

Adiabatic Processes in the Liquid–Vapor Two-Phase Region. 1. Pure Fluids

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ABSTRACT: Adiabatic processes in the liquid–vapor two-phase region were studied with several equations of state. The comparison of the resulting isentropes, particularly their patterns in quality (fraction of vapor phase) vs temperature diagrams, indicates that there are two different classes of fluids: One class shows a simple pattern where isentropes entering the two-phase region never leave it again; the other shows a more complicated pattern with reentrant isentropes, which may either cross the entire two-phase region or exhibit a retrograde behavior. The existence of these two classes can be related to the shapes of entropy–volume or temperature–entropy curves, and these in turn to the temperature dependence of ideal-gas heat capacities. The two-phase isentrope that runs to the critical point approaches it with an infinite slope in the quality–temperature diagram. The slope is positive for reference equations of state, but negative for all other equations of state used in this work.

1. INTRODUCTION

Adiabatic processes involving gases or supercritical fluids occur within many heat engines, from internal combustion engines to turbines, and their optimization is essential for the energy efficiency of motors, power plants, or refrigeration machinery. Of course, true adiabatic processes, i.e., processes during which the heat exchange with the environment is exactly zero, are idealizations only. But processes involving large amounts of substance or rapid changes of thermodynamic states can come close to the ideal case.

A special subset of adiabatic processes is the two-phase adiabatic processes during which a liquid and a vapor phase are in equilibrium. An example is the adiabatic expansion of a compressed, hot liquid or a supercritical fluid: The process can eventually lead to a state on the vapor pressure curve; further expansion then causes the formation of a vapor phase, accompanied by rapid cooling of the system.

The Clausius–Rankine cycle, the model process upon which most thermal power plants are based, involves an adiabatic expansion of the superheated working fluid which may take it into the two-phase region.¹ As the original (and still the predominant) working fluid for Clausius–Rankine cycles is water, most of the thermodynamic studies were made for this fluid. Over the previous decades, however, other substances have been investigated as working fluids in the context of “organic Rankine cycles” (ORC) in order to recover energy from low- and intermediate-temperature heat reservoirs.^{2,3}

An example of an adiabatic two-phase expansion from the field of equipment safety is the escape of hot, pressurized

cooling water in a power plant from a broken pipe;⁴ at least the early phase of such an accident can be considered adiabatic. The scenario may be complicated by metastability issues (superheating or subcooling). Examples are the LOCA (“loss of coolant accident”) in a nuclear power plant, which involves so-called flash-boiling, and the BLEVE (“boiling-liquid expanding-vapor explosion”), which can occur after a fast depressurization of liquefied natural gas.^{5,6}

Adiabatic two-phase decompression can also take place in volcanic eruptions, where water gets into contact with hot magma and rapidly evaporates, and the superheated steam thus produced seeks an outlet. The explosivity of water has been extensively discussed by Thiéry and Mercury.⁷

One should suppose that two-phase adiabatic processes have been studied exhaustively and that—as they (in pT space) follow the vapor pressure curve—their computation is a trivial problem. But this is not quite the case. While adiabatic compressions or expansions of fluids *in the single phase state* are discussed in most textbooks on thermodynamics (at least for ideal gases), two-phase adiabatic processes are either not mentioned at all or treated superficially, i.e., their discussion is reduced to their courses in temperature–entropy diagrams.

In this work, we propose calculation methods—a differential and an algebraic equation—for adiabatic processes in two-

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phase systems and then compute isentropes for several fluids of technical importance, using some equations of state of varying complexity, which are relevant for chemical engineering. Furthermore, we investigate the question whether a two-phase adiabatic expansion can result in a single-phase state.

2. EQUATIONS OF ADIABATIC PROCESSES

In this section, equations for reversible adiabatic expansions and compressions of pure fluids are derived. For simplicity's sake, only expansion processes are mentioned, but the following derivations can be applied to compression processes as well.

2.1. Single-Phase Isentropes. Before tackling the problem of computing adiabatic processes in the liquid–vapor two-phase region, it may be useful to briefly review the case of adiabatic processes in a single-phase fluid.

In the course of an adiabatic expansion, there is no heat exchange with the environment

$$dQ = T dS = 0 \quad (1)$$

and the entropy is constant (assuming that the process is carried out reversibly). The system gives off mechanical work to its environment; the required energy is taken entirely from its internal energy. According to the first law, and if no other forms of energy are exchanged, such a process in a closed system is described by

$$dU = -p dV \quad (2)$$

for a pure fluid. The total differential of U in terms of temperature and volume is

$$dU = C_V dT + \left(T \left(\frac{\partial p}{\partial T} \right)_V - p \right) dV \quad (3)$$

Combining these two equations leads to the well-known differential equation for the adiabatic expansion or compression of a pure fluid:

$$\frac{dT}{dV} = -\frac{T}{C_V} \left(\frac{\partial p}{\partial T} \right)_V \quad (4)$$

or, using the density instead of the volume and switching to molar variables,

$$\frac{dT}{d\rho} = \frac{T}{\rho^2 C_{V,m}} \left(\frac{\partial p}{\partial T} \right)_V \quad (5)$$

Assuming $(\partial p/\partial T)_V = R/V_m$ and $C_V = \text{const}$ leads to the well-known isentropic formula for ideal gases. But it is not necessary to make such approximations. $C_{V,m}$ and $(\partial p/\partial T)_V$ can be obtained from an equation of state of the fluid, $p(\rho, T)$, and its ideal-gas heat capacity function, $C_{p,m}^{\text{id}}(T)$. Then, eq 5 can be integrated numerically.

2.2. Two-Phase Isentropes. In this work, the special case is considered where the system is a fluid in a liquid–vapor two-phase state. It is assumed that the phase equilibrium is maintained throughout the expansion process, i.e., that there is no overheating or subcooling, and that liquid and vapor always have the same temperature.

2.2.1. Algebraic Equation. A simple and straightforward way to calculate two-phase isentropes can be based on the constancy of entropy during an adiabatic process. The total entropy of a two-phase system is of course the sum of the contributions of the two phases:

$$S_m = (1 - q)S_m(\rho^l, T) + qS_m(\rho^g, T) \quad (6)$$

where the ρ^ϕ with $\phi = \{l, g\}$ denote the molar densities of the coexisting liquid and vapor phase, respectively. q is the fraction of the system that is in the vapor phase, $q = n^g/(n^l + n^g)$; this property is often called the quality or the dryness of the system. Equation 6 holds at the initial state of the two-phase isentrope, (q_0, T_0) , too. Hence q at any other temperature can be obtained by

$$q = \frac{S_{m,0} - S_m(\rho^l, T)}{S_m(\rho^g, T) - S_m(\rho^l, T)} \quad (7)$$

A result outside of the range $0 \leq q \leq 1$ indicates that the two-phase state is no longer stable, and that a single-phase isentrope should be computed instead.

For the evaluation of eq 7, it is necessary to know the full Helmholtz energy function, which we write here as

$$A_m(\rho, T) = A_m^{\text{id}}(T) + RT \ln \left(\frac{\rho}{\rho^\ominus} \right) + A_m^r(\rho, T) \quad (8)$$

where $\rho^\ominus = RT^\ominus/p^\ominus$ is a reference density, namely the density of an ideal gas at standard temperature, T , and standard pressure, p^\ominus . The Helmholtz energy function consists of the density-independent part of the ideal-gas contribution, its density-dependent part, and the residual term. The first term can be calculated from ideal gas heat capacity data, as described in the Appendix. The residual term can be obtained from a thermal equation of state, $p(\rho, T)$:

$$\frac{A_m^r(\rho, T)}{RT} = \int_0^\rho \left(\frac{p(\rho, T)}{RT\rho^2} - \frac{1}{\rho} \right) d\rho \quad (9)$$

In principle, any thermal equation of state—from simple cubic equations to high-precision reference equations—can be used.

From the Helmholtz energy function, all other thermodynamic functions can be obtained by well-known standard relations. For the readers' convenience, the relations needed in this work are listed in the Appendix.

The orthobaric densities and the vapor pressure p^σ can then be obtained by numerically solving the phase equilibrium conditions:

$$A_m(\rho^g, T) - A_m(\rho^l, T) = -p^\sigma \left(\frac{1}{\rho^g} - \frac{1}{\rho^l} \right) \quad (10)$$

$$p(\rho^\phi, T) = p^\sigma \quad \phi = \{l, g\}$$

for the given temperature T . For this, fast and reliable algorithms exist (e.g., ref 8, section 5.2.3 or the area method of Elhassan et al.⁹). Once the orthobaric densities are known, the heat of vaporization and the isobaric heat capacities can be computed in a straightforward manner.

For completeness' sake, we wish to point out that eq 7 can also be applied to solid–vapor (sublimation) equilibria after merely replacing $S_m(\rho^l, T)$ by its counterpart for solid phases. The entropies of the solid phases—there can be more than one—of most substances that can be used in adiabatic processes have been tabulated. Such tabulations are usually for a fixed pressure of 0.1 MPa, but pressure effects in the typical range of sublimation pressures tend to be negligible. Alternatively, the entropies can be obtained from the sublimation pressure curves: As the Gibbs energy of the solid

and the vapor are the same along the sublimation pressure curve, the Helmholtz energy of the solid can be expressed as

$$A_m^s(T) = A_m(\rho^g, T) + p^{sg} \left(\frac{1}{\rho^g} - \frac{1}{\rho^s} \right) \quad (11)$$

where ρ^g and ρ^s denote the molar densities of the vapor and the solid at the sublimation pressure p^{sg} . The Helmholtz energy of the vapor is of course given by eq 8. Differentiation with respect to temperature yields the solid-phase entropy.

2.2.2. Differential Equation. Alternatively, and in analogy to section 2.1, it is possible to obtain two-phase isentropes from a differential equation.

Let V_m^l and V_m^g denote the orthobaric molar volumes of the liquid and the vapor, respectively. Lowering the temperature by the infinitesimal amount dT liberates the heat

$$dQ^\phi = n^\phi C_{\sigma m}^\phi dT \quad (12)$$

from the phase $\phi = \{l, g\}$, where n^ϕ is the amount of substance of the phase ϕ and $C_{\sigma m}^\phi$ denotes the molar heat capacity along the saturation curve, i.e., the heat capacity of the liquid in the presence of an infinitesimal amount of vapor, or that of the vapor in the presence of an infinitesimal amount of liquid.

This heat is then used to move a small amount of substance from the liquid to the vapor phase. The heat balance of the process is therefore

$$dQ^l + dQ^g + \Delta_{\text{vap}} H_m dn = 0 \quad (13)$$

where $\Delta_{\text{vap}} H_m$ denotes the enthalpy of vaporization.

The saturation heat capacities can be related to more common thermodynamic derivatives by invoking the second law (assuming that the expansion process is reversible) and considering the total differential of the entropy of a phase

$$dQ^\phi = T dS^\phi = n^\phi \left(C_{p m}^\phi dT + T \left(\frac{\partial S_m^\phi}{\partial p} \right)_T dp \right) \quad (14)$$

The required pressure change is given by Clapeyron's equation:

$$dp = \frac{dp^\sigma}{dT} dT = \frac{\Delta_{\text{vap}} H_m}{T(V_m^g - V_m^l)} dT \quad (15)$$

Insertion into eq 14 and observing the relation $(\partial S_m / \partial p)_T = -(\partial V_m / \partial T)_p$ leads to

$$dQ^\phi = C_{p m}^\phi dT - T \left(\frac{\partial V_m^\phi}{\partial T} \right)_p \frac{\Delta_{\text{vap}} H_m}{T(V_m^g - V_m^l)} dT \quad (16)$$

from which the definition of the saturation heat capacity immediately follows:

$$\begin{aligned} C_{\sigma m}^\phi &= C_{p m}^\phi - T \left(\frac{\partial V_m^\phi}{\partial T} \right)_p \frac{\Delta_{\text{vap}} H_m}{T(V_m^g - V_m^l)} \\ &= C_{p m}^\phi - \alpha_p^\phi V_m^\phi \frac{\Delta_{\text{vap}} H_m}{V_m^g - V_m^l} \end{aligned} \quad (17)$$

Here, α_p^ϕ denotes the isobaric thermal expansivity. Equation 17 as well as some alternative expressions can be found in the textbook of Rowlinson and Swinton [ref 10, section 2.1].

With the saturation heat capacities, eq 13 can be written as

$$n^l C_{\sigma m}^l dT + n^g C_{\sigma m}^g dT = -\Delta_{\text{vap}} H_m dn \quad (18)$$

Introducing the quality q (fraction of the amount of substance that is in the vapor phase) leads to

$$-\frac{1}{\Delta_{\text{vap}} H_m} [(1-q)C_{\sigma m}^l + qC_{\sigma m}^g] = \frac{dq}{dT} \quad (19)$$

This is an ordinary differential equation for $q(T)$, which can be conveniently solved numerically, for example by the method of Runge and Kutta.¹¹

For practical purposes, it may be desirable to study a modified adiabatic process in which the experimental apparatus provides an additional (constant) heat capacity, perhaps the heat capacity of the wall material of the pressure vessel. This case can be modeled by including an additional, "environmental" heat capacity term in eq 19:

$$-\frac{1}{\Delta_{\text{vap}} H_m} [(1-q)C_{\sigma m}^l + qC_{\sigma m}^g + C_e] = \frac{dq}{dT} \quad (20)$$

$C_e = 0$ evidently corresponds to the original adiabatic process and $C_e \rightarrow \infty$ to an isothermal process.

All numerical calculations in this work were carried out with the *ThermoC* software package.¹²

3. CALCULATION OF ISENTROPES

3.1. Simple Behavior. Figure 1a and b show the adiabatic expansion of liquid, compressed propane and carbon dioxide, respectively, calculated with the Peng–Robinson equation of state.^{13,14} Starting at state A, the system follows the single-phase isentrope to the phase boundary at B, then switches to the two-phase isentrope, which of course coincides with the vapor pressure curve in this pT projection.

The single-phase isentrope can be extended—at least theoretically—into the metastable and then through the unstable region of the phase diagram; it exhibits a kind of van der Waals loop. For propane, this loop is easily discernible, whereas for carbon dioxide the maximum lies at very low temperatures. In practice, however, the system must switch from the single-phase to the two-phase isentrope at the latest where the former meets the spinodal curve. This transition is indicated in the diagrams by arrows; it is accompanied by a significant pressure increase and is potentially dangerous.

The relationships between single-phase and two-phase curves are perhaps easier recognizable in a pressure–density diagram, Figure 2: The adiabatic expansion takes the system along a single-phase isentrope from A to B¹, where it splits into a liquid and a vapor phase. In this representation, the two-phase isentrope consists of two branches, which of course coincide with the boundary of the vapor–liquid two-phase region. Inside this region, the isotherms of the equation of state exhibit van der Waals loops; their minima and maxima are the spinodal states. The single-phase isentrope, if extended into the two-phase region, exhibits a van der Waals loop, too. But at the osculation point of the isentrope with the spinodal, a phase split is unavoidable; the arrows in the diagram show the effect of an adiabatic–isochoric spinodal decomposition.

It should be noted that the single-phase isentrope, after passing through the unstable region, does not intersect the two-phase isentrope again. Consequently, the system does not completely evaporate when the expansion proceeds but remains in a two-phase state.

This fact is easier to see in a qT representation, Figure 3a. The initial liquid state corresponds to $q = 0$. When the expansion sets in, some liquid evaporates (q increases). But at

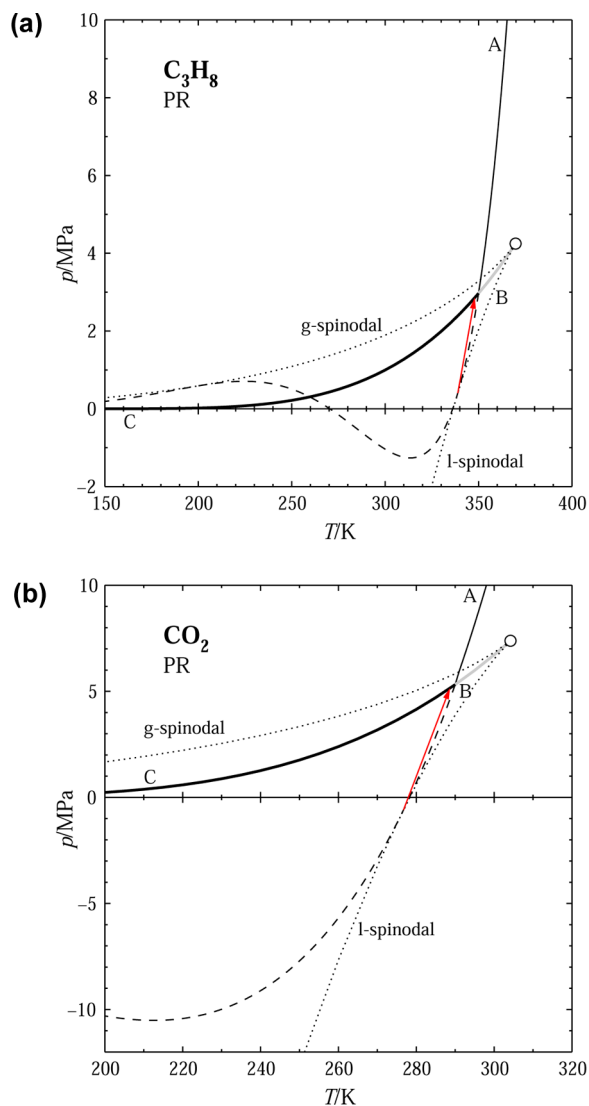


Figure 1. Adiabatic expansion of a fluid, starting at a compressed liquid state, calculated with the Peng–Robinson equation of state:^{13,14} pressure–temperature relation. (—) Single-phase isentrope, stable portion; (---) meta- and unstable portions; (bold —) two-phase isentrope (gray: vapor–pressure curve); (···) spinodal; (arrow) isochoric spinodal decomposition; (O) critical point. (a) Adiabatic expansion of compressed, liquid propane. (b) Adiabatic expansion of compressed, liquid carbon dioxide.

the same time, the temperature decreases, and so does the vapor pressure. As a consequence, q never exceeds 0.5 for this example, and for large expansions even decreases. This behavior can be explained with eq 7: As the vapor pressure decreases, the molar volume and therefore the molar entropy of the vapor phase grow without bounds, whereas the molar entropy of the liquid changes slowly. Consequently, q must approach zero.

Below the triple point temperature of carbon dioxide (approximately 216 K), crystallization is possible, and thus the vapor–liquid isentropes become metastable. At the triple point, the solid–vapor equilibrium and the vapor–liquid equilibrium have the same pressure. As the solid has a lower molar entropy than the liquid, eq 7 yields a higher q value for the solid–vapor equilibrium. But as the sublimation pressure decreases with decreasing temperature more rapidly than the

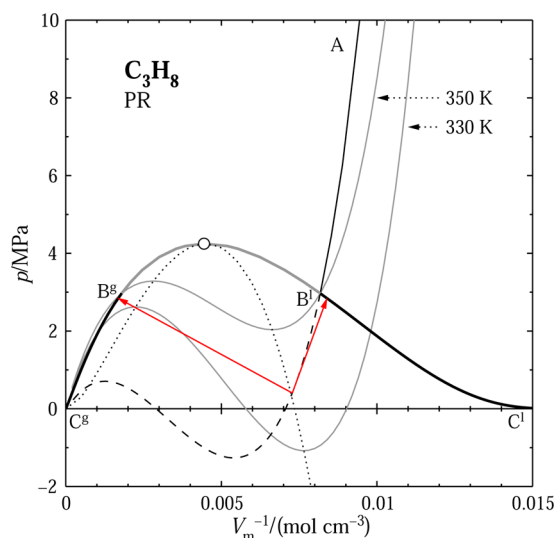


Figure 2. Adiabatic expansion of propane, starting at a compressed liquid state, calculated with the Peng–Robinson equation of state:^{13,14} pressure–density relation. (—) Single-phase isentrope, stable portion (gray: single-phase isotherm); (---) single-phase isentrope, meta- and unstable portions; (bold —) two-phase isentrope (gray: boundary of two-phase region); (···) spinodal, (arrow) isochoric spinodal decomposition; (O) critical point.

vapor pressure, the vapor entropy of the solid–vapor equilibrium is larger, and therefore its q drops to zero faster.

The other curves in Figure 3a show the influence of the environmental heat capacity. For approximately $C_e > 150 \text{ J}/(\text{mol K})$, complete evaporation can be achieved by adiabatic expansion.

Figure 3b shows the corresponding T S diagrams. The entropy is that of the carbon dioxide only, without the environmental contribution. In this representation, the expansion paths are the same for liquid–vapor and solid–vapor equilibria, but of course, the molar entropies of the coexisting phases differ, and so do the qualities along the expansion curves. If the environmental heat capacity is zero, the entropy of the carbon dioxide (i.e., the sum of the contributions of the two phases) is constant, and hence the expansion path in the diagram is vertical. A positive environmental heat capacity makes the expansion path bend away from the vertical, so that it can eventually touch the phase envelope. An infinite environmental heat capacity would cause the expansion path to become horizontal, which means that the expansion would become isothermal.

Figure 4a and b show the adiabatic expansion of a saturated vapor state (initially $q = 1$). In contrast to an isothermal process, an *expansion* is needed to enter the two-phase region. Below the triple point temperature, the liquid–vapor two-phase isentrope becomes metastable with respect to the solid–vapor isentrope. In both cases, stable or metastable, the systems remain in a two-phase state. For an environmental heat capacity $C_e \approx 60 \text{ J}/(\text{mol K})$, however, the expansion curve turns back to the vapor axis of the diagram. This means that, during the expansion, a transient condensation occurs. This phenomenon will be discussed in more detail in section 3.2.

Figure 5 gives an overview over the two-phase isentropes of carbon dioxide. Adiabatic expansions of saturated liquid ($q = 0$) or vapor ($q = 1$) states always lead to a two-phase state; it is not possible to reach a single phase state. The isentrope starting at

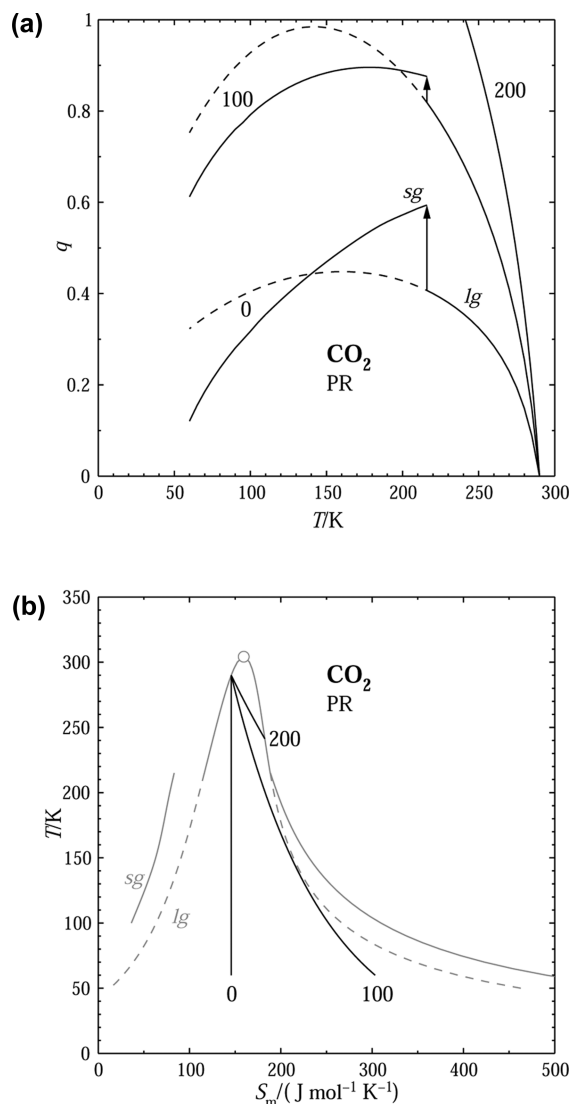


Figure 3. Adiabatic expansion of carbon dioxide, starting at a saturated liquid state, calculated with the Peng–Robinson equation of state.^{13,14} (—) stable expansion path; (---) metastable. Parameter: environmental heat capacity $C_e/(J mol^{-1} K^{-1})$. (a) Quality–temperature relation (solid–vapor and liquid–vapor equilibria; an expansion corresponds to a temperature decrease). (b) Temperature vs entropy of carbon dioxide (i.e., without the environmental contribution). Gray curves: boundaries of two-phase regions (solid–vapor and liquid–vapor).

the critical point (at $q = 0.5$; see section 4 for the proof) runs to $q = 0.5958$ at 210 K.

This isentrope pattern can be explained with entropy–volume or temperature–entropy diagrams. Carbon dioxide belongs to a class of substances which has been named “wet working fluids,” because the adiabatic expansion step of the ORC leads to a two-phase state. Figure 6a shows the SV diagram of methane, another “wet fluid,” along the liquid–vapor phase boundary, together with its constituents, namely

- the equation of state part, which consists of the residual entropy plus a volume term, $R \ln(V_m/V_m^\ominus)$ with $V_m^\ominus = 1 \text{ cm}^3/\text{mol}$; the residual term is negligible for the larger part of the vapor branch
- and the “intrinsic” term, which is obtained by integrating the isochoric heat capacity of the ideal gas

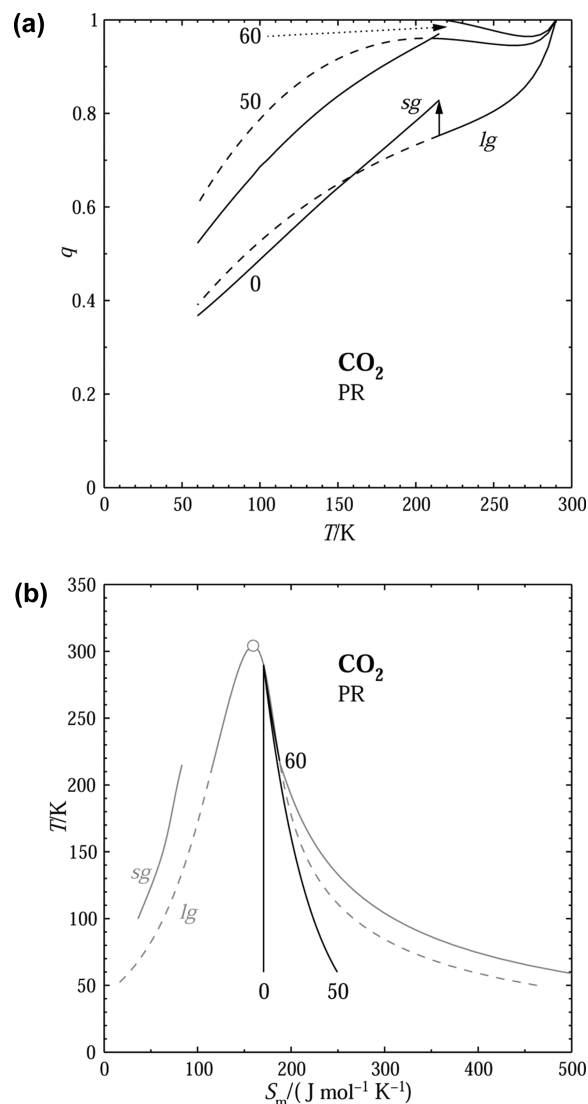


Figure 4. Adiabatic expansion of carbon dioxide, starting at a saturated vapor state, calculated with the Peng–Robinson equation of state.^{13,14} See Figure 3 for an explanation of the line types. (a) Quality–temperature relation (solid–vapor and liquid–vapor equilibria; an expansion corresponds to a temperature decrease). (b) Temperature vs entropy of carbon dioxide (i.e., without the environmental contribution).

$$S_m^{\text{id}}(T) = \int_{T^\ominus}^T \frac{C_{V,m}^{\text{id}}(T)}{T} dT + S_m^{\text{id}}(T^\ominus) \quad (21)$$

The curves were computed with the van der Waals equation of state¹⁵ in order to show that the phenomena discussed here are not due to features of a particular equation of state but can be reproduced with all equations of state.

The equation of state term increases monotonically with volume. The intrinsic term exhibits a weak maximum; the total entropy still increases monotonically. From a state on the phase boundary—either liquid or vapor—an expansion (which corresponds to a horizontal displacement to the right in Figure 6a) takes the system into the two-phase region and further expansion cannot get it out again. The same can be seen from the TS diagram in Figure 6b, where an adiabatic expansion corresponds to a vertical downward movement.

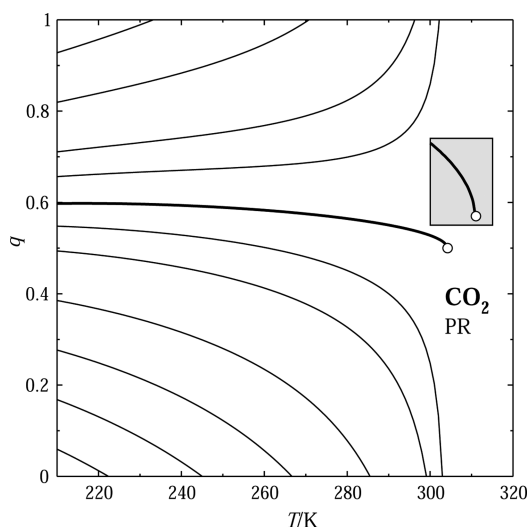


Figure 5. Overview over two-phase isentropes of carbon dioxide: quality (fraction of substance in the vapor phase) vs temperature, calculated with the Peng–Robinson equation of state.^{13,14} (—) Two-phase isentropes; (bold —) two-phase isentrope ending in the critical point (O). Inset: magnification of the critical region.

3.2. Isentropes Crossing the Two-Phase Region.

Benzene exhibits a rather different pattern of isentropes, as shown in Figure 7: Isentropes starting at saturated *liquid* states run to lower temperatures; i.e., they are expansion isentropes, and they lead to two-phase states. This is similar to the situation for carbon dioxide, but now the isentropes reach much larger q values. Isentropes starting at saturated *vapor* states are expansion isentropes at low temperatures only; at high temperatures, they exhibit negative slopes; i.e., they are compression isentropes.

Comparing the entropy values associated with the isentropes leads to the insight that there are three different kinds of isentropes in this diagram:

- There are “normal” isentropes starting from two-phase states with $q \leq 0.9$ at 250 K. Adiabatic compression along these isentropes leads to saturated liquid states. This behavior is the same as in the previous section.
- For $q > 0.9$ at 250 K, there are “re-entrant” isentropes: They run toward a saturated vapor state (as the isentropes of carbon dioxide in the previous section), pass virtually through the single phase region, and re-enter at higher temperatures. “Virtually” means that the two-phase isentropes can be computed but reach q values above 1; in reality, the two stable portions of the two-phase isentrope are connected by a single-phase isentrope. Isentropes running below the critical isentrope (i.e., the isentrope that passes through the critical point) of this kind then run to a saturated liquid state. Consequently, these are “crossing” isentropes; i.e., they cross the entire two-phase region, and hence it is possible to achieve a complete evaporation of a liquid by expansion, or a complete condensation of a vapor, along one of these isentropes.
- Finally, there are re-entrant isentropes above the critical isentrope. After reappearing in the diagram at high temperatures, they turn back and end in saturated vapor states. Consequently, the compression of a saturated vapor state in this region would show a “retrograde” behavior; i.e., there would be a transient condensation.

In Figure 7, the critical isentrope begins—at 240 K—at $q = 0.9814$. The isentrope just below it, with an initial q of 0.95, is

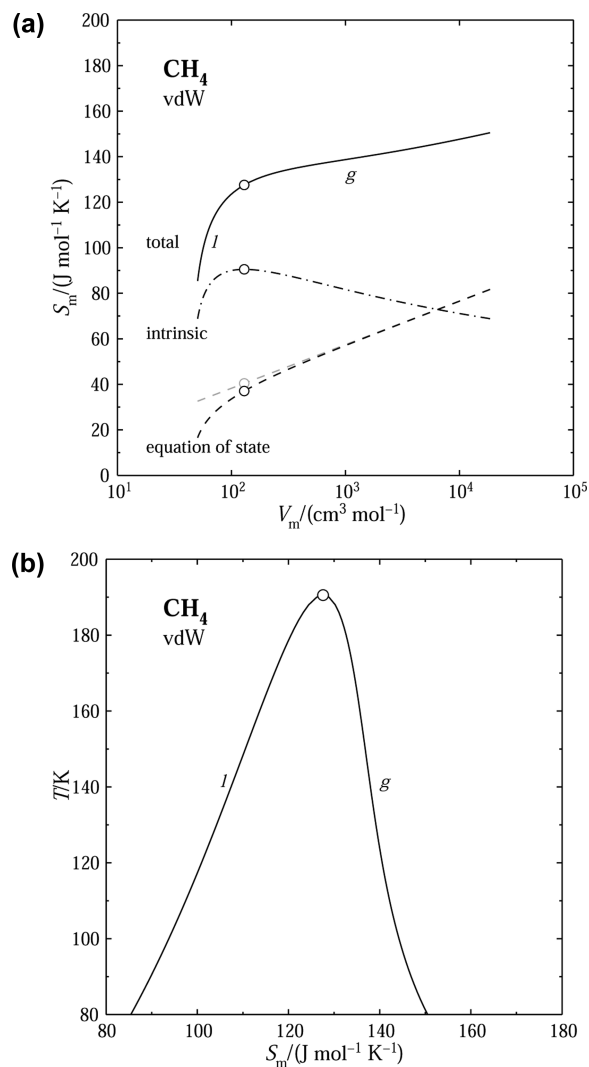


Figure 6. Molar entropy of methane along the vapor–liquid phase boundary, computed with the van der Waals equation of state.¹⁵ (a) Dependence of the molar entropy on molar volume (logarithmic volume scale). (—) Total molar entropy; (---) equation of state contribution (gray curve: without the residual entropy); (---) intrinsic contribution; (O) critical point. (b) Temperature–molar entropy relation.

of the re-entrant crossing type, and the one above it, with an initial q of 0.99, is of the re-entrant retrograde type.

Around 350 K, there is a saturated vapor state from which adiabatic compression or expansion will both take the fluid into the two-phase region.

The qT map of decane, Figure 8, corresponds to that of benzene, but without the low-temperature part. In the temperature range considered here, all isentropes starting at vapor states are of the re-entrant type. Consequently, there is now a wide range of temperatures with “crossing” isentropes, and complete evaporation of liquid decane by adiabatic expansion is the normal behavior above 480 K initial temperature.

This is illustrated by Figure 9a and b: Starting at a compressed liquid state (A), the single-phase isentrope passes through a kind of van der Waals loop to a single-phase vapor state, intersecting the two-phase isentrope (in the pT diagram coinciding with the vapor pressure curve) twice (states B and C). This means that the system will follow the single-phase

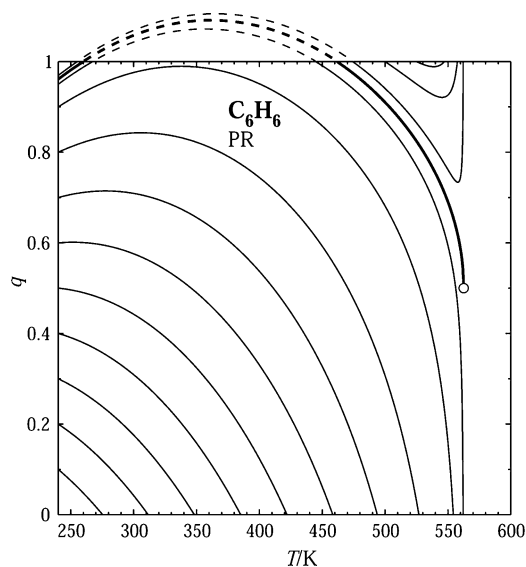


Figure 7. Overview over two-phase isentropes of benzene: quality vs temperature, calculated with the Peng–Robinson equation of state.^{13,14} For an explanation of the curves, see Figure 5. Dashed curves: the portions of the isentropes below the triple point temperature (278.5 K) are metastable with respect to crystallization.

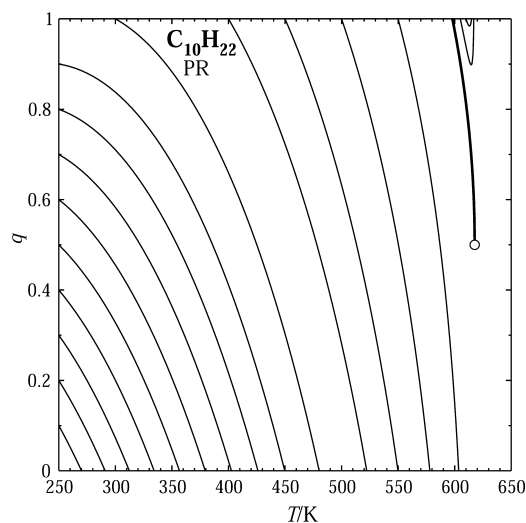


Figure 8. Overview over two-phase isentropes of decane: quality (fraction of substance in the vapor phase) vs temperature, calculated with the Peng–Robinson equation of state.^{13,14} For an explanation of the lines, see Figure 5.

isentrope to the first intersection point B, then follow the two-phase isentrope to C, and finally switch back to the single-phase isentrope and run to D.

If the adiabatic expansion is done quickly, it may be possible to follow the single-phase isentrope into the metastable portion of the two-phase region. But the system has to switch to the two-phase isentrope at the latest at the osculation points with the spinodals.

Again, the explanation for the behavior of the isentropes can be found in the SV or TS diagrams. Benzene, octane, and decane are so-called “dry fluids.” Figure 10a, the SV diagram of octane, shows that the maximum of the intrinsic term is so high that the total entropy passes through a maximum. The TS diagram contains a vapor branch with a positive slope.

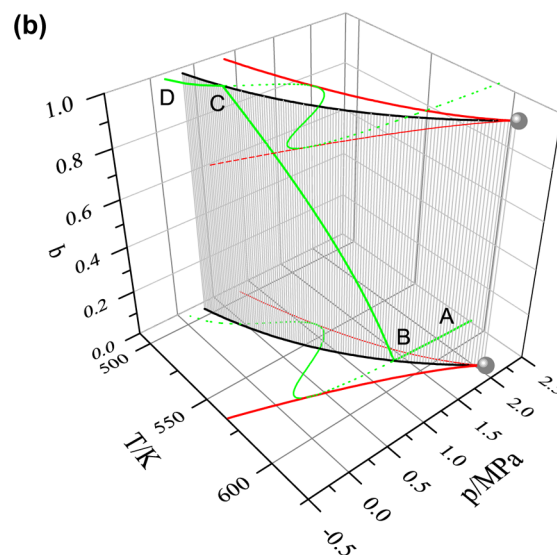
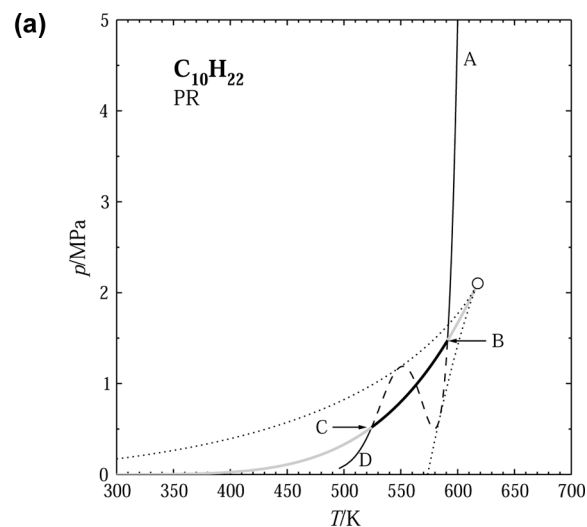


Figure 9. Adiabatic expansion of compressed liquid decane (state A), calculated with the Peng–Robinson equation of state.^{13,14} (a) Pressure–temperature relation. See Figure 1 for an explanation of the symbols. (b) Quality–pressure–temperature relation. Surface, vapor pressure relation; red, spinodals (bold, relevant branch); bold green, path of the adiabatic process (AB, CD, single-phase isentrope; BC, two-phase isentrope); thin green, metastable and unstable portions of single-phase isentrope.

Consequently, an adiabatic expansion of a saturated liquid can take the system to a single-phase (“dry”) vapor state.

We can therefore conclude that the intrinsic term decides to which class—“dry” or “wet”—a substance belongs.

A closer inspection of the critical region in Figure 10a reveals that the maximum of the entropy curve is on the vapor branch (see the inset). This is due to the fact that the maximum of the intrinsic term coincides with the critical point (T_c is the highest temperature along the vapor pressure curve, and here the integral in eq 21 covers the widest range), while the equation of state term increases monotonically with volume. Consequently, isentropes originating at saturated vapor states with an entropy below the critical entropy pass through the two-phase region and reach states on the liquid branch: these are the “crossing isentropes” characteristic of dry fluids; isentropes with an entropy above the critical entropy pass through the two-phase

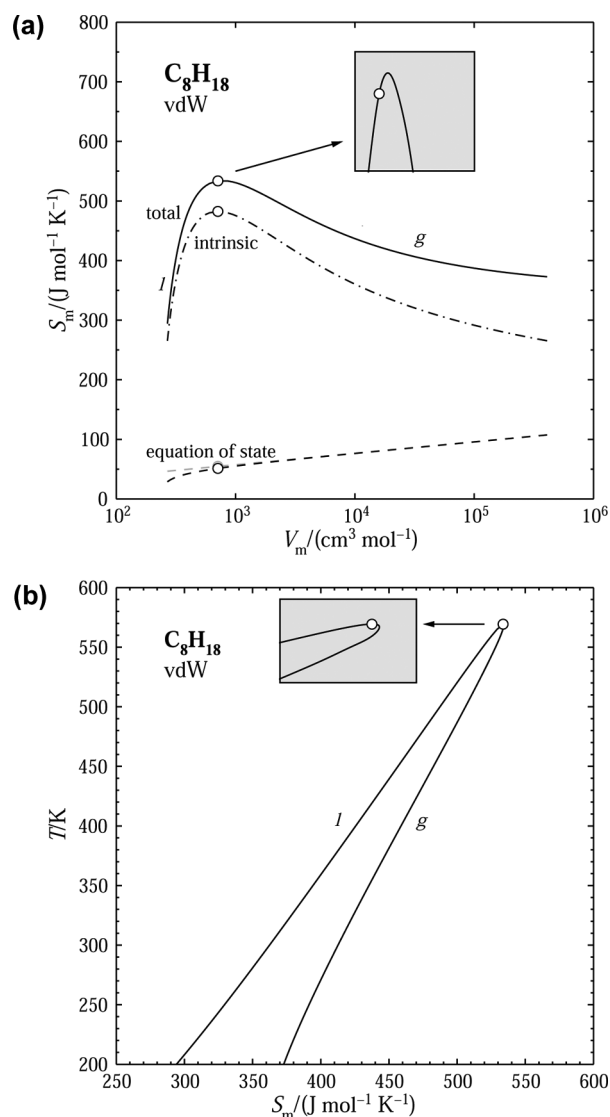


Figure 10. Molar entropy of octane along the vapor–liquid phase boundary, computed with the van der Waals equation of state. See Figure 6a for an explanation of the symbols and lines. (a) Dependence of the molar entropy on molar volume. (b) Temperature–molar entropy relation.

region and reach states on the vapor branch: these are the “retrograde isentropes.”

It is possible that the SV curve of a fluid, after passing through the maximum, exhibits a shallow minimum and then increases again. An example is benzene (see Figure 11). For a vapor state at this minimum, an adiabatic expansion or compression would drive the fluid into the two-phase region. Evidently, this is the explanation for the behavior shown in Figure 7.

3.3. Substance Classes. The distinction between “wet” and “dry” fluids, which have been used here, is usually based on the slope of the vapor branch in a TS diagram.² This criterion is not quite sharp, however, for even a substance like octane must have a portion of that branch with a negative slope close to the critical point (see the inset of Figure 10b). It would be better to base the distinction on whether the vapor branch exhibits an entropy maximum in the SV or TS diagram. We will adopt this definition henceforth.

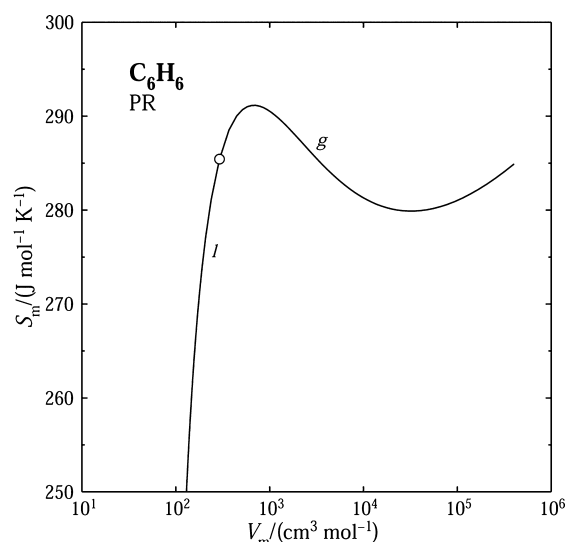


Figure 11. Molar entropy of benzene along the vapor–liquid phase boundary, computed with the Peng–Robinson equation of state, as a function of molar volume (logarithmic volume scale). (O) Critical point.

3.3.1. Qualitative Classification. We thus can distinguish two classes of isentropic behavior:

“wet”: Adiabatic expansion of saturated liquid states ($q = 0$) as well as expansion of saturated vapor states ($q = 1$) drives the system into the vapor–liquid two-phase region. The expansion never leads to a single-phase state; the isentropes do not leave the two-phase region again. Adiabatic compression of saturated vapor states leads to single-phase states only. The vapor branch in the SV diagram has a positive slope and in the TS diagram a negative slope. Examples of such fluids are argon, methane, carbon dioxide, or water.

“dry”: Fluids of this class exhibit “crossing” two-phase isentropes, so that it is possible to achieve complete evaporation of saturated liquid states or complete condensation of saturated vapor states by adiabatic processes. Adiabatic compression of saturated vapor states close to the critical temperature may cause transient condensation (“retrograde” isentropes). The crossing and retrograde isentropes are the high-temperature portions of re-entrant isentropes; their low-temperature parts may be experimentally accessible (dry-1: butane, benzene) or not (dry-2: hexane, octane, decane).

In Figure 12, the TS curves along the liquid–vapor two-phase boundary are compared for some small alkanes. It is easy to see whether (or how often) an isentropic (vertical) path from a given initial state will cross the phase envelope. The trend from “wet” to “dry” behavior with increasing chain length is evident.

Figure 13 indicates the class memberships of several substances in relation to their critical pressures and temperatures. The isentropes patterns were calculated with the Peng–Robinson equation of state. Evidently, the distribution is not random: The “dry” substances can all be found at high critical temperatures and relatively low critical pressures.

3.3.2. Semiquantitative Classification. These considerations can be used for a semiquantitative classification of substances: The slope of the total entropy function with respect to volume along the two-phase boundary is

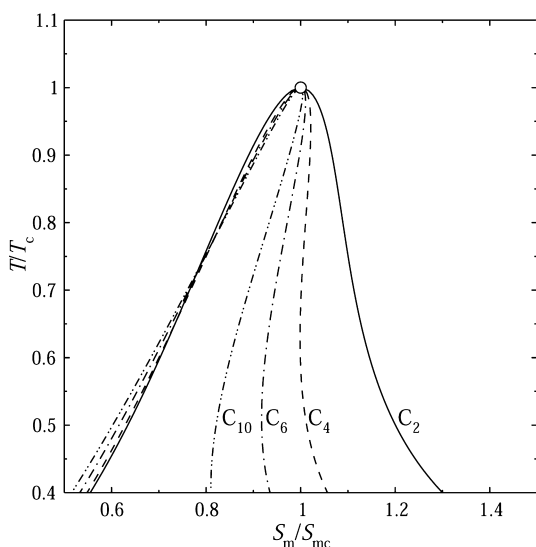


Figure 12. Reduced temperature vs reduced entropy along the liquid–vapor two-phase boundary for some alkanes computed with the Peng–Robinson equation of state. (—) ethane, (---) butane, (---) hexane, (---) decane.

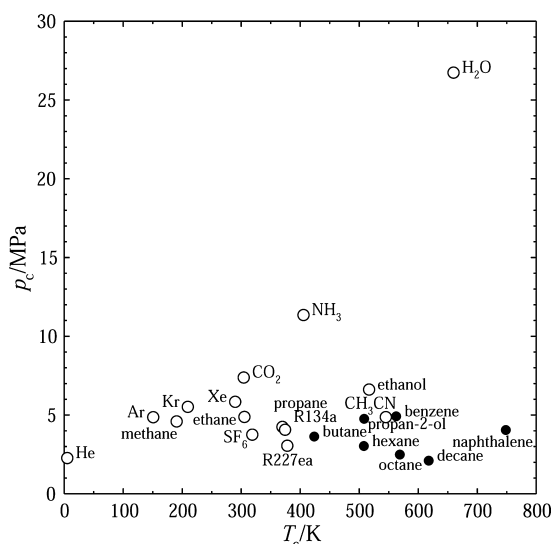


Figure 13. Critical pressures and temperatures of some technically important fluids, and classification of their isentrope pattern, based on the Peng–Robinson equation of state. (O) “wet” fluids, (●) “dry” fluids.

$$\frac{dS_m^\phi}{dV_m^\phi} = \frac{dS_m^\phi}{dT} \frac{dT}{dV_m^\phi} = \frac{C_{\sigma m}^\phi}{T} \frac{dT}{dV_m^\phi} \quad (22)$$

as V_m^ϕ and T are not independent.

dT/dV_m^ϕ along the phase boundary can be obtained from the total differential of V_m by substituting Clapeyron’s equation, eq 15,

$$\begin{aligned} \frac{dV_m^\phi}{dT} &= \left(\frac{\partial V_m^\phi}{\partial T} \right)_p + \left(\frac{\partial V_m^\phi}{\partial p} \right)_T \frac{dp}{dT} \\ &= V_m^\phi \left(\alpha_p^\phi - \kappa_T^\phi \frac{\Delta_{\text{vap}} H_m}{T(V_m^g - V_m^l)} \right) \end{aligned} \quad (23)$$

where κ_T denotes the isothermal compressibility. For the vapor phase, dT/dV_m^g is always negative.

Sufficiently far away from the critical point, the vapor pressure is low, and the vapor phase therefore behaves as an ideal gas ($C_{pm}^g \rightarrow C_{pm}^{\text{id}}$, $\kappa_T^g \rightarrow V_m^g/(RT)$, and $\alpha_p^g \rightarrow T^{-1}$); moreover, the orthobaric liquid volume can be neglected against the vapor volume. Then, eq 17 becomes

$$C_{\sigma m}^g \rightarrow C_{pm}^{\text{id}} - \frac{\Delta_{\text{vap}} H_m}{T} \quad (24)$$

eq 23 turns into

$$\frac{dV_m^g}{dT} \rightarrow \frac{V_m^g}{T} \left(1 - \frac{\Delta_{\text{vap}} H_m}{RT} \right) \quad (25)$$

and hence eq 22 turns into

$$\frac{dS_m^g}{dV_m^g} \rightarrow \frac{1}{V_m^g \left(1 - \frac{\Delta_{\text{vap}} H_m}{RT} \right)} \left(C_{pm}^{\text{id}} - \frac{T_b}{T} \frac{\Delta_{\text{vap}} H_m}{T_b} \right) \quad (26)$$

Here, T_b denotes the normal boiling temperature. $\Delta_{\text{vap}} H_m/T_b$ is Trouton’s constant, which amounts to about 90 J/(mol K) for many nonpolar or weakly polar fluids. As $\Delta_{\text{vap}} H_m/(RT) > 1$ for subcritical systems far away from the critical point, the sign of the whole expression thus depends mostly on the ideal gas heat capacity C_{pm}^{id} .

For a small nonlinear molecule at a low temperature at which vibrations are still not excited, C_{pm}^{id} amounts to $4R \approx 33$ J/(mol K), which is considerably less than Trouton’s constant; for noble gases or linear molecules, the isobaric heat capacity is even lower. Thus, argon has a C_{pm}^{id} of about 20.8 J/(mol K), and methane one of 33.3–33.4 J/(mol K) in the temperature range 0.5–1 T_c . Consequently, the slope of the entropy function must be positive for these substances, and hence they are “wet.”

Large molecules, however, have low-frequency bending vibrations and librations which can be excited to a significant extent even at low temperatures. Octane, for instance, has a C_{pm}^{id} of about 181–315 J/(mol K) in the temperature range 0.5–1.0 T_c (285–569 K), which evidently outweighs Trouton’s constant: it belongs to class “dry-2” (see Figure 14). Butane has 79–131 J/(mol K) and is therefore in class “dry-1”.

These considerations are crude approximations only; for an accurate classification of isentrope behavior, SV or TS diagrams should be constructed.

Figure 15 shows the distribution of substances with respect to their isobaric ideal-gas heat capacities and enthalpies of vaporization, both computed at $0.7T_c$. In agreement with the previous considerations, “wet” substances occupy the lower part of the diagram. The diagram depends to some extent on the equation of state used for the calculation of isentropes (here: the Peng–Robinson equation); for other equations, the locations of the points and the class assignments might be slightly different. For instance, propane is “dry” if the van der Waals equation is used.

The boundary of the shaded area in Figure 15 merely indicates a trend; it was calculated by setting the parameters of the equation of states and the heat capacity function to rather artificial values. Most fluids have a $\Delta_{\text{vap}} H_m/(RT)$ in a rather narrow range of 8–12 (at $0.7T_c$); for them, the boundary between “wet” and “dry” runs at $C_{pm}^{\text{id}}(0.7T_c)/R \approx 11$.

At sufficiently low temperatures, the excitation of vibrations becomes unlikely, and then even large molecules must theoretically exhibit a constant ideal-gas heat capacity C_{pm}^{id} of

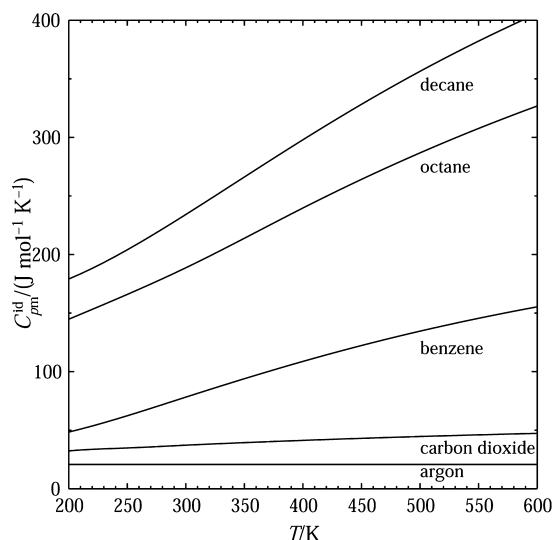


Figure 14. Isobaric ideal-gas heat capacities of various substances as functions of temperature.

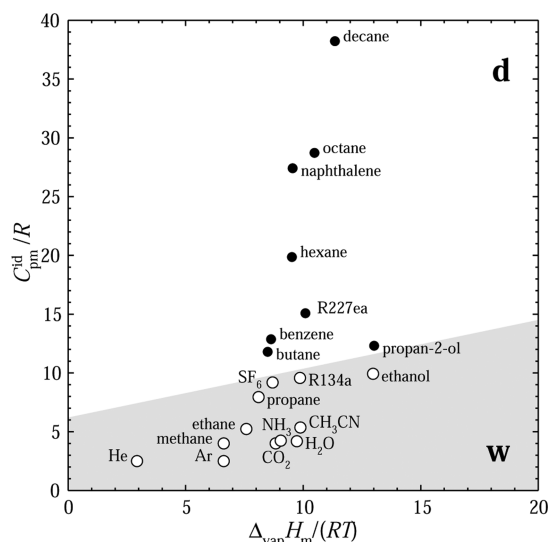


Figure 15. Isobaric ideal-gas heat capacities, C_{pm}^{id}/R , and heats of vaporization, $\Delta_{vap}H_m$, of some technically important fluids at $T = 0.7T_c$, and classification of their isentrope pattern, based on the Peng–Robinson equation of state. (○) “wet” fluids, (●) “dry” fluids.

merely $4R \approx 33.25 \text{ J}/(\text{mol K})$ (assuming a nonlinear molecule). Then the equation of state contribution to the entropy necessarily causes a positive slope in the SV diagram. Consequently, all “dry” fluids must in principle conform to the SV diagram (Figure 11) and to the isentrope pattern Figure 7: Adiabatic expansion will ultimately lead to a two-phase state, but for some substances the minimum of the entropy curve may be practically inaccessible because of crystallization or because the vapor pressure is too low.

4. ISENTROPES AT THE CRITICAL POINT

Figures 5, 7, and 8 show that the “critical isentrope,” i.e., the isentrope that passes through the critical point, approaches this point in a qT diagram with a large negative slope. In order to analyze the limiting behavior of the critical isentrope, it is useful to consider the Taylor series expansion of the molar entropy around a state (T, V_m) in the vicinity of the critical point with

respect to the reduced temperature and volume deviations, $\delta\tilde{T} = T/T_c - 1$ and $\delta\tilde{V} = V_m/V_{mc} - 1$, respectively. The entropy at the critical point can then be expressed as

$$\begin{aligned} S_{mc} = S_m - T_c \left(\frac{\partial S_m}{\partial T} \right)_{V_m} \delta\tilde{T} - V_{mc} \left(\frac{\partial S_m}{\partial V_m} \right)_T \delta\tilde{V} \\ + \frac{1}{2} T_c^2 \left(\frac{\partial^2 S_m}{\partial T^2} \right) (\delta\tilde{T})^2 + T_c V_{mc} \left(\frac{\partial^2 S_m}{\partial T \partial V_m} \right) \delta\tilde{T} \delta\tilde{V} \\ + \frac{1}{2} V_{mc}^2 \left(\frac{\partial^2 S_m}{\partial V_m^2} \right) (\delta\tilde{V})^2 + \dots \end{aligned} \quad (27)$$

Close to the critical point, the thermodynamic properties of fluids can be described by power laws,^{10,16} for example the isochoric heat capacity

$$C_{V_m} = RB_\alpha (-\delta\tilde{T})^{-\alpha} \quad (28)$$

the orthobaric densities

$$\delta\tilde{\rho}^\phi = \frac{\rho^\phi - \rho_c}{\rho_c} = \pm B_\beta (-\delta\tilde{T})^\beta \quad \delta\tilde{V}^\phi = -\delta\tilde{\rho}^\phi \quad (29)$$

the isothermal compressibility along the critical isochore (negative for subcritical temperatures)

$$\kappa_T = -\frac{B_\gamma}{RT_c \rho_c} (-\delta\tilde{T})^{-\gamma} \quad (30)$$

the isochoric pressure coefficients on the phase boundary

$$\beta_V^\phi - \beta_{V_c} = \pm R \rho_c B_\epsilon (-\delta\tilde{T})^\epsilon \quad \text{with } \beta_V = \left(\frac{\partial p}{\partial T} \right)_{V_m} \quad (31)$$

and the curvature of the vapor pressure curve

$$\frac{d^2 p^\sigma}{dT^2} = \left(\frac{\partial^2 p}{\partial T^2} \right)_{V_m} \bigg|_\sigma = \frac{R \rho_c B_\theta}{T_c} (-\delta\tilde{T})^{-\theta} \quad (32)$$

α – θ are so-called critical exponents, B_α – B_ϵ (dimensionless) critical amplitudes. Equations 29–32 are valid for subcritical conditions, $\delta\tilde{T} \leq 0$, but some can be extended to supercritical conditions (but then may have different amplitudes). The upper signs in eqs 29 and 31 refer to the liquid, the lower to the vapor. Equations 29–32 are not independent, but can be derived from an underlying “scaling equation of state” [ref 17, eq 1.22]. The critical exponents are connected by “scaling equalities”

$$\begin{aligned} \gamma &= 2 - \alpha - 2\beta \\ \epsilon &= 1 - \alpha - \beta \\ \theta &= \alpha + \beta \end{aligned} \quad (33)$$

Classical theories of the fluid state yield $\alpha = 0$ and $\beta = 0.5$. Experiments as well as renormalization group theory give exponents in the range $0 \leq \alpha \leq 0.15$ and $0.32 \leq \beta \leq 0.36$.^{10,16}

With these power laws, it is possible to express some of the coefficients in eq 27:

$$\begin{aligned}
 \left(\frac{\partial S_m}{\partial T}\right)_{V_m} &= \frac{C_{V_m}}{T} = \frac{RB_\alpha}{T}(-\delta\tilde{T})^{-\alpha} \\
 \left(\frac{\partial S_m}{\partial V_m}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_{V_m} = \beta_{V_c} \pm R\rho_c B_\epsilon(-\delta\tilde{T})^{1-\alpha-\beta} \\
 \left(\frac{\partial^2 S_m}{\partial T^2}\right) &= -\frac{C_{V_m}}{T^2} + \frac{1}{T}\left(\frac{\partial C_{V_m}}{\partial T}\right)_{V_m} \\
 &= -\frac{RB_\alpha}{T^2}(-\delta\tilde{T})^{-\alpha} + \frac{\alpha RB_\alpha}{TT_c}(-\delta\tilde{T})^{-1-\alpha} \\
 \left(\frac{\partial^2 S_m}{\partial T \partial V_m}\right) &= \left(\frac{\partial^2 p}{\partial T^2}\right) = \frac{RB_\theta \rho_c}{T_c}(-\delta\tilde{T})^{-\alpha-\beta} \\
 \left(\frac{\partial^2 S_m}{\partial V_m^2}\right) &= -\left(\frac{\partial}{\partial T}\left(\frac{1}{\kappa_T V_m}\right)\right)_{V_m} = -\frac{\gamma R \rho_c \rho}{B_\gamma}(-\delta\tilde{T})^{1-\alpha-2\beta}
 \end{aligned}
 \tag{34}$$

Inserting these relations as well as the density power law, eq 29, into the entropy series, keeping the relevant terms only, then leads to

$$\begin{aligned}
 S_{mc} - S_m &= \frac{T_c}{T} RB_\alpha(-\delta\tilde{T})^{1-\alpha} \left[1 + \frac{\alpha}{2} + \dots\right] \pm B_\beta V_{mc} \\
 &\quad \beta_{V_c}(-\delta\tilde{T})^\beta + RB_\beta B_\epsilon(-\delta\tilde{T})^{1-\alpha} \\
 &\quad \pm RB_\theta B_\beta(-\delta\tilde{T})^{1-\alpha} - \left[\frac{\gamma}{2} + \dots\right] \frac{RB_\beta^2 \rho}{B_\gamma \rho_c} \\
 &\quad (-\delta\tilde{T})^{1-\alpha} + \dots
 \end{aligned}
 \tag{35}$$

The derivation of this equation is complicated by the fact that the third- and higher-order terms of the series expansion of S_m contain terms proportional to $(-\delta\tilde{T})^{1-\alpha}$, too. These terms, however, are smaller and do not change the outcome significantly. So the α series in eq 35 converges against $(1-\alpha)^{-1}$ and the γ series to $\gamma 2^{\gamma-2}$. With these results, eq 7 can be turned into

$$\begin{aligned}
 q &= \frac{S_{mc} - \frac{1}{2}(S_m^g + S_m^l)}{S_m^g - S_m^l} + \frac{\frac{1}{2}(S_m^g - S_m^l)}{S_m^g - S_m^l} \\
 &= \frac{\frac{1}{2}(S_{mc} - S_m^g) + \frac{1}{2}(S_{mc} - S_m^l)}{(S_{mc} - S_m^l) - (S_{mc} - S_m^g)} + \frac{1}{2} \\
 &= \frac{\left(\frac{1}{1-\alpha} \frac{T_c}{T} RB_\alpha + RB_\beta B_\epsilon - \frac{\gamma 2^{\gamma-2} RB_\beta^2 \rho}{B_\gamma \rho_c} + \dots\right)(-\delta\tilde{T})^{1-\alpha} + \dots}{2V_{mc} \beta_{V_c} B_\beta (-\delta\tilde{T})^\beta + \dots} + \frac{1}{2}
 \end{aligned}
 \tag{36}$$

From this equation, it is evident that $q_c = (1/2)$ at the critical point. Furthermore, $q - q_c$ vanishes as $(-\delta\tilde{T})^{1-\alpha-\beta}$, and consequently the slope of the critical isentrope diverges as $(-\delta\tilde{T})^{1-\alpha-\beta}$.

The leading factor in the numerator of eq 36 contains a negative term. For cubic equations, it tends to be small; hence $q > (1/2)$ close to the critical point and $(dq/dT) \rightarrow -\infty$. More accurate equations of state usually have rather large B_β amplitudes in order to represent the fluctuation-caused widening of the phase boundary; consequently such equations may generate critical isentropes with $q > (1/2)$ and $(dq/dT) \rightarrow +\infty$.

So the reference equation of state of carbon dioxide by Span and Wagner¹⁸ yields a qT diagram, Figure 16, that is very

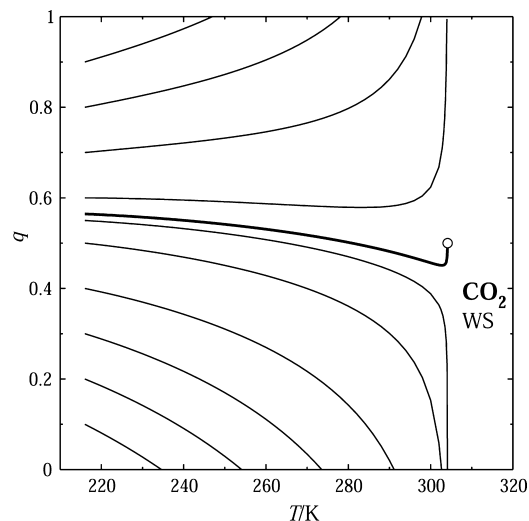


Figure 16. Overview over two-phase isentropes of carbon dioxide: quality vs temperature, calculated with the reference equation of state of Span and Wagner.¹⁸ For an explanation of the lines, see Figure 5

similar to that of the Peng–Robinson equation. The critical isentrope has a slightly lower initial q of 0.5645; here, however, the critical isentrope turns upward close to the critical point and ends there with a positive-infinite slope.

The isentropes of water show a similar behavior, as can be seen in Figure 17. The calculations were made with the IAPWS

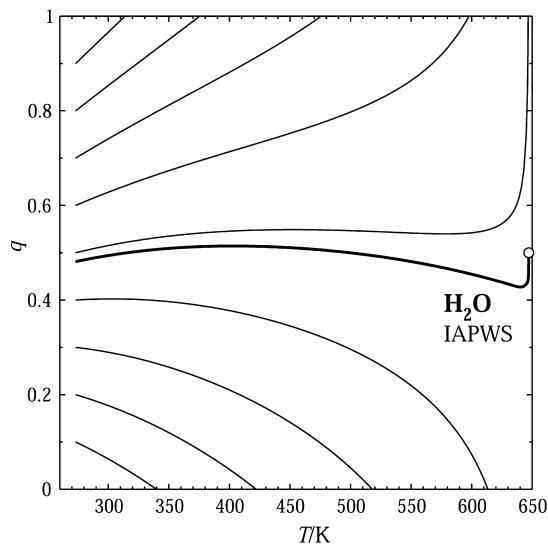


Figure 17. Overview over two-phase isentropes of water: quality vs temperature, calculated with a reference equation of state.¹⁹ For an explanation of the lines, see Figure 5.

reference equation of state by Wagner and Prüss.¹⁹ In contrast to carbon dioxide, the initial quality of the “critical isentrope” is lower, about 0.4813; furthermore, near-critical isentropes exhibit a maximum at relatively high reduced temperatures.

That indeed the ability of an equation of state to represent the near-critical behavior decides the terminal slope of the critical isentrope can be seen in Figure 18: This diagram was computed with the “short Span–Wagner” equation,^{20–22} a

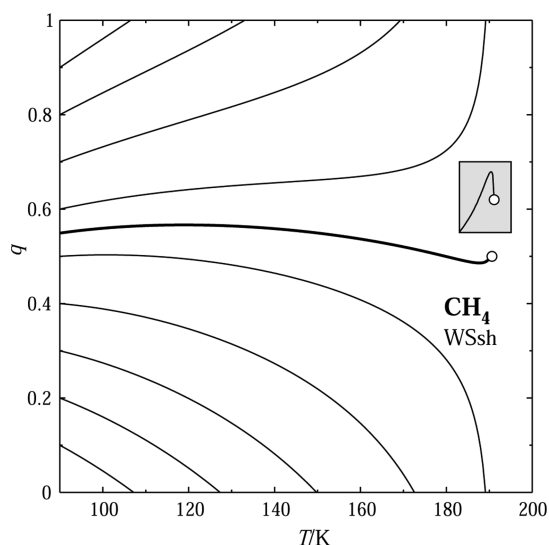


Figure 18. Overview over two-phase isentropes of methane: quality vs temperature, calculated with the “short Span–Wagner” equation of state.^{20–22} For an explanation of the lines, see Figure 5.

simplified version of the Setzmann–Wagner reference equation for methane.²³ The short equation represents the thermodynamic properties of methane very well, and thus the critical isentrope shows the typical approach “from below,” but very close to the critical point the classical behavior dominates, causing a negative infinite terminal slope.

5. CONCLUSION

The adiabatic expansion or compression of a fluid in the vapor–liquid two phase region has to follow the vapor pressure curve, if phase equilibrium is maintained during the process. The “quality” (fraction of substance that is in the vapor phase) can be calculated either from an ordinary differential equation or—perhaps more efficiently—from the entropy balance, using arbitrary equations of state in combination with the ideal-gas heat capacity function.

A systematic survey of quality vs temperature isentrope diagrams for many substances reveals that there are two different isentrope patterns, namely,

- a simple pattern (called here the “wet” fluid pattern, after the classification of ORC fluids), where two-phase isentropes starting at all-liquid or all-vapor states never reach the opposite state; i.e., the adiabatic expansion of a liquid never leads to complete evaporation,
- and a complicated pattern (called here the “dry” fluid pattern), where two-phase isentropes can cross the vapor–liquid coexistence region, so that the adiabatic expansion of a liquid can achieve a complete evaporation, or an adiabatic compression of a vapor, a complete condensation. The crossing isentropes are the high-temperature portions of re-entrant isentropes. For expansions or compressions of saturated vapor states close to the critical temperature, the calculations predict transient condensation.

These two classes can be found for all equations of state, from simple cubic to reference equations. They can be explained with the shape of entropy–volume curves along the phase boundary, which may or may not exhibit a maximum, or with temperature–entropy diagrams. A crude test can be based

on the ideal-gas heat capacity function: substances with $C_{pm}^{id}(0.7T_c)/R > 11$ are likely to belong to the “dry” class.

For a more accurate test, the heat of vaporization should also be taken into account. But its influence is positively inferior to that of the ideal-gas heat capacity.

The critical isentrope (i.e., the isentrope that runs through the critical point) approaches the critical point with an infinite slope, $dq/dT \rightarrow \pm\infty$. For simple equations of state, the slope is usually negative; more accurate equations that account for critical fluctuations, in particular reference equations, may exhibit a positive terminal slope. Hence, simple equations of state and reference equations give *qualitatively different* predictions close to the critical point: A small adiabatic expansion of a critical fluid will result in either a depression of the meniscus (simple equation of state) or a rise (reference equation of state).

■ APPENDIX. AUXILIARY EQUATIONS

1. Ideal-Gas Functions

The isochoric heat capacity function of the ideal gas, $C_{vm}^{id}(T)$, can be conveniently set up by constructing a natural cubic spline function over a tabulation of experimental heat capacities ($C_{pm}^{id}(T) - R$), but of course other functions can be used, too. In some modern reference equations of state (e.g., the IAPWS equation for water¹⁹), the ideal-gas heat capacity is modeled after the heat capacity function of the harmonic oscillator.

Once $C_{vm}^{id}(T)$ is given, the other thermodynamic functions of the ideal gas (density-independent parts only) are obtained as

$$U_m^{id}(T) = U_m^{id}(p^\ominus, T^\ominus) + \int_{T^\ominus}^T C_{vm}^{id} dT \quad (37)$$

$$S_m^{id}(T) = S_m^{id}(p^\ominus, T^\ominus) + \int_{T^\ominus}^T \frac{C_{vm}^{id}}{T} dT \quad (38)$$

$$C_{pm}^{id}(T) = C_{vm}^{id} T + R \quad (39)$$

$$A_m^{id}(T) = U_m^{id}(T) - TS_m^{id}(T) \quad (40)$$

Here, $p^\ominus = 0.1$ MPa and $T^\ominus = 298.15$ K are the thermodynamic standard conditions. If a cubic spline function is used for C_{vm}^{id} , the integrations can be carried out analytically.

2. Functions of the Real Fluid

Let the residual Helmholtz energy be given by eq 9. Then the other thermodynamic functions required in this work are obtained as

$$\frac{U_m^r(\rho, T)}{RT} = -T \left(\frac{\partial A_m^r(\rho, T)/(RT)}{\partial T} \right)_\rho \quad (41)$$

$$\frac{H_m^r(\rho, T)}{RT} = \frac{U_m^r(\rho, T)}{RT} + \frac{p(\rho, T)}{\rho RT} - 1 \quad (42)$$

$$\frac{S_m^r(\rho, T)}{R} = \frac{U_m^r(\rho, T) - A_m^r(\rho, T)}{RT} \quad (43)$$

$$\begin{aligned} \frac{C_{vm}^r}{R} = & -2T \left(\frac{\partial A_m^r(\rho, T)/(RT)}{\partial T} \right)_\rho \\ & - T^2 \left(\frac{\partial^2 A_m^r(\rho, T)/(RT)}{\partial T^2} \right)_\rho \end{aligned} \quad (44)$$

$$\frac{C_{pm}^r(\rho, T)}{R} = \frac{C_{vm}^r(\rho, T)}{R} + \frac{T\alpha_p^2(\rho, T)}{\rho\kappa_T(\rho, T)} - 1 \quad (45)$$

The heat of vaporization is then

$$\Delta_{\text{vap}}H_m(T) = H_m^r(\rho^g, T) - H_m^r(\rho^l, T) \quad (46)$$

and the full functions referenced here

$$\frac{A_m(\rho, T)}{RT} = \frac{A_m^{\text{id}}(T)}{RT} + \ln \frac{\rho}{\rho^\ominus} + \frac{A_m^r(\rho, T)}{RT} \quad (47)$$

$$\frac{S_m(\rho, T)}{R} = \frac{S_m^{\text{id}}(T)}{R} - \ln \frac{\rho}{\rho^\ominus} + \frac{S_m^r(\rho, T)}{R} \quad (48)$$

$$\frac{C_{pm}(\rho, T)}{R} = \frac{C_{pm}^{\text{id}}(T)}{R} + \frac{C_{pm}^r(\rho, T)}{R} \quad (49)$$

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Notes

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SYMBOLS

A = Helmholtz energy
 B_x = critical amplitude (of a “power law”) associated with the critical exponent x
 C = heat capacity
 H = enthalpy
 n = amount of substance
 p = pressure
 Q = heat
 q = “quality”, $q = n^g/n$
 R = gas constant
 S = entropy
 T = temperature
 U = internal energy
 V = volume
 α = critical exponent of the isochoric heat capacity along the critical isochore
 α_p = isobaric thermal expansivity
 β = critical exponent of the orthobaric densities
 β_V = isochoric pressure coefficient
 γ = critical exponent of the isothermal compressibility
 $\delta\tilde{X}$ = relative deviation of property X from its critical value, $(X - X_c)/X_c$
 ϵ = critical exponent of the isochoric pressure coefficient along the phase boundary
 θ = critical exponent describing the curvature of the vapor pressure curve and the isochoric pressure coefficient along the phase boundary

κ_T = isothermal compressibility

ρ = molar density, $\rho = 1/V_m$

Subscripts

b = normal boiling point

c = critical point

e = environmental heat capacity

m = molar

p = derivative at constant pressure

T = derivative at constant temperature

V = derivative at constant volume

vap = vaporization

σ = along the vapor pressure curve, at saturation

0 = initial state, starting point of an isentrope

Superscripts

g = gas, vapor phase

l = liquid

id = ideal gas

r = residual

s = solid

ϕ = arbitrary phase

\ominus = reference state

\tilde{X} = reduced (dimensionless) property X

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