the quantity in braces (Γ, say).

For the purpose of this comparison, the determinations of the pressure of the saturated vapour by Sydoriak and Roberts (1960) and Sreedhar and Daunt (1960) have been preferred as being more reliable than those of earlier investigators. The results of Sreedhar and Daunt are of interest as distinctly suggesting that there is *no* discontinuity in the slope of the vapour pressure curve at T_λ, but only a relatively rapid change of slope.

The plots (figure 2) exhibit reasonable linearity, but the slopes (0·8 K for $x_3^l = 0·04$, and 1·0 K for $x_3^l = 0·30$) are distinctly less than $-dT_{\lambda\text{sat}}/dx_3^l$. (There is, however, some indication that points for temperatures *above* T_λ would give a slope greater than $-dT_{\lambda\text{sat}}/dx_3^l$, thus 'bracketing' the slope of the λ curve between those of Pippard-like plots for temperatures above and below T_λ—as envisaged in I.)
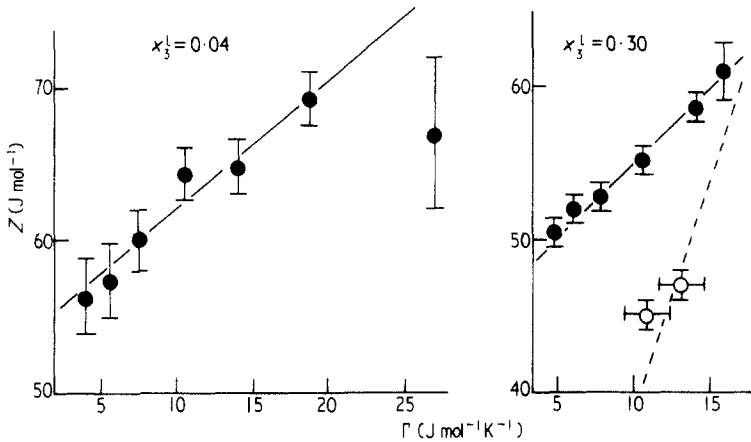

Figure 2. Plots based on the change in the slope of the vapour pressure curve as the λ temperature is approached.

Ordinate: $Z \equiv \dfrac{1}{x_3^g} R \left(\dfrac{\partial \ln(p_{\text{sat}}/p_4^0)}{\partial(1/T)} \right)_{x_3^l}$

Abscissa: $\Gamma \equiv C_{\text{sat}}^l - \dfrac{x_3^l}{x_3^g} \left(C_{\text{sat}}^l - \dfrac{1}{x_3^l} \int_0^{x_3^l} C_{\text{sat}}^l \, dx_3^l \right)$

Points over a range of temperature from 1·4 K upwards for $x_3^l = 0·04$, from 1·2 K upwards for $x_3^l = 0·30$. Open circles are points for temperatures above T_λ.

There is in principle no need to restrict attention to the case in which the vapour may be treated as if a classical ideal gas, with a density much less than that of the liquid. In any attempt at a completely general treatment, the exact relation

$$\left(\frac{\partial p_{\text{sat}}}{\partial T} \right)_{x_3^l} = \frac{(S^g - S^l) - (x_3^g - x_3^l)(\tilde{S}_3^l - \tilde{S}_4^l)}{(V^g - V^l) - (x_3^g - x_3^l)(\tilde{V}_3^l - \tilde{V}_4^l)}$$

(where S^g, S^l, V^g, V^l are the entropies per mole and volumes per mole for the two phases)

would be used as starting point, and, under comparison (ii) of I and a variant of comparison (i), the quantities to be considered for how nearly they may replace the differences $\tilde{V}^1_3 - \tilde{V}^1_4$ and $\tilde{S}^1_3 - \tilde{S}^1_4$ would be

$$\text{constant} + \left(-\frac{\partial T_\lambda}{\partial x^1_3}\right)_p \left(\frac{\partial V^1}{\partial T}\right)_{p,x^1_3}$$

and

$$\text{constant} + \left(-\frac{\partial T_\lambda}{\partial x^1_3}\right)_p \frac{C^1_p}{T}.$$

This expression for $(\partial p_{sat}/\partial T)_{x^1_3}$, if appreciably different from the preceding, would contain a second 'anomalous' term in the denominator, instead of one in the numerator alone.

An exactly similar expression would apply to the slope of the freezing curve. It would merely be necessary to replace each quantity referring to the vapour by the corresponding quantity for the solid. It would be in this context that the denominator could be of particular importance.

Similarly, the dependence of boiling point on composition could be represented by the exact relation

$$\left(\frac{\partial T_b}{\partial x^1_3}\right)_p = -\left\{\left(\frac{\partial \mu^1_3}{\partial x^1_3}\right)_{T,p} + \left(\frac{\partial \mu^1_4}{\partial x^1_4}\right)_{T,p}\right\}\left(\frac{S^g - S^1}{x^g_3 - x^1_3} - (\tilde{S}^1_3 - \tilde{S}^1_4)\right)^{-1}$$

and then, under comparison (vi) of I, what is to be considered is how nearly the numerator may be replaced by

$$\text{constant} + \left(-\frac{\partial T_\lambda}{\partial x^1_3}\right)_p (\tilde{S}^1_3 - \tilde{S}^1_4)$$

(with a possible further replacement in terms of C^1_p).

An exactly similar discussion could be made of the dependence of the freezing point on composition. A similar discussion of the boundary of the miscibility gap, near its intersection with the λ curve, would be appropriate if this intersection were to lie away from the critical solution temperature. However, it appears (Graf *et al* 1967) that the intersection occurs *at* the critical solution temperature, coinciding with the ordinary critical point for partial miscibility.

References

Coulson E A and Herington E F G 1948 *Trans. Faraday Soc.* 44 629–36
De Boer J and Gorter C J 1950 *Physica* 16 225–38
—— 1952 *Physica* 18 565–8
De Bruyn Ouboter R and Beenakker J J M 1961 *Physica* 27 219–29, 1074–82
De Bruyn Ouboter R, Beenakker J J M and Taconis K W 1959 *Physica* 25 1162–76
De Bruyn Ouboter R, Taconis K W, Le Pair C and Beenakker J J M 1960 *Physica* 26 853–88
Dokoupil Z, Kapadnis D G, Sreeramurty K and Taconis K W 1959 *Physica* 25 1369–75
Dokoupil Z, Van Soest G, Wansink D H N and Kapadnis D G 1954 *Physica* 20 1181–8
Esel'son B N and Berezniak N G 1956 *Sov. Phys.–JETP* 3 568–79 (1956 *Zh. eksp. teor. Fiz.* 30 628–39)
Esel'son B N, Kaganov M I and Lifshitz I M 1958 *Sov. Phys.–JETP* 6 719–26 (1958 *Zh. eksp. teor. Fiz.* 33 936–44)
Esel'son B N, Lazarev B G and Lifshitz I M 1950 *Zh. eksp. teor. Fiz.* 20 748–58

Graf E H, Lee D M and Reppy J D 1967 *Phys. Rev. Lett.* **19** 417–9

Le Pair C, Taconis K W, De Bruyn Ouboter R and Das P 1962 *Physica* **28** 305–6

Le Pair C *et al* 1965 *Physica* **31** 764–812

Redlich O and Kister A T 1948 *Ind. Engng Chem.* **40** 345–8

Rice O K 1967 *Phys. Rev. Lett.* **19** 295–7

Roberts T R and Swartz B K 1960 *Proc. 2nd Symp. on Liquid and Solid ³He* (Ohio: Ohio State University)
     p 158

Sanikidze D G 1962 *Sov. Phys.–JETP* **15** 922–3 (1962 *Zh. eksp. teor. Fiz.* **42** 1330–2)

Sommers H S Jr. 1952 *Phys. Rev.* **88** 113–27

Sreedhar A K and Daunt J G 1960 *Phys. Rev.* **117** 891–6

Stout J W 1948 *Phys. Rev.* **74** 605–9

—— 1949 *Phys. Rev.* **76** 864–5

Sydoriak S G and Roberts T R 1960 *Phys. Rev.* **118** 901–12

Taconis K W and De Bruyn Ouboter R 1964 *Progress in Low Temperature Physics* vol 4 (Amsterdam: North
     Holland pp 38–96

Wansink D H N, Taconis K W and Staas F A 1956 *Physica* **22** 449–64