

Pippard relations and critical phenomena in binary liquid mixtures

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MS received 18 April 1974; after revision 10 September 1974

Abstract. The cylindrical approximation originally proposed by Pippard for the λ -transitions in one-component systems is extended to multicomponent systems. The application of the generalised Pippard relations to binary liquid mixtures is considered. The relations for $\text{He}^3 + \text{He}^4$ mixtures are shown to be equivalent to those obtained by earlier workers. The validity of the relation relating specific heat and thermal expansion for binary liquid systems is discussed on the basis of the measurements performed on the system methanol + *n*-heptane. Lack of information on the behaviour of a few quantities prevents a quantitative test of the relation.

Keywords. Pippard relations; multicomponent systems; thermal expansion; specific heat; methanol + *n*-heptane system; critical phenomena.

1. Introduction

The approach to infinitely large values of the various thermodynamic properties such as the specific heat and thermal expansion was originally discussed by Pippard (1956) for a one-component system on the basis of the cylindrical approximation of the entropy and volume surfaces close to a λ -transition. Several other equivalent methods to describe the interrelations among the thermodynamic quantities (Pippard 1956, Buckingham and Fairbank 1961, Tisza 1961, Rice 1967, Zemansky 1968, Wright 1969) have also been developed. During recent years, Pippard relations have been extended to crystalline media (Tisza 1961, Viswanathan 1963, Garland 1964, Janovec 1966), magnetic transitions (Gambhir *et al* 1967, Wright 1972 *c*), ferroelectric transitions (Viswanathan *et al* 1968) and to λ -transitions in mixtures (Wright 1972 *a, b*, Chang 1973). The choice of fields and densities in the thermodynamic description of these phase changes has also been critically discussed by Griffiths and Wheeler (1970).

In multicomponent systems, qualitative and quantitative differences may be expected because of the increased degrees of freedom. Certain features like the applicability of the Pippard relations to two-phase regions and the quantitative relationships between specific heat, thermal expansion and compressibility have remained ambiguous largely because relevant experimental studies on the appropriate systems have been lacking. However, measurements of specific heat and thermal expansion have been recently reported close to critical solution temperature and composition in two binary liquid systems. In view of the availability of such experimental observations, it seems worthwhile to investigate the Pippard relations in multicomponent systems.

2. Generalised Pippard relations

in discussing multicomponent systems, the method followed by Buckingham and Fairbank (1961) to obtain Pippard relations for one-component systems is outlined here. The other equivalent methods also lead to the same final results (Ramachandra 1973).

For a system with C components exhibiting p phases, the total number of variables would be $C + 2$ and the degrees of freedom $C - p + 2$; if the independent variables are denoted by a_1, a_2, \dots, a_f then any state function Z can be expressed in terms of the free variables by the identity

$$dZ = (\partial Z/\partial a_1)_{a_2, \dots, a_f} da_1 + (\partial Z/\partial a_2)_{a_1, a_3, \dots, a_f} da_2 + \dots \\ + (\partial Z/\partial a_f)_{a_1, \dots, a_{f-1}} da_f$$

or

$$\left(\frac{dZ}{da_1}\right) = (\partial Z/\partial a_1)_{a_2, \dots, a_f} + (\partial Z/\partial a_2)_{a_1, a_3, \dots, a_f} (da_2/da_1) + \dots \\ + (\partial Z/\partial a_f)_{a_1, \dots, a_{f-1}} (da_f/da_1) \quad (1)$$

If the thermodynamic variables are chosen in the following manner, $Z \leftrightarrow S$, $a_1 \leftrightarrow T$, $a_2 \leftrightarrow P$, $a_3 \leftrightarrow X_1, \dots, a_f \leftrightarrow X_{C-p}$ then, along the λ -line,

$$(dS/dT)_\lambda = (\partial S/\partial T)_{P, X_1, \dots, X_{C-p}} + (\partial S/\partial P)_{T, X_1, \dots, X_{C-p}} (dP/dT)_\lambda \\ + \sum_{\substack{i=1 \text{ to } C-p \\ j \neq i}} \left(\frac{\partial S}{\partial X_i}\right)_{P, T, \{X_j\}} (dX_i/dT)_\lambda$$

$(dS/dT)_\lambda$, $(dP/dT)_\lambda$ and $(dX_i/dT)_\lambda$ are the slopes along the λ line and hence can be taken as 'constants', that is to say much less temperature-dependent than the divergent quantities like specific heat. This is equivalent to the cylindrical approximation introduced by Pippard (1956).

Writing

$$(\partial S/\partial T)_{P, X_1, \dots, X_{C-p}} = (C_{P, X_1, \dots, X_{C-p}}/T) \\ (\partial S/\partial P)_{T, X_1, \dots, X_{C-p}} = -(\partial V/\partial T)_{P, X_1, \dots, X_{C-p}} = -V\beta_{P, X_1, \dots, X_{C-p}} \\ (dP/dT)_\lambda = \alpha \quad \text{and} \quad (dX_i/dT)_\lambda = \eta_i$$

the above equation can be written as

$$(dS/dT)_\lambda = (C_{P, X_1, \dots, X_{C-p}}/T) - V\beta_{P, X_1, \dots, X_{C-p}} \alpha \\ + \sum_{\substack{i=1 \text{ to } C-p \\ j \neq i}} (\partial S/\partial X_i)_{P, T, \{X_j\}} \eta_i \quad (2)$$

This equation relates specific heat and thermal expansion coefficient.

Substitution of volume V for Z in eq. (1) gives the following relation between thermal expansion coefficient and isothermal compressibility $K_{T, X}$.

$$(dV/dT)_\lambda = V\beta_{P, X_1, \dots, X_{C-p}} - VK_{T, X_1, \dots, X_{C-p}} \alpha \\ + \sum_{i=1 \text{ to } C-p} (\partial V/\partial X_i)_{P, T, \{X_j\}} \eta_i \quad (3)$$

Similarly, substitution of chemical potential μ for Z gives

$$(d\mu/dT)_\lambda = (\partial\mu/\partial T)_{P, x_1, \dots, x_{C-p}} + (\partial\mu/\partial P)_{T, x_1, \dots, x_{C-p}} \alpha + \sum_{\substack{i=1 \text{ to } C-p \\ j \neq i}} (\partial\mu/\partial X_i)_{P, T, \{x_j\}} \eta_i \quad (4)$$

The relations (2), (3) and (4) show that the plot of any one of heat capacity, thermal expansion coefficient, isothermal compressibility, etc., against any other of these quantities must be a straight line asymptotically. If any one of these tends to infinity at the λ -transition then every other quantity must also tend to infinity. Equations of this type have been obtained by many earlier workers. As mentioned above, other alternative approaches to the derivation of these equations are possible (Ramachandra 1973).

3. Pippard relations for different systems

Pippard relations for different systems follow from the above generalization.

For a one-component system in one phase, the number of variables is 3 and the number of degrees of freedom is 2. Choosing the variables $a_1 \leftrightarrow T$, $a_2 \leftrightarrow P$, and taking $Z \leftrightarrow S$ and $Z \leftrightarrow V$, one gets

$$(dS/dT)_\lambda = (C_P/T) - V\beta\alpha \quad \text{and} \quad (dV/dT)_\lambda = V\beta - VK_T \alpha \quad (5)$$

These relations are the same as the relations obtained earlier by Pippard, Buckingham and Fairbank and others.

In the vicinity of λ -transitions in magnetic materials for the one-phase region (*i.e.*, above the critical point) the independent variables may be taken as T , P and H^2 . The following relations are obtained for $Z \leftrightarrow S$, $Z \leftrightarrow V$ and $Z \leftrightarrow \chi$ respectively

$$(dS/dT)_\lambda = (C_{PH}/T) + (\partial S/\partial P)_{TH} (dP/dT)_\lambda + (\partial S/\partial H^2)_{TP} (dH^2/dT)_\lambda \quad (6)$$

$$(dV/dT)_\lambda = (\partial V/\partial T)_{PH} + (\partial V/\partial P)_{TH} (dP/dT)_\lambda + (\partial V/\partial H^2)_{TP} (dH^2/dT)_\lambda \quad (7)$$

$$(d\chi/dT)_\lambda = (\partial\chi/\partial T)_{PH} + (\partial\chi/\partial P)_{TH} (dP/dT)_\lambda + (\partial\chi/\partial H^2)_{TP} (dH^2/dT)_\lambda \quad (8)$$

For fixed field, eqs (6) and (7) lead to

$$(C_{PH}/T) = (dS/dT)_{\lambda H} + (\partial V/\partial T)_{PH} (dP/dT)_{\lambda H} \quad (9)$$

$$(\partial V/\partial T)_{PH} = (dV/dT)_{\lambda H} - (\partial V/\partial P)_{TH} (dP/dT)_{\lambda H} \quad (10)$$

At constant pressure, eqs (6), (7) and (8) lead to the following equations:

$$(\partial\chi/\partial T)_{PH} = 2 (dS/dT)_{\lambda P} (dT/dH^2)_{\lambda P} - 2 (C_{PH}/T) (dT/dH^2)_{\lambda P} \quad (11)$$

$$(\partial V/\partial H^2)_{TP} = (dV/dT)_{\lambda P} (dT/dH^2)_{\lambda P} - (\partial V/\partial T)_{PH} (dT/dH^2)_{\lambda P} \quad (12)$$

$$(\partial\chi/\partial H^2)_{TP} = (d\chi/dT)_{\lambda P} (dT/dH^2)_{\lambda P} - (\partial\chi/\partial T)_{PH} (dT/dH^2)_{\lambda P} \quad (13)$$

Substituting in eq. (9), the values of C_{PH}/T and $(\partial V/\partial T)_{PH}$ from eqs (11) and (12), one gets

$$(\partial\chi/\partial T)_{PH} = -2 (dV/dT)_{\lambda P} (dT/dH^2)_{\lambda P} (dP/dT)_{\lambda H} + 2 (\partial V/\partial H^2)_{TP} (dP/dT)_{\lambda H} \quad (14)$$

The relations (11) to (14), together with the relations (9) and (10), are called magnetic Pippard relations and are equivalent to the following relations obtained by Wright (1972 c):

$$(C_{PH}/T) = \text{constant} + (dP/dT)_{\lambda H} (\partial V/\partial T)_{PH}$$

$$(\partial V/\partial T)_{PH} = \text{constant} + (dP/dT)_{\lambda H} (-\partial V/\partial P)_{TH}$$

$$(\partial \chi/\partial T)_{PH} = \text{constant} - 2 (dT/dH^2)_{\lambda P} (C_{PH}/T)$$

$$(\partial V/\partial H^2)_{PT} = \text{constant} - (dT/dH^2)_{\lambda P} (\partial V/\partial T)_{PH}$$

$$(\partial \chi/\partial H^2)_{PT} = \text{constant} - (dT/dH^2)_{\lambda P} (\partial \chi/\partial T)_{PH}$$

and $(\partial \chi/\partial T)_{PH} = \text{constant} + 2 (dP/dT)_{\lambda H} (\partial V/\partial H^2)_{TP}$

Replacing the magnetic field H by electric field E , one gets dielectric Pippard relations.

Considering one more independent variable X , for composition, in addition to T , P and H^2 (E^2), one gets the following additional Pippard relations for the effect of change of composition on (magnetic or electric) Curie points and Neel points of mixtures:

$$(\partial \chi/\partial X)_{TPH} = (d\chi/dT)_{\lambda PH} (dT/dX)_{\lambda PH} - (\partial \chi/\partial T)_{PHX} (dT/dX)_{\lambda PH} \quad (15)$$

$$(\partial V/\partial X)_{TPH} = (dV/dX)_{\lambda PT} - (\partial V/\partial H^2)_{TPX} (dH^2/dX)_{\lambda PT} \quad (16)$$

These are equivalent to the following relations obtained by Wright (1972 b):

$$(\partial \chi/\partial X)_{TPH} = \text{constant} - (dT/dX)_{\lambda PH} (\partial \chi/\partial T)_{PHX}$$

$$(1/V) (\partial V/\partial X)_{TPH} = \text{constant} - (dT/dX)_{\lambda PH} (1/V) (\partial V/\partial T)_{PHX}$$

4. Pippard relations in binary liquid mixtures

For a binary liquid mixture in one phase, the number of variables is 4 and the number of degrees of freedom is 3. Taking the thermodynamic variables as T , P and X the following relations are obtained from the relations (2), (3) and (4):

$$(dS/dT)_{\lambda} = (C_{PX}/T) - V\beta_{PX}^{\alpha} + (\partial S/\partial X)_{PT} \eta \quad (17)$$

$$(dV/dT)_{\lambda} = V\beta_{PX} - VK_{TX}^{\alpha} + (\partial V/\partial X)_{PT} \eta \quad (18)$$

and

$$(d\mu/dT)_{\lambda} = (\partial \mu/\partial T)_{PX} + (\partial \mu/\partial P)_{TX} \alpha + (\partial \mu/\partial X)_{PT} \eta \quad (19)$$

where $\alpha = (dP/dT)_{\lambda}$ and $\eta = (dX/dT)_{\lambda}$

In the case of binary liquid mixtures, one has to consider two categories, one corresponding to $\text{He}^3 + \text{He}^4$ type and the other corresponding to ordinary binary liquid mixtures.

4.1. $\text{He}^3 + \text{He}^4$ mixtures

In mixtures of this type, the line of critical points is obtained by keeping either the pressure or the composition constant. If the pressure is kept constant, the following relations are obtained from the relations (17), (18) and (19);

$$(\partial S/\partial X)_{TP} = (dS/dT)_{\lambda P} (dT/dX)_{\lambda P} - (C_{PX}/T) (dT/dX)_{\lambda P} \quad (20)$$

$$(\partial V/\partial X)_{TP} = (dV/dT)_{\lambda P} (dT/dX)_{\lambda P} - (\partial V/\partial T)_{PX} (dT/dX)_{\lambda P} \quad (21)$$

$$- (\partial \mu/\partial X)_{TP} = - (d\mu/dT)_{\lambda P} (dT/dX)_{\lambda P} - (\partial S/\partial X)_{PT} (dT/dX)_{\lambda P} \quad (22)$$

These relations are equivalent to the following relations obtained by Wright (1972 a)

$$\tilde{S}_2 - \tilde{S}_1 = \text{constant} - (C_{PX}/T) (dT/dX)_{\lambda P}$$

$$\tilde{V}_2 - \tilde{V}_1 = \text{constant} - (\partial V/\partial T)_{PX} (dT/dX)_{\lambda P}$$

$$- \left[\frac{\partial (\mu_2 - \mu_1)}{\partial X} \right] = \text{constant} - (\tilde{S}_2 - \tilde{S}_1) (dT/dX)_{\lambda P}$$

where the notations \tilde{S}_2 , etc., stand for partial molar quantities, the subscripts 1 and 2 denoting the components.

Applying these relations to two phases on both sides in the vicinity of λ -line and taking differences, one gets

$$\begin{aligned} (dT/dX)_{\lambda P} &= - T(\Delta \tilde{S}_2 - \Delta \tilde{S}_1)/\Delta C_{PX} \\ &= - (\Delta \tilde{V}_2 - \Delta \tilde{V}_1)/V \Delta \beta_{PX} \\ &= \Delta [\partial(\mu_2 - \mu_1)/\partial X]/(\Delta \tilde{S}_2 - \Delta \tilde{S}_1) \end{aligned}$$

where the notation Δ stands for the difference between the quantities in the two phases. These expressions for $(dT/dX)_{\lambda P}$ are the same as those obtained by Stout (1948).

4.2. Ordinary binary liquid mixtures

For ordinary partially miscible binary liquid mixtures there is only one line of critical points along which none of T , P and X is constant. The relations (17), (18) and (19) are directly applicable to this situation. These equations are similar to the relations valid for a one-component system except for the terms containing η .

A discussion of the experimental situation in relation to these generalized Pippard relations is given later.

4.3. Two-phase region

The two-phase region is complicated by the presence of the different phases and the interfacial effects. So far no completely satisfactory treatment has been possible. All the same, the experimental evidence, to be discussed below, suggests the validity of the same type of relations as in the one-phase region,

A plausible, though not rigorous, approach is to apply eqs (17)–(19) to the individual phases, neglecting the phase boundary effects. In the vicinity of T_c , the two phases are very similar to each other with $V' \approx V''$, $(dS/dT)_{\lambda}' = (dS/dT)_{\lambda}''$, etc. Therefore, taking the averages

$$(dS/dT)_{\lambda} = (\overline{C_{PX}/T}) - V\overline{\beta_{PX}}\alpha + (\overline{\partial S/\partial X})_{PT} \eta \quad (23)$$

$$(dV/dT)_{\lambda} = V\overline{\beta_{PX}} - V\overline{K_{TX}}\alpha + (\overline{\partial V/\partial X})_{PT} \eta \quad (24)$$

and

$$(d\mu/dT)_{\lambda} = (\overline{\partial\mu/\partial T})_{PX} + (\overline{\partial\mu/\partial P})_{TX} \alpha + (\overline{\partial\mu/\partial X})_{TP} \eta \quad (25)$$

These equations imply, for example, an asymptotic linear relationship between the average specific heat and the average coefficient of thermal expansion. This is similar to the situation in the one-phase region, although eqs (23)–(25) cannot be fully justified by theory.

5. Discussion

There have been many studies on the thermodynamic properties of binary liquids near their critical solution temperature, but very few systems have been studied for specific heat, thermal expansion and compressibility at the same time. Hildebrand and coworkers (Jura *et al* 1953) measured the thermal expansion and specific heat of the system $C_7F_{16} + i-C_8H_{18}$ in the critical region. The data were not presented in detail and so one cannot analyse their experiments.

Near the LCST of the triethylamine + water system thermal expansion data (Semenchenko *et al* 1952) and specific heat data (Krichevski *et al* 1955) have been reported and these will be discussed below. Following the measurement of the specific heat of the system $CS_2 + CH_3OH$ in the critical region (Gambhir *et al* 1971), Lele measured the thermal expansion of the same system (Lele 1971, Lele *et al* 1973). The plot of specific heat against thermal expansion was found to be linear, giving two parallel straight lines for $T > T_c$ and $T < T_c$. This behaviour is similar to that given by eq. (17) for the one-phase region and by eq. (23) for the two-phase region.

A study of the system methanol + *n*-heptane has now been completed regarding the specific heat (Viswanathan *et al* 1973) and the thermal expansion (Ramachandra 1973, Gopal *et al* 1974) in the critical region, and it is now possible to discuss eqs (17) and (23) in some detail. The variation of the specific heat with thermal expansion for the critical composition $X_c = 0.6136$ mole fraction of methanol is shown in figure 1. It is seen that the plot is asymptotically a straight line showing a linear relationship between C_{PX} and β_{PX} . Secondly, the fact that linear variations are obtained for $T > T_c$ and $T < T_c$, shows that the Pippard relations are valid for the two-phase region also, if the system average quantities are used.

A quantitative analysis of the data reveals, however, some difficulties. Consider eq. (17) valid for the one-phase region. While $(dX/dT)_{\lambda} = \eta$ may be finite non-zero, no measurement of the quantity $(\partial S/\partial X)_{PT}$ is available in the critical region. Theoretical estimates also appear lacking. Griffiths and Wheeler (1970) suggest that close to the λ -line $C_{PX}/TV\beta_{PX}$ and (β_{PX}/K_{TX}) should both approach $(dP/dT)_{\lambda}$. This implies that $(\partial S/\partial X)_{PT}$, $(\partial V/\partial X)_{PT}$ are nonsingular and hence negligible

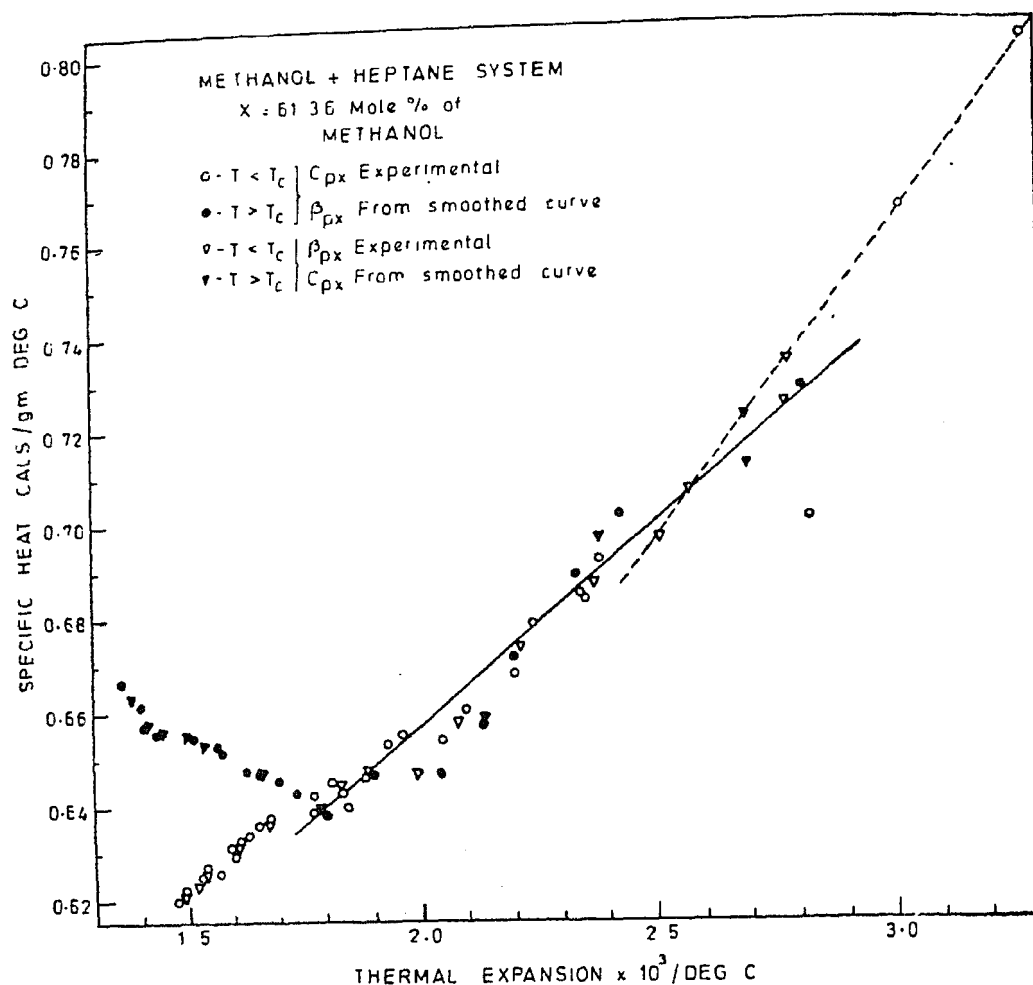


Figure 1. Variation of specific heat with thermal expansion of the methanol + *n*-heptane system at critical composition $X_c = 61.36$ mole % of CH_3OH . Full line fit yields $(dT_c/dP) \approx 120$ mdeg/atm and broken line fit yields ≈ 85 mdeg/atm. Data points obtained in various experiments are clearly distinguished.

compared to C_{PX} , β_{PX} and K_{TX} which assume anomalously large values. Under such conditions, eqs (17) and (18) reduce to the form of the relations valid for a one-component one-phase system.

This suggestion can be quantitatively tested by calculating the asymptotic slope of the C_{PX} against β_{PX} plot which must have a value $TV(dP/dT)_\lambda$. For the methanol + heptane system at its critical composition, the data given in figure 1, converted to molar units to perform the standard calculations, yield $(dT_c/dP)_X \approx 85 - 120$ mdeg/atm. Though $(dT_c/dP)_X$ has not been measured for the methanol + heptane system, this value is much larger than $(dT_c/dP)_X \approx 20$ mdeg/atm observed in many binary liquid systems (Schneider 1970).

A second difficulty appears when compositions close to the critical composition are considered. The mixtures with compositions 0.6191, 0.6064 and 0.6246 have been investigated and they all show peaks in C_{PX} and β_{PX} . The plots of their interrelationships are given in figure 2 and the $(dT/dP)_\lambda$ values obtained are respectively 230, 240 and 230 mdeg/atm. These values are also different and have a dependence on $|X - X_c|$. In other words, if one uses the relation

$$C_{PX} = TV\beta_{PX}(dP/dT)_\lambda + \text{constant} \quad (26)$$

the calculated values of $(dT/dP)_\lambda$ are too high and also depend upon the composition.

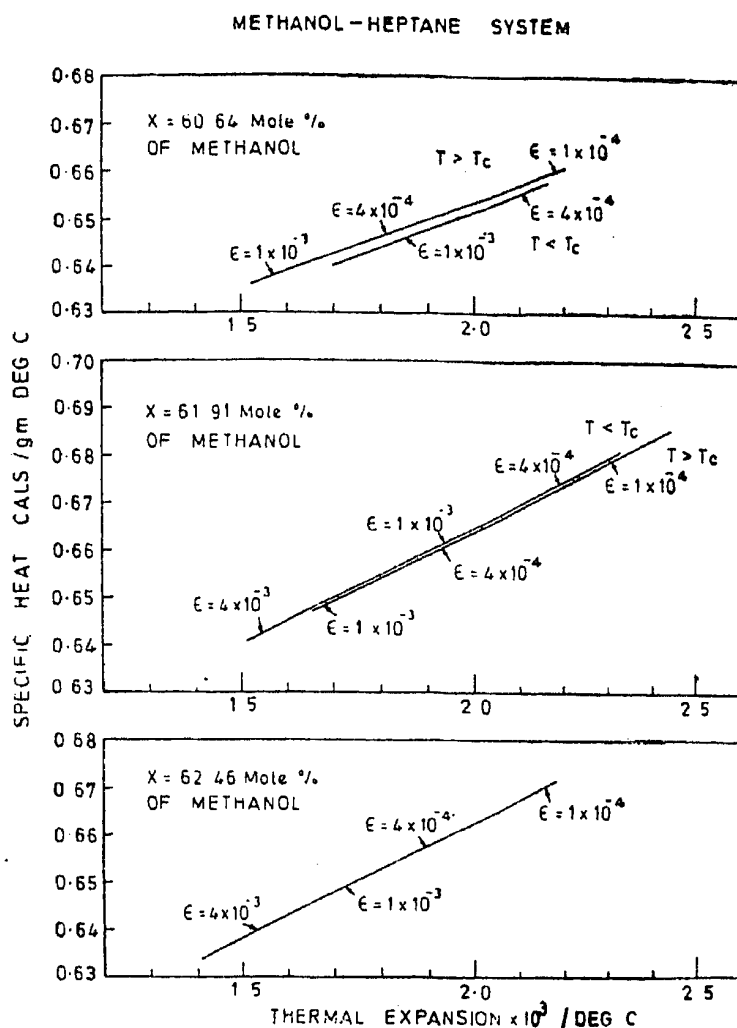


Figure 2. Variation of specific heat with thermal expansion of the system methanol + *n*-heptane for $X = 60.64$, 61.91 and 62.46 mole % of CH_3OH . Only asymptotic lines based on smooth fit to experimental data are shown for the sake of clarity.

The situation is similar in the case of $\text{CS}_2 + \text{CH}_3\text{OH}$ system (Lele 1971). The analysis based on specific heat data (Gambhir *et al* 1971) and thermal expansion data (Lele *et al* 1973) on the system $\text{CS}_2 + \text{CH}_3\text{OH}$ gives the values of effective $(dT/dP)_\lambda$ as 130 mdeg/atm and 185 mdeg/atm for compositions 80.1 and 79.55 wt% of CS_2 , close to critical composition.

An analysis based on the published thermal expansion (Krichevski *et al* 1955) and specific heat (Semenchenko *et al* 1952) data for the system triethylamine + water exhibiting LCST, gives the values of effective $(dT/dP)_\lambda$ as 9, 12 and 20 mdeg/atm for compositions 20.7, 27.6 and 38.6 wt% of triethylamine, for $T < T_c$.

If eq. (26) were correct, one should get the same value of $(dT/dP)_\lambda$ for all the compositions showing anomalous peaks. Not only are the effective calculated values different for the different compositions, but also they deviate substantially from the direct experimental values of $(dT_c/dP)_\lambda$. This discrepancy needs to be resolved.

Three possibilities exist which can resolve this discrepancy. Firstly, all the different experiments of the various workers may contain unsuspected systematic errors which render the data unreliable near the critical temperature. Against this, one may point out that the anomalies are of the order expected on the basis of scaling and universality considerations. A second possibility is that the asymptotic limit may not have been reached at $\epsilon \sim 10^{-4}$ and that one should approach ppm resolution in temperature to achieve this. Here one may point out that the critical exponents seem to have reached the asymptotic region in the analysis

of the individual experiments. A third possibility* is that $(\partial S/\partial X)_{PT}$ in eq. (17) has the same α -singularity as C_{PX} and β_{PX} . If so, the earlier difference between the observed slope of the $C_{PX} - \beta_{PX}$ plot and the theoretically estimated value, mentioned above, is a measure of the contribution from $(\partial S/\partial X)_{PT}$ term. Using a value $(dT/dP)_\lambda = 20$ mdeg/atm the values of $(\partial S/\partial X)_{PT} (dX/dT)_\lambda$ at $\epsilon = 1 \times 10^{-4}$ for the four compositions 0.6136, 0.6191, 0.6064 and 0.6246 mole fraction of methanol are 9.44×10^6 , 8.86×10^6 , 8.75×10^6 and 8.22×10^6 C.G.S. units and the four compositions have respectively $|X - X_c| \sim 0$, 0.0055, 0.0072 and 0.0110. The data are not enough to obtain unambiguously the functional dependence on $|X - X_c|$.

Acknowledgements

The authors thank the authorities of the National College, Bangalore, for study leave to R. R. and the PL-480 programme for financial assistance.

*Note added in proof:

Using scaling arguments (*Physica*, to be published), it can be shown that $(\partial\mu/\partial T)$, $(\partial S/\partial X)$ go to zero as $\epsilon \rightarrow 0$ and hence this possibility is ruled out.

References

- Buckingham M. J. and Fairbank W M 1961 *Progress in Low Temperature Physics* 3 80 ed. C J Gorter (North Holland, Amsterdam)
- Chang D R 1973 *Phys. Lett.* 44 A 411
- Gambhir R D, Vaidya S N and Gopal E S R 1967 *J. Indian Inst. Sci.* 49 48
- Gambhir R D, Viswanathan B and Gopal E S R 1971 *Indian J. Pure Appl. Phys.* 9 787
- Garland C W 1964 *J. Chem. Phys.* 41 1005
- Gopal E S R, Ramachandra R, Lele M V, Chandra Sekhar P and Nagarajan N 1974 *J. Indian Inst. Sci.* 56 193
- Griffiths R B and Wheeler J C 1970 *Phys. Rev. A* 2 1047
- Janovec V 1966 *J. Chem. Phys.* 45 1874
- Jura G, Praga D, Maki G and Hildebrand J H 1953 *Proc. Nat. Acad. Sci. (U.S.A.)* 39 19
- Krichevskii I F, Khazanova N E and Linshitz 1955 *Zhur. Fiz. Khim* 29 547
- Lele M V 1971 Some thermal instrumentation for investigations on the critical phenomena in binary liquid systems. M.Sc. Thesis, Indian Institute of Science, Bangalore
- Lele M V, Subramanyam S V and Gopal E S R 1973 *Ind. J. Pure and Appl. Phys.* 11 228
- Pippard A B 1956 *Phil. Mag.* 1 473
- Ramachandra R 1973 Some aspects of critical point phenomena in binary liquid systems. Ph.D. Thesis, Indian Institute of Science, Bangalore
- Ramachandra R, Nagarajan N, Subramanyam S V and Gopal E S R 1973 *Proc. Nucl. Phys. Solid State Phys. Symp.* 16 C 244
- Rice O K 1967 *Phys. Rev.* 153 275
- Schneider W G 1970 *Advances in chemical physics* Vol VI, 1 ed, Prologine I (Interscience, New York)
- Semenchenko V K and Skripov V P 1952 *Dokl. Akad. Nauk. SSSR* 85 1325
- Stout, J W 1948 *Phys. Rev.* 74 605
- Tisza L 1961 *Ann. Phys. (NY)* 1 13
- Viswanathan R 1963 *Physica* 29 18
- Viswanathan B, Vaidya S N and Gopal E S R 1968 *J. Ind. Inst. Sci.* 50 83
- Viswanathan B, Govindarajan K and Gopal E S R 1973 *Ind. J. Pure and Appl. Phys.* 11 157
- Wright P G 1969 *J. Phys. A* 2 226
- Wright P G 1972 a *J. Phys. A* 5 1004
- Wright P G 1972 b *J. Phys. A* 5 1018
- Wright P G 1972 c *J. Phys. A* 5 1206
- Zemansky M W 1968 *Heat and thermodynamics* 5th ed, ch. 12 (McGraw-Hill, New York)