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On the Thermodynamics of Partially Miscible Liquid Binary Systems

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Isobaric coexistence curves of two liquid phases are predicted from the temperature and composition at the consolute point of binary solutions consisting of a hydrocarbon and the corresponding perfluorocarbon. Excess enthalpies obtained from the free volume theory of *Flory* as well as from calorimetric measurements are used to account for the temperature dependence of the *Gibbs* energy of mixing. The treatment is based on the extension of the *Flory-Huggins* model to nonathermal polymer solutions. Formal applicability to mixtures of molecules not largely differing in size is achieved by introducing generalized variables characterizing composition in place of volume fractions. Phase diagrams of following systems are predicted and compared with experimental results: methane + carbontetrafluoride, *n*-hexane + perfluoro-*n*-hexane, *n*-heptane + perfluoro-*n*-heptane, methylcyclohexane + perfluoromethylcyclohexane.

(Keywords: Binary liquid mixtures, thermodynamics of; Liquid-liquid phase equilibria)

Zur Thermodynamik beschränkt mischbarer flüssiger Zweistoffsysteme

Isobare Koexistenzkurven zweier flüssiger Phasen werden aus Temperatur und Zusammensetzung am kritischen Entmischungspunkt binärer Lösungen bestehend aus einem Kohlenwasserstoff und dem entsprechenden Perfluorkohlenstoff vorausgesagt. Die Temperaturabhängigkeit der *Gibbs*-Energie der Mischung wird mit Hilfe von Mischungsenthalpien, die sowohl der Freien Volumentheorie von *Flory* als auch kalorimetrischen Messungen entstammen, berücksichtigt. Als Berechnungsgrundlage dient das auf nichtathermische Polymerlösungen erweiterte *Flory-Huggins*-Modell. Die Einführung verallgemeinerter Variablen zur Charakterisierung der Zusammensetzung an Stelle von Volumenbrüchen ermöglicht die formale Anwendbarkeit auf Mischungen von Molekülen mit wenig verschiedener Größe. Zustandsdiagramme folgender Mischsysteme werden vorausberechnet und mit experimentellen Ergebnissen verglichen: Methan + Tetrafluorkohlenstoff, *n*-Hexan + Perfluor-*n*-Hexan, *n*-Heptan + Perfluor-*n*-Heptan, Methylcyclohexan + Perfluormethylcyclohexan.

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1. Introduction

The success of a thermodynamic description of the isobaric coexistence curve of two liquid phases in a binary system of incompletely miscible components is largely dependent on the form of the function relating the molar excess *Gibbs* energy ΔG^E to concentration and temperature. The accuracy of the binodial curve predicted from a certain mixture model is a very sensitive test of its theoretical basis.

In the simplest possible case, when ΔG^E is represented by a one-parameter expression of *Porter* type, the resulting phase-boundary curve is symmetrical in the mole fractions and the equilibrium temperature is explicitly expressible as a function of composition of the coexisting phases. In the present concept, the *Porter* formalism having for practical purposes the advantage of simple mathematical tractability, is extended to binodials of unsymmetrical shape. This is most easily accomplished by introducing new variables characterizing the composition of the binary system: a parameter taken constant throughout the whole range of concentration relates these variables to the mole fractions.

Solubility-temperature curves are calculated from the coordinates of the critical solution point (CSP) and the molar enthalpies of mixing ΔH^E for solutions of the following pairs consisting of a hydrocarbon and the corresponding perfluorocarbon: $CH_4 + CF_4$, $n\text{-}C_6H_{14} + n\text{-}C_6F_{14}$, $n\text{-}C_7H_{16} + n\text{-}C_7F_{16}$, $c\text{-}CH_3C_6H_{11} + c\text{-}CF_3C_6F_{11}$. The CSPs of these systems have been predicted already by *Abe* and *Flory*[1], but no other points of the phase diagram have been calculated. The influence of the results of *Flory*'s free volume model on the theoretical form of the binodial is discussed.

2. Formulation of Phase Equilibrium Conditions

The condition for a system to be in thermodynamic equilibrium at constant temperature and pressure, requires its *Gibbs* energy to be a minimum. If the system consists of two components and two coexisting liquid phases, it follows from this condition that the chemical potential μ_i for any component i is equal in both liquid phases symbolized by (′) and (″)

$$\mu_i' = \mu_i'' \quad (i = 1, 2). \tag{1}$$

In addition to this general prerequisite, some special assumption on the dependence of μ_i on concentration and temperature is necessary.

For the sake of algebraic simplicity, we shall use, as proposed by

Wohl[2], what may be termed "generalized volume fractions" ξ_i defined as:

$$\xi_1 = \frac{x_1}{x_1 + x_2 B} \qquad \xi_2 = \frac{x_2 B}{x_1 + x_2 B}, \tag{2}$$

where x_i are the mole fractions.

In the particular case of a mixture of a solvent and a monodisperse polymer, i.e. a polymer consisting of only one kind of species, where the polymer is considered as built up of segments which are of the same volume as a solvent molecule, one may set ξ_1 equal to the volume fraction of the solvent and B to the number of segments in the polymer species. Taking segments instead of molecules as basic units in the solution, we may then write the *Gibbs* energy in terms of the new concentration variables in analogy to the *Porter* expression

$$\frac{\Delta \overline{G}}{x_1 + x_2 B} = A\,\xi_1 \xi_2 + RT\left(\xi_1 \ln \xi_1 + \frac{\xi_2}{B} \ln \xi_2\right), \tag{3}$$

where $\Delta \overline{G} = \Delta G^E + \Delta G^{id}$ and ΔG^{id} is the excess of the molar *Gibbs* energy of an ideal mixture over the contribution of the pure components, R is the molar gas constant and T the thermodynamic temperature. For $B = 1$ eq. (3) reduces to $\Delta \overline{G} = A x_1 x_2 + \Delta G^{id}$.

Rewriting eq. (3) in the form

$$\Delta \overline{G} = A\,\xi_1 \xi_2 (x_1 + x_2 B) + RT(x_1 \ln \xi_1 + x_2 \ln \xi_2), \tag{4}$$

we note that $\Delta \overline{G}$ may be represented as a sum of a term ΔG^R of *Scatchard-Hildebrand* type (following *Flory*, we call it the "residual" term) and of a *Flory-Huggins* (*FH*) combinatorial part ΔG^c:

$$\begin{aligned} \Delta G^R &= A\,\xi_1 \xi_2 (x_1 + x_2 B) = \frac{A B x_1 x_2}{x_1 + x_2 B} \\ \Delta G^c &= RT(x_1 \ln \xi_1 + x_2 \ln \xi_2). \end{aligned} \tag{5}$$

As shown in standard texts, the corresponding chemical potentials $\Delta \mu_i$ may be derived from eq. (4)

$$\begin{aligned} \Delta \mu_1 &= A\,\xi_2^2 + RT[\ln \xi_1 + \xi_2 (B - 1)/B] \\ \Delta \mu_2 &= AB\,\xi_1^2 + RT[\ln \xi_2 + \xi_1 (1 - B)]. \end{aligned} \tag{6}$$

From eqs. (6) and (11) one obtains at the critical solution point rium

$$A\,\xi_2'^2 + RT\,[\ln \xi_1' + \xi_2'(B-1)/B] = A\,\xi_2''^2 + RT\,[\ln \xi_1'' + \xi_2''(B-1)/B] \tag{7a}$$

$$AB\,\xi_1'^2 + RT\,[\ln \xi_2' + \xi_1'(1-B)] = AB\,\xi_1''^2 + RT\,[\ln \xi_2'' + \xi_1''(1-B)]. \tag{7b}$$

Setting

$$\begin{aligned} \xi_1' + \xi_1'' &= 2\,\bar{\xi}_1 \\ \xi_2' + \xi_2'' &= 2\,\bar{\xi}_2, \end{aligned} \tag{8}$$

where $\bar{\xi}_i$ denotes the mean composition of the two conjugate phases, combination of eq. (8) with eqs. (7a) and (7b), respectively, under elimination of ξ_1'' and ξ_2'' yields

$$RT = \frac{4\,AB\,\bar{\xi}_2\,(\xi_2' - \bar{\xi}_2)}{2\,(1-B)\,(\xi_2' - \bar{\xi}_2) + B \ln [(1 + \xi_2' - 2\,\bar{\xi}_2)/(1 - \xi_2')]} \tag{9a}$$

$$RT = \frac{4\,AB\,\bar{\xi}_1\,(\xi_1' - \bar{\xi}_1)}{2\,(B-1)\,(\xi_1' - \bar{\xi}_1) + \ln [(1 + \xi_1' - 2\,\bar{\xi}_1)/(1 - \xi_1')]}. \tag{9b}$$

Combining eqs. (9a) and (9b) and expressing ξ_1' and $\bar{\xi}_1$ by ξ_2' and $\bar{\xi}_2$, we obtain after some algebraic rearrangement the following implicit relation between ξ_2' and $\bar{\xi}_2$

$$2\,(B-1)\,(\bar{\xi}_2 - \xi_2') + B\,(1 - \bar{\xi}_2) \ln \frac{1 - (2\,\bar{\xi}_2 - \xi_2')}{1 - \xi_2'} + \bar{\xi}_2 \ln \frac{2\,\bar{\xi}_2 - \xi_2'}{\xi_2'} = 0. \tag{10}$$

Assuming that the FH term does not contribute to the enthalpy of mixing ΔH^E, that is, if we take the parameter B as independent of temperature, we must, according to eq. (10), allow for $\bar{\xi}_2$ being a function of ξ_2' in order to satisfy the equilibrium conditions. Extending eq. (3) to binary systems which do not strictly correspond to the molecular theoretical basis of the FH equation, we replaced the volume fractions by the generalized concentration variables ξ_i. This seems legitimate in the absence of any specific interactions in the solution.

3. Calculation of the Binodial

The conditions for critical mixing are usually derived from stability considerations implying that at the point at which the two coexisting phases become identical, there should be simultaneously for any component:

$$\left(\frac{\partial\,\Delta\,\mu_i}{\partial\,x_i}\right)_{T_c,P} = 0 \quad \text{and} \quad \left(\frac{\partial^2\,\Delta\,\mu_i}{\partial\,x_i^2}\right)_{T_c,P} = 0. \tag{11}$$

From eqs. (6) and (11) one obtains at the critical solution point

$$\xi_{1c} = \frac{B^{1/2}}{1+B^{1/2}} \qquad \xi_{2c} = \frac{1}{1+B^{1/2}}. \tag{12}$$

Using eq. (2), we may express the critical composition in mole fractions

$$x_{1c} = \frac{B^{3/2}}{1+B^{3/2}} \qquad x_{2c} = \frac{1}{1+B^{3/2}}. \tag{13}$$

The value of the parameter A at the critical temperature, A_c, follows from eq. (6), (11) and (12)

$$A_c = \frac{RT_c}{2\,\xi_{1c}^2} = \frac{RT_c\,(1+B^{1/2})^2}{2\,B} \tag{14}$$

and the residual *Gibbs* energy $\Delta\,G_c^R$ at the critical temperature T_c results from eqs. (5), (13) and (14):

$$\Delta\,G_c^R = \frac{RT_c\,B^{1/2}\,(1+B^{1/2})}{2\,(1+B^{3/2})}. \tag{15}$$

It is appropriate to note here that in applying simple classical thermodynamics to a critical point, we made implicitly a somewhat questionable assumption postulating the chemical potential to be a continous function through stable and unstable phases. This can be avoided if we derive eq. (12) and (14) on extrapolating eq. (9a) or (9b) to the critical temperature instead of differentiating $\Delta\,\mu_i$ in the unstable portion of the curve that has no physical significance, since mixtures in this range of compositions are not observable.

Looking for the limiting values of ξ_2' and A as T approaches T_c, we introduce the approximation $\ln(1+\delta) \simeq \delta$ in eq. (9a, b). Now, for instance, eq. (9a) becomes

$$\frac{RT_c}{2\,A_c\,B} = \frac{\xi_{2c}\,(1-\xi_{2c})}{(1-\xi_{2c})+\xi_{2c}\,B}.$$

As there is only one critical composition at a certain CSP, this quadratic equation should yield a pair of identical roots for ξ_{2c}, a requirement that cannot be satisfied unless A_c is in agreement with eq. (14). The result for ξ_{2c} is the same as given by eq. (12).

In order to perform the calculation of the binodial, we first neglect the temperature dependence of A in eq. (9a, b) setting $A = A_c$. The corresponding (uncorrected) equilibrium temperature may be denoted by T_0. At any temperature sufficiently close to the critical, we may modify our crude approximation by a linear variation of A with T:

$$A = A_c + \left(\frac{\partial A}{\partial T}\right)_p \Delta T \qquad \Delta T = T - T_c. \tag{16}$$

We now insert into eq. (9a) or (9b) the correction term of eq. (16), $(\partial A/\partial T)_p \Delta T$, giving $T/A\ (\partial A/\partial T)_p \Delta T$. The corrected temperature T is then:

$$T = T_0 + \frac{T}{A}\left(\frac{\partial A}{\partial T}\right)_p \Delta T,$$

or equivalently

$$\frac{\Delta T_0}{\Delta T} = 1 - \left(\frac{\partial \ln A}{\partial \ln T}\right)_p, \tag{17}$$

where $\Delta T_0 = T_0 - T_c$.

Relating the temperature dependence of A to experimentally determined quantities, we derive from eq. (5)

$$\Delta S^R = \frac{\Delta H^E - \Delta G^R}{T} = -\Delta G^R \left(\frac{\partial \ln A}{\partial T}\right)_p, \tag{18}$$

ΔS^R being the residual entropy. From eq. (18) it follows that

$$1 - T\left(\frac{\partial \ln A}{\partial T}\right)_p = \frac{\Delta H^E}{\Delta G^R}. \tag{19}$$

Thus, eq. (17) reduces to

$$\frac{\Delta T}{\Delta T_0} = \left(\frac{\Delta G^R}{\Delta H^E}\right)_{T \to T_c} \tag{20}$$

Eq. (20) provides a simple means to predict the critical solution line from the position of the CSP, characterized by x_{2c} and T_c, and the enthalpy of mixing. ΔG^R is determined by A_c and B which are functions of x_{2c} and T_c.

Carrying out the numerical computations, one obtains the parameter B from x_{2c} using eq. (13) and A_c is related to B and T_c by eq. (14). For any value of ξ_2' the appropriate parameter $\bar{\xi}_2$ is found by a trial and error solution of eq. (10). With the data A_c, ξ_2' and $\bar{\xi}_2$ one may evaluate ΔT_0 from either of the eqs. (9a, b); the temperature T then follows from eq. (20). In most cases it would be sufficient to approximate $\bar{\xi}_2$ by ξ_{2c} and to determine the resulting error at one single point of the phase diagram. Corrections for temperatures between this point and T_c may then be estimated with sufficient accuracy from a linear interpolation.

4. Results

All of the four binary mixtures considered here exhibit an upper CSP. Due to the scarcity of experimental data it is not easy to give some general answer to the question of how far the investigated solutions satisfy the assumptions on which eq. (6) is based.

We first deal with the system n-C_6H_{14} + n-C_6F_{14} where an objective comparison of observed and calculated results is least difficult. *Williamson* and *Scott*[3] have measured enthalpies of mixing at a temperature as close as 2 °C above the CSP. If in eq. (5) the parameter A is assumed as independent of concentration, then, according to eq. (19), the same will be true for $\Delta H^E/\Delta G^R$. Hence, the variation of A with temperature is readily obtained from the ratio $\Delta H^E/\Delta G^R$ at a mole fraction of 0.5, ΔG^R being evaluated from critical miscibility data. Fig. 1 presents the phase diagram of this system. Curves were calculated with ΔH^E supplied by the *Flory* theory as well as from calorimetric measurements and were fitted to the CSP. Moreover, the form of the theoretical curve is shown when A is kept constant everywhere ($A = A_c$). Best results are obtained if ΔH^E from experimental determinations is used, although in the medium section of the predicted curve a major discrepancy can be observed, whereas towards the ends disagreement with measured points becomes less. With ΔH^E taken from the *Flory* theory, eq. (20) yields predictions of worse quality, which are, however, still better than those resulting from the crude approximation $A = A_c$.

For the system c-$CH_3C_6H_{11}$ + c-$CF_3C_6F_{11}$ only ΔH^E data of minor accuracy reported by *Dyke*[4] et al. were available. The authors have derived ΔH^E from the temperature dependence of ΔG^E and added two calorimetrically determined points. Finally, the enthalpies of mixing refer to 65 °C, a temperature that is about 20 °C above that of the CSP. Nevertheless, the resulting phase boundary curve (Fig. 2) is closer to the experimental points than that obtained from ΔH^E calculated on the basis of the *Flory* theory.

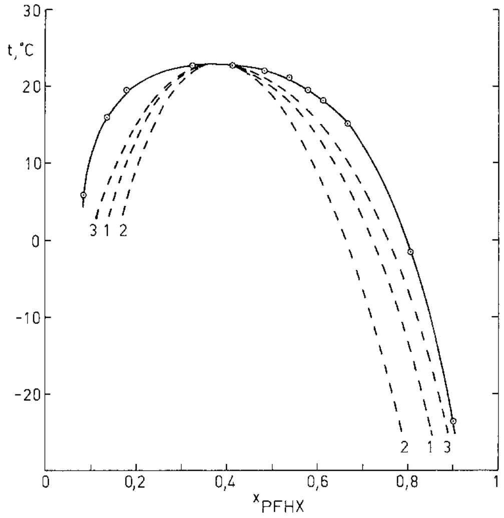

Fig. 1. Liquid-liquid phase separation in the system *n*-hexane + perfluoro-*n*-hexane. Experimental results[6] (solid curve); theoretical results (dotted curves) calculated with: *1* ΔH^E from *Flory* theory; *2* $A = A_c$; *3* ΔH^E from measurements

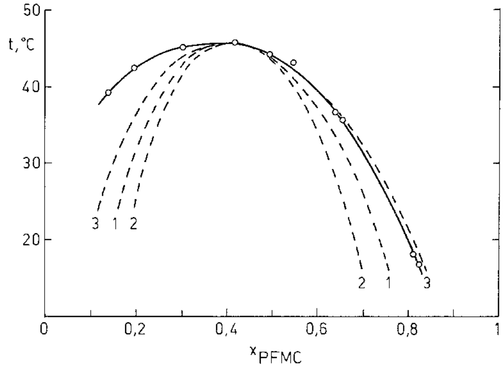

Fig. 2. Liquid-liquid phase separation in the system methylcyclohexane + perfluoromethylcyclohexane. Experimental results[4] (solid curve); theoretical results (dotted curves) calculated with: *1* ΔH^E from *Flory* theory; *2* $A = A_c$; *3* ΔH^E from measurements

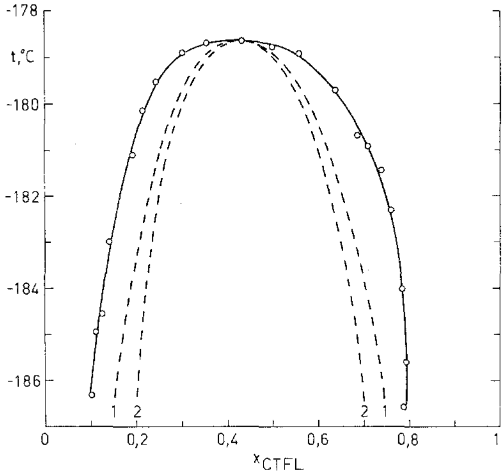

Fig. 3. Liquid-liquid phase separation in the system methane + carbontetrafluoride. Experimental results[5] (solid curve); theoretical results (dotted curves) calculated with: *1* ΔH^E from *Flory* theory; *2* $A = A_c$

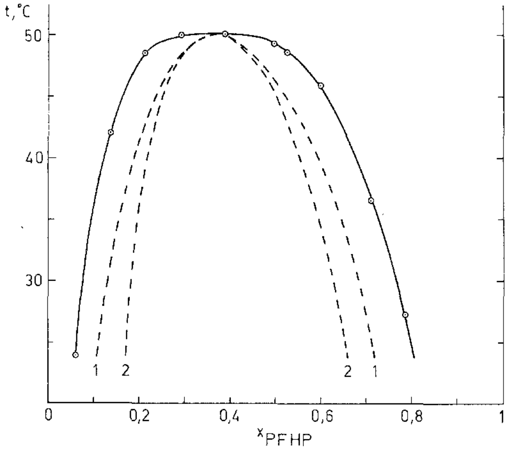

Fig. 4. Liquid-liquid phase separation in the system *n*-heptane + perfluoro-*n*-heptane. Experimental results[7] (solid curve); theoretical results (dotted curves) calculated with: *1* ΔH^E from *Flory* theory; *2* $A = A_c$

In default of experimental ΔH^E data, mutual solubilities of $CH_4 + CF_4$ and n-C_7H_{16} + n-C_7F_{16} (Fig. 3 and 4) were calculated with ΔH^E estimated from the *Flory* theory and with $A = A_c$.

In Table 1, critical solution properties of the individual systems and values of ξ_{2c}, A_c and B calculated therefrom on the basis of eqs. (12)-(14), are recorded. Excess *Gibbs* energies obtained from A_c and B are, where adequate information was available, compared with experimental results at the composition midpoint. Enthalpies of mixing are listed in the paper of *Abe* and *Flory*[1].

Table 1. *Data of studied binary systems. Upper critical solution temperature* t_c *(in °C), critical compositions* x_{2c} *and* ξ_{2c} *of the perfluorinated components, parameters* A_c *(in J/mol) and* B*, predicted and observed excess Gibbs energies* $\Delta G^E_{0.5}$ *(in J/mol) for equimolar mixtures*

System	t_c	x_{2c}	ξ_{2c}	A_c	B	$\Delta G^E_{0.5}$ calc.	$\Delta G^E_{0.5}$ obs.
$CH_4 + CF_4$ [5]	—179	0.43	0.477	1433	1.207	388	—
n-C_6H_{14} + n-C_6F_{14} [3,6]	23	0.37	0.456	4151	1.426	1181	1360
n-C_7H_{16} + n-C_7F_{16} [7,8]	50	0.356[a]	0.451	4451	1.485	1278	1310
c-$CH_3C_6H_{11}$ + c-$CF_3C_6F_{11}$ [4]	46	0.40[a]	0.466	4652	1.310	1295	—

[a] Data from *Abe* and *Flory*[1].

5. Discussion

Eq. (4) is equal to the extended form of the *FH* equation as used in the treatment of nonathermal polymer solutions. As to the temperature dependence of $\Delta \bar{G}$ it is worth noting that in the original concept of *Flory*[9] ΔG^R, defined in eq. (5), was identified with ΔH^E and considered as a relatively small term correcting the predominant combinatorial part in $\Delta \bar{G}$ for deviations of the solution from athermal behavior. ΔG^R is connected with ΔG^c through the parameter B, whilst A is of no influence on the combinatorial contribution to $\Delta \bar{G}$. Also the critical compositions are due to eq. (12) and (13) completely determined by the parameter B, whereas T_c, as indicated in eq. (14), is a function of A as well as of B.

For mixtures of molecules not largely differing in size, eq. (4) is in many cases still a quite useful approximation. With the aid of eq. (15) it may be shown that the greatest possible value of ΔG^R at the CSP, $RT_c/2$, is obtained at $B = 1$. The assumptions of the model impose on the parameter B the condition that $B \geq 1$, and, as a consequence, eq. (13) requires to select as component 2 that one which has a critical composition $x_{2c} \leq 0.5$.

From eq. (15) it follows that at the consolute point (and also in some interval above and below the critical solution temperature) $\Delta G^R > 0$. This argument would lead to the conclusion that the CSP of a system where A is independent of T ($A = A_c$) should always be an upper CSP, provided the following considerations formulated by *Rehage*[10] hold.

If we accept that a *Taylor* series expansion of ΔG is valid near the critical point (see comment in Section 3), then we may apply the necessary conditions[10] for the existence of a CSP:

$$\left(\frac{\partial^2 \Delta H^E}{\partial x_i^2}\right)_{P,T_c} \neq 0,$$

where

$$\left(\frac{\partial^2 \Delta H^E}{\partial x_i^2}\right)_{P,T_c} < 0 \qquad \text{at the upper CSP}$$

and

$$\left(\frac{\partial^2 \Delta H^E}{\partial x_i^2}\right)_{P,T_c} > 0 \qquad \text{at the lower CSP.} \tag{21}$$

From eq. (5) we obtain

$$\left(\frac{\partial \ln \Delta G^R}{\partial x_1}\right)_{P,T} = \frac{1}{x_1} - \frac{1}{x_2} - \frac{1 - B}{x_1 + x_2 B} = \frac{\xi_2}{x_1} - \frac{\xi_1}{x_2}$$

$$\text{or} \quad \left(\frac{\partial \Delta G^R}{\partial x_1}\right)_{P,T} = A\,(\xi_2^2 - B\,\xi_1^2).$$

Thus

$$\left(\frac{\partial^2 \Delta G^R}{\partial x_1^2}\right)_{P,T} = -2\,A\,(\xi_2 + \xi_1 B)\left(\frac{\partial \xi_1}{\partial x_1}\right)_{P,T},$$

where

$$\left(\frac{\partial \xi_1}{\partial x_1}\right)_{P,T} = \frac{\xi_1 \xi_2}{x_1 x_2}.$$

Therefore we may write

$$\left(\frac{\partial^2 \Delta G^R}{\partial x_1^2}\right)_{P,T} = -2\,\Delta G^R \frac{\xi_1 \xi_2}{(x_1 x_2)^2}. \tag{22}$$

Assuming $A = A_c$ for any temperature along the critical solution line, we conclude from eq. (18) that in this particular case $\Delta H^E = \Delta G^R$, where $\Delta G^R > 0$ at the CSP as shown earlier. Considering now eq. (22), we get $(\partial^2 \Delta H^E/\partial x_1^2)_{P,T_c} < 0$, a necessary condition for the occurrence of an upper CSP according to eq. (21).

It is now possible to test some predictions of eq. (20) on the behavior of the thermodynamic excess functions at the consolute point.

Due to eq. (20), the CSP of a binary system should be an upper CSP, if the sign of ΔT and ΔT_0 is the same, in other words, if $\Delta H^E > 0$ at the CSP.

As obvious from eq. (19) and (22),

$$\left(\frac{\partial^2 \Delta H^E}{\partial x_1^2}\right)_{P,T_c} = -2\,\Delta G_c^R \left(\frac{\xi_1 \xi_2}{x_1^2 x_2^2}\right)_c \left[1 - T\left(\frac{\partial \ln A}{\partial T}\right)_P\right] = -2\,\Delta H_c^E \left(\frac{\xi_1 \xi_2}{x_1^2 x_2^2}\right)_c .$$

Therefore $(\partial^2 \Delta H^E/\partial x_1^2)_{P,T_c}$ can only be negative, if, in agreement with eq. (20), at the CSP $\Delta H^E > 0$.

Using eq. (21), one may similarly verify the following assertion based on eq. (20): If the binary system exhibits a lower CSP, then $\Delta H^E < 0$ there and on account of $\Delta G^R > 0$, $\Delta S^R < 0$, too.

Another consequence of eq. (20) is that $\Delta H^E \neq 0$ at the CSP. This statement is again confirmed by eq. (21).

The basic features of the model underlying eq. (4) may be summarized as follows:

(1) The parameters A and B are considered as independent of concentration, B also of temperature.

(2) At fixed T and P, the proportion of ΔG^R, ΔH^E and $T \Delta S^R$ remains on account of eq. (18) and (19) constant over the whole range of compositions.

(3) Since eq. (22) implies ΔG^R to be a function free from points of inflection, one may establish as a general rule valid at any concentration in a temperature interval around the consolute point that

(a) $\Delta G^R > 0$ and $\Delta H^E \neq 0$.

(b) In the vicinity of an upper CSP $\Delta G^R > 0$ and $\Delta H^E > 0$.

(c) In the vicinity of a lower CSP $\Delta G^R > 0$, $\Delta H^E < 0$, $\Delta S^R < 0$.

The statements made in point (3) (a)-(c) are in agreement with experience. Other consequences of the basic equations such as ΔG^R and especially ΔH^E and ΔS^R should be functions without any points of inflection are of less rigorous validity even in the close vicinity of the CSP thus indicating the limitations of the treatment. This shortcomings cannot be removed by the free volume theory of *Flory* unless additional assumptions are made, since the reduced equation of state in the free volume concept in its original form does solely correlate various thermodynamic properties at the same concentration without supplying any information on their functional dependence on composition. For that reason it is not unusual in the treatment of polymer mixtures to combine eq. (4) representing $\Delta \bar{G}$ for any composition with the free volume theory predicting its dependence on temperature[11]. It is difficult to give a more detailed description of consolute behavior by a refined treatment without thereby introducing a major number of adjustable parameters.

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