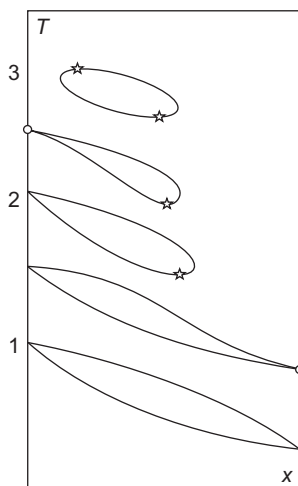
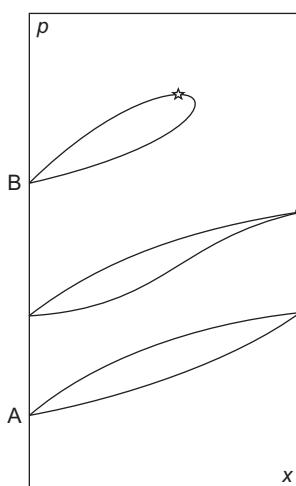


**FIGURE 2.18** Phase diagram class I. Note that the pure-fluid critical point with the lower temperature belongs to component 1.



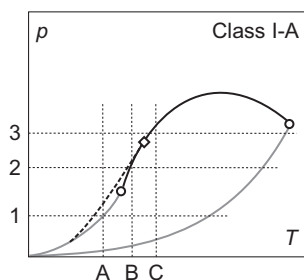
**FIGURE 2.19** Class I  $Tx$  cross sections.



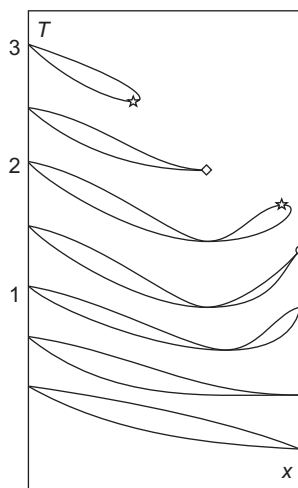
**FIGURE 2.20** Class I  $px$  cross sections.

An isothermal  $px$  cross section can be constructed in an analogous way by plotting a vertical line in the  $pT$  projection. The intersections of the curves with this line are plotted into a  $px$  diagram in Fig. 2.20.

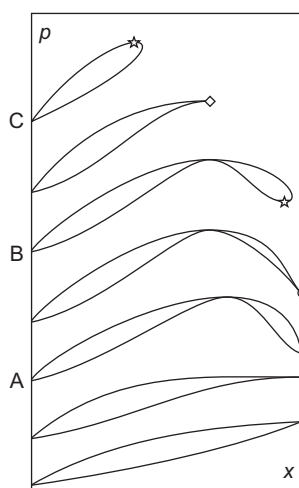
- At low temperatures, the vapor pressure curves of both substances are intersected, yielding a regular vapor–liquid coexistence region in the  $px$  diagram such as cross section A in Fig. 2.20.
- At the critical temperature of the more volatile substance, this vapor–liquid region detaches from the pressure axis at  $x=1$  (cross section between A and B). Then a coexistence region connected to the ordinate at  $x=0$  forms, as shown in cross section B. Its pressure maximum is a binary critical point.
- This coexistence region finally contracts and vanishes at  $x=0$ , when the critical temperature of the less volatile substance is reached.



**FIGURE 2.23** Class I-A phase diagram.



**FIGURE 2.24** Corresponding  $Tx$  cross sections.



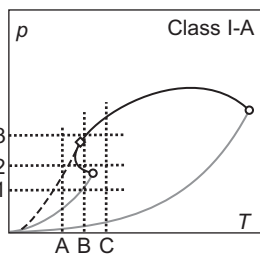
**FIGURE 2.25** Corresponding  $Tx$  cross sections.

are nonazeotropic. Then border azeotropy develops: the bubble point curve and the dew point curve come together in a cusp at  $x=1$  with a horizontal tangent. A further increase of temperature or pressure lets the (still subcritical) azeotrope move away from  $x=1$ . Then the two-phase region detaches from the  $x=1$  ordinate and contracts, until it vanishes in a critical azeotropic point.

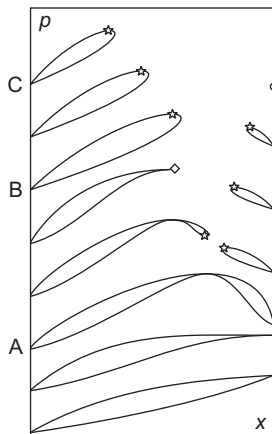
Examples for this subclass are the systems {ethane + hydrogen sulfide} [10], {carbon dioxide + ethane} [11], and – most important – {ethanol + water}.

It is very easy to confuse the phase envelopes of border azeotropes and critical azeotropes: in both, the bubble point curve and the dew point curve meet in a horizontal cusp; both look like half a regular azeotropic curve. The border azeotrope, however, is a subcritical two-phase state, whereas the critical azeotrope is a one-phase state.

A schematic phase diagram of class I-A with a temperature minimum along the critical curve is shown in Fig. 2.26. The  $Tx$  cross sections are topologically



**FIGURE 2.26** Class I-A phase diagram with a temperature minimum in the critical curve.



**FIGURE 2.27** Corresponding  $px$  cross sections.

the same as those without the temperature minimum, but the  $px$  cross sections differ, as shown in Fig. 2.27. In cross section B, the critical curve is intersected two times; hence, there are two critical points in the  $px$  cross section. These two critical points merge at the temperature minimum of the critical curve. Above that temperature, the two-phase region splits into two parts; below that temperature, it is a regular azeotropic diagram.

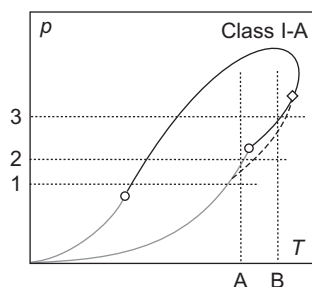
Examples for this kind of phase diagram topology are {ethane + dinitrogen oxide} [12] and {ethane + hydrogen chloride} [13].

### 2.2.1.3 Variants of Class I: Negative Azeotropy

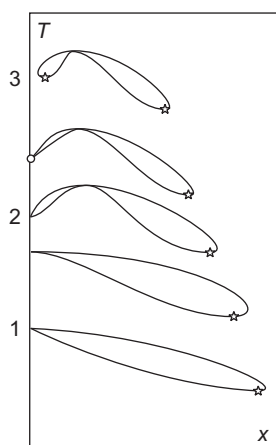
Negative azeotropy is seldomly observed for mixtures of nonpolar compounds. The phenomenon is usually caused by attractive interactions between unlike molecules which are stronger than those between like molecules, and this is often the result of chemical interactions. Examples are {hydrogen chloride + methanol}, where there is strong hydrogen bonding or even proton transfer between the acid and the alcohol,<sup>8</sup> and {hydrogen bromide + water}. In the case of {carbon disulfide + acetone}, the negative azeotropy is explained with the existence of a charge transfer complex.

A schematic binary phase diagram with negative azeotropy is shown in Fig. 2.28. The azeotropic curve originates at the vapor pressure curve of the less volatile substance and terminates in a critical azeotropic point at high temperature. The  $Tx$  cross sections (Fig. 2.29) and the  $px$  cross sections (Fig. 2.30) may differ, depending on the pressure at which the azeotropy sets in at  $x=0$ . The

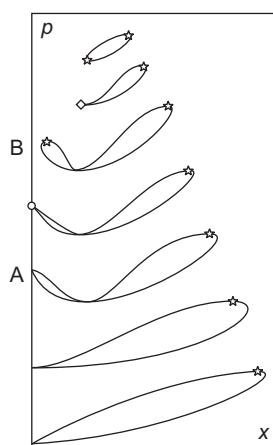
<sup>8</sup>This is probably not the best example, for here chemical reactions producing methyl chloride, dimethyl ether, and water may take place, so that this is not really a binary mixture.



**FIGURE 2.28** Class I-A phase diagram with negative azeotropy.



**FIGURE 2.29** Corresponding  $Tx$  cross sections.



**FIGURE 2.30** Corresponding  $px$  cross sections.

sequence begins with a regular vapor–liquid phase equilibrium with a binary critical point, followed by the formation of an azeotropic point at  $x=0$ , and the detachment from the ordinate at the critical point of the less volatile substance. The  $Tx$  and  $px$  cross sections are topologically similar; merely minima and maxima appear to be switched. At high pressures or temperatures beyond the critical azeotropic point, closed-loop phase envelopes appear. Closed-loop two-phase regions in  $Tx$  diagrams are nothing special; they occur also in the regular class I. But closed-loop two-phase regions in  $px$  diagrams are a rare phenomenon.

If the azeotropic curve ends on the critical curve, it is unavoidable that the critical curve runs through regions above the critical temperature of the less volatile component. Negative azeotropy is, therefore, one of the rather few phenomena that causes phase separation above the critical temperatures of the mixture components.

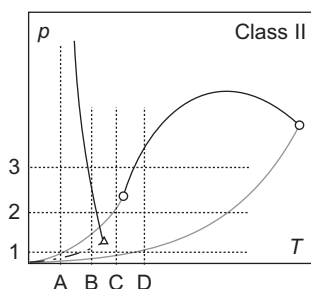


FIGURE 2.36 Class II phase diagram.

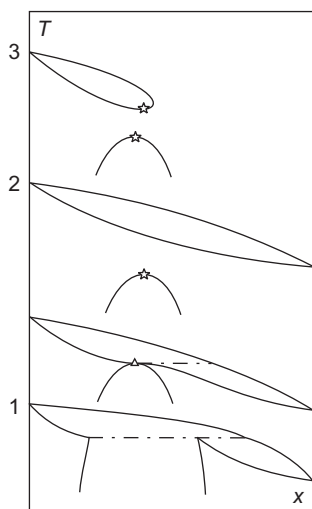


FIGURE 2.37 Corresponding  $Tx$  cross sections.

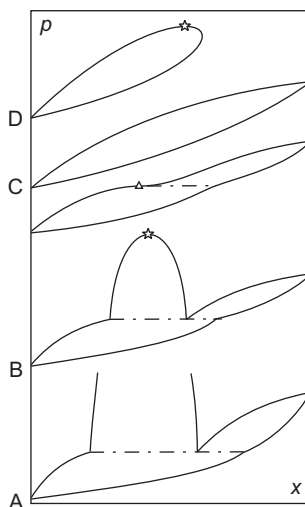


FIGURE 2.38 Corresponding  $px$  cross sections.

on the shape of the  $l=l$  critical curve, one can distinguish several subclasses. In the subclass shown in Fig. 2.36, the  $l=l$  critical curve has a negative slope in the  $pT$  projection. The corresponding  $Tx$  and  $px$  cross sections are displayed in Figs 2.37 and 2.38, respectively.

- In the  $Tx$  cross section at low pressure (section 1 in Fig. 2.37), a vapor–liquid coexistence region “overlaps” with a liquid–liquid phase equilibrium coming up from low temperatures. A three-phase line  $llg$  (more precisely:  $l_1l_2g$ ) splits the vapor–liquid region in two parts,  $l_1g$  and  $l_2g$ . The two parts are connected to the boiling points of the pure components at  $x=0$  and  $x=1$ .
- With increasing temperature, the liquid–liquid coexistence region detaches from the vapor–liquid region at a critical endpoint.
- In cross section 2, the two regions are separated.

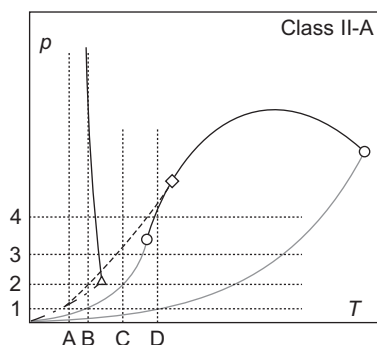


FIGURE 2.43 Class II-A phase diagram.

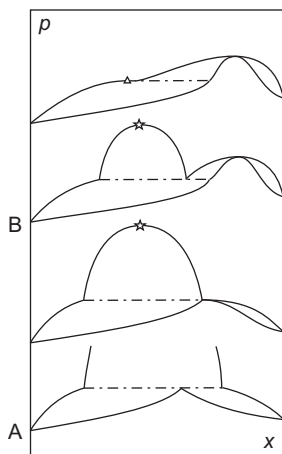
### 2.2.2.3 Variants of Class II: Azeotropy

Azeotropy can appear in connection with class II, too. In the  $pT$  projection (Fig. 2.43), the three-phase curve is located above the vapor pressure curve of the more volatile substance. Azeotropy starts somewhere along the three-phase curve and terminates at the critical curve in a critical azeotrope.

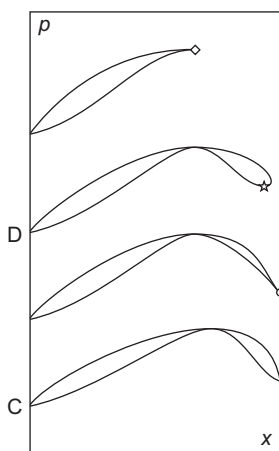
- The  $px$  cross section A at low temperature (Fig. 2.44) contains two vapor–liquid coexistence regions connected to a liquid–liquid coexistence region at higher pressure; between them, a three-phase state  $lg$  is formed. Cross section type A is called *heteroazeotropic*.

In a heteroazeotropic system, there are two distinct liquid–gas phase equilibrium regions at a given pressure and temperature, like in a regular azeotropic system. At the highest possible pressure (or the lowest possible temperature) for vapor–liquid equilibria, however, these two regions merge to form a three-phase state  $lg$ . This is in contrast to a regular azeotropic system (cf. Fig. 2.45 curve C), where the vapor–liquid equilibrium with the highest pressure (lowest temperature) is reached in an azeotropic two-phase state  $(lg)^{az}$ .

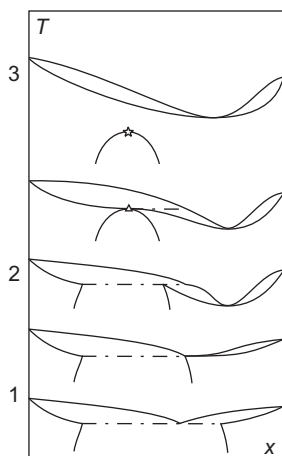
- With increasing temperature, the vapor–liquid region at high mole fraction develops an azeotrope connected to the three-phase line. Such an  $l(lg)^{az}$  three-phase state is called an *azeotropic endpoint*. As for a regular azeotrope, the slopes of both phase boundary curves are here zero.
- In cross section B, above that temperature, the vapor–liquid coexistence region exhibits a regular azeotrope connected to the other two coexistence regions through a three-phase state.
- With increasing temperature, the liquid–liquid immiscibility region shrinks and finally terminates in a critical endpoint  $l=lg$ .
- In cross section C (Fig. 2.45), a regular vapor–liquid azeotrope exists.
- If the critical azeotrope lies at a higher temperature than the critical point of the more volatile component, first a vapor–liquid critical point appears at



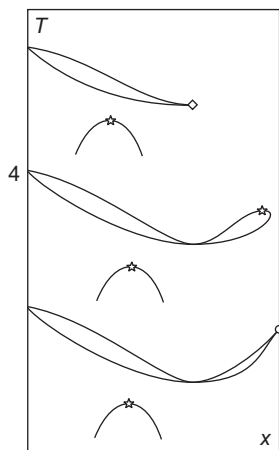
**FIGURE 2.44** Class II-A: corresponding  $px$  cross sections.



**FIGURE 2.45** More corresponding  $px$  cross sections.



**FIGURE 2.46**  $Tx$  cross sections of class II-A.



**FIGURE 2.47** More  $Tx$  cross sections.

high mole fraction (cross section D) before the azeotropic curve ends in a critical azeotrope.

The  $Tx$  cross sections of class II-A (Figs 2.46 and 2.47) behave similarly as the  $px$  sections, although with the difference that the liquid–liquid immiscibility region is detached from the vapor–liquid region at the critical endpoint. Between cross sections 1 and 2, three-phase states and azeotropy occur together. Above cross section 4, there is a cross section with a critical azeotrope, and at still higher pressures, the cross sections are similar to those of class I.