

## Chapter 2

# The Thermodynamic Properties of the Working Fluids

The most common working fluids in power generation plants are water, in steam plants, and air and the gaseous combustion products in gas turbines and in internal combustion engines. Within certain limits, the air and gases produced by combustion can be treated as ideal gases. In the case of steam, when calculating the thermodynamic properties, reference needs to be made to the specific tables and diagrams. In closed gas cycles (Brayton or Stirling) the working fluid, under the usual operating conditions, is an ideal gas (helium, hydrogen etc.). Other fluids are successfully used in Rankine cycles (the so-called ORC engines, see Chap. 3) and mixtures of water and ammonia have been adopted in the so-called Kalina cycles.

Carbon dioxide and hydrocarbons are widely used as fluids in a whole variety of industrial sectors. Sodium (in liquid phase) is used as a cooling fluid in fast nuclear reactors and other liquid metals are currently proposed for future projects concerning nuclear reactors. Binary cycles with mercury and water vapour were adopted between 1930 and 1950 (see Chap. 5).

Therefore, many different working fluids are used or potentially usable in energy conversion systems and it is scarcely ever sufficient just calculating their thermodynamic properties by means of models and simplified hypotheses (as in the case of perfect or ideal gases or incompressible liquids). When detailed thermodynamic tables are not available, it is necessary to refer to equations that will give a reasonable estimate of the true thermodynamic behaviour of a working fluid, in order to make the necessary comparisons, the performance analysis and, even, a preliminary sizing of the machinery and components that will make up the thermodynamic engines.

The systems of energy conversion may also use more than one working fluid (for example, the combined cycles) and the fluid may be present in different states of aggregation.

This chapter will summarise and discuss the behaviour of fluids with regard to their possible use as working fluids in energy conversion systems.

## 2.1 The Thermodynamic Plane of the Substances

As we know, the reasons for the deviation of a substance from the behaviour of an ideal gas are, usually, phase changes, high densities and the dissociation of the fluid. In the case of pure substances, as the pressure gradually approaches the critical pressure  $P_{cr}$ , the two phases (liquid and vapour) become increasingly indistinguishable, and at the critical pressure and critical temperature  $T_{cr}$ , the change of phase is no longer apparent. The values of  $P_{cr}$  and  $T_{cr}$  identify a particular point, called “critical point”.<sup>1</sup>

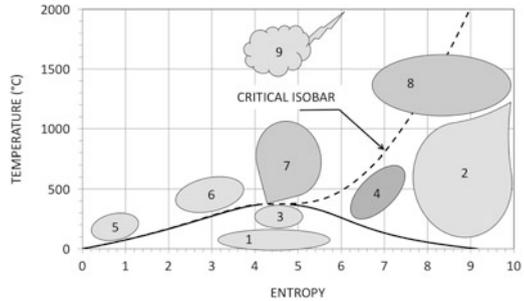
Referring to Fig. 2.1 (relative to water, for the sake of simplicity), a state diagram distinguishes different regions, which are characterised by a different thermodynamic behaviour of the fluid [20]:

- Region 1 Within the saturation curves (the saturation dome), enclosed in a temperature range that corresponds to a modest vapour pressure. If there are no changes of state, the aeriform state closely obeys the law of ideal gases. Generally, though, the variability of the vapour quality during the transformations of technical interest and the latent heat exchanged in the vaporization or condensation phases, prevents the use of transformation equations which are valid for ideal gases.
- Region 2 To the right of the saturation dome, characterised by moderate pressures and widely varying temperatures. The vapour behaves like an ideal gas at specific heats that rise with the temperature. It is the only region where it is permissible to use equations valid for ideal gases.
- Region 3 Within the saturation dome and at high pressure. On account of the significant “real gas effect”, we cannot apply the laws of ideal gases rigorously even in the gaseous phase.
- Region 4 At high pressure, in the zone of the moderately heated vapour. The high density of the vapour leads to a noticeable, although not great, deviation in the fluid behaviour from that predicted by the laws of ideal gases; generally speaking, though, it is permissible to apply the equations valid for the latter.
- Region 5 To the left of the saturation dome and at low temperature. The behaviour is typical of liquids in the proper sense, characterised by negligible mechanical compressibility and a very small, though not to be overlooked, thermal dilation.
- Region 6 To the left of the limit curve, for high temperatures, but subcritical. This is a liquid whose specific volume, mechanical compressibility and thermal dilation all have unusually high values. Applying the usual equations for liquids in the proper sense, in this zone, may lead to numerous mistakes (for example, the temperature rise in an ideal compression cannot usually be overlooked). In this region, we sometimes find the feed pumps for the high-pressure regenerative steam cycles.

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<sup>1</sup>A critical point also exists for fluid mixtures, although, for a prefixed composition, it is not usually the point on the saturation dome at the maximum pressure and temperature (see, for example [1, p. 306]).

**Fig. 2.1** Thermodynamic diagram T-S for a substance like water. Limit curves and zones with different thermodynamic behaviour



**Region 7** At hypercritical pressure and temperature. Here we have a fluid with highly unusual properties, in some intermediate state between liquid and gas. Without a simple intuitive model to act as a guide for the physical compression of the phenomena, any extrapolation at that state of the liquid or gas behaviour is unadvisable.

**Region 8** At high pressure and temperature. The real gas effects diminish and the steam once more conforms reasonably well to the laws for an ideal gas. In the specific case of water vapour, the high temperature (over 1,500 °C) limits the interest for this region, at least as far as industrial applications are concerned.

**Region 9** At very high temperatures (2,000–3,000 °C). A new effect of the real gas appears, due to molecular dissociation, which prevents the correct use of equations valid for ideal gases. This region is of strong interest for high temperature combustion (internal combustion engines, rocket engines) where there is usually a great quantity of water vapour among the reaction products.

As a result of what we have said, only on very limited occasions and when the precision required of the calculations is not too high is it possible to use the laws of ideal gases or consider the fluid as incompressible.

Furthermore, there are essentially two different effects of a real gas. The first is apparent at high densities and in proximity to the limit curve (the saturation dome). The second, at high temperature, occurs together with the phenomena of dissociation and recombination.

## 2.2 The Simplified Thermodynamic Systems and the Equations of State

As we know from thermodynamics [2], the properties of a simplified thermodynamic system which is composed of  $r$  substances in a condition of stable equilibrium depend only on the internal energy  $U_T$ , the volume  $V_T$  and the number of moli  $N_1, N_2 \dots N_r$ .

In particular,  $S_T = S_T(U_T, V_T, N_1, N_2 \dots N_r)$  takes the name of “fundamental equation in the entropic form”, which, resolved with respect to the variable  $U_T$ , gives  $U_T = U_T(S_T, V_T, N_1, N_2 \dots N_r)$  or the “fundamental equation in the energetic form”. From the expression  $U_T(S_T, V_T, N_1, N_2 \dots N_r)$  we can derive the other useful properties that are characteristic of the stable thermodynamic equilibrium or the equations of state:

$$T(S_T, V_T, N_1, N_2, \dots N_r) = \left( \frac{\partial U_T}{\partial S_T} \right)_{V_T, N_1, N_2 \dots N_r} \quad (2.1a)$$

$$P(S_T, V_T, N_1, N_2, \dots N_r) = - \left( \frac{\partial U_T}{\partial V_T} \right)_{S_T, N_1, N_2 \dots N_r} \quad (2.1b)$$

$$\mu_i(S_T, V_T, N_1, N_2, \dots N_r) = \left( \frac{\partial U_T}{\partial N_i} \right)_{S_T, V_T, N_1, N_2 \dots N_{r-1}} \quad \text{for } i = 1, 2 \dots r \quad (2.1c)$$

with  $\mu_i$  the chemical potential of the  $i$ -th constituent. We can also calculate the enthalpy  $H_T = U_T + PV_T$ , the Helmholtz free energy  $A_T = U_T - TS_T$  and the Gibbs free energy  $G_T = U_T - TS_T + PV_T = H_T - TS_T$ .

Introducing the specific variables, referring to the mole (or mass) unit, all the extensive thermodynamic functions can be reduced to their respective specific values. For example,  $U = U_T/N$ ,  $V = V_T/N \dots$ , with  $N = N_1 + N_2 + \dots + N_r$ . Defining the molar fractions  $y_1 = N_1/N$ ,  $y_2 = N_2/N \dots$  and remembering that  $y_1 + y_2 + \dots + y_r = 1$ , we get, for example,  $T = T(S, V, y_1, y_2 \dots y_r)$ ,  $P = P(S, V, y_1, y_2 \dots y_r)$  etc.

Since a simple thermodynamic system may have various forms of aggregation (liquid and vapour, for example), the phases are defined and a heterogeneous system is defined as a system in stable equilibrium with coexisting phases that are not separated by materialised constraints. If the phase is just one, then the system is homogeneous. As we know, a heterogeneous system has discontinuous variations in its specific properties, passing from one to another of its homogeneous parts (namely, the phases). The necessary condition for equilibrium between the various phases requires that the pressure, temperature and chemical potential of each component be the same in each phase. Under certain conditions, varying the state of equilibrium of a heterogeneous system, there may appear phase transitions (of a different order).

The limit curve in Fig. 2.1 is, for a pure fluid, the result of variations in the specific entropy  $S$  passing from the liquid to the vapour phase (example of a first order transition phase for a mono-component system<sup>2</sup>). The two phases—liquid and vapour—have different entropy values<sup>3</sup> but the variation between the value

<sup>2</sup>The phase transition is said to be of the first order if, in the transition point, the derivatives of the chemical potential show discontinuity of the first kind.

<sup>3</sup>The difference between specific entropies, multiplied by the temperature at which the phase transition takes place is the latent heat of evaporation.

corresponding to the liquid phase and that of the vapour phase occurs with continuity and is a function of the molar (or mass) fraction present in the various phases. Finally, we should remember that the slope of the coexistence curve for the phases on the plane  $P$ – $T$  for a mono-component heterogeneous system is represented by the Clausius–Clapeyron equation.

In the case of simple homogeneous systems, the fundamental equation  $U(S, V, y_1, y_2 \dots y_r)$  contains all the thermodynamic information. From this equation we can derive the equations of state (2.1a), (2.1b) and (2.1c). Knowing all the equations of state is the equivalent, therefore, of knowing the fundamental equation: knowing just one equation of state is to have incomplete information. However, knowing all of them bar one, it is possible to deduce the missing one, unless there is an indeterminate constant. Usually, it is relatively easy to correlate the quantities  $P$ ,  $T$  and  $V$ , once we know the composition of the system, and to obtain the volumetric equation of state

$$f(P, T, V, y_1, y_2 \dots y_r) = 0 \quad (2.2)$$

Complete knowledge of the system, though, requires a second equation which defines its thermal behaviour. This second equation of state generally correlates the specific heat at constant pressure with the temperature and pressure

$$C_P = C_P(P, T, y_1, y_2 \dots y_r) = 0 \quad (2.3)$$

In the next section, we shall discuss the volumetric equations of state for the case of mono-component simple systems

## 2.3 The Volumetric Equation of State for the Pure Fluids

The numerous volumetric equations of state proposed by various authors over the years try to take into account the peculiarities of “real gases”: above all, the liquid to vapour phase transitions, the volumetric behaviour in proximity to the critical point and the effects of high pressure on the density.

Of the two typical approaches to formulating the equations of state, the first based on the methods of mechanical statistics, which takes a rigorous approach to the interaction between molecules, and the second, which proposes the use of empirical or semiempirical equations based on the analysis of experimental data, we shall consider only the latter, which, for our purposes, gives simpler equations that are easy to apply.

The semiempirical and analytical equations include the so-called cubic equations. A summary of the limits and characteristics that distinguish the various equations of state is given in [3], together with suggestions and recommendations on how to develop and present any new equations of state. In [4] are presented, discussed and compared numerous cubic equations. The semiempirical equations of state generally express the pressure as the sum of two terms, a repulsive term  $P_R$  and

an attractive term  $P_A$ . According to this model, no single molecule can move freely, but interacts with the molecules near to it, via the forces of cohesion and repulsion.

The general formulation of a cubic equation of state is the following:

$$P = P_R + P_A = \frac{RT}{V - b} - \frac{\Theta (V - \eta)}{(V - b)(V^2 + \delta V + \epsilon)} \quad (2.4)$$

All cubic equations derive from the equation of van der Waals,<sup>4</sup> the first equation of state proposed in order to describe the properties of a real gas qualitatively. Equation (2.4) is reduced to the equation of van der Waals, supposing  $\delta = \epsilon = 0$ ,  $\eta = b$  e  $\Theta = a$  (constant).

The parameters which appear in (2.4) may be constants or vary with the temperature or the composition (in the case of mixtures, see Sect. 2.6). In general, they are specifics of each fluid.

Among the numerous equations proposed, one of the most used is the equation of Peng–Robinson [5]. In this,  $\delta = 2b$ ,  $\epsilon = -b^2$ ,  $\eta = b$  and  $\Theta = a_{cr}\alpha(\omega, T_r)$ , with  $T_r = T/T_{cr}$  (reduced temperature) and  $\omega$ , a parameter called “acentric factor”:

$$P = \frac{RT}{V - b} - \frac{a_{cr}\alpha(\omega, T_r)}{V(V + b) + b(V - b)} \quad (2.5a)$$

$$a_{cr} = \frac{0.457235R^2T_{cr}^2}{P_{cr}} \quad (2.5b)$$

$$b = \frac{0.077796RT_{cr}}{P_{cr}} \quad (2.5c)$$

$$\alpha(\omega, T_r) = \left(1 + \kappa \left(1 - \sqrt{T_r}\right)\right)^2 \quad (2.5d)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (2.5e)$$

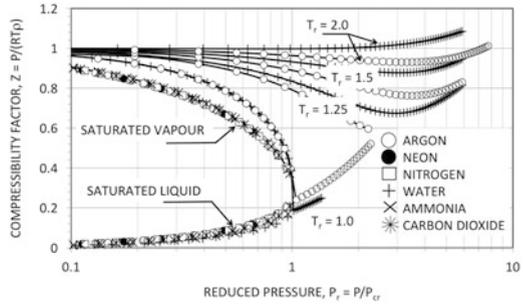
The acentric factor,  $\omega$ , was introduced by Pitzer et al. [6] as a measure of the difference in the structure of a molecule of any substance compared to that of a gas with a spherical molecule (for which  $\omega$  is zero). This is defined as

$$\omega = -\log [P_{vp,r}]_{T_r=0.7} - 1 \quad (2.6)$$

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<sup>4</sup>Johannes Diderik van der Waals (1837–1923). In his degree thesis, in 1873, he provided a semi-quantitative description of the phenomena of condensation and the critical point and derived the equation which bears his name. The equation of state which he developed derives from one describing the behaviour of an ideal gas, corrected in order to take into account the two special aspects of a real gas: the finite dimensions of the molecules and the intermolecular forces of attraction. In 1880, van der Waals also derived the Law of Corresponding States, showing that the equation of state which he had formulated could be expressed in a completely general form, by substituting the coefficients  $a$  and  $b$ , specifics of every fluid, with two universal parameters that are independent from the compound being considered.

**Fig. 2.2** Compressibility chart for various fluids. The values of the compressibility factor  $Z$  have been calculated from the equation of state (2.5a)



with  $[P_{vp,r}]_{T_r=0.7} = [P_{vp}]_{T_r=07}/P_{cr}$  which is the reduced vapour pressure calculated at the reduced temperature  $T_r = 0.7$ .

Introducing into (2.5a) the reduced variables  $T_r = T/T_{cr}$ ,  $P_r = P/P_{cr}$  and  $V_r = V/V_{cr}$ , we get

$$P_r = \frac{T_r}{Z_{cr} V_r - b^*} - \frac{a_{cr}^* \alpha(\omega, T_r)}{Z_{cr}^2 V_r^2 + 2b^* Z_{cr} - b^{*2}} \tag{2.7}$$

with  $b^* = 0.077796$ ,  $a_{cr}^* = 0.457235$  and  $Z_{cr} = P_{cr} V_{cr}/RT_{cr}$  the compressibility factor at the critical point. Equation (2.7) corresponding to the critical point ( $T_r = P_r = V_r = 1$ ) gives  $Z_{cr} = 0.307$  constant for any fluid: in the limits of validity of (2.7), all the fluids showed the same volumetric behaviour, except for the effects of the acentric factor  $\omega$  and considering the reduced variables as variables (see Fig. 2.2). A similar result is obtained from any cubic equation expressed by (2.4) and goes under the name of the Law of Corresponding States. The Law of Corresponding States, verified experimentally, may be theoretically justified by resorting to mechanical statistics, assuming the appropriate hypotheses on the nature of the intermolecular forces. In its simplest formulation, it is expressed by the equation  $Z = f(T_r, P_r)$  with two parameters, with  $Z = PV/RT$  the compressibility factor. With three parameters, the compressibility factor is more easily estimated and, historically, as the third parameter, it is the factor  $Z_{cr}$  which is introduced first and then, as an alternative, the acentric factor  $\omega$  (see [6, 7]). The parameter  $Z$  tends towards unity when the fluid behaves in a way that tends towards that of an ideal gas.

Starting with the Law of Corresponding States, various equations of state have been formulated, some of them very precise and with general validity, but, they are usually very complex. By way of example, we cite those discussed in [8, 9] and the one presented in [10, Sect. 4].

Observing that in the description of the volumetric properties of a fluid (and mixtures of fluids) it is definitely advantageous to use models with a solid physical base and, for this very reason, the equations of state deriving from mechanical statistics have a great potential, many studies into the research for new formulations of equations of state go back to appropriate molecular models, taking into account

interaction potentials that are both inter- and intra-molecular. One example of this approach is the equation PC-SAFT (Perturbed-Chain Statistical Associating Fluid Theory) with three (or more, depending on the system considered) coefficients [11].

In the considerations that follow and for the calculations in the rest of the book, for the sake of simplicity and practicality, we shall refer to the Peng–Robinson equation of state (2.5).

In (2.5a) it is possible to introduce the factor of compressibility  $Z = RT/PV$  and the reduced variables  $T_r$  and  $P_r$ , obtaining

$$Z^3 - (1 - B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \quad (2.8)$$

with

$$A = a_{\text{cr}}^* \alpha(\omega, T_r) \frac{P_r}{T_r^2} \quad (2.9a)$$

$$B = b^* \frac{P_r}{T_r} \quad (2.9b)$$

Equations (2.8) with (2.9a) and (2.9b) is another form of (2.7) and allows the factor of compressibility to be calculated directly from the reduced variables  $T_r$  and  $P_r$ .

For example, if we consider nitrogen and carbon dioxide at  $T = 25^\circ\text{C}$  and  $P = 100$  bar, the compressibility factor  $Z$  is equal to 0.989 and 0.249, respectively: nitrogen is, to all effects, an ideal gas, whilst carbon dioxide, under fixed conditions, has a density that is four times greater than that which would result from calculation with hypotheses of an ideal gas.

### ***The Influence of Compressibility on the Work of Expansion and Compression***

The volumetric effects of a real gas (represented and described by means of the compressibility factor  $Z$ ), in general, reduce the molar work of compression and expansion. In fact, referring to an isentropic expansion (ideal and adiabatic) in a turbomachine from pressure  $P_1$  to final pressure  $P_2$ :

$$W_T = \int_{P_1}^{P_2} \left( \frac{\partial H}{\partial P} \right)_S dP = \int_{P_1}^{P_2} \frac{1}{\rho} dP = \int_{P_1}^{P_2} V dP = \int_{P_1}^{P_2} Z \frac{RT}{P} dP \quad (2.10)$$

and having set  $T$  and  $P$ , being mostly  $Z < 1$ , the specific work is less than that which the fluid would provide if it were an ideal gas.

Furthermore, the work of compression and expansion diminishes with the molar mass of the working fluid. Still referring to an isentropic expansion in a turbomachine:

$$\begin{aligned}
W_T &= \int_{P_1}^{P_2} V dP = \int_{P_1}^{P_2} Z \frac{RT}{P} dP \\
&= \int_{P_{r,1}}^{P_{r,2}} Z \frac{T_r}{P_r} RT_{cr} dP_r \quad \text{or} \\
\frac{W_T}{RT_{cr}} &= \int_{P_{r,1}}^{P_{r,2}} Z \frac{T_r}{P_r} dP_r
\end{aligned} \tag{2.11}$$

Having set the law of variation  $T_r$  as a function of  $P_r$ , the ratio  $W_T/RT_{cr}$  is constant for any fluid (generally speaking, by virtue of the Law of Corresponding States). So, as a result, the specific work is inversely proportional to the molar mass of the working fluid. The variation in the work with the molar mass of the fluid has, for example, a direct effect on the performance and size of the turbomachinery in a thermodynamic cycle with a perfect gas (see Sect. 1.7).

## 2.4 The Evaluation of the Thermodynamic Properties of a Real Gas

From the volumetric equation of state  $f(P, V, T) = 0$  and from the equation  $C_p^0 = C_p^0(T)$  for the ideal gas, it is possible to derive the thermodynamic properties that interest us. We report the necessary equations, with reference to a monophasic and mono-component fluid system, following the procedure described in detail in [12, Chap. 8].

We shall start by considering the isothermal variations of a generic thermodynamic property; subsequently, we shall take into account the effects of variations in temperature.

To calculate the variations in a thermodynamic property at constant temperature, we use “departure functions”, defined as functions that represent the difference between a generic thermodynamic property in the state of a real gas (at fixed temperature  $T$  and corresponding to a defined specific volume  $V$  or a pressure  $P$ ) and the corresponding property for an ideal gas, at the same temperature  $T$  and pressure  $P$  but with a volume  $V^0$  calculated by means of  $V^0 = RT/P$ . The choice of the two independent variables  $T$  and  $P$  or  $T$  and  $V$  is arbitrary and dictated by convenience.

Thus, if  $X$  represents any thermodynamic property (enthalpy, entropy etc.), the departure function will be defined as

$$X(T, P) - [X(T, P)]_{\text{ideal gas}} = X(T, P) - X^0(T, P) \tag{2.12a}$$

$$X(T, V) - [X(T, V^0)]_{\text{ideal gas}} = X(T, V) - X^0(T, V^0) \tag{2.12b}$$

Since (2.5a) is explicit in  $P$ , it is more convenient to use temperature and volume as independent variables.

Proceeding and using (2.12b), we get the departure function relative to the Helmholtz free energy:

$$A(T, V) - A^0(T, V^0) = - \int_{\infty}^V \left( P - \frac{RT}{V} \right) dV + RT \ln \frac{V^0}{V} \quad (2.13)$$

Note that for  $A$ , the departure function is calculated for the entropy  $S$  as

$$\left( \frac{\partial A}{\partial T} \right)_V = -S$$

We obtain

$$S(T, V) - S^0(T, V^0) = \left[ \frac{\partial}{\partial T} \int_{\infty}^V \left( P - \frac{RT}{V} \right) dV \right]_V + R \ln \frac{V^0}{V} \quad (2.14)$$

From (2.13) and (2.14), we can calculate

$$U(T, V) - U^0(T, V^0) = (A - A^0) + T(S - S^0) \quad (2.15a)$$

$$H(T, V) - H^0(T, V^0) = (U - U^0) + PV - RT \quad (2.15b)$$

At this point, to determine the difference between the generic thermodynamic property  $X$  between two states 1 and 2 which also differ in temperature, it is possible to use

$$\begin{aligned} X(T_2, V_2) - X(T_1, V_1) &= [X(T_2, V_2) - X^0(T_2, V_2^0)] \\ &\quad - [X(T_1, V_1) - X^0(T_1, V_1^0)] \\ &\quad + [X^0(T_2, V_2^0) - X^0(T_1, V_1^0)] \end{aligned} \quad (2.16)$$

in which, the first two terms used on the right side represent the departure functions at temperatures  $T_1$  and  $T_2$ ; the third term represents the difference in  $X$  under the conditions of an ideal gas, easily calculated from the specific heats of the ideal gas. For example,

$$U^0(T_2, V_2^0) - U^0(T_1, V_1^0) = \int_{T_1}^{T_2} C_V^0 dT \quad (2.17a)$$

$$H^0(T_2, V_2^0) - H^0(T_1, V_1^0) = \int_{T_1}^{T_2} C_p^0 dT \quad (2.17b)$$

$$S^0(T_2, V_2^0) - S^0(T_1, V_1^0) = \int_{T_1}^{T_2} \frac{C_V^0}{T} dT + R \ln \frac{V_2^0}{V_1^0} \quad (2.17c)$$

The departure functions (2.13), (2.14), (2.15a) and (2.15b) depend only on the volumetric behaviour of the fluid. The specific heat (at constant pressure and volume) comes into play only in the definition of the properties of the ideal gas.

Equation (2.13) may be expressed also as a function of the reduced variables  $T_r$ ,  $P_r$  and  $V_r$  and of the compressibility factor. With reference to (2.7),

$$\begin{aligned} \frac{A(T, V) - A^0(T, V^0)}{RT_{\text{cr}}} &= -Z_{\text{cr}} \int_{\infty}^{V_r} \left( P_r - \frac{T_r}{V_r Z_{\text{cr}}} \right) dV_r + T_r \ln Z \\ &= g_A(T_r, V_r, \omega) \\ &= f_A(T_r, P_r, \omega) \end{aligned} \quad (2.18)$$

In the approximation of (2.7) (and of the Law of the Corresponding States), therefore, all the fluids have the same departure function  $A(T, V) - A^0(T, V^0)/RT_{\text{cr}}$  (except for the effects of the acentric factor  $\omega$ ).

Since the departure functions regarding entropy, internal energy and enthalpy derive from the departure function of the free energy of Helmholtz, generally speaking, it is also true

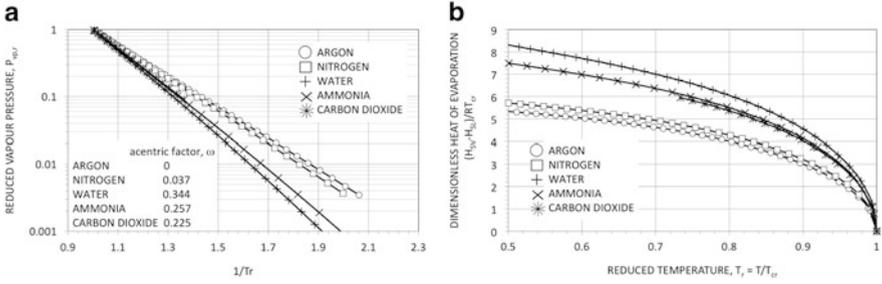
$$\frac{H(T, V) - H^0(T, V^0)}{RT_{\text{cr}}} = f_H(T_r, P_r, \omega) \quad (2.19a)$$

$$\frac{S(T, V) - S^0(T, V^0)}{R} = f_S(T_r, P_r, \omega) \quad (2.19b)$$

For the mono-component systems, as we know, at the liquid–vapour equilibrium the chemical potentials of the two phases are the same:  $\mu_{l,\text{sat}}(T, P_{\text{vp}}) = \mu_{v,\text{sat}}(T, P_{\text{vp}})$ . Since the chemical potential is  $\mu = H - TS$ , it is also true that  $\mu_{l,\text{sat}}(T_r, P_{\text{vp},r}) = \mu_{v,\text{sat}}(T_r, P_{\text{vp},r})$ . It follows that, within the limits of (2.7) (and of the Law of the Corresponding States), the relation between the reduced temperature  $T_r$  and the reduced vapour pressure  $P_{\text{vp},r}$  is a universal function for all pure fluids:

$$P_{\text{vp},r} = f_P(T_r, \omega) \quad (2.20)$$

Calculation results of the vapour pressure for certain fluids are shown in Fig. 2.3a. The fluids with the same value of acentric factor have, at the same  $T_r$ , a similar reduced vapour pressure. The observations above have a direct consequence on the evaporation heat and the shape of the limit curve.



**Fig. 2.3** (a) Reduced vapour pressure as a function of the reciprocal of the reduced temperature for certain fluids. (b) Dimensionless heat of evaporation as a function of the reduced temperature for some fluids. The results are those given by the equation of state (2.5a)

### *The Influence of the Nature of the Fluid on the Evaporation Heat*

The evaporation heat can be derived directly from the difference between the departure functions calculated for the steam and the saturated liquid, using (2.19a), or by means of the Clapeyron equation:

$$\begin{aligned} \frac{dP_{vp}}{dT} &= \frac{H_{SV} - H_{SL}}{T(V_{SV} - V_{SL})} \\ &= \frac{H_{SV} - H_{SL}}{RT_{cr}} \frac{P_r}{T_r^2} \frac{P_{cr}}{(Z_{SV} - Z_{SL}) T_{cr}} \end{aligned} \quad (2.21)$$

since

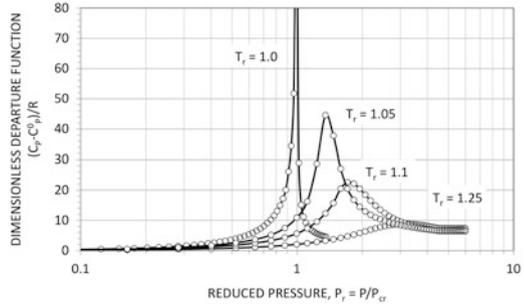
$$\frac{dP_{vp}}{dT} = \frac{P_{cr}}{T_{cr}} \frac{dP_{vp,r}}{dT_r} = \frac{P_{cr}}{T_{cr}} \frac{df_P}{dT_r}$$

We obtain for the dimensionless molar evaporation heat, with regard to  $RT_{cr}$ ,

$$\frac{H_{SV} - H_{SL}}{RT_{cr}} = \frac{T_r^2 (Z_{SV} - Z_{SL})}{P_r} \frac{df_P}{dT_r} \quad (2.22)$$

Therefore, the dimensionless evaporation heat is a universal function (except for the effects of the acentric factor  $\omega$ ) of just the reduced temperature (see Fig. 2.3b). In fact, it represents a particular enthalpic correction of the real gas: the correction, at constant pressure and temperature, corresponding to the phase change. The specific evaporation heat, once the reduced temperature is set, is more or less inversely proportional to the molar mass of the fluid. Several results are reported in Fig. 2.3b.

**Fig. 2.4** Dimensionless departure function for the heat capacity  $C_p$  as a function of the reduced pressure and for several values of the reduced temperature. The results are relevant to water [13]



### *The Specific Heats of a Real Gas*

The difference between the specific heats of a real gas under conditions  $T, V$  and the corresponding values for the ideal gas can be determined directly from the equation of state. In fact, since

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \text{and}$$

$$C_P = C_V - \frac{T(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T},$$

we obtain

$$C_V(T, V) - C_V^0(T) = T \int_{\infty}^V \left(\frac{\partial^2 P}{\partial T^2}\right)_V dV \quad (2.23a)$$

$$C_P(T, V) - C_P^0(T) = T \int_{\infty}^V \left(\frac{\partial^2 P}{\partial T^2}\right)_V dV - \frac{T(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T} - R \quad (2.23b)$$

At the critical point  $(\partial P/\partial V)_T$  is nullified and the departure function (2.23b) tends to infinity. Consequently, there exists a zone of the thermodynamic diagram inside of which there appear high and rapid variations in the specific heat. Figure 2.4 reports some results (for water) of the specific heat departure function. The behaviour evident in the figure is common to all pure fluids. The dependence of the heat capacity  $C_p$  on the pressure, as well as the temperature, introduces a difference in heat capacity which, in regenerative gas cycles operating with working fluids that have notable real gas effects, causes an irreversibility in the heat transmission to the recuperators even with infinite surfaces (ideal recuperator).

### ***The Speed of Sound in a Real Gas***

The speed of sound  $v_s$ , or the speed at which the small perturbations of pressure propagate through a pure substance, is defined, for a single phase, as

$$v_s^2 = \left( \frac{\partial P}{\partial \rho} \right)_S = -V^2 \frac{C_P}{C_V} \left( \frac{\partial P}{\partial V} \right)_T \quad (2.24)$$

If the behaviour of the fluid is assimilable to that of a perfect gas, the speed of sound is

$$v_s^2 = \gamma(R/M)T \quad \text{or} \\ \frac{v_s^2}{(R/M)T_{cr}} = \gamma T_r \quad (2.25)$$

and, therefore, with the reduced temperature set,  $v_s^2/(R/M)T_{cr}$  diminishes as the molecule complexity increases (or, with the increase in the number of atoms constituting the molecule, see Fig. 1.30) and  $v_s^2$  diminishes with the molar mass of the gas.

If the gas is a real gas, the parameters which appear in (2.24) can be calculated by means of an equation of state, for example, using (2.5a). Then, within the limits of validity of the equation of state (and the Law of Corresponding States),

$$v_s^2 = -\frac{C_P}{C_V} P_{cr} V_{cr} k_1 \\ = -\left[ 1 - \frac{k_2}{\frac{C_V^0}{Z_{cr} R} + k_3} \right] Z_{cr} (R/M) T_{cr} k_1 \quad \text{or} \\ \frac{v_s^2}{(R/M)T_{cr}} = -k_1 Z_{cr} \left[ 1 - \frac{k_2}{\frac{C_V^0}{Z_{cr} R} + k_3} \right] \quad (2.26)$$

with

$$k_1 = V_r^2 \left( \frac{\partial P_r}{\partial V_r} \right)_{T_r} \\ k_2 = \frac{T_r (\partial P_r / \partial T_r)_{V_r}^2}{(\partial P_r / \partial V_r)_{T_r}} \\ k_3 = T_r \int_{\infty}^{V_r} \left( \frac{\partial^2 P_r}{\partial T_r^2} \right)_{V_r} dV_r$$

Equation (2.26) shows that, with equal  $T_r$  and  $P_r$ , as the  $C_V^0/R$  increases, the ratio  $v_s^2/(R/M)T_{cr}$  diminishes and if  $C_V^0/R$  tends to infinity, then  $v_s^2/(R/M)T_{cr}$  tends to the value  $(-k_1 Z_{cr})$ .

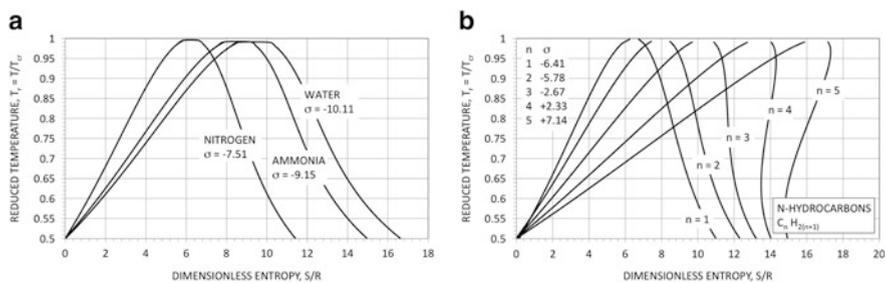
The speed of sound is important, for example, in calculating the critical mass flow in nozzles [14]. Furthermore, the low speed of sound of gas and vapour, with complex molecules (consisting of numerous atoms) and high molar mass, could represent a significant limitation to fluid dynamics when designing turbine stages, with the possibility of shock waves and heavily penalised performance. The speed value  $v_s$ , as indicated in (2.26), is influenced decisively by the molecular complexity of the fluid, its molar mass, but also its volumetric behaviour. One example of an extreme condition caused by the effects of a real gas is the possibility that high values of the ratio  $C_V^0/R$  (around 50–70), associated with the intense effects of a real gas in proximity to the critical point of a fluid ( $0.95 < T_r < 1.04$ ,  $0.7 < P_r < 1.15$ , see [15]), could introduce non-linear fluid dynamics, bringing about rarefaction shock waves and compression fans (the opposite of what would normally happen with an ideal gas). The study of the gas dynamics of heavy fluids near their critical point is known as “dense gas dynamics” and is a relatively modern field of study and research [16].

## 2.5 The Molecular Complexity of the Fluid and the Shape of the Limit Curve

The physical quantity which is most directly correlated to the molecular complexity of a fluid, as we have seen, is its specific molar heat ( $C_p$  or  $C_V$ , which are strictly correlated). The slope of the saturated vapour line can be calculated and a  $\sigma$  parameter introduced which, in its turn, can be assumed to be a parameter linked to the molecular complexity of the fluid [17]

$$\begin{aligned}\sigma &= \frac{T_{cr}}{R} \left[ \frac{dS_{SV}}{dT} \right]_{T_r=0.7} \\ &= \frac{T_{cr}}{R} \left[ \left( \frac{\partial S}{\partial T} \right)_p + \left( \frac{\partial S}{\partial P} \right)_T \frac{dP_{vp}}{dT} \right]_{SV, T_r=0.7} \\ &= \frac{T_{cr}}{R} \left[ \frac{C_p}{T} - \left( \frac{\partial V}{\partial T} \right)_p \frac{dP_{vp}}{dT} \right]_{SV, T_r=0.7}\end{aligned}\quad (2.27)$$

For a real gas, the  $\sigma$  parameter is calculated by means of an equation of state (for example, using (2.5a)). The  $\sigma$  coefficient is primarily a function of the heat capacity of the saturated vapour and, as a consequence, is directly correlated to the molecular structure of the fluid. The qualitative effects of the fluid’s molecular structure on the  $\sigma$  value can easily be shown if the vapour is assimilated to an ideal gas. In which case,



**Fig. 2.5** Tendency of the saturation dome in the plane of reduced temperature-reduced entropy for various fluids. The results are those given by the equation of state (2.5a). (a) Typical fluids with simple molecular structure. (b) First compounds in the series of aliphatic alkane hydrocarbons

$$\begin{aligned} \sigma &\approx \frac{T_{cr}}{R} \left[ \frac{C_p^0}{T} - \frac{R}{P} \frac{dP_{vp}}{dT} \right]_{T_r=0.7} \\ &= \left[ \frac{\gamma}{\gamma-1} \frac{1}{T_r} - \frac{1}{P_r} \frac{df_p}{dT_r} \right]_{T_r=0.7} \end{aligned} \quad (2.28)$$

The slope of the upper limit curve, in the thermodynamic plane T-S, may then be negative, null or positive according to which of the two terms included within square brackets prevails. The fluids with a complex molecular structure, i.e. formed by a large number of atoms, tend to have a high specific molar heat and the ratio  $\gamma = C_p/C_v$  tends to unity (see Fig. 1.30). Consequently, they are characterised by a slope of the upper limit curve that is markedly positive. Fluids with a simple molecular structure, like water and ammonia, have modest specific heat values and, therefore, the  $\sigma$  is negative for them. Figure 2.5 shows several examples of limit curves for different fluids.

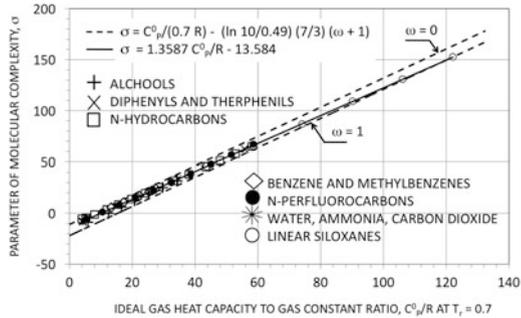
The vapour pressure for any pure fluid may be expressed by means of an equation such as (see (2.20) and Fig. 2.3a):

$$\log P_{vp,r} = A + \frac{B}{T_r}$$

Using the definition (2.6) of the acentric factor and the condition  $P_r = 1$  when  $T_r = 1$ , the two parameters  $A$  and  $B$  can be calculated and the vapour pressure curve can be expressed as

$$\log P_{vp,r} = \frac{7}{3} (\omega + 1) \left( 1 - \frac{1}{T_r} \right)$$

**Fig. 2.6** Parameter of molecular complexity sigma, evaluated by means of (2.29), as a function of the ratio  $C_p^0/R$  for some pure fluids



which, substituted in (2.28), gives for the  $\sigma$  parameter

$$\sigma \approx \frac{C_p^0}{0.7R} - \frac{\ln 10}{0.49} \times \frac{7}{3} (\omega + 1) \tag{2.29}$$

The slope of the upper limit curve is positive if  $\sigma \geq 0$  or if  $C_p^0/R$  is higher than the value  $7.67(\omega + 1)$ . Figure 2.6 reports the  $\sigma$  parameter, calculated for several fluids by means of (2.29). The effect of the acentric factor on the  $\sigma$  value is modest and, generally speaking,  $\sigma$  is primarily a function of the ratio  $C_p^0/R$ , which changes 30 times in passing from the more simple molecule structures (water, ammonia, carbon dioxide) to those which are more complex (like, for example, the linear siloxanes).

As we shall see in Chap. 3, the shape of the limit curve, its slope in particular, is important because, of the numerous thermo-physical properties that characterise each fluid, only a few play a significant role in determining the “quality” of a thermodynamic cycle on the limit curve. Generally speaking, two properties, above all, are responsible for both the cycle performance and the degree of suitability of the fluid for heat recovery from a determined heat source: the critical temperature  $T_{cr}$  and the parameter of molecular complexity  $\sigma$ . In general, at least for homologous fluids, an increase in the molecular complexity is accompanied by a decrease in the critical pressure and a rise in the critical temperature of the fluid.

## 2.6 The Equations of State for Mixtures

For the multicomponent mixtures in a single phase, it is usual to define the volumetric equation of state (2.2), starting with a valid equation for pure fluids and introducing appropriate terms which, correlating between them the valid parameters for pure fluids, provide (via the so-called mixing rules) the corresponding parameters of the mixture.

In the case of (2.5), the mixture parameters are defined, for example, by the following mixing rules [5]:

$$a = \sum_i \sum_j y_i y_j a_{ij} \quad (2.30a)$$

$$b = \sum_i y_i b_i \quad \text{where} \quad (2.30b)$$

$$a_{ij} = (1 - \delta_{ij}) a_i^{1/2} a_j^{1/2} \quad i \neq j \quad (2.30c)$$

and  $a_{ii} = a_i$ ,  $a_{jj} = a_j$ ,  $\delta_{ii} = \delta_{jj} = 0$ .

The coefficient  $\delta_{ij}$  is the specific “binary interaction coefficient” of the couple  $i - j$ . The binary interaction parameters are often estimated on the basis of experimental data for the liquid–vapour equilibrium relative to the mixture.

The departure functions defined for the pure fluid are also valid for the mixtures, provided that the parameters  $a$  and  $b$  of the mixture are used with its specific composition. The specific heats under conditions of an ideal gas for the mixture should be calculated using the following equations:

$$C_V^0 = \sum_i y_i C_{V,i}^0 \quad (2.31a)$$

$$C_P^0 = \sum_i y_i C_{P,i}^0 \quad (2.31b)$$

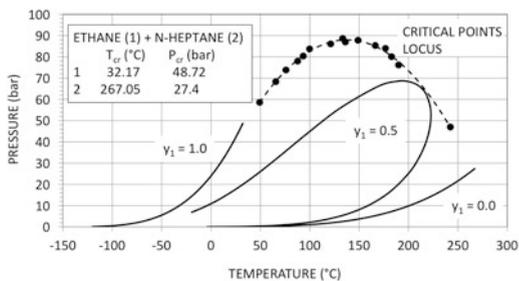
or as weighted mean with the molar fractions of the pure components of the mixture. A critical point can be defined and calculated also for the mixtures, applying the appropriate conditions of stability [4, p. 6.30], [12, Chap. 7].

## Exercises

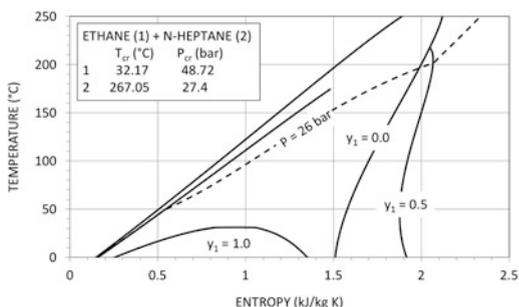
**2.1.** Figure 2.7 reports the liquid–vapour equilibrium pressures for pure ethane (fluid number 1), for pure n-heptane (fluid number 2) and for an equimolar mixture of the two ( $y_1 = y_2 = 0.5$ ). The figure also shows the critical point locus, that is, the variations in pressure and critical temperature with the composition of the mixture (the experimental results are taken from [18]). Calculations of the liquid–vapour equilibrium were made using the equation of state (2.2), with the mixing rules (2.30), assuming  $\delta_{12} = \delta_{21} = 6.7 \times 10^{-3}$ .

As can be seen from the figure, mixing the two fluids, the pressure and the critical temperature vary with continuity from the values relative to the case of pure ethane ( $y_1 = 1$ ) to the values of pure n-heptane ( $y_1 = 0$ ). These variations, though, are not linear: firstly, the critical pressure increases, reaching its maximum value of around 88 bar in correspondence to  $y_1 \approx 0.78$ , then dropping to a minimum value that

**Fig. 2.7** Bubble and dew pressure curves per ethane, per n-heptane and for a mix of the two



**Fig. 2.8** Trend of the limit curve in the thermodynamic plane T-S for pure ethane, for pure n-heptane and for a mixture of the two. For the mixture, there is also shown the isobar at 26 bar



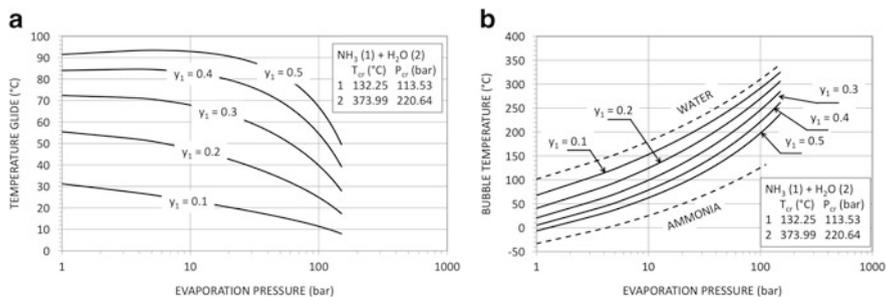
corresponds to the case of pure n-heptane. The mixing of two (or more) compounds represents, therefore, an efficient instrument for varying the critical point of a fluid.

As can be seen, though, in the case of the equimolar mixture, the mixture, once the pressure has been fixed, is characterised by a difference between the bubble and the dew temperatures (the so-called temperature glide). For example, in this specific case, at the pressure of 26 bar, the bubble point is reached at the temperature of about 50 °C and the corresponding dew point is around 200 °C. The temperature glide diminishes as the pressure increases.

Figure 2.8 shows the limit curves in the thermodynamic plane T-S. As we can see, as the composition varies, as well as the pressure and the temperature at the critical point, there is also a significant change in the molecular complexity (the slope of the upper limit curve changes). The figure also clearly shows the temperature glide associated with the isobar of 26 bar.

The results shown here for the mixture of ethane and n-heptane are basically and qualitatively indicative of the thermodynamic behaviour of all the mixtures known as non-azeotropic.<sup>5</sup>

<sup>5</sup>An azeotrope is a mixture of two or more substances with a composition that cannot be distilled. That is, the glide temperature at constant pressure is null and the mixture behaves, from this point of view, as if it were a pure fluid. The composition of the liquid phase is the same of the composition of the vapour phase.



**Fig. 2.9** Temperature glide and bubble temperature for ammonia–water mixtures, with various compositions. The results are those given by the equation of state (2.5a)  $\delta_{12} = -0.2589$

**2.2.** The mixture of water–ammonia has been proposed—and occasionally used—as the working fluid in special steam cycles (see, for example [19]). Figure 2.9a shows the temperature glide, for different compositions of the mixture, as a function of the evaporation pressure: it is always particularly high and grows rapidly with the molar fraction of ammonia. For example, at 1 bar of pressure, the temperature glide is about 31 °C when  $y_1 = 0.1$  and about 92 °C when  $y_1 = 0.5$ .

Having set the composition, the temperature glide falls as the evaporation pressure increases. For example, when  $y_1 = 0.3$ , we get 72 °C at the evaporation pressure of 1 bar and 29 °C at the pressure of 150 bar. To get significant temperature glide at high pressure (advantageous, in principle, if the mixture is used in heat engines that recover heat from heat sources with variable temperature), we need mixtures that are sufficiently rich in ammonia; modest temperature glide in condensation (not excessively penalising from a thermodynamic point of view) is obtained, though, when the molar fraction of ammonia is small.

Figure 2.9b shows the bubble temperature as a function of the evaporation pressure for mixtures of water and ammonia, with different compositions. Bubble temperature values close to the environmental values are obtained when  $y_1 \approx 0.3$ , which could represent the composition of the base mixture in a thermodynamic cycle that uses a water–ammonia mixture as working fluid.

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