

## Adiabatic Processes in the Vapor–Liquid Two-Phase Region. 2. Binary Mixtures

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**ABSTRACT:** The phase equilibrium conditions and entropy balance equations for multicomponent fluid mixtures are expressed with a density-based formalism (“isochoric thermodynamics”), and isentropes in the one- and two-phase region are computed from equations of state; here the Peng–Robinson equation is used as an example. Griffiths’ theorem—one- and two-phase isentropes meet at a maxcondensar point (pressure maximum of an isopleth) with equal slopes—could be confirmed. For chemically similar compounds at subcritical conditions, the resulting isentrope patterns are similar to those of pure fluids. If one of the components is supercritical, it is possible that, along a part of a two-phase isentrope, the liquid phase has a higher molar entropy than the vapor phase (“entropic inversion”). The phenomenon not only poses a numerical problem, but is also relevant for the question whether a two-phase isentrope can run into the lg three-phase curve.

### 1. INTRODUCTION

Modern power technology strives to increase the efficiency of power plants, industrial installations, but also vehicle motors, by utilizing their waste heats. Some new power plant types, e.g., combustion power plants using biogenic fuels or solarthermal plants, have to use heat at unusually low temperature levels. Under these conditions, the obtainable efficiency depends very much on working fluids used, and consequently the number of publications dealing with “organic Rankine cycles” (ORC) and similar concepts is rapidly increasing.

Another challenge that modern power technology is facing is the need for flexibility, that is, the need to achieve a good efficiency under partial load. This is particularly important for refrigeration and air conditioning applications, which consume a large amount of energy, and that at steadily increasing costs. Improving process efficiencies is therefore mandatory, and this means, among other things, the optimization of the working fluids. For fine-tuning the working fluids as well as for achieving optimal performance under varying operating conditions, the use of mixed fluids is seriously considered. This means, of course, that the processes typical of power plants, for example, adiabatic compressions and expansions, have to be studied for mixtures.

An example of a highly efficient power cycle using a mixed working fluid is the Kalina cycle.<sup>1</sup>

Another application for the adiabatic expansion of mixtures is the processing of natural gas and oil, where again the

energetical efficiency, but also the condensation behavior is really important. Here, too, the Kalina cycle is considered because of its good performance.<sup>2,3</sup>

We will therefore consider some aspects of the adiabatic compression or expansion of binary fluid mixtures, with particular emphasis on high-pressure regions where retrograde phenomena can be found.

In the preceding article<sup>4</sup> a differential equation and an algebraic scheme for the computation of isentropes of *pure fluids* in the vapor–liquid region were given. The usual distinction between “wet” and “dry” working fluids was discussed with  $TS$  (temperature–entropy),  $SV$  (entropy–volume) as well as  $qT$  (quality–temperature) diagrams, and then related to molecular properties.

For the calculation of two-phase isentropes in *mixtures* Cowperthwaite and Ahrens<sup>5</sup> presented a mathematical solution to the problem already in 1967. This solution, however, is a set of ordinary differential equations which not only describes the adiabatic process itself, but also the phase equilibrium by a generalization of the Gibbs–Konowalow equations; it is so complicated that one is tempted to doubt whether it has ever been practically applied. Rowlinson et al.<sup>6</sup> used a more

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straightforward method which, however, is limited to binary mixtures and cannot be easily adapted for machine calculation.

Instead, we will concentrate here on easily applicable numerical solutions of the problem.

## 2. THEORY

**2.1. Calculation of Isentropes.** Following our previous work<sup>4</sup> about two-phase adiabatic processes in pure fluids, we shall assume that the two phases are always in equilibrium, i.e., that temperatures, pressures, and the chemical potentials of all components match at all times.

While an adiabatic process in the vapor–liquid two-phase region evidently has to follow the vapor pressure curve (as far as its  $pT$  projection is concerned), this is no longer true for mixtures. Still, the computation method proposed in the previous article can be used after minor modification. We assume that there are two fluid phases, denoted by  $\phi = ', ''$ , with mole fractions  $x_i^\phi$ ,  $i = 1, \dots, N$  and overall molar densities  $\rho^\phi$ . Alternatively we can characterize the phases by their density vectors,

$$\rho^\phi = (\rho_1^\phi, \rho_2^\phi, \dots, \rho_N^\phi) \quad \text{with} \quad \rho_i^\phi = \rho^\phi x_i^\phi \quad (1)$$

The total molar entropy of the two-phase system is then

$$S_m = (1 - q)S_m(\rho', T) + qS_m(\rho'', T) \quad (2)$$

where  $q$  denotes the “quality” of the system, that is, the fraction of the '' phase in the system:  $q = n''/(n' + n'')$ . At the beginning of the adiabatic process, eq 2 can be written as

$$S_{m,0} = (1 - q_0)S_m(\rho'_0, T_0) + q_0S_m(\rho''_0, T_0) \quad (3)$$

Then the quality at any point of a two-phase adiabatic process can be obtained as

$$q = \frac{S_{m,0} - S_m(\rho', T)}{S_m(\rho'', T) - S_m(\rho', T)} \quad (4)$$

The phase density vectors are linked by a material balance equation:

$$(1 - q)\mathbf{x}' + q\mathbf{x}'' = (1 - q_0)\mathbf{x}'_0 + q_0\mathbf{x}''_0 \quad (5)$$

or, written with densities,

$$\frac{1 - q}{\rho'}\rho' + \frac{q}{\rho''}\rho'' = \frac{1 - q_0}{\rho'_0}\rho'_0 + \frac{q_0}{\rho''_0}\rho''_0 \quad (6)$$

Of course,  $\rho^\phi/\rho^\phi$  is equal to the mole fraction vector  $\mathbf{x}^\phi$  of phase  $\phi$ .

In a density-based system of variables, the phase equilibrium criterion of each component having equal chemical potentials in both phases can be written as<sup>7,8</sup>

$$\nabla\Psi' = \nabla\Psi'' \quad (7)$$

where  $\Psi^\phi = A_m^\phi/\rho^\phi$  denotes the Helmholtz energy density of the phase  $\phi$  and  $\nabla$  the gradient operator; the gradients have to be computed with respect to all component densities, that is,  $\nabla = (\partial/\partial\rho_1, \partial/\partial\rho_2, \dots, \partial/\partial\rho_N)$ . The equal-pressure criterion then becomes

$$\nabla\Psi \cdot (\rho'' - \rho') = \Psi'' - \Psi' \quad (8)$$

For a given temperature  $T$ , the system is characterized by  $2N + 1$  variables ( $\rho', \rho''$ , and  $q$ ) and four eqs 4, 6–8, of which eq 6 is a vector equation with  $N - 1$ , and eq 7 is one with  $N$  independent components. The computation of mixture

isentropes is therefore a well-defined task. The system of nonlinear equations outlined in this section can be solved numerically, for example with a Marquardt–Levenberg method;<sup>9</sup> an algorithm has been implemented in the *ThermoC* computation package.<sup>10</sup> Convergence was found to be unproblematic if the densities and mole fractions of the initial phase pair were known. The density-based formulation of the phase equilibrium conditions has the advantage that convergence is not affected by azeotropic or critical states.

The computation can, in principle, yield a  $q$  value below 0 or above 1. Such a result indicates that the computed two-phase state is not realistic, and that a single-phase isentrope should be calculated instead.

**2.2. Thermodynamic Functions.** We write the total Helmholtz energy of a fluid mixture with the density vector  $\rho$  and the temperature  $T$  as a sum of an ideal-gas part and a residual part,<sup>7</sup>

$$\begin{aligned} A_m(\rho, T) &= A_m^{\text{id}}(\rho, T) + A_m^{\text{r}}(\rho, T) \\ &= \left[ \sum_{i=1}^N x_i \left( G_{m,i}^\ominus(T) + RT \ln \left( \frac{\rho_i}{\rho^\ominus} \right) \right) - RT \right] \\ &\quad + RT \int_0^\rho \frac{Z(\rho, T) - 1}{\rho} d\rho \end{aligned} \quad (9)$$

where  $G_{m,i}^\ominus(T)$  denotes the Gibbs energy of pure component  $i$  at the reference density  $\rho^\ominus$ . For  $\rho^\ominus$  a very small value is assumed, at which the substance can be regarded as an ideal gas. The actual value is irrelevant, as it cancels out in the subsequent calculations.  $Z(\rho, T) = p(\rho, T) V_m/(RT)$  is the compression factor of the mixture. Then the Helmholtz energy density is given by

$$\begin{aligned} \Psi(\rho, T) &= \left[ \sum_{i=1}^N \rho_i \left( G_{m,i}^\ominus(T) + RT \ln \left( \frac{\rho_i}{\rho^\ominus} \right) \right) - \rho RT \right] \\ &\quad + \rho RT \int_0^\rho \frac{Z(\rho, T) - 1}{\rho} d\rho \end{aligned} \quad (10)$$

Throughout this work, the Peng–Robinson equation of state<sup>11,12</sup> is used to compute residual properties:

$$p = \frac{RT}{V_m - v^*} - \frac{a_c \alpha(T, \omega)}{V_m(V_m + v^*) + v^*(V_m - v^*)} \quad (11)$$

Here  $v^*$  and  $a_c \equiv 8 RT^* v^*$  are substance-specific parameters, which can be readily computed from the critical pressure and temperature;  $\alpha(T, \omega)$  describes the temperature dependence of the attraction part. We use here the Soave-style  $\alpha(T)$  function proposed by Peng and Robinson in 1978,<sup>12</sup> which contains another substance-dependent parameter, namely the acentric factor  $\omega$ . The critical data and parameters used in this work are listed in Table 1.

Switching to reduced variables  $\tilde{p} = v^*/V_m$  and  $\tilde{T} = T/T^*$ , the compression factor and the residual Helmholtz energy can then be expressed as

$$\begin{aligned} Z &= \frac{1}{1 - \tilde{p}} - \frac{8\tilde{p}}{1 + 2\tilde{p} - \tilde{p}^2} \frac{\alpha(\tilde{T}, \omega)}{T} \\ \frac{A_m^{\text{r}}}{RT} &= -\ln(1 - \tilde{p}) - 2\sqrt{2} \ln \frac{1 + \tilde{p}(\sqrt{2} + 1)}{1 - \tilde{p}(\sqrt{2} - 1)} \frac{\alpha(\tilde{T}, \omega)}{\tilde{T}} \end{aligned} \quad (12)$$

**Table 1.** Parameters of the Peng–Robinson Equation of State<sup>a</sup>

	$p_c$ /MPa	$T_c$ /K	$\omega$
methane	4.60848	190.778	0.0110
ethane	4.88000	305.400	0.0990
propane	4.24800	369.825	0.1531
butane	3.63480	423.675	0.1929
pentane	3.37000	469.700	0.2510
nitrogen	3.32598	126.303	0.0370
		$k_{12}$	
methane–propane		+0.042546	
butane–pentane		PPR78	
nitrogen–ethane		+0.026302	
nitrogen–pentane		PPR78	

<sup>a</sup>For pure fluids the critical pressure, critical temperature, and acentric factor; for mixtures  $k_{12}$ . “PPR78” indicates that the (temperature-dependent) group contribution method of Jaubert, Qian et al.<sup>13,14</sup> was used.

according to Appendix C.4 of the textbook of Deiters and Kraska.<sup>7</sup>

These equations can be generalized to mixtures with the following combining rules:

$$a_c \alpha = \sum_{i=1}^N \sum_{j=1}^N x_i x_j (1 - k_{ij}) \sqrt{a_{c,i} \alpha(\tilde{T}_i, \omega_i) a_{c,j} \alpha(\tilde{T}_j, \omega_j)}$$

$$v^* = \sum_{i=1}^N x_i v_i^* \quad (13)$$

The binary interaction parameters  $k_{ij}$  were either fitted to experimental data or obtained with the PPR78 (predictive Peng–Robinson equation) group contribution method of Jaubert, Qian et al.<sup>13,14</sup>

The Peng–Robinson equation is known to give reasonably good results for mixtures of nonpolar and weakly polar compounds. While certainly more sophisticated equations of state can be found in the literature, these will not predict qualitatively different thermodynamic properties.

Differentiation of eq 10 with respect to the temperature yields the entropy,

$$S_m(\rho, T) = -\frac{1}{\rho} \left( \frac{\partial \Psi(\rho, T)}{\partial T} \right)_\rho$$

$$= \sum_{i=1}^N x_i \left( S_{m,i}^\ominus(T) - R \ln \left( \frac{\rho_i}{\rho^\ominus} \right) \right) + S_m^i(\rho, T) \quad (14)$$

The *ThermoC* software obtains the residual entropy from  $\Psi^r$  by numerical differentiation.

The reference entropies in eq 14 are calculated from the ideal-gas isobaric heat capacities of the compounds,

$$S_{m,i}^\ominus(T) = S_{m,i}^\ominus(T^\ominus) + \int_{T^\ominus}^T \frac{C_{V,m,i}^{\text{id}}(T)}{T} dT \quad (15)$$

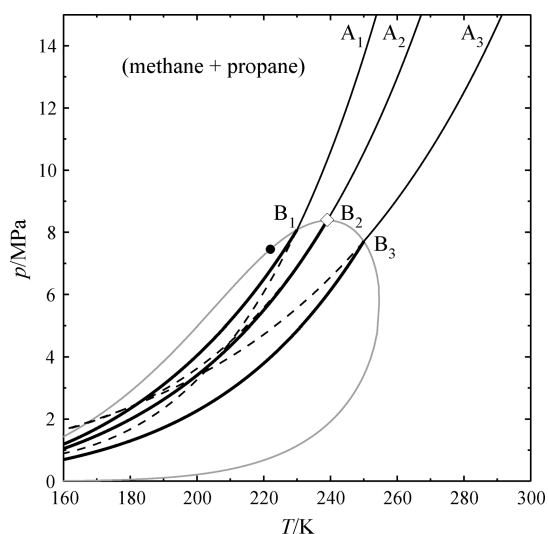
The ideal-gas heat capacities can be conveniently expressed as (smoothing) spline functions over appropriate data tables;<sup>15,16</sup> then the integration can be carried out analytically.  $S_{m,i}^\ominus(T^\ominus)$  is the value of the ideal-gas entropy at the reference temperature  $T^\ominus$ . The value should be chosen in such a way that eq 14, when

applied to a pure compound at thermodynamic standard conditions, reproduces its standard (Third Law) entropy. For the calculations reported in his article, however, the value of  $S_{m,i}^\ominus(T^\ominus)$  is not relevant.

### 3. APPLICATION

**3.1. (Methane + Propane).** Methane and propane are chemically similar, but their critical temperatures differ by a factor of almost 2. Still the system (methane + propane) belongs to the most simple phase diagram class, namely Class I according to the classification of Scott and van Konynenburg,<sup>17,18</sup> or 1<sup>P</sup> according to the rational nomenclature of Bolz et al.<sup>19</sup>

Figure 1 shows the adiabatic expansion of a (methane + propane) mixture with a methane overall mole fraction  $x_1 = 0.9$

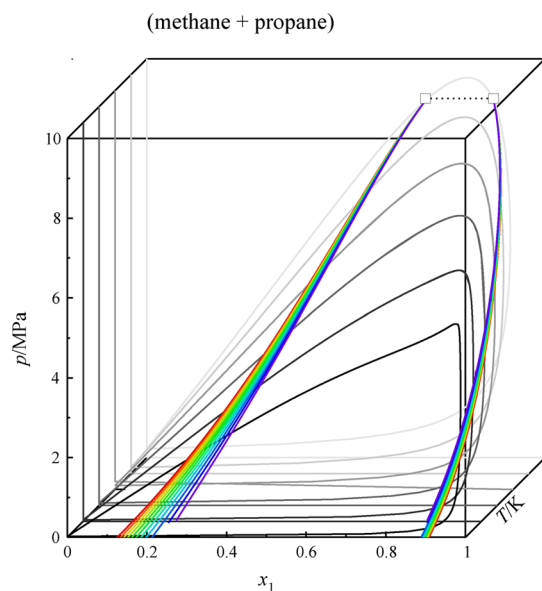


**Figure 1.** Pressure–temperature diagram of (methane + propane) for  $x_1 = 0.9$ , for three different initial states, computed with the Peng–Robinson equation of state. (black line) single-phase isentropes (stable); (dashed line) single-phase isentropes (metastable); (bold line) two-phase isentropes, (gray line) phase envelope  $x_1 = 0.9$ ; (●) binary critical point; (◇) maxcondenbar point.

for three different initial states,  $A_1$ – $A_3$ . These states lie in the single-phase region; consequently, the expansion follows single-phase isentropes, until these intersect the  $x_1 = 0.9$  phase envelope (states  $B_1$ – $B_3$ ). Here the expansion process switches to the two-phase isentropes. As methane as well as propane are “wet” fluids (i.e., their adiabatic expansion does not take them out of the vapor–liquid two-phase region anymore), it is not surprising that the two-phase isentropes of their mixture stay inside the phase envelope.

It should be noted that, for the initial state  $A_3$ , the two-phase isentrope runs below the metastable part of the single-phase isentrope and has a larger slope at the intersection with the phase envelope. For the initial state  $A_1$ , the slope of the two-phase isentrope is smaller. Only for an expansion that passes through the pressure maximum of the phase envelope, the so-called maxcondenbar point  $B_2$ , the two slopes are the same. A formal proof of this phenomenon (and an analogous one concerning the behavior of isochors at the maxcondenbar point) was given by Griffiths<sup>6,20</sup> (also published in Appendix B.2 of the textbook of Deiters and Kraska<sup>7</sup>).

Figure 2 shows two-phase isentropes of (methane + propane) originating at an equilibrium state at 250 K and



**Figure 2.** Adiabatic expansion of a (methane + propane) mixture starting at a two-phase state at 250 K, 9 MPa:  $pT x_1$  representation. (Gray curves) isothermal phase diagrams 200–250 K; ( $\square \cdots \square$ ) initial states (connode); (color lines) isentropes. The color indicates the initial quality  $q_0$  (“rainbow encoding”: red = 0.0, magenta = 1.0).

9 MPa, with the equilibrium mole fractions 0.705 and 0.870, on a background of isothermal phase diagrams. Methane is supercritical in the temperature range considered (200–250 K), and the isothermal phase diagrams are therefore looplike. As the temperature decreases during the adiabatic expansion, the two-phase isentropes move along the sequence of the isothermal phase diagrams.

The expansion processes were calculated for a range of initial qualities from  $q_0 = 0$  (all liquid) to 1 (all vapor); the corresponding overall mole fractions varied from 0.705 to 0.870. It should be noted that a given two-phase equilibrium state ( $p$ ,  $T$ ,  $x'_1$ ,  $x''_1$ ) can be reached via more than one single-phase isentrope; isentropes belonging to different overall mole fractions result in different  $q$  values for the two-phase state.

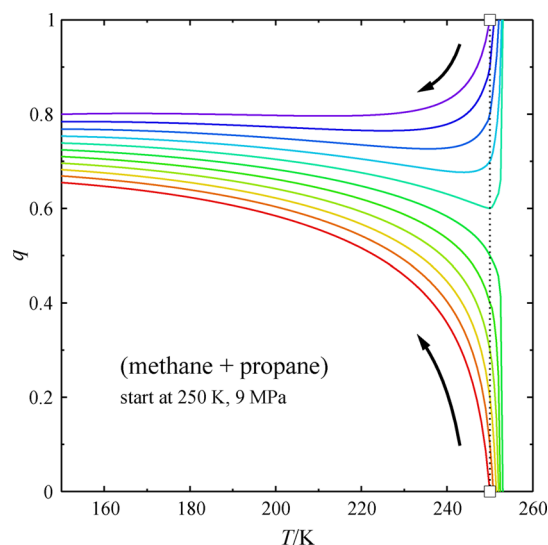
For this system and for these initial conditions, the calculated isentropes do not coincide: the course of the expansion depends on the initial quality. The  $qT$  diagram in Figure 3 shows the expected pattern: the isentropes run to lower temperatures and remain at  $q$  values between 0 and 1; that is, the expansion stays in the two-phase region.

The corresponding  $TS$  diagram, Figure 4, shows a rather surprising pattern: The entropy curves of the coexisting phases intersect. If this happens, eq 4 is no longer applicable, and the computation may encounter convergence problems.

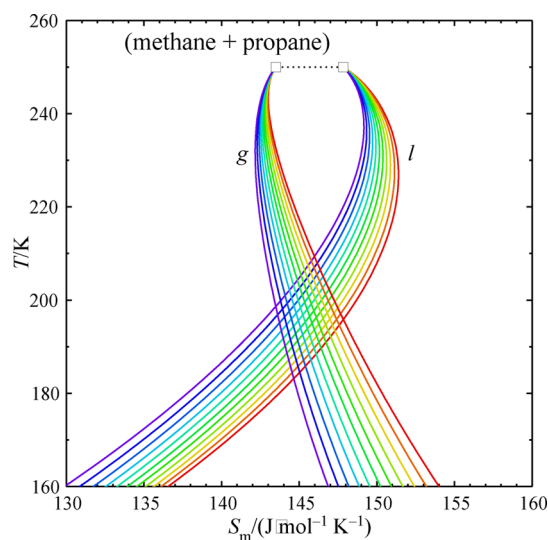
The intersection means that, in some portion of the phase diagram, the vapor phase has a lower molar entropy than the liquid phase. Figure 5 panels a and b demonstrate that this phenomenon can also be found along two-phase isotherms. In analogy to the “barotropic inversion”, at which the specific gravity of the vapor becomes higher than that of the liquid, we propose the name “entropic inversion” for the switching of molar entropies.

At a first glance, it may seem paradox that the molar entropy of the vapor can be lower than that of the liquid. But there are two reasons for this:

(i) The entropy difference between vapor and liquid is to a large extent due to their density ratio,  $-R \ln(\rho^g/\rho^l)$ . In low-



**Figure 3.** Adiabatic expansion of a (methane + propane) mixture starting at a two-phase state at 250 K, 9 MPa:  $qT$  representation. ( $\square \cdots \square$ ) Initial state; (color lines) isentropes. The color indicates the initial quality  $q_0$  (rainbow encoding: red = 0.0, magenta = 1.0). The arrows indicate the direction of the expansion.

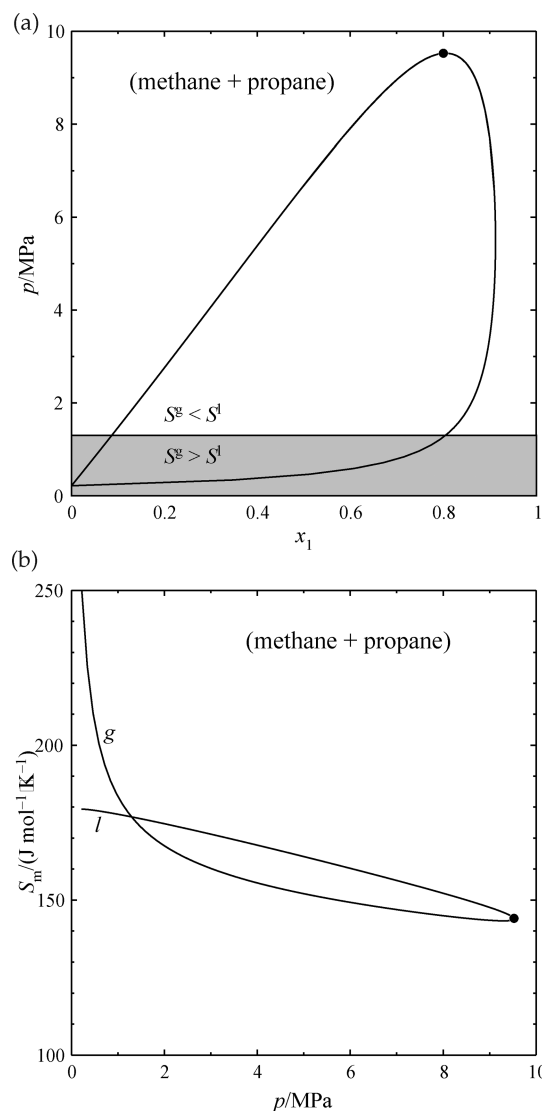


**Figure 4.** Adiabatic expansion of a (methane + propane) mixture starting at a two-phase state at 250 K, 9 MPa for various quality values: entropies of the coexisting phases along the isentropes. ( $\square \cdots \square$ ) Initial state; (color lines) isentropes. The color indicates the initial quality  $q_0$  (rainbow encoding: red = 0.0, magenta = 1.0).

pressure vapor–liquid equilibria, the vapor density is much smaller than that of the liquid, and hence this term is large. At high pressures, however, the vapor densities tend to be of a similar order of magnitude as the liquid densities. For “asymmetric mixtures”, that is, mixtures of compounds with very different molecular sizes, it is even possible that the vapor phase (more precisely, the phase with the higher fraction of the light component) can have the larger molar density.<sup>21</sup>

(ii) For mixtures, coexisting liquid and vapor phases usually have different compositions. It turns out that propane, which is enhanced in the liquid phase, has a much higher ideal-gas entropy than methane (64.46 over 34.27 J mol<sup>-1</sup> K<sup>-1</sup> at 250 K) because of its larger number of thermally excitable vibrations.

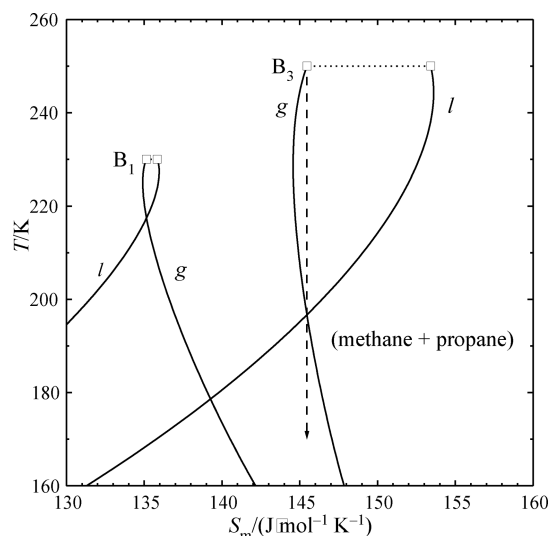




**Figure 5.** Isothermal phase equilibria of (methane + propane) at 250 K, computed with the Peng–Robinson equation of state: (●) binary critical point.

Consequently, whenever compounds of very different complexity (more accurately, with very different ideal-gas heat capacities) or very different molecular sizes are mixed and studied at high, near-critical pressures, an entropic inversion is likely.

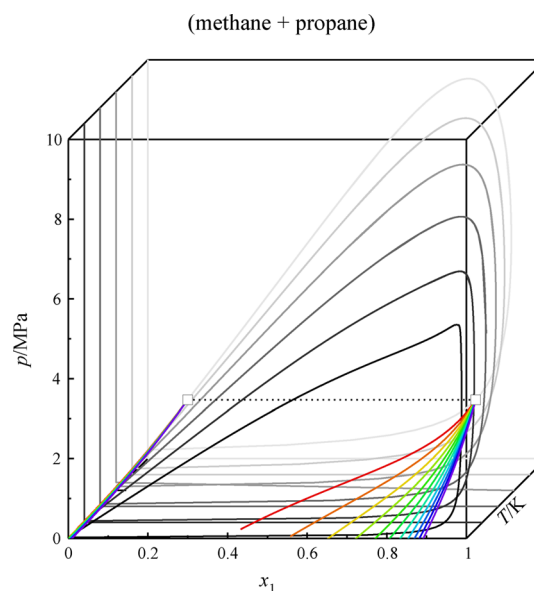
Figure 6 gives a clearer picture of the adiabatic expansion of a mixture exhibiting entropic inversion: For the isentrope 3 in Figure 1, the initial state of the two-phase part is an all-vapor state ( $q_0 = 1.0$ ) at 250 K and 7.7 MPa. This corresponds to the left initial state in Figure 6,  $B_3$ . The adiabatic expansion, which is characterized by  $S_m = S_{m,0}$ , is represented by a vertical arrow in the diagram. Usually the coexisting vapor and liquid have different molar entropies, and then  $q$  adjusts in such a way that eq 2 yields the constant overall entropy. But at the entropic inversion  $S'_m(\rho, T) = S''_m(\rho, T)$  holds, and then the isentropic condition can only be fulfilled if  $S'_m(\rho, T) = S''_m(\rho, T) = S_{m,0}$ ;  $q$  becomes irrelevant. In other words: at the entropic inversion, the entropies of the coexisting phases must both equal that of the initial state. Therefore, the arrow in Figure 6 must pass exactly through the entropic inversion state.



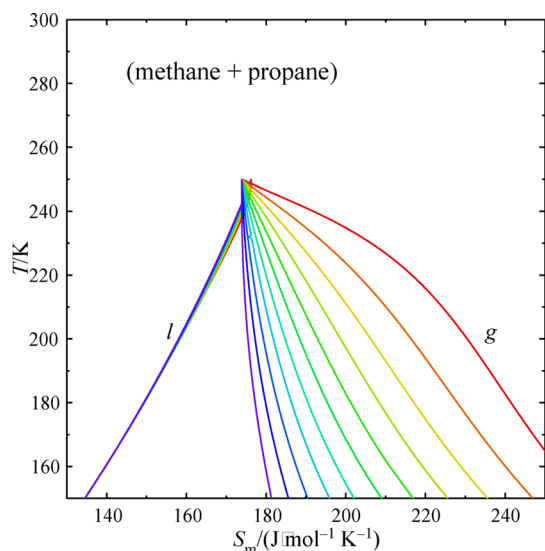
**Figure 6.** Temperature–entropy curves for two-phase isentropes from Figure 1: (□··□) initial states (connodes); (—) two-phase isentropes belonging to an initial quality of 1.0 (all-vapor state); (arrow) total entropy during expansion.

The consequence for the computation of isentropes is that the system of eqs 4, and 6–8 is no longer well-defined and hence cannot be solved at the entropic inversion; this may lead to convergence problems in numeric calculations. But immediately above and below the entropic inversion the system of equations has physically reasonable solutions, so that an analytic continuation of the isentropes exists.

Figure 7 shows an adiabatic two-phase expansion starting at 250 K, just as in Figure 2, but at a lower pressure—below the maxcondentherm pressure, but above the entropic inversion; the latter is revealed by the  $TS$  diagram, Figure 8. In contrast to the expansion from the high-pressure equilibrium state, but also



**Figure 7.** Adiabatic expansion of a (methane + propane) mixture starting at a two-phase state at 250 K, 1.5 MPa:  $pTx_1$  representation. Gray curves: isothermal phase diagrams 200–250 K, (□··□) initial state (connode). Color lines: isentropes. The color indicates the initial quality  $q_0$  (rainbow encoding: red = 0.0, magenta = 1.0).



**Figure 8.** Adiabatic expansion of a (methane + propane) mixture starting at a two-phase state at 250 K, 1.5 MPa ( $\square \cdots \square$ ): entropies of the coexisting phases. (Color lines) isentropes. the color indicates the initial quality  $q_0$  (rainbow encoding: red = 0.0, magenta = 1.0).

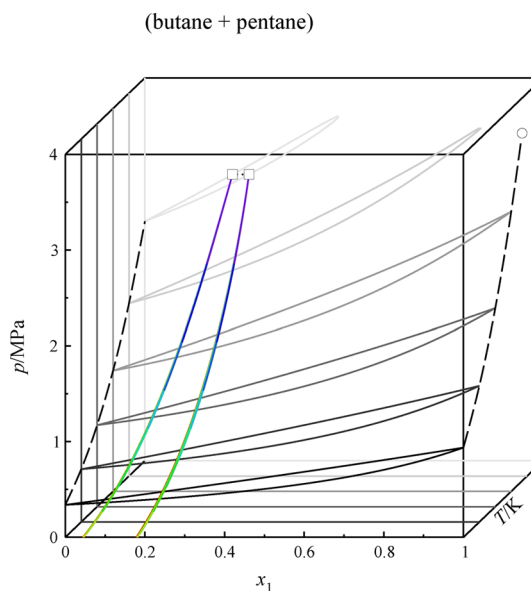
to the (butane + pentane) system, the vapor branches of the isentropes are very sensitive to the initial  $q$ .

**3.2. (Butane + Pentane).** Both compounds are alkanes, and their molecular sizes are similar. It is therefore not surprising that their mixtures exhibit nearly ideal behavior. The (butane + pentane) system belongs to the phase diagram class I according to Scott and van Konynenburg,<sup>17,18</sup> or  $1^P$  according to the rational nomenclature of Bolz et al.,<sup>19</sup> which means that it exhibits a continuous critical curve connecting the critical points of butane and pentane, and that no liquid–liquid immiscibility exists.

Figure 9 shows the two-phase isentropes (liquid and vapor branches) of the (butane + pentane) system originating at an equilibrium state at 450 K and 3 MPa on a background of isothermal phase diagrams. The two-phase isentropes necessarily have common points with the phase diagrams. As the temperature drops during the expansion, the isothermal phase diagrams change their shapes—from a looplike shape at 450 K (where butane is supercritical) to a spindle shape at 350 K (where butane is subcritical). All curves were computed with PPR78 interaction parameters.<sup>13,14</sup>

The expansion process was calculated for various initial qualities, ranging from  $q_0 = 0.0$  (= all liquid) to  $q_0 = 1.0$  (= all vapor). But the mole fractions of the initial coexisting phases are rather similar, and therefore the variation of  $q$  corresponds to a variation of the overall mole fraction from merely 0.220 to 0.261. It is therefore not surprising that the resulting isentropes—vapor as well as liquid branches—almost coincide. Only the color gamut along the isentropes shows that the initial quality has some influence: The isentropes with high  $q_0$  values end sooner than those with low  $q_0$  values, that is, they run to  $q = 1$ , and then the expansion process continues along single-phase isentropes.

The situation can be explained with temperature–entropy diagrams. Figure 10a shows  $TS$  curves for the expansion process considered here. One can see that the isentrope with the initial quality of 1.0 reaches the boundary of the two-phase region already at 430 K, whereas the isentropes starting at 0.5 or 0.0 reach it at 360 K or below 300 K, respectively. Figure 10b



**Figure 9.** Adiabatic expansion of a (butane + pentane) mixture starting at a two-phase state at 450 K, 3 MPa:  $pTx_1$  representation. (Gray curves) isothermal phase diagrams 350–450 K; (dashed line) vapor pressure curves of the pure fluids; (O) pure-component critical point; ( $\square \cdots \square$ ) initial states (connode); (color lines) isentropes. The color indicates the initial quality  $q_0$  (rainbow encoding: red = 0.0, magenta = 1.0).

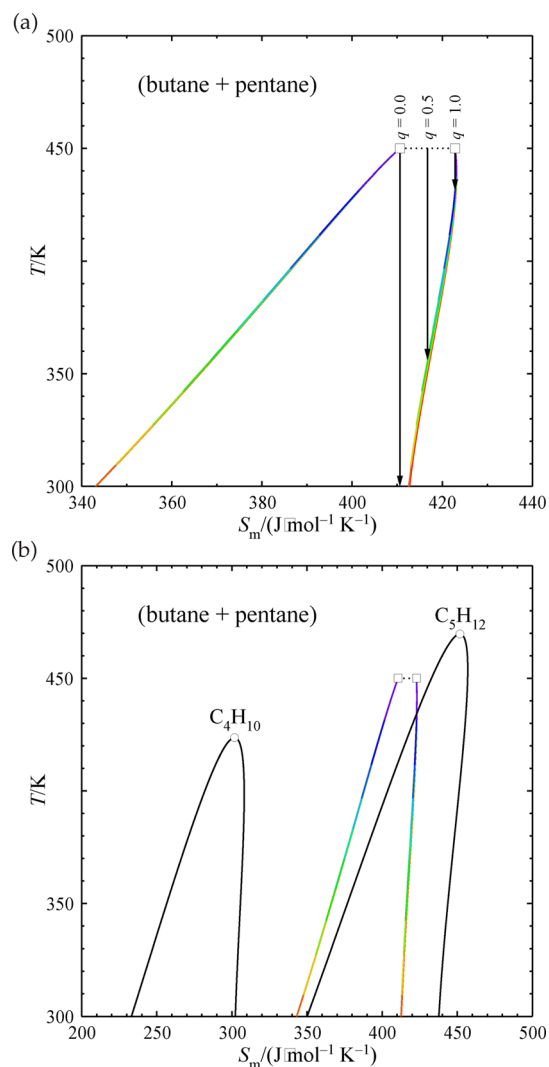
compares the mixture  $TS$  curve with those of the pure components. Both butane and pentane are “dry” fluids in the temperature range of the diagrams, that is, the vapor branches have regions with positive slopes, so that an isentropic expansion can run to a single-phase vapor state. Evidently the mixture shows a similar, intermediate behavior. It is thus possible to tune the  $TS$  slopes by mixing suitable components.

The quality versus temperature diagram Figure 11 reveals that the isentrope that starts from an all-liquid state ( $q_0 = 0$ ) in the direction of the arrow (expansion) remains in the two-phase region. The other isentropes ( $q_0 \geq 0.1$ ) run to single-phase vapor states, which is typical for “dry” systems. A closer inspection of the computation results shows that these isentropes are of the reentrant type,<sup>4</sup> that is, they do not end here, but continue virtually and become real again at lower temperatures. A real mixture would, of course, follow its two-phase isentrope to complete evaporation ( $q = 1$ ), then switch to a single-phase isentrope, and then back to the two-phase isentrope. The expansion curve for  $q_0 = 1.0$ , that is, for an all-vapor initial state, exhibits a transient condensation: an expansion experiment would show first condensation and then evaporation, a single-phase vapor state below about 440 K, and finally condensation again below about 190 K.

These considerations are for an expansion from an equilibrium state at 450 K and 3 MPa. Figure 11 also shows that a compression of this initial two-phase state would cause complete condensation for initial qualities less than 0.7, and complete evaporation for  $q_0 > 0.7$ . The isentrope belonging to  $q_0 \approx 0.7$  terminates in a critical point.

**3.3. (Nitrogen + Ethane).** The binary interaction parameters for this systems were fitted to experimental data of Stryk et al.<sup>22</sup> (see Table 1).

This system belongs to the phase diagram class III according to the classification of Scott and van Konynenburg,<sup>17,18</sup> or  $1^C1^Z$  according to the rational nomenclature of Bolz et al.<sup>19</sup> It

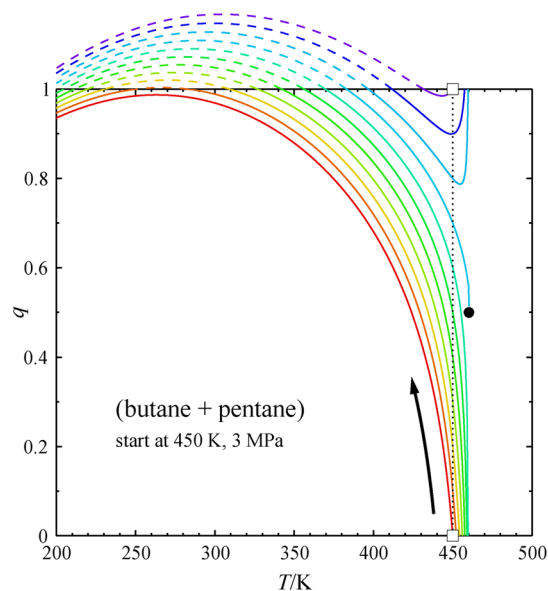


**Figure 10.** Temperature–entropy relation of coexisting liquid and vapor phases for the adiabatic expansion of a (butane + pentane mixture) originally in a two-phase equilibrium at 450 K and 3 MPa. The color indicates the initial quality  $q_0$  (rainbow encoding: red = 0.0, magenta = 1.0).

contains two critical curves, one of which runs from the critical point of ethane to high pressures (“ $1^C$ ”), whereas the other one originates at the critical point of nitrogen and ends at an upper critical end point (“ $1^Z$ ”), where it meets an llg three-phase curve. A  $pT$  phase diagram is shown in Figure 12.

The complication that the (nitrogen + ethane) system offers is, evidently, the existence of a liquid–liquid phase split at low temperatures. The figure illustrates what happens when a mixture with a nitrogen mole fraction of 0.9 is adiabatically expanded from the indicated initial state A: The system follows the single-phase isentrope until it reaches the isopleth at the point B, then follows the lg two-phase isentrope until it reaches the llg three-phase curve at point C; from then on it follows the three-phase isentrope (which coincides with the llg three-phase curve in this projection). Below point C, the two-phase isentrope is metastable.

The metastable portion of the two-phase isentrope shows a “wriggle”, which is analogous to the behavior of single-phase isentropes of pure fluids.<sup>4</sup> In both cases, the phenomenon is



**Figure 11.** Adiabatic expansion of a (butane + pentane) mixture starting at a two-phase state at 450 K, 3 MPa ( $\square \cdots \square$ )  $qT$  representation. The colors indicate the initial quality  $q_0$  (rainbow encoding: red = 0.0, magenta = 1.0). The arrow shows the direction of the expansion.

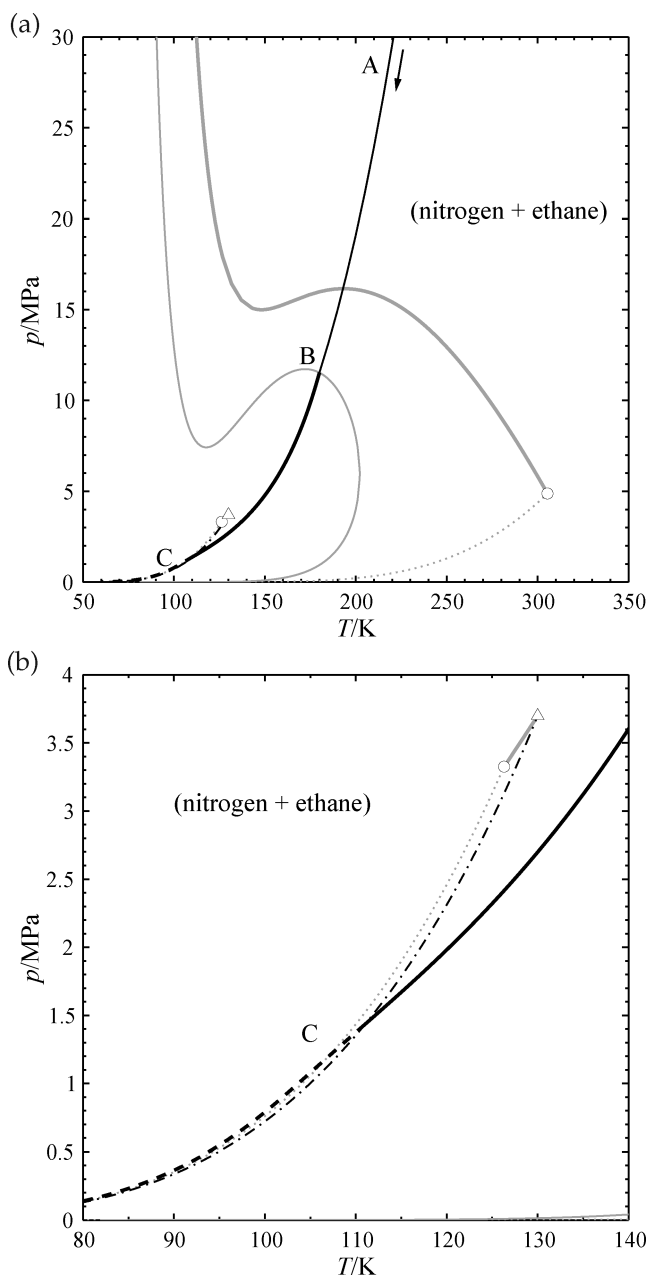
related to the existence of a stability boundary (spinodal curve) in the vicinity.

For the (nitrogen + ethane) system, the metastable two-phase isentrope lies always above the llg three-phase curve, which means that the system cannot return to a two-phase or single-phase expansion anymore.

Figure 13 shows the corresponding  $TS$  diagram. It should be noted that the curves are projections onto the  $TS$  plane: The two-phase isentrope has a lower pressure than the three-phase curve above state C, and a higher pressure below this state. When the two-phase expansion reaches C, a new liquid phase is formed, which is very rich in nitrogen. The amounts of the three phases can be calculated from the mass and entropy balances by extending eqs 2 and 6 to three-phase systems.

At sufficiently low temperatures and pressures, the vapor phase contains mostly the light component, nitrogen. It is therefore not surprising that the  $T(S)$  relations of the vapor branches of the two- and three-phase isentropes are very similar to that of pure nitrogen vapor, with a negative slope. The (nitrogen + ethane) system can therefore be classified as “wet”: The single-phase isentrope cannot intersect the vapor branch of the two-phase isentrope a second time, and therefore the system cannot reach a single-phase state by adiabatic expansion. But whether the system will remain in a two-phase or a three-phase state is more difficult to decide. In this case, however, the three-phase state persists.

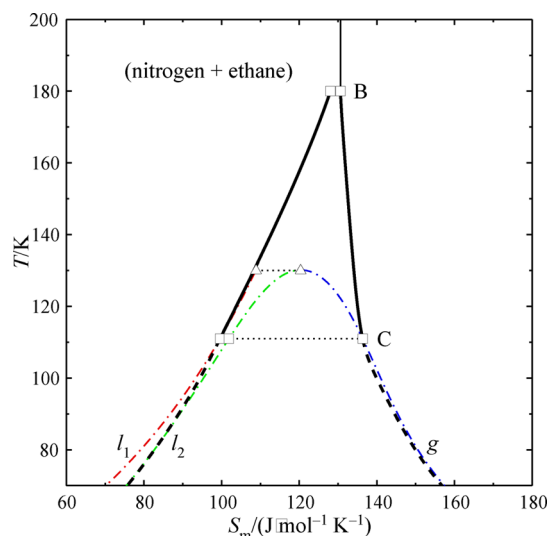
Figure 14 describes the adiabatic expansion of a (nitrogen + ethane) mixture with  $x_1 = 0.9$  at a lower temperature. On reaching state B, a second phase is formed, which is richer in ethane. This is similar to the behavior shown in Figure 12, but now the new phase has a lower molar density than the original one. Evidently, along the isopleth there is a state at which the (molar) phase densities change places. Such an isopycnic state is sometimes regarded as the boundary between vapor–liquid and liquid–liquid phase equilibria.<sup>21</sup> The ethane-rich phase, however, has always the higher mass density; a (mass) barotropic inversion does not occur in this system.



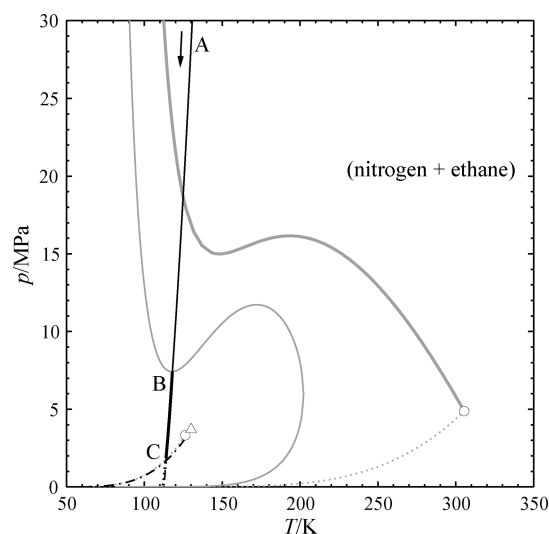
**Figure 12.** Phase diagram of the (nitrogen + ethane) system:  $pT$  projection. (○) Pure-component critical point; (△) critical end point. Gray curves: (heavy line) critical curve; (dotted line) vapor pressure curve; (line) phase envelope  $x_1 = 0.9$ . Black curves: (solid = stable, broken = metastable): (solid line) single-phase isentrope; (bold solid line) two-phase isentrope; (dash-dot line) lg three-phase curve.

Incidentally, Griffiths' theorem is also applicable to isentropes passing through a *minimum* of an isopleth. In the  $pT$  projection Figure 14, the two-phase isentrope coincides with the single-phase isentrope between the states B and C.

**3.4. (Nitrogen + Pentane).** As the system (nitrogen + ethane) belongs to phase diagram class III (rational name:  $1^C 1^Z$ ), one might expect the same to be true for (nitrogen + pentane). Figure 15 shows, however, that the phase diagram class might rather be V (rational name:  $2^P$ ). The distinction is difficult, for the course of the low-temperature portion of the critical curve is very sensitive to the choice of the interaction parameters (here: PPR78 group contribution method<sup>13,14</sup>) and



**Figure 13.** Temperature–entropy diagram of the system (nitrogen + ethane). See Figure 12 for an explanation of the symbols. (□...□) Coexisting phases marking the transition between single-, two-, and three-phase expansion. The colors merely serve to improve the visibility of the three-phase curves.

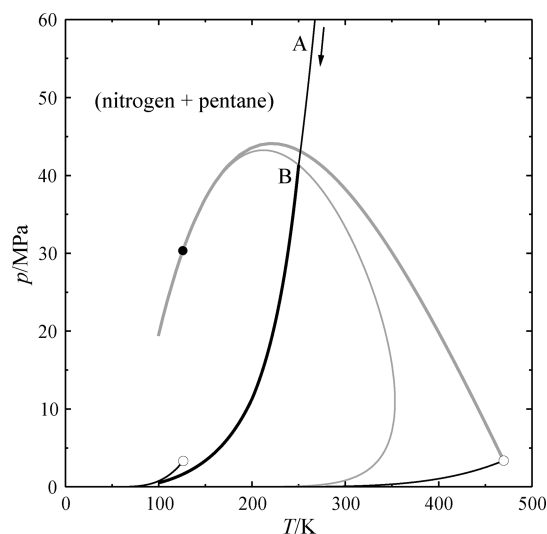


**Figure 14.** Phase diagram of the (nitrogen + ethane) system:  $pT$  projection; expansion of a mixture with  $x_1 = 0.9$  at low temperatures. (○) Pure-component critical point; (△) critical end point. Gray curves: (heavy line) critical curve; (dotted line) vapor pressure curve; (line) phase envelope  $x_1 = 0.9$ . Black curves (solid = stable, broken = metastable): (line) single-phase isentrope, (heavy line) two-phase isentrope; (dash-dot line) lg three-phase curve.

the pure-fluid parameters. The point is probably moot, as the triple point of pentane is at 143 K, so that the low-temperature portion of the critical curve lies behind the crystallization surface.

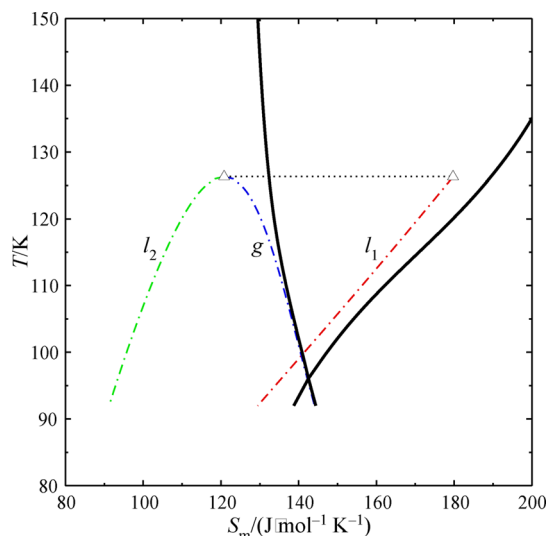
The diagram illustrates the adiabatic expansion of a sample with the composition  $x_1 = 0.9$  from a high-pressure state. As for the previous examples, the system switches to the two-phase isentrope at the intersection with the isopleth. The two-phase isentrope runs to the low-pressure and low-temperature region, where the three-phase equilibrium curve lies (not visible at the resolution of the diagram).





**Figure 15.** Phase diagram of the (nitrogen + pentane) system:  $pT$  projection; expansion of a mixture with  $x_1 = 0.9$  at low temperatures. (O) pure-component critical point, (●) binary critical point for  $x_1 = 0.9$ . Gray curves: (heavy line) critical curve; (dotted line) vapor pressure curve; (line) phase envelope  $x_1 = 0.9$ . Black curves: (line) single-phase isentrope, (heavy line) two-phase isentrope.

As for the previous system, the vapor phase of the three-phase equilibrium is almost pure nitrogen, and so appears as a curve with a negative slope in the  $TS$  diagram Figure 16. The



**Figure 16.** Temperature–entropy diagram of the system (nitrogen + pentane). (Δ) Critical end point. Color curves: (dash dot line)  $l_2$  three-phase curves; (solid line) two-phase isentrope. The colors merely serve to improve the visibility of the three-phase curves ( $l_1$ , pentane-rich liquid;  $l_2$ , nitrogen-rich liquid;  $g$ , vapor).

curve of the pentane-rich liquid crosses the curves of the other phases because of entropic inversion. But the two-phase isentrope shows entropic inversion, too. As a consequence, the two-phase isentrope misses the three-phase separation. In the  $pT$  diagram Figure 15, the two-phase isentrope passes under the vapor pressure curve of nitrogen and under the three-phase curve.

## 4. CONCLUSION

A method for the calculation of the isentropes of mixtures in the vapor–liquid two-phase region was proposed, and isentropes were calculated for some binary fluid mixtures with the Peng–Robinson equation of state,<sup>11,12</sup> using the common quadratic mixing rules and interaction parameters either fitted to experimental data or computed with a group contribution method.<sup>13,14</sup>

Comparison of single-phase and two-phase isentropes confirms Griffiths' prediction that their slopes must be identical at pressure extrema of isopleths—particularly the maxcondensar point, but also at pressure minima—and different elsewhere.

Calculations of isentropes starting at a given two-phase equilibrium state, but with different qualities (vapor/liquid ratios) show that the isentropes depend little on the initial quality  $q_0$  if the mole fractions of the starting phases were similar, but can differ considerably otherwise. Adiabatic expansions of mixtures containing a supercritical component can exhibit an “entropic inversion”, that is, a situation in which the vapor has a lower molar entropy than the liquid.

Fluid mixtures exhibiting large nonideality may eventually have regions of liquid–liquid immiscibility. In such a case, a two-phase isentrope can possibly intersect the  $l_2l_3$  three-phase curve. Beyond this intersection, an adiabatic process would follow the three-phase curve, while the two-phase isentrope becomes metastable. But if an entropic inversion takes place along the two-phase isentrope, this can affect the topology of the phase diagram in such a way that the isentrope misses the three-phase curve and therefore remains stable.

Evidently, the patterns of two-phase isentropes of fluid mixtures can be varied and sometimes rather complicated. Further research on this subject is certainly indicated.

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### Notes

The authors declare no competing financial interest.

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## ■ SYMBOLS

- $a_c$  = attraction parameter of the Peng–Robinson equation
- $A$  = Helmholtz energy
- $C$  = heat capacity
- $G$  = Gibbs energy
- $n$  = amount of substance
- $N$  = number of components
- $p$  = pressure
- $q$  = “quality”,  $q = n''/(n' + n'')$
- $R$  = gas constant
- $S$  = entropy
- $T$  = temperature
- $T^*$  = characteristic temperature, parameter of the PR equation,  $a_c = 8RT^*v^*$

$v^*$  = characteristic volume, parameter of the PR equation  
 $V$  = volume  
 $x$  = mole fraction  
 $Z$  = compression factor,  $Z = p V_m / (R T)$   
 $\alpha(T)$  = temperature dependence of the attraction term of the PR equation  
 $\rho$  = molar density,  $\rho = 1/V_m$   
 $\Psi$  = Helmholtz energy density,  $\Psi = A/V$   
 $\omega$  = acentric factor, parameter of the PR equation

### Subscripts

$c$  = critical point  
 $m$  = molar  
 $i$  = belonging to component  $i$   
 $p$  = derivative at constant pressure  
 $T$  = derivative at constant temperature  
 $V$  = derivative at constant volume  
 $0$  = initial state, starting point of an isentrope

### Superscripts

$g$  = gas, vapor phase  
 $l$  = liquid  
 $id$  = ideal gas  
 $r$  = residual  
 $\phi$  = arbitrary phase  
 $\ominus$  = reference state  
 $\tilde{X}$  = reduced (dimensionless) property  $X$   
 $*$  = characteristic (substance-specific) parameter

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