

Revised thermodynamic relations for lambda transitions in mixtures. I. Examination in terms of properties generally relevant

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Revised thermodynamic relations for λ transitions in mixtures

I. Examination in terms of properties generally relevant

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Abstract. It is proposed that thermodynamic relations to be used for λ transitions in mixtures will normally follow the lines of Pippard's relations for λ transitions in pure substances. The relations given by Stout, treating C_p as finite but discontinuous, will usually be irrelevant.

1. Introduction

For λ transitions in mixtures, the effect of change of composition was treated by Stout (1948) on the hypothesis that what is involved is a transition of the second order in Ehrenfest's sense. That is, it was assumed that C_p , the coefficient of expansion, and the isothermal compressibility, were all three finite but discontinuous at the λ temperature. The λ transition in isotopic mixtures of ^3He with ^4He has been considered in such terms (Stout 1948, De Bruyn Ouboter and Beenakker 1961 and Le Pair *et al* 1965).

However, it is nearly always more realistic (Tisza 1951) to adopt the hypothesis that C_p is either infinite or else merely very large but continuous. When employed for λ transitions in pure substances, this hypothesis leads to the valuable relations obtained by Pippard (1956 and 1957).

The purpose of the present communication is, as far as such is possible, to obtain relations for λ transitions in mixtures on *this* hypothesis. Such relations would ordinarily be more appropriate than the corresponding relations deduced by Stout (1948).

2. Contours relevant to a thermodynamic treatment of λ transitions in mixtures

For λ transitions in pure substances, Pippard's (1956) relations can be obtained by an argument (Rice 1954 and compare Rice 1967, Wright 1969) in which the basic approximation is made that the slope of the λ line is nearly equal to the slope of neighbouring contours of constant C_p or constant C_p/T , constant coefficient of expansion, etc.

For λ transitions in mixtures, there are two distinct situations to be considered.

In the first (figures 1 and 2), it happens that either for all compositions of the mixture (figure 1) or else for a wide range of compositions (figure 2) C_p rises to a maximum that is either infinite or very high. Over ranges of composition for which this applies, a situation obtains which is analogous to that for pure substances. In a diagram plotted, for constant pressure, with coordinates x_B (the mole fraction of substance B in a mixture

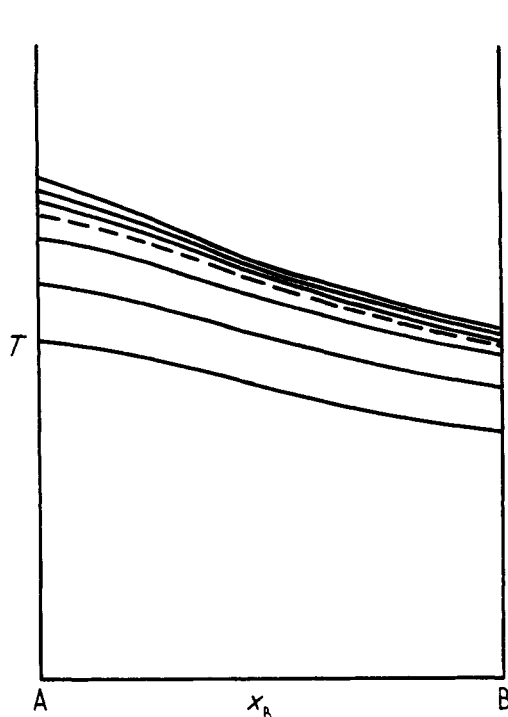


Figure 1. Schematic contours of constant C_p for a λ transition for which the maximum in C_p is very large at all compositions. The broken line denotes the locus of maxima in C_p .

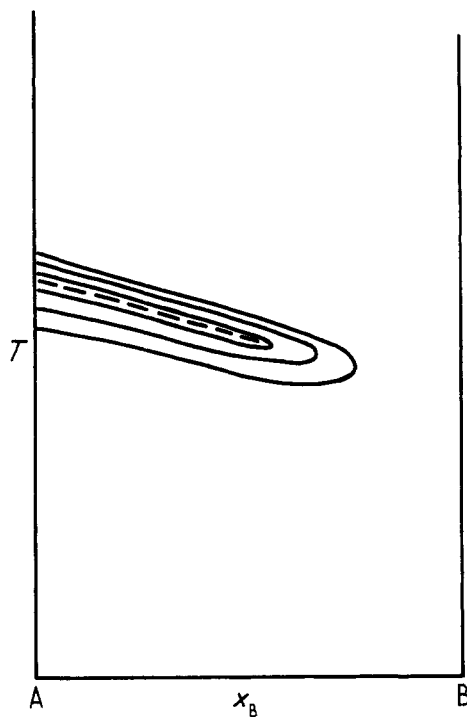


Figure 2. Schematic contours of constant C_p for a λ transition for which the maximum in C_p remains very large for a substantial range of composition (though not for all compositions).

of A and B) and T , the slope of a λ curve approximates to that of neighbouring contours of constant C_p (or C_p/T). That is

$$\left(\frac{\partial T_\lambda}{\partial x_B}\right)_p \simeq \text{values, at neighbouring points, of } \left(\frac{\partial T}{\partial x_B}\right)_{p, C_p}.$$

This is illustrated in figures 1 and 2. As in the case of a pure substance, contours of constant $(\partial V/\partial T)_{p, x_B}$, or of constant $(-\partial V/\partial p)_{T, x_B}$, would likewise serve.

On the other hand (and this seems to be the more usual case), C_p may rise to a maximum whose height varies greatly with the composition of the mixture (figures 3 and 4). It is then to be expected that only over short ranges will contours of constant C_p , or of constant $(\partial V/\partial T)_p$, or of constant $(-\partial V/\partial p)_T$, approximate in slope to the λ curve. The most, then, that could ordinarily be obtained would be an *inequality* requiring that the slope of the λ curve lie between the values taken, at neighbouring points one to one side and the other to the other side, by the slope of a contour of constant C_p (etc).

The slopes of the various contours required are found by straightforward exercises in partial differentiation, analogous to those previously employed for a pure substance. Subject to appropriate conditions of continuity, the slopes are as stated in table 1.

The reason for the inclusion of some of the contours in table 1 is indicated subsequently.

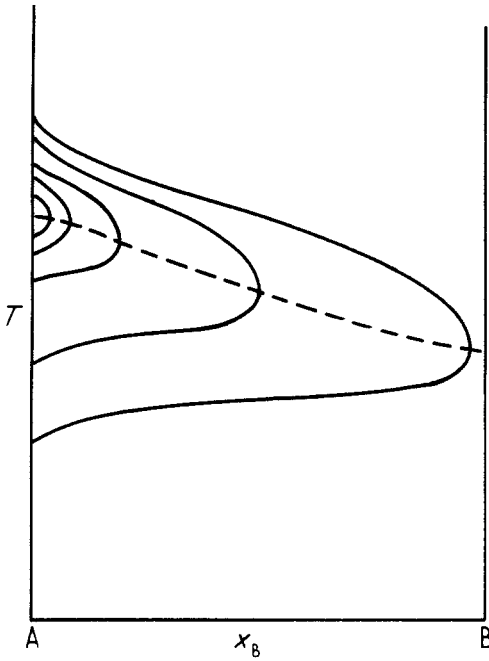


Figure 3. Schematic contours of constant C_p for a λ transition for which the maximum in C_p varies greatly in height as the composition of the mixture varies.

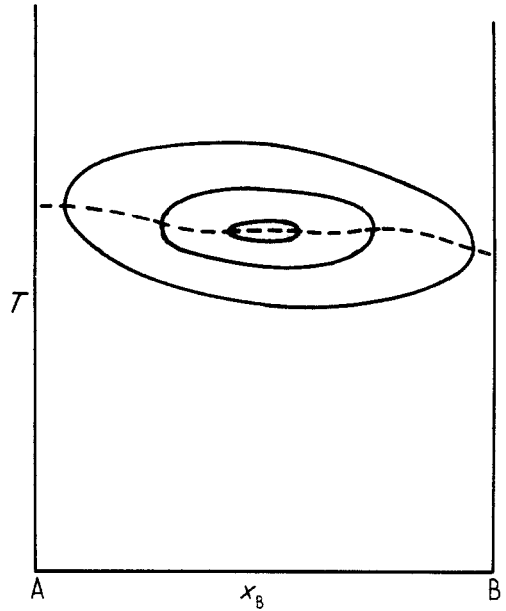


Figure 4. Another conceivable case of a maximum varying greatly in height.

Alternative forms included in table 1 follow from expressions

$$\left(\frac{\partial H}{\partial x_B}\right)_{T,p} = \tilde{H}_B - \tilde{H}_A \quad \left(\frac{\partial V}{\partial x_B}\right)_{T,p} = \tilde{V}_B - \tilde{V}_A$$

in terms of partial molar quantities \tilde{H}_i, \tilde{V}_i .

The λ curves in figures 1 to 4 have been drawn with negative slopes ($(\partial T_\lambda/\partial x_B)_p < 0$) since the usual case is that in which addition of a solute depresses the λ temperature. This is the effect observed, for example, for solutions of ^3He in liquid ^4He (Taconis and De Bruyn Ouboter 1964), krypton in solid methane (Eucken and Bartholomé 1936), parahydrogen in solid ordinary hydrogen (Hill and Ricketson 1954) and copper in nickel (Grew 1934).

3. Relations holding when the λ curve and the contours are almost parallel

In the special situations exemplified in figure 1 and the left hand part of figure 2, the contours of constant C_p are almost parallel to each other and to the λ curve. The same applies to contours of constant $(\partial V/\partial T)_{p,x_B}$ and to contours of constant $(-\partial V/\partial p)_{T,x_B}$.

Consequently, by arguments of the kind used by Rice (1954 and 1967), there result analogues of Pippard's relations:

Table 1. Contours along which, in the $x_B T$ plane, certain quantities are at a fixed pressure constant

The slope of a contour of constant is equal to the negative of the slope of a graph of values of	C_p	$(\partial V/\partial T)_{p,x_B}$	$(-\partial V/\partial p)_{T,x_B}$	$\bar{H}_B - \bar{H}_A$	$\bar{V}_B - \bar{V}_A$	$\bar{S}_B - \bar{S}_A$	
for various	$(\partial \bar{H}/\partial x_B)_{T,p}$ or $\bar{H}_B - \bar{H}_A$	$(\partial V/\partial x_B)_{T,p}$ or $\bar{V}_B - \bar{V}_A$	$(\partial V/\partial x_B)_{T,p}$ or $\bar{V}_B - \bar{V}_A$	$(\partial H/\partial x_B)_{T,p}$ or $\bar{H}_B - \bar{H}_A$	$(\partial V/\partial x_B)_{T,p}$ or $\bar{V}_B - \bar{V}_A$	$(\partial S/\partial x_B)_{T,p}$ or $\bar{S}_B - \bar{S}_A$	$-\left(\frac{\partial}{\partial x_B}\right)_{T,p} (\mu_B - \mu_A)$
at fixed	temperatures	temperatures	pressures	compositions	compositions	compositions	temperatures
plotted against the	pressure and composition	pressure and composition	temperature and composition	temperature and pressure	temperature and pressure	temperature and pressure	pressure and composition
corresponding values of	C_p	$(\partial V/\partial T)_{p,x_B}$	$(\partial V/\partial T)_{p,x_B}$	C_p	$(\partial V/\partial T)_{p,x_B}$	C_p/T	$\bar{S}_B - \bar{S}_A$

(i) In the vicinity of a λ transition, for various temperatures at a fixed pressure and composition

$$\tilde{H}_B - \tilde{H}_A \simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial x_B} \right)_p C_p.$$

(ii) In the vicinity of a λ transition, for various temperatures at a fixed pressure and composition

$$\tilde{V}_B - \tilde{V}_A \simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial x_B} \right)_p \left(\frac{\partial V}{\partial T} \right)_{p, x_B}.$$

(iii) In the vicinity of a λ transition, for various pressures at a fixed temperature and composition

$$\tilde{V}_B - \tilde{V}_A \simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial x_B} \right)_p \left(\frac{\partial V}{\partial T} \right)_{p, x_B}.$$

Since C_p becomes very large as a λ transition is approached, relation (i) requires that $\tilde{H}_B - \tilde{H}_A$ passes either through a maximum (if $(\partial T_\lambda / \partial x_B)_p$ is negative) or through a minimum (if $(\partial T_\lambda / \partial x_B)_p$ is positive), unless $(\partial T_\lambda / \partial x_B)_p$ is extremely close to zero. The occurrence of such maxima or minima suggests that the λ curve might be almost parallel to neighbouring contours of constant $\tilde{H}_B - \tilde{H}_A$. If this is so, then, using the relations of table 1:

(iv) In the vicinity of a λ transition, for various compositions at a fixed temperature and pressure

$$\tilde{H}_B - \tilde{H}_A \simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial x_B} \right)_p C_p.$$

Similarly, by considering cases where $(\partial V / \partial T)_{p, x_B}$ becomes either large and positive or large and negative, it is seen that save in exceptional circumstances there will be either a maximum or a minimum in $\tilde{V}_B - \tilde{V}_A$. The λ curve might then be almost parallel to neighbouring contours of constant $\tilde{V}_B - \tilde{V}_A$, whence it would follow that:

(v) In the vicinity of a λ transition, for various compositions at a fixed temperature and pressure

$$\tilde{V}_B - \tilde{V}_A \simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial x_B} \right)_p \left(\frac{\partial V}{\partial T} \right)_{p, x_B}.$$

For dilute solutions of B in A, variants of these last two relations could be obtained by noting that, for a dilute solution, a maximum in $\tilde{H}_B - \tilde{H}_A$ or $\tilde{V}_B - \tilde{V}_A$ necessarily implies a maximum in \tilde{H}_B or \tilde{V}_B . Contours of constant \tilde{H}_B , or of constant \tilde{V}_B , could then be considered.

The set of relations still contains no analogue of the first forms given by Stout (1948). Such would be obtained by invoking contours of constant $\tilde{S}_B - \tilde{S}_A$:

(vi) In the vicinity of a λ transition, for various temperatures at a fixed pressure and composition

$$- \left\{ \left(\frac{\partial \mu_B}{\partial x_B} \right)_{T, p} + \left(\frac{\partial \mu_A}{\partial x_A} \right)_{T, p} \right\} \simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial x_B} \right)_p (\tilde{S}_B - \tilde{S}_A).$$

There would also be obtained:

(vii) In the vicinity of a λ transition, for various compositions at a fixed temperature and pressure

$$\tilde{S}_B - \tilde{S}_A \simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial x_B} \right)_p \frac{C_p}{T}.$$

Where relations (iv), (v) and (vii) are applicable, they may be replaced by equivalent relations expressed in terms of activities a_i or activity coefficients γ_i .

The first two give

$$\begin{aligned} \text{(iv')} \quad -RT^2 \left(\frac{\partial}{\partial T} \right)_{p, x_B} \ln \frac{a_B}{a_A} &= -RT^2 \left(\frac{\partial}{\partial T} \right)_{p, x_B} \ln \frac{\gamma_B}{\gamma_A} \\ &\simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial x_B} \right)_p C_p. \end{aligned}$$

$$\begin{aligned} \text{(v')} \quad RT \left(\frac{\partial}{\partial p} \right)_{T, x_B} \ln \frac{a_B}{a_A} &= RT \left(\frac{\partial}{\partial p} \right)_{T, x_B} \ln \frac{\gamma_B}{\gamma_A} \\ &\simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial x_B} \right)_p \left(\frac{\partial V}{\partial T} \right)_{p, x_B}. \end{aligned}$$

Similarly, in (vi), the left hand side may be equated to

$$-RT \left(\frac{\partial}{\partial x_B} \right)_{T, p} \ln \frac{a_B}{a_A} = -RT \left\{ \frac{1}{x_B} - \frac{1}{x_A} + \left(\frac{\partial}{\partial x_B} \right)_{T, p} \ln \frac{\gamma_B}{\gamma_A} \right\}.$$

For an ideal dilute solution of a gas B in a liquid or solid A exhibiting a λ transition, an alternative form of (i) can be given in terms of the Henry's law coefficient for the solubility of B

$$f_B \equiv \frac{x_B}{p_B}$$

where p_B is the partial pressure of B in the vapour in equilibrium with the condensed phase.

In the vicinity of a λ transition for an ideal dilute solution of B in A, for various temperatures at a fixed pressure

$$H_B^\ddagger + RT^2 \frac{d \ln f_B}{dT} - H_A^0 \simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial x_B} \right) C_p$$

where H_B^\ddagger is the value of H per mole of gaseous B, and H_A^0 is the value of H per mole for pure liquid or solid A. The values of C_p may be taken to be those of pure A.

4. The case of peaks of greatly varying height, when the ' λ curve' and the contours are not even approximately parallel

The more usual situation for λ transitions in mixtures seems to be that, exemplified in particular in figure 3, wherein the peak in C_p varies drastically as the composition alters, and the ' λ -curve' and the contours are not even approximately parallel.

For such cases, the above relations would be replaced by corresponding inequalities. For example, for the situation exemplified in figure 3, plots of $\tilde{V}_B - \tilde{V}_A$ against $(\partial V/\partial T)_{p,x_B}$ would consist of points constituting two curves probably quite different in slope. One would give the slopes of contours to one side of the 'λ curve', and the other the slopes of contours to the other side.

Such plots, while capable of furnishing only approximate upper and lower bounds to the slope of a 'λ curve', could give at least qualitative information on the effect of composition on the height of the peak. If the two 'branches' of a contour of constant C_p seem to be approaching each other on moving to the right, then, as can be seen from a simple sketch, the height of a finite peak in C_p is decreasing towards the right.

While such an application might sometimes be of use, it must be borne in mind that the experimental data available will often already consist of measurements of C_p as a function of temperature and composition.

5. Some exact relations for finite peaks

Especially when considering mixtures of two substances only one of which exhibits a peak in C_p , maxima in C_p may often be associated with no discontinuity either in C_p or in any of its derivatives. A 'λ curve' is then the locus of points at which, for given pressure and composition, C_p passes through a maximum; and so is a locus of points at which $(\partial C_p/\partial T)_{p,x_B} = 0$. That is, it is, exactly, a contour of constant $(\partial C_p/\partial T)_{p,x_B}$. Thus

$$\left(\frac{\partial T_\lambda}{\partial x_B}\right)_p = -\frac{\partial^2 C_p}{\partial x_B \partial T} / \frac{\partial^2 C_p}{\partial T^2}$$

(where this relation is exact). The crossed second derivatives being continuous, it follows that

$$\left(\frac{\partial T_\lambda}{\partial x_B}\right)_p = \left(\frac{\partial}{\partial T}\right)_{p,x_B} (\tilde{C}_{pB} - \tilde{C}_{pA}) / \left(-\frac{\partial^2 C_p}{\partial T^2}\right)_{p,x_B}$$

In principle, though almost certainly not in practice, this might be obtainable as the slope of a graph of $\tilde{C}_{pB} - \tilde{C}_{pA}$ against $(-\partial C_p/\partial T)_{p,x_B}$, plotting the corresponding values of these quantities, for a fixed pressure and composition, for various temperatures around the top of the peak in C_p .

Similarly, relations (table 2) may be formulated on the basis of treating the 'λ curve' as the locus of maxima in other quantities than C_p . For peaks which are not very sharp, a 'λ curve' so defined is not necessarily coincident with the 'λ curve' defined as the locus of maxima in C_p . Various aspects of such 'fuzziness' have been expressed by Giauque *et al* (1965).

5.1. Initial slope of the λ curve

The relation given above, for the slope of the λ curve treated as a contour of constant $(\partial C_p/\partial T)_{p,x_B}$, reduces to a simpler form if only the initial slope is considered—as, for example, when considering the effect of small quantities of an impurity.

Table 2. Exact relations for peaks involving no discontinuities

The locus of maxima, or minima, in	C_p	$(\partial V/\partial T)_{p,x_B}$	$(-\partial V/\partial p)_{T,x_B}$
(maxima, or minima, at fixed pressure and composition) is a contour of constant	$(\partial C_p/\partial T)_{p,x_B}$	$(\partial^2 V/\partial T^2)_{p,x_B}$	$-\partial^2 V/\partial T \partial p$
As such, its slope $\partial T/\partial x_B$ is equal to the negative of	$\frac{\partial^2 C_p/\partial x_B \partial T}{\text{or } (\partial/\partial T)_{p,x_B}(\tilde{C}_{pB} - \tilde{C}_{pA})}$	$\frac{\partial^3 V/\partial x_B \partial T^2}{\text{or } (\partial^2/\partial T^2)_{p,x_B}(\tilde{V}_B - \tilde{V}_A)}$	$-\frac{\partial^3 V/\partial x_B \partial T \partial p}{\text{or } -(\partial^2/\partial T \partial p)(\tilde{V}_B - \tilde{V}_A)}$
divided by	$(\partial^2 C_p/\partial T^2)_{p,x_B}$	$(\partial^3 V/\partial T^3)_{p,x_B}$	$-\partial^3 V/\partial T^2 \partial p$
Alternatively, its slope is equal to the negative of the slope of a graph of values of	$\frac{(\partial C_p/\partial x_B)_{T,p}}{\text{or } \tilde{C}_{pB} - \tilde{C}_{pA}}$	$\frac{\partial^2 V/\partial x_B \partial T}{\text{or } (\partial/\partial T)_{p,x_B}(\tilde{V}_B - \tilde{V}_A)}$	$-\frac{\partial^2 V/\partial x_B \partial p}{\text{or } (-\partial/\partial p)_{T,x_B}(\tilde{V}_B - \tilde{V}_A)}$
for various temperatures at fixed pressure and composition, plotted against the corresponding values of	$\frac{(\partial C_p/\partial T)_{p,x_B}}{\text{or } x_A \left(\frac{\partial \tilde{C}_{pA}}{\partial T} \right)_{p,x_B} + x_B \left(\frac{\partial \tilde{C}_{pB}}{\partial T} \right)_{p,x_B}}$	$\frac{(\partial^2 V/\partial T^2)_{p,x_B}}{\text{or } x_A \left(\frac{\partial^2 \tilde{V}_A}{\partial T^2} \right)_{p,x_B} + x_B \left(\frac{\partial^2 \tilde{V}_B}{\partial T^2} \right)_{p,x_B}}$	$-\partial^2 V/\partial T \partial p$

Table 2—continued

	$\tilde{H}_B - \tilde{H}_A$	$\tilde{V}_B - \tilde{V}_A$	$\tilde{S}_B - \tilde{S}_A$
The locus of maxima, or minima, in (maxima, or minima, at fixed pressure and composition) is a contour of constant	$\tilde{C}_{pB} - \tilde{C}_{pA}$	$(\partial/\partial T)_{p,x_B}(\tilde{V}_B - \tilde{V}_A)$	$(\tilde{C}_{pB} - \tilde{C}_{pA})/T$ $\left. \begin{array}{l} \\ \\ \end{array} \right\} - (\partial^2/\partial T^2)_{p,x_B}(\mu_B - \mu_A)$
As such, its slope $\partial T/\partial x_B$ is equal to the negative of	$(\partial^2 C_p/\partial x_B^2)_{T,p}$ or $(\partial/\partial x_B)_{T,p}(\tilde{C}_{pB} - \tilde{C}_{pA})$	$\partial^3 V/\partial T \partial x_B^2$ or $(\partial^2/\partial T \partial x_B)(\tilde{V}_B - \tilde{V}_A)$	
divided by	$(\partial/\partial T)_{p,x_B}(\tilde{C}_{pB} - \tilde{C}_{pA})$	$(\partial^2/\partial T^2)_{p,x_B}(\tilde{V}_B - \tilde{V}_A)$	
Alternatively, its slope is equal to the negative of the slope of a graph of values of	$(\partial^2 H/\partial x_B^2)_{T,p}$	$(\partial^2 V/\partial x_B^2)_{T,p}$	$-\left(\frac{\partial}{\partial T}\right)_{p,x_B} \left\{ \left(\frac{\partial \mu_A}{\partial x_A}\right)_{T,p} + \left(\frac{\partial \mu_B}{\partial x_B}\right)_{T,p} \right\}$
for various temperatures at fixed pressure and composition, plotted against the corresponding values of	$\tilde{C}_{pB} - \tilde{C}_{pA}$	$\partial^2 V/\partial T \partial x_B$ or $\left(\frac{\partial}{\partial T}\right)_{p,x_B}(\tilde{V}_B - \tilde{V}_A)$	$(\tilde{C}_{pB} - \tilde{C}_{pA})/T$ $-(\partial^2/\partial T^2)_{p,x_B}(\mu_B - \mu_A)$

\tilde{C}_{pA} and C_p both approximate to C_{pA}^0 , the value of C_p for pure A. Further, since each quantity takes the value appropriate to the top of the peak, $(\partial C_{pA}^0 / \partial T)_p$ is to be equated to zero. Thus the slope

$$\left(\frac{\partial T_\lambda}{\partial x_B} \right)_{p, x_B=0} = \left(\frac{\partial \tilde{C}_{pB}^\oplus}{\partial T} \right)_p / \left(- \frac{\partial^2 C_{pA}^0}{\partial T^2} \right)_p$$

where \tilde{C}_{pB}^\oplus is the limiting value of \tilde{C}_{pB} for infinite dilution.

The initial slope is thus determined exclusively by:

- (a) The variation of \tilde{C}_{pB}^\oplus , a property of the solute, with temperature.
- (b) The curvature at the top of the peak for pure substance A.

Since the denominator will always be numerically large, it constitutes a factor tending to make the initial slope small. There being no obvious analogous factor in effects on the height of the peak, it is hardly surprising that small traces of impurity usually have a much more drastic effect on the *height* of the peak than on its position.

The sign of the numerator $(\partial \tilde{C}_{pB}^\oplus / \partial T)_p$ corresponds unambiguously to the sign of the initial slope, since the denominator is always positive. The usual case is that in which addition of a solute depresses the λ temperature (initial slope negative). Then at a temperature equal to the λ temperature of the solvent

$$\left(\frac{\partial \tilde{C}_{pB}^\oplus}{\partial T} \right)_p < 0.$$

While this is the usual case, the reverse situation seems to occur for solutions in liquid sulphur (Scott 1965 and Larkin *et al* 1967).

5.2. Final disappearance of a broadened peak

Addition of successively larger quantities of a substance B can result in a peak first becoming broader and lower, and finally disappearing. The quantity

$$\left(\frac{\partial C_p}{\partial T} \right)_{p, x_B} = x_A \left(\frac{\partial \tilde{C}_{pA}}{\partial T} \right)_{p, x_B} + x_B \left(\frac{\partial \tilde{C}_{pB}}{\partial T} \right)_{p, x_B}$$

is zero both for a maximum and for a minimum in C_p , and disappearance of a maximum will occur at a point where a maximum and a minimum coincide, that is, at a point where

$$\left(\frac{\partial^2 C_p}{\partial T^2} \right)_{p, x_B} = x_A \left(\frac{\partial^2 \tilde{C}_{pA}}{\partial T^2} \right)_{p, x_B} + x_B \left(\frac{\partial^2 \tilde{C}_{pB}}{\partial T^2} \right)_{p, x_B}$$

also is zero.

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