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Thermodynamics in CEDRE

The CEDRE thermophysics model combines all the data and procedures that allow the calculation of the thermodynamic properties and transport coefficients of the material media that make up the multi-physics system to be analyzed. This document is more specifically concerned with the thermodynamics of compressible fluids and is limited to the study of homogenous mixtures of chemical species. Starting from the different forms of the fundamental equation of thermodynamics, it involves some useful concepts: state variables and functions, extensive and intensive properties, specific (or molar) properties of the mixture, partial properties of species in the mixture and properties of pure substances. It is shown that, in the pressure-temperature-composition variable system, the free enthalpy is a potential that all the other properties are derived from (volume, entropy, enthalpy, etc.), from which arises a set of general relations between calorific and thermoelastic coefficients. Then, different models for the calculation of the properties of pure substances are presented, from the "perfect gas" limit through real gases, to compressible liquids. These are then reused in the section that covers the way in which the properties of the mixture are calculated from those of its components. Finally, the document briefly describes how the computer data management and the thermophysics computing service are organized in an independent library called *ThermoLib*.

Introduction

As its name indicates, numerical fluid mechanics is nothing but numerical calculation applied to solving fluid flow equations and so much the better for the reader, who will see this definition as merely obvious. Historically, this discipline was first limited to the study of potential flows. Then, it undertook the solution of the Euler equations, thus confronting the characteristics of compressible media, and, in parallel, the solution of the Navier-Stokes equations, which at first only concerned the motion of fluids with constant density. Today, the description "Navier-Stokes Code" has a nebulous coverage that includes the solution of the aerothermochemical transport equations. We recall that this hyperbolic (in time) system expresses the conservation of the extensive quantities that characterize the state of a flow: the linear momentum vector, the total energy and as many masses as the number of independent chemical species of the phase being considered (homogeneous mixture).

It was when NFM entered the world of compressible flows that thermodynamics invited itself in, through the state equations chosen to model the fluid properties. For obvious reasons, the first model used was that of the perfect gases, and it is within this restricted context that most numerical models have been developed today. In this regard we note that, based on the formalism presented in [3], the numerical flow models used by the CEDRE CODE [12, 2] were programmed

from the start with a view to using any thermodynamics whatsoever: this investment has allowed the fluid models presented here to be integrated very rapidly, and to develop them without risk of overlapping other developments.

If the only purpose of the CEDRE code was to simulate the flight of aircraft in cloud free skies, its fluid model could be described in few words: a mixture of chemical species with a fixed composition, whose behavior is similar to that of a perfect gas with constant specific heat. If it was a matter of explaining the concepts and models used in chemical engineering [19] in detail, not even several pages would suffice. The field of application of CEDRE [14] being situated well beyond the first example cited, it is the same for its modeling domain, and in particular for its fluid models: compressible, single or multiple species, possibly reactive, even multiple phase.

The CEDRE thermophysics model brings together all the data and procedures that allow the calculation of the thermodynamic properties and transport coefficients for any material medium likely to be involved in a multi-physics system, as it has been defined by the user: compressible, for which the CHARME solver calculates the flow, dispersed phases handled by the SPARTE (Lagrangian) and SPIREE (Euler) solvers, and solid materials on which the Acacia solver works. This document is more specifically concerned with the thermodynamics of the main fluid (that of Charme), and it is limited to the study

of homogenous mixtures of chemical species. For greater detail, the reader could refer to the references [1, 19], in the first chapter of the thesis report [8] and to the CEDRE theoretical manual [4].

§ "Theoretical framework" sets the theoretical framework for the modeling and states its notations. Starting from the different forms of the fundamental equation of thermodynamics, it summarizes some useful concepts: state functions and independent variables, extensive properties and intensive properties, thermodynamic potentials, specific (or molar) properties of the mixture, partial properties of species in the mixture and properties of pure substances (not mixed). § "Fluids properties" recalls that, in the so called system of natural variables (pressure, temperature and composition), the free enthalpy of the mixture is a potential from which all other first order quantities (volume, entropy, internal energy, enthalpy, etc.) are derived, and deduces all the relations between second order calorific and thermoelastic properties. Also indicated there is how it is possible to calculate, without limitation to the special case of perfect gases, data that is indispensable to any code handling fluid mechanics, such as the specific heat ratio, the speed of sound or the partial derivatives of pressure with respect to the conservative volume quantities (mass and energy). § "Properties of species" presents different models for calculating the properties of species (not mixed), from the "perfect gas" limit, through the various models for real gases (the Viriel law and cubic state equations), to compressible liquids. These models are reused in § "Mixture models", which shows how the properties of the mixture are calculated from its components. Finally, § "The CEDRE ThermoLib library" briefly describes how the computer management of the thermophysics calculation service is organized in an independent library called *ThermoLib*.

Theoretical framework

The flow of a compressible fluid comprising n_e chemical species is considered, and it is assumed that this system changes sufficiently slowly for thermodynamic equilibrium to be preserved at any point in space and time (local equilibrium). In these conditions, the state of each fluid particle is defined uniquely by $n_e + 2$ extensive quantities (i.e. proportional to the size): the volume occupied by the component considered, its internal energy E and the masses M_j of the species that it contains.

Although this set of independent variables, which will be called basic variables (or primitives) here, is sufficient to describe the state of any continuous medium in equilibrium, even if it is composed of different phases, and thus offers access to all of its properties, we will limit this dissertation to the special case of single phase fluids.

Fundamental equation

Applied to systems of this type, thermodynamics postulates the existence of an extensive quantity called entropy, a homogenous first degree function of the basic variables, or:

$$S = S(E, V, M_j) = \frac{1}{\lambda} S(\lambda E, \lambda V, \lambda M_j), \forall \lambda > 0 \quad (1)$$

This state function only defines a stable physical system if it satisfies certain conditions of monotonicity and convexity. In particular, it must increase strictly with energy and volume, which implies that

the corresponding partial derivatives are positive. Applying the Euler theorem to the first degree homogeneous functions, postulate (1) can be written:

$$S = \frac{1}{T} E + \frac{p}{T} V - \sum_{j=1}^{n_e} \frac{g_j}{T} M_j$$

$$\Leftrightarrow dS = \frac{1}{T} dE + \frac{p}{T} dV - \sum_{j=1}^{n_e} \frac{g_j}{T} dM_j \quad (2)$$

or in the following (more classical) form:

$$E = TS - pV + \sum_{j=1}^{n_e} g_j M_j \Leftrightarrow dE = TdS - pdV + \sum_{j=1}^{n_e} g_j dM_j \quad (3)$$

Thus, the pressure p, temperature T and thermodynamic potentials per unit mass g_j for the species in the mixture are defined by:

$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_{V, M_j} \quad , \quad \frac{p}{T} = \frac{\partial S}{\partial V}\bigg|_{E, M_j} \quad , \quad \frac{g_i}{T} = -\frac{\partial S}{\partial M_i}\bigg|_{E, V, M_{j \neq i}}$$

These new quantities, which only have meaning with the assumption of local equilibrium and are described as intensive because they do not depend on the size of the system, are homogenous zero degree functions of the primitive variables.

Free energy and volume-temperature variables

If the free energy $F = E - TS$, also called the Helmoltz function, is used, equation (3) becomes:

$$F = -pV + \sum_{j=1}^{n_e} g_j M_j \Leftrightarrow dF = -pdV - SdT + \sum_{j=1}^{n_e} g_j dM_j \quad (4)$$

From this the partial derivatives of the free energy in the system of variables are deduced:

$$p = -\frac{\partial F}{\partial V}\bigg|_{T, M_j} \quad , \quad S = -\frac{\partial F}{\partial T}\bigg|_{V, M_j} \quad , \quad g_i = \frac{\partial F}{\partial M_i}\bigg|_{V, T, M_{j \neq i}}$$

Free enthalpy and pressure-temperature variables.

By replacing the internal energy by the enthalpy $H = E \times pV$ in equation (3), we immediately obtain:

$$H = TS + \sum_{j=1}^{n_e} g_j M_j \Leftrightarrow dH = TdS + Vdp + \sum_{j=1}^{n_e} g_j dM_j \quad (5)$$

From which, by introducing the free enthalpy $G = H - TS$, also called the Gibbs function:

$$G = \sum_{j=1}^{n_e} g_j M_j \Leftrightarrow dG = Vdp - SdT + \sum_{j=1}^{n_e} g_j dM_j \quad (6)$$

This new form of the thermodynamic postulate (Gibbs) means that, in the $[p, T, M_j]$ system of variables, we have:

$$V = \frac{\partial G}{\partial p}\bigg|_{T, M_j} \quad , \quad S = -\frac{\partial G}{\partial T}\bigg|_{p, M_j} \quad , \quad g_i = \frac{\partial G}{\partial M_i}\bigg|_{p, T, M_{j \neq i}}$$

In this regard, we note that the change of variables $\left[V, E, M_j\right] \to \left[p, T, M_j\right]$ leads to a loss of information on the zones where different phases coexist. This is the case, for example, on the phase change curves for pure substances $(n_e = 1)$: the pressure and temperature being related there, these two variables do not permit a complete description of the state of the system in equilibrium.

Molar approach

Chemists prefer to measure the quantities of matter in numbers of moles. Let N_j be the number of moles of the species j, N the total number, m_j the molar masses of the species and m that of the mixture. The change from M_j to N_j is immediate:

$$M_j = N_j m_j \Rightarrow M = \sum N_j m_j = Nm$$

In the new variables $\left[p, T, N_j\right]$, the equations (6) are written

$$G = \sum_{j=1}^{n_e} \mu_j N_j \Leftrightarrow dG = Vdp - SdT + \sum_{j=1}^{n_e} \mu_j dN_j$$

Here, the partial derivatives μ_j (also denoted by $g_{m,j}$) are the molar thermodynamic potentials of the species in the mixture:

$$\mu_i = m_i \, g_i = \left.\frac{\partial F}{\partial N_i}\right|_{V,T,N_{j \neq i}} = \left.\frac{\partial G}{\partial N_i}\right|_{p,T,N_{j \neq i}}$$

Partial quantities

In the $\left[p, T, N_j\right]$ system of variables, the free enthalpy is a homogenous first degree function of the masses. It is the same for any extensive quantity Ψ, which can be translated into the following form:

$$\Psi = \sum_{j=1}^{n_e} \psi_j M_j \Leftrightarrow d\Psi = \frac{\partial \Psi}{\partial p}dp + \frac{\partial \Psi}{\partial T}dT + \sum_{j=1}^{n_e} \psi_j dM_j \qquad (7)$$

The quantities ψ_j thus defined are called specific (per unit mass) partial quantities of the species in the mixture. In general, they are a function of all of the variables chosen to define the state of the system, which distinguishes them from the intrinsic properties of the same species (measured when not mixed), which only depend on the pressure and temperature, and that will be denoted here by ψ_j^*. We will return to these two important concepts later.

In terms of molar variables $\left[p, T, N_j\right]$, the equations (7) are written:

$$\Psi = \sum \psi_{m,j} N_j \Leftrightarrow d\Psi = \frac{\partial \Psi}{\partial p}dp + \frac{\partial \Psi}{\partial T}dT + \sum \psi_{m,j} dN_j \qquad (8)$$

Here, $\psi_{m,j} = m_j \psi_j$ is the partial molar quantity of the species j in the mixture, to be distinguished from the molar property $\psi_{m,j}^*$ of the pure substance.

Mass specific (or molar) quantities

The homogeneity of the state functions, such as free enthalpy relative to the masses of the species allows the study of the relations

between thermodynamic quantities to be reduced to that of a system whose total mass M remains equal to unity. The composition of such a mixture is defined by the n_e mass specific fractions $y_j = M_j / M$, it being understood that these new state variables are not independent because their sum is equal to unity. In the rest of this presentation, we will call any extensive quantity referred to the unit mass of the system being studied a mass specific property (or property per unit mass), that is:

$$\upsilon = \frac{V}{M}, \; s = \frac{S}{M}, \; e = \frac{E}{M}, \; h = \frac{H}{M} = e + p\upsilon, \; g = \frac{G}{M} = h - Ts, \text{ etc...}$$

We note that neither the density of the mixture $\left(\rho = \upsilon^{-1}\right)$ nor that of the species $\left(\rho_j = \rho y_j\right)$ are specific properties in the sense that is understood here. For any extensive quantity $\Psi = M\psi$, the equations (7) are written:

$$\psi = \sum \psi_j y_j \Leftrightarrow d\psi = \frac{\partial \psi}{\partial p}dp + \frac{\partial \psi}{\partial T}dT + \sum \psi_j dy_j \qquad (9)$$

If the composition is measured in moles (8), the following molar fractions are introduced:

$$x_j = \frac{N_j}{N} = \frac{m}{m_j} y_j \text{ where } m = \sum x_j m_j = \left(\sum \frac{y_j}{m_j}\right)^{-1}$$

and the fluid is characterized by its molar properties:

$$\psi_m = m\psi = \sum \psi_{m,j} x_j \Leftrightarrow d\psi_m = \frac{\partial \psi_m}{\partial p}dp + \frac{\partial \psi_m}{\partial T}dT + \sum \psi_{m,j} dx_j$$

To go from the specific approach (which is preferred in this presentation) to the molar approach, it is sufficient to replace the mass fractions by the molar fractions $\left(y_j \to x_j\right)$ in all the mathematical expressions below, and the specific quantities by the corresponding molar quantities $\left(\psi \to \psi_m\right)$.

Fluid properties

Free enthalpy and derived properties

On condition of the assumptions stated at the start of the previous section, and subject to the constraint $\Sigma y_j = 1$, the fundamental equation (6) becomes:

$$g = \sum_{j=1}^{n_e} y_j g_j \Leftrightarrow dg = \upsilon dp - sdT + \sum_{j=1}^{n_e} g_j \, dy_j \qquad (10)$$

Of course, these relations are only valid if the function g is continuously differentiable, in other words, free of singularities related to phase changes (figure 1). As has already been remarked above, they throw light on the special status of the pressure-temperature-composition variables relative to the free enthalpy g. In this space with $n_e + 1$ independent coordinates, the function:

$$g = g(p, T, y_j) \parallel p, T > 0, \sum y_j = 1$$

is a thermodynamic potential, which, among other things, implies that any specific property of the fluid (in the sense stated in § "Mass specific (or molar) quantities" is a linear form of g and its partial derivatives, or, with the first order of differentiation:

$$\upsilon = \frac{\partial g}{\partial p}, \quad s = -\frac{\partial g}{\partial T}, \quad g_j = \frac{\partial g}{\partial y_j} \Rightarrow h = g - T\frac{\partial g}{\partial T} = -T^2 \frac{\partial}{\partial T}\left(\frac{g}{T}\right)$$

$$and \quad e = g - p\frac{\partial g}{\partial p} - T\frac{\partial g}{\partial T}$$

It is the same for the specific heat at constant pressure, or

$$c_p = \frac{\partial h}{\partial T} = T\frac{\partial s}{\partial T} = -T\frac{\partial^2 g}{\partial T^2}$$

and for any first order partial derivative of the properties. Because of the commutativity of the differentiation operators, these second order quantities (relative to the potential g) are related to each other (Maxwell). Thus, in the pressure-temperature plane, we have:

$$\frac{\partial s}{\partial p} = -\frac{\partial \upsilon}{\partial T}, \quad \frac{\partial h}{\partial p} = \upsilon - T\frac{\partial \upsilon}{\partial T}, \quad \frac{\partial e}{\partial p} = \upsilon - p\frac{\partial \upsilon}{\partial p} - T\frac{\partial \upsilon}{\partial T}$$

As regards the derivatives of the first order quantities in the composition space, these are related to those of the thermodynamic potentials g_j with respect to pressure or temperature, for example:

$$\upsilon_j = \frac{\partial \upsilon}{\partial y_j} = \frac{\partial g_j}{\partial p}, \quad s_j = \frac{\partial s}{\partial y_j} = -\frac{\partial g_j}{\partial T}, \quad h_j = \frac{\partial h}{\partial y_j} = g_j - T\frac{\partial g_j}{\partial T} \text{ etc...}$$

It is easily shown that these quantities ψ_j are identical to the partial properties whose definition was given in § "Partial quantities". Subsequently, we will show how these are calculated from the properties of pure substances ψ_j^* via a mixture model. First, we present a series of relations between thermodynamic functions that any mechanical fluid code is able to use.

Thermodynamic relations

To simplify the expressions that follow, let:

$$r = \frac{p\upsilon}{T} = r\,(p, T, y_j)$$

and let the thermoelastic coefficients α_p (isobaric expansion) and χ_T (isothermal compressibility) be made dimensionless in the following way:

$$\omega_p = \chi_T p = -\frac{p}{\upsilon}\frac{\partial \upsilon}{\partial p}\bigg|_{T,y_j} \quad and \quad \omega_T = \alpha_T T = \frac{T}{\upsilon}\frac{\partial \upsilon}{\partial T}\bigg|_{p,y_j}$$

We note that the factor r thus defined is a specific property in the same way as the volume, that it is measured in the same units as entropy or specific heat, and that the equation that defines it as a function of the variables (p, T, y) plays the role of the equation of state for the mixture. To return to more classical notations, it is sufficient to note that:

$$r = \frac{RZ}{m} \quad (J/K/kg) \quad then \quad r_m = RZ \quad (J/K/mol)$$

where R is the universal gas constant, m is the molar mass of the mixture and Z is the compressibility factor from the theory of real gases.

From the relations stated in § " Free enthalpy and derived properties ", it is easily deduced that any specific quantity derived from a first order property is expressed as a function of volume (or, what amounts to the same thing, from the factor r), the specific heat at constant pressure and the two dimensionless thermoelastic coefficients. Here, presented in differential form and still in the system of natural variables (p, T, y), is the table of these partial derivatives:

$$dr = (1-\omega_p)r\frac{dp}{p} + (\omega_T - 1)r\frac{dT}{T} + \sum_{j=1}^{n_e} r_j dy_j$$

$$d\upsilon = -\omega_p \upsilon\frac{dp}{p} + \omega_T \upsilon\frac{dT}{T} + \sum_{j=1}^{n_e} \upsilon_j dy_j$$

$$ds = -\omega_T r\frac{dp}{p} + c_p\frac{dT}{T} + \sum_{j=1}^{n_e} s_j dy_j$$

$$dh = (1-\omega_T)\upsilon dp + c_p dT + \sum_{j=1}^{n_e} h_j dy_j$$

$$de = (\omega_p - \omega_T)\upsilon dp + (c_p - \omega_T r)dT + \sum_{j=1}^{n_e} e_j dy_j$$

We recall that these partial derivatives r_j, v_j, s_j, h_j et e_j are partial mass specific quantities (9), and that they are related by the same type of relations as the properties from which they are derived, for example:

$$r_j = \frac{p\upsilon_j}{T}, \quad h_j = e_j + r_j T, \quad \frac{\partial h_j}{\partial p} = \upsilon_j - T\frac{\partial \upsilon_j}{\partial T} \quad etc...$$

It may be necessary to use the volume rather than the pressure as the independent variable, with a state equation of the form:

$$r = \frac{p\upsilon}{T} = r\,(\upsilon, T, y_j)$$

In this case, let:

$$\pi_\upsilon = \omega_p^{-1} = -\frac{\upsilon}{p}\frac{\partial p}{\partial \upsilon}\bigg|_{T,y_j} \quad and \quad \pi_T = \omega_p^{-1}\omega_T = \frac{T}{p}\frac{\partial p}{\partial T}\bigg|_{\upsilon,y_j}$$

By combining the previously obtained results, it is found that in the new system of variables :

$$dr = (1-\pi_\upsilon)r\frac{d\upsilon}{\upsilon} + (\pi_T - 1)r\frac{dT}{T} + \sum_{j=1}^{n_e} \pi_\upsilon r_j dy_j$$

$$dp = -\pi_\upsilon p\frac{d\upsilon}{\upsilon} + \pi_T p\frac{dT}{T} + \sum_{j=1}^{n_e} \pi_\upsilon p\frac{\upsilon_j}{\upsilon} dy_j$$

$$ds = \pi_T r\frac{d\upsilon}{\upsilon} + c_v\frac{dT}{T} + \sum_{j=1}^{n_e} (s_j - \pi_T r_j)dy_j$$

$$dh = (\pi_T - \pi_\upsilon)\, p d\upsilon + (c_\upsilon + \pi_T r) dT + \sum_{j=1}^{n_e} \left[h_j + (\pi_\upsilon - \pi_T) r_j T \right] dy_j$$

$$de = (\pi_T - 1)\, p d\upsilon + c_\upsilon dT + \sum_{j=1}^{n_e} \left[e_j + (1 - \pi_T) r_j T \right] dy_j$$

where $\quad c_\upsilon = c_p - \omega_T \pi_T r = c_p - \dfrac{\omega_T^2}{\omega_p} r$

In particular, Mayer's relation is deduced, which expresses the difference between the specific heat at constant pressure and the specific heat at constant volume:

$$c_p - c_\upsilon = \frac{\omega_T^2 r}{\omega_p} \tag{11}$$

and the specific heat ratio:

$$\gamma \equiv \frac{c_p}{c_\upsilon} = 1 + \frac{\omega_T^2 r}{\omega_p c_\upsilon} = \frac{\omega_p c_p}{\omega_p c_p - \omega_T^2 r} \tag{12}$$

As for the speed of sound in the mixture, it is easily obtained by changing to the (p, s, y) system of variables. It is found that:

$$c^2 \equiv \left. \frac{\partial p}{\partial \rho} \right|_{s, y_j} = \frac{\gamma r T}{\omega_p} \tag{13}$$

The last two equations show that a fluid model defined by an equation of the form $g = g(p, T, y_j)$ is only stable if the following two conditions are satisfied:

$$\omega_p > 0 \text{ and } \omega_p c_p > \omega_T^2 r$$

Finally, we note that in the (υ, T, y) system of variables, the free energy $f = e - Ts$ is a more suitable state function for the calculation of its derivative properties:

$$f = f(\upsilon, T, y) \Rightarrow df = -p d\upsilon - s dT + \sum_{j=1}^{n_e} g_j\, dy_j$$

Volume specific variables

The $\left[\rho_j, \rho e \right]$ system of variables is important for the Euler approach to fluid mechanics: the masses of species and the internal energy per unit volume are the thermostatic part (i.e. without motion) of the so-called conservative quantities. In the transport equations, the fluid properties intervene via the pressure (Euler flux) and the temperature (heat flux). The result of this is that the functions:

$$p = p(\rho_j, \rho e) \Rightarrow dp = \pi_e d\rho e + \sum \pi_j d\rho_j$$

$$T = T(\rho_j, \rho e) \Rightarrow dT = \vartheta_e d\rho e + \sum \vartheta_j d\rho_j$$

and their partial derivatives, here denoted by π and ϑ, play an important role. The simplest way to express these as a function of the mass specific quantities and coefficients defined in the $\left[p, T, y_j \right]$ system of variables, is to go through the variables $\left[\rho_j, T \right]$. After some elementary analytic developments, we find:

$$\pi_e = \frac{\pi_T r}{c_\upsilon} = \frac{\omega_T c^2}{c_p T}, \quad \pi_j = c^2 \frac{r_j}{r} - \pi_e h_j \text{ and}$$

$$\vartheta_e = \frac{1}{\rho c_\upsilon}, \quad \vartheta_j = \vartheta_e \left(\frac{\omega_T}{\omega_p} r_j T - h_j \right)$$

It is easily verified that the speed of sound c and the partial derivative of the pressure are linked by the following relation (which can moreover be proven):

$$c^2 = h \pi_e + \sum y_j \pi_j$$

Properties of species

As has already been noted in § "Partial quantities " and "Mass specific (or molar) quantities", any extensive quantity referred to the unit of mass of the mixture can be written

$$\psi = \sum_{j=1}^{n_e} y_j \psi_j \text{ where } \psi_j = \psi_j(p, T, y_k) = \left. \frac{\partial \psi}{\partial y_j} \right|_{p, T, y_{k \neq j}}$$

the ψ_j being, by definition, the partial mass specific properties of the species in the mixture. As for the properties of pure substances (i.e. measured outside a mixture), which, let us recall, generally differ from those above, these will be denoted by ψ_j^*:

$$\psi_j^* = \psi_j^*(p, T) = \psi_j(p, T, y_k = \delta_{jk})$$

The second equality means that the intrinsic properties and partial quantities are only equal if the mixture is composed only of the species being considered.
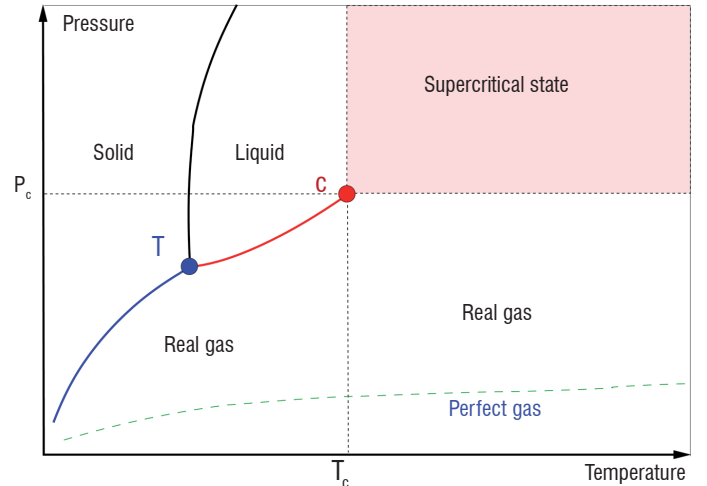

Figure 1 - Phase diagram for a pure substance

To calculate the properties of pure substances, it is normal to refer to those that are measured along a particular isobar, that is $p = p_o = 10^5\, Pa$, and for which the variations as a function of temperature are listed in thermodynamic tables. These quantities are generally described as properties in the standard state:

$$\psi_j^o = \psi_j^o(T) = \psi_j^*(p_o, T)$$

Applied to the free enthalpy, this concept allows the following equation to be written for each substance j:

$$g_j^*(p, T) = g_j^o(T) + \int_{p_o}^{p} \upsilon_j^*(p, T) dp = g_j^o(T) + T \int_{p_o}^{p} r_j^* \frac{dp}{p} \tag{14}$$

Thus, the properties of the species j are entirely defined by its state equation, that is,

$$\upsilon_j^* = \upsilon_j^*(p,T) \text{ or } r_j^* = \frac{p\upsilon_j^*}{T} = r_j^*(p,T)$$

and its free enthalpy g_j^o in the standard state. To calculate these explicitly, it is sufficient to apply the results of Section 3 to this single species system. In the paragraphs below, we will temporarily drop the index j and the exponent "*", it being understood that the results presented here concern either the intrinsic properties of any constituent of the mixture, or what amounts to the same thing, the properties of any single species fluid.

Perfect gases

This is the case of any gas subject to a sufficiently low pressure for the molecules to be considered as material points (zero covolume) whose interactions are negligible, except for impacts. This purely fictitious state, or ideal state according to Anglo-Saxon terminology, can be defined without prejudging the stability of the real physical system. For example: Water vapor at atmospheric pressure and at 0° C ...

The universal molar gas constant is denoted by R, m is the molar mass of the species considered and r_o is its specific constant per unit mass. The state equation is written

$$r^{(id)} = r_o = \frac{R}{m} \Leftrightarrow \upsilon^{(id)} = \frac{r_o T}{p} \qquad \omega_p^{(id)} = \omega_T^{(id)} = 1$$

and the free enthalpy (14) becomes

$$g^{(id)}(p,T) = g^o(T) + r_o T \ln \frac{p}{p_o} \text{ where } g^o = h^o(T) - Ts^o(T)$$

Thermophysical databases such as the NIST-JANAF tables supply the information needed for the calculation of the properties in the standard state $(p = p_o)$ for a large number of ordinary gases. In addition to the molar masses, the following can be found:
• the enthalpies and entropies of formation measured at a reference state (p_o, T_o),
• and a tabulation of the specific heats at constant pressure (p_o), from which it is possible, by using the least squares method, to draw a polynomial representation over a range of temperatures suited to the calculations, that is, a limited set of species parameters and physical constants that can be combined in a reasonably sized database. This is the case for the thermog.xml file of the CEDRE calculation chain. From this, it is possible to calculate explicitly the intrinsic properties of any "perfect gas" type component, first in the standard state (isobar (p_o)):

$$h^o(T) = h_f^o + \int_{T_o}^{T} c_p^o dT, s^o(T) = s_f^o + \int_{T_o}^{T} c_p^o \frac{dT}{T}, \text{ etc...}$$

And then in the entire plane (p,T) :

$$c_p^{(id)} = c_p^o(T), h^{(id)} = h^o(T), s^{(id)} = s^o(T) - r_o \ln \frac{p}{p_o}, \text{ etc...}$$

Compressible liquids

Here is an example of a simplified state equation for a compressible liquid, valid in the vicinity of a reference state (p_o, T_o) :

$$\upsilon = \upsilon_o \frac{1 + \alpha(T - T_o)}{1 + \beta(p - p_o)} \text{ where } \alpha T_o \ll 1 \text{ et } \beta p_o \ll 1$$

In these conditions, the dimensionless thermoelastic coefficients are:

$$\omega_p \sim \beta p \qquad \text{and} \qquad \omega_T \sim \alpha T$$

Equation (14) become:

$$g \sim g^o(T) + \upsilon_o(p - p_o) \text{ hence } h \sim h^o(T) + \upsilon_o(p - p_o), c_p = c_p^o(T)$$

It is easily shown that if the fluid cannot be expanded ($\alpha = 0$), the ratio γ is strictly equal to unity. In CEDRE, this model for a fluid with little compressibility is used to evaluate the robustness and stability of numerical models initially developed for gas flows.

Real gases

When a gas is subject to high pressures, the molecules can no longer be considered as material points and their interactions can no longer be neglected. As a result, the compressibility factor:

$$Z = \frac{\upsilon}{\upsilon^{(id)}} = \frac{r}{r_o} = \frac{p\upsilon}{r_o T}, \quad r_o = \frac{R}{m} \tag{15}$$

differs from unity, as does the fugacity coefficient (φ), a dimensionless parameter whose logarithm measures the difference between the free enthalpy of a mole of real gas and the value that a perfect gas would have at the same temperature, that is, in terms of mass specific properties:

$$g(p,T) = g^{(id)}(p,T) + r_o T \ln \varphi = g^o(T) + r_o T \ln \frac{p}{p_o} + r_o T \ln \varphi \tag{16}$$

By combining equation (14) and the definition of the fugacity coefficient (16), we obtain:

$$\ln \varphi = \frac{g - g^{(id)}}{r_o T} = \frac{1}{r_o T} \int_{p_o}^{p} \left(\upsilon - \upsilon^{(id)} \right) dp \tag{17}$$

In this paragraph, we will assume on the one hand that the pressure p_o is sufficiently low for the standard state to coincide with that of the perfect gas (or $Z^o \sim 1$) and, on the other hand, that the state equation can be written in one of the two forms below:

$$Z = \mathcal{Z}(p,T) \qquad \text{or} \qquad Z = \mathcal{Z}(\upsilon,T) \tag{18}$$

In these conditions and depending on the case, the logarithm of the fugacity coefficient is written:

$$\ln \varphi = \int_0^p (\mathcal{Z} - 1) \frac{dp}{p} \tag{19}$$

$$\text{or } \ln \varphi = Z - 1 - \ln Z - \int_{\infty}^{\upsilon} (\mathcal{Z} - 1) \frac{d\upsilon}{\upsilon} \tag{20}$$

We note in passing that the two forms (18) are only equivalent if, at a given temperature, pressure and volume vary in opposite directions,

which must be the case for the speed of sound in the substance to be calculable (see § "Thermodynamic relations").

Principle of corresponding states

In what follows, the critical pressure of the gas that is being considered will be denoted by P_c , its critical temperature will be denoted by T_c , and this data will be used to make the state variables dimensionless:

$$P_r = \frac{p}{p_c}, \quad T_r = \frac{T}{T_c} \quad \text{and} \quad V_r = \frac{p_c \upsilon}{r_o T_c} = Z_c \frac{\upsilon}{\upsilon_c} \quad (21)$$

According to the "principle" of corresponding states, the volume factor must be a universal function of the reduced variables. Experience shows that this is only the case for rigorously symmetrical molecules, in other words, for monatomic substances. This is why Pitzer and other authors have introduced the concept of the acentric factor ω , this dimensionless number being assumed to represent the molecular characteristics of the gas being considered. They let:

$$Z = \frac{P_r V_r}{T_r} = \mathcal{Z}(P_r, T_r, \omega)$$

the function $\mathcal{Z}$ being common to all species. This approximation, which is found to be fairly close to reality for most ordinary gases, allows considerable simplification of the relation between the calculation library and the thermophysical database: so that a chemical species for which "perfect gas" data is available, via the thermog.xml file for example (see § "Perfect gases"), can be treated as a real gas, it is sufficient to add the three additional constants p_c, T_c and ω to the data for the standard state.

Viriel expression

At moderate pressure, we can be content to express the volume factor by means of a limited expression around the perfect gas state, or

$$Z = 1 + \sum_{k>0} \frac{A_k}{V_r^k} = 1 + \sum_{k>0} B_k \left(\frac{P_r}{T_r} \right)^k$$

the coefficients A_k and B_k (related to each other) only depend on the reduced temperature and the Pitzer acentric factor.

$$A_k = A_k(T_r, \omega), \quad B_1 = A_1, \quad B_2 = A_2 - A_1^2,$$

As for the free enthalpy and the other calorific properties, they can be deduced from the fugacity coefficient (19), which here has the value:

$$\ln \varphi = \sum_{k>0} \frac{B_k}{k} \left(\frac{P_r}{T_r} \right)^k$$

Cubic state equations

At higher pressure, it is preferable to use one of the state equations derived from the Van der Waals equation. This is the general form, with the two numbers σ_1 and σ_2, as parameters and expressed as a function of the molar volume:

$$p = \frac{RT}{\upsilon_m - b} - \frac{a\alpha(T)}{(\upsilon_m + \sigma_1 b)(\upsilon_m + \sigma_2 b)} \quad \text{where} \quad \alpha(T_c) = 1 \quad (22)$$

After changing to reduced variables (21), and once we let:

$$b_r = \frac{p_c b}{RT_c} \quad \text{and} \quad a_r = \frac{p_c a}{(RT_c)^2}$$

Equation (22) becomes:

$$P_r = \frac{T_r}{V_r - b_r} - \frac{a_r \alpha(T_r, \omega)}{(V_r + \sigma_1 b_r)(V_r + \sigma_2 b_r)}$$

Both dimensional constants b_r (reduced covolume) and a_r (internal pressure coefficient) are such that the first and second derivatives of the function (23) with respect to the volume are zero at the critical point, or $P_r = T_r = 1$. Table 1 shows the constants for four of the best known models: Van der Waals (VdW, [18]), Redlich-Kwong (RK, [11]), Soave-Redlich-Kwong (SRK, [16]) and Peng-Robinson (PR, [9]). The first is mainly of historical interest. The correction to the Redlich-Kwong equation by Soave permits a better representation of the behavior of hydrocarbon gases close to the saturation curve.

EOS	σ_1	σ_2	b_r	a_r	Z_C	$\alpha(T_r, \omega)$
VdW	0	0	0.125	0.421875	0.375	1
RK	0	1	0.08664	0.42748	0.333	$T_r^{-0.5}$
SRK	0	1	0.08664	0.42748	0.333	$\left[1 + m(1 - T_r^{0.5}) \right]^2$
PR	$1-\sqrt{2}$	$1+\sqrt{2}$	0.07780	0.45724	0.305	$\left[1 + m(1 - T_r^{0.5}) \right]^2$

SRK	$m = 0.48508 + 1.54171\omega - 0.17613\omega^2$
PR	$m = 0.37464 + 1.54226\omega - 0.26992\omega^2$

Table - 1 Cubic state equations

As for the performance of the Peng and Robinson model, it is better on the liquid side and in the vicinity of the critical point [17]. Here we let:

$$\xi = \frac{b_r P_r}{T_r}, \quad \eta = \frac{b_r}{V_r} \quad \text{and} \quad \Theta = \frac{a_r \alpha}{b_r T_r} = \Theta(T_r)$$

The covolume b_r being the threshold value for the reduced volume, the variable η defined above varies between 0 (perfect) and 1 (infinite pressure). With this notation, the state equation (23) becomes:

$$\xi = \frac{\eta}{1-\eta} - \frac{\Theta \eta^2}{(1+\sigma_1\eta)(1+\sigma_2\eta)} \tag{24}$$

hence, the compressibility factor is:

$$Z = \frac{\xi}{\eta} = \frac{1}{1-\eta} - \frac{\Theta \eta}{(1+\sigma_1\eta)(1+\sigma_2\eta)} \tag{25}$$

The fugacity coefficient (20) is deduced from the state equation (25). After integration of the function Z along each isotherm, we find:

$$\ln \varphi = Z - 1 - \ln Z - \ln(1-\eta) - \Theta U(\eta) \tag{26}$$

the function being defined by

$$U = \int_o^\eta \frac{d\eta}{(1+\sigma_1\eta)(1+\sigma_2\eta)} \quad \text{or} \quad U = \frac{1}{\sigma_2-\sigma_1} \ln\left(\frac{1+\sigma_2\eta}{1+\sigma_1\eta}\right) \text{ if } \sigma_1 \neq \sigma_2$$

üütüäűůűůűűűűűűűß$_1 = \sigma_2 = \sigma$
$$\frac{\eta}{1+\sigma\eta}$$

From equation 26, we deduce the free energy of the real gas

$$f = g - p\upsilon = f^{(id)} - r_o T \left[\ln(1-\eta) + \Theta U(\eta)\right]$$

then, by differentiation with respect to temperature, all the calorific properties, for example:

$$e = e^{(id)} - r_o T \left[T \frac{d\Theta}{dT} U(\eta)\right]$$

$$h = h^{(id)} + r_o T \left[Z - 1 + T \frac{d\Theta}{dT} U(\eta)\right]$$

$$s = s^{(id)} + r_o \left[\ln Z + \ln(1-\eta) + \left(\Theta + T \frac{d\Theta}{dT}\right) U(\eta)\right]$$
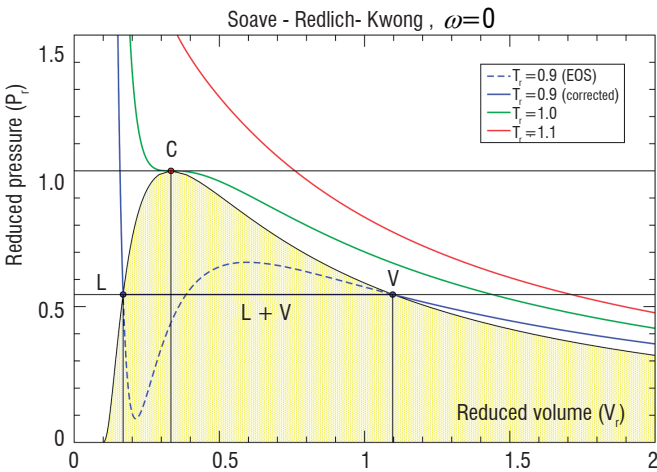

Figure 2 - Cubic state equation, Clapeyron diagram.

The state equations (22-25) are described as cubic because the calculation of the volume (or factor) from the intensive parameters (pressure and temperature) involves the solution of a third degree equation. This does not present any difficulty in the supercritical domain $(T_r > 1)$: the solution there is necessarily unique. Otherwise, the problem can have three solutions, as shown in figure 2. The one located in the increasing part of the curve can be eliminated automatically because it is not physical, which does not necessarily mean that the other two will be. In fact, over the entire domain above the saturation curve, each isotherm from the cubic equation must be replaced by a horizontal plateau (isobar) whose level is the saturated vapor pressure, and whose two ends are the values of the volume on the saturated liquid side (to the left) and that on the just dry vapor side (to the right), or:

$$\forall T_r < 1, \quad P_r = P_r^{(sat)}(T_r) \text{ if } V_r^{(sat,l)} \leq V_r \leq V_r^{(sat,v)}$$

Thus, for any state equation of the form (23) and for any fixed temperature above the critical point, the saturated vapor pressure is determined by the fact that, on the one hand, the reduced volumes $V_r^{(sat,l)}$ and $V_r^{(sat,v)}$ are respectively the smallest and the greatest of the three real solutions of the equation

$$P_r^{(sat)} = \frac{T_r}{V_r} \mathcal{Z}(V_r, T_r)$$

And, on the other hand, the free enthalpy is continuous across the saturation curve. This equilibrium condition between coexisting phases comes down to writing the equality of the fugacity coefficients (26), or:

$$\varphi(V_r^{(sat,l)}, T_r) = \varphi(V_r^{(sat,v)}, T_r)$$

This type of problem can only be solved iteratively: starting from a pressure level between the two extremes of the isotherm under consideration, the volumes corresponding to the two intersection points L and V are calculated (see figure 2), then the two related fugacity coefficients are calculated by applying the formula (26), and the pressure is iterated using the following recurrence:

$$P_r = P_r \times \frac{\varphi^{(L)}}{\varphi^{(V)}}$$

until the fugacities are equal. Figure 3 shows the result obtained with the Soave-Redlich-Kwong equation in the case where the acentric factor is zero. We note that the leaps in the derived properties are linked to the slope of the saturation curve via the Clapeyron relation:

$$L_v = \Delta h^{(sat)} = T \, \Delta s^{(sat)} = r_o T_c \left[\frac{T_r^2}{P_r} \frac{dP_r}{dT_r}\right]^{(sat)} \Delta Z^{(sat)}$$

If we assume that the specific heat of vaporization L_v is proportional to the variation of the compressibility ratio, or

$$\frac{L_v}{r_o T_c} \approx A \times \Delta Z^{(sat)} \text{ where } A = \frac{7}{3} \ln 10 \times (1+\omega)$$

an expression analogous to Antoine's law is deduced from the Clapeyron equation,

$$ln \, P_r^{(sat)} = A \times \left(1 - \frac{1}{T_r}\right)$$

which, as can been seen in figure 3, is close to that obtained from the state equation.

Figure 4 shows, as a function of the ratio P_r / T_r and of the values of T_r, from 0.5 to 2, the compressibility factor resulting from the Soave equation and with a correction for the Maxwell plateaux procedure. It shows, if this was needed, that in the zone of coexistence between liquid and vapor (colored yellow), where pressure and temperature are related, the fluid properties can only be calculated if additional information is available, such as the liquid mass (or volume) fraction. Furthermore, it is noted that, even at moderate pressure, the perfect gas assumption $(Z = 1)$ is only really justified (as close as five per cent, for example) if the temperature is greater than one and a half times the critical temperature.
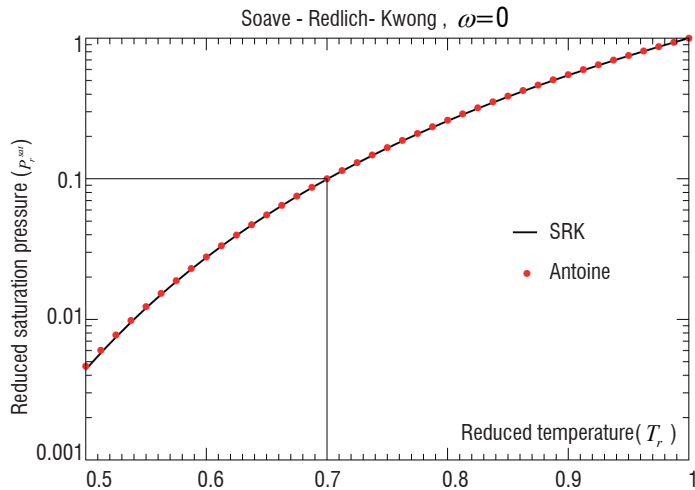

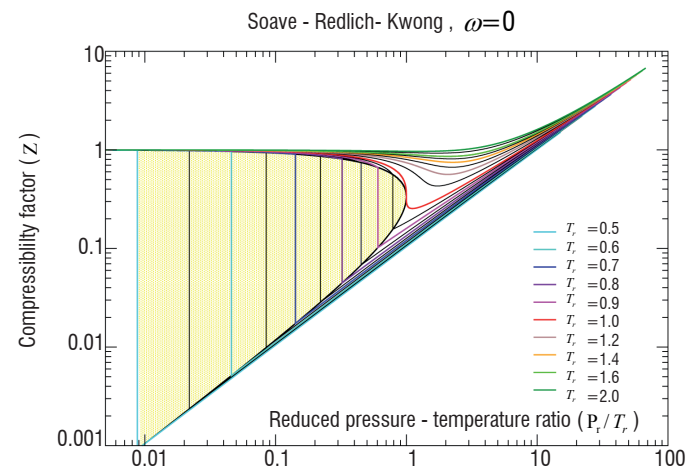Figure - 3 - Cubic state equation, saturation curve.

Figure 4 - Cubic state equation, compressibility factor.

Mixture models

Ideal mixture

We will consider the special case of an ideal mixture of perfect gases. Let x_j denote the molar fraction of the species and let j and $p_j = p x_j$ be its partial pressure. Once this constituent is placed in the mixture (and after homogenization), its thermodynamic potential becomes:

$$g_j(p,T,y_j) = g_j^*(p,T) + r_j^o T \ln x_j = g_j^o(T) + r_j^o T \ln \frac{p_j}{p_o}$$

We recall that $r_j^o = R / m_j$ is the mass specific gas constant and that the molar fractions only depend on the composition. As a result, for an ideal mixture, and only in this case, the partial volume and enthalpy of each species in the mixture are respectively identical to the volume and enthalpy of the pure substance:

$$\upsilon_j = \frac{\partial \upsilon}{\partial y_j} = \frac{\partial g_j}{\partial p} = \frac{r_j^o T}{p}, \quad h_j = \frac{\partial h}{\partial y_j} = g_j - T \frac{\partial g_j}{\partial T} = h_j^o(T)$$

More generally, in any ideal mixture, we have:

$$\upsilon = \sum y_j \upsilon_j^*(p,T), \quad h = \sum y_j h_j^*(p,T), \quad e = \sum y_j e_j^*(p,T)$$

but

$$s = \sum y_j s_j^*(p,T) - \frac{R}{m} \sum x_j \ln x_j \quad \text{where} \quad m = \sum x_j m_j$$

Other models

In general, the chemical activity of a component j in the mixture is defined as follows:

$$g_j(p,T,y_j) = g_j^o(T) + r_j^o T \ln \mathfrak{a}_j$$

It has been seen that, for ideal mixtures of perfect gases, this intensive quantity only depends on the partial pressure of the constituent in the mixture, that is:

$$\mathfrak{a}_j^{(id)} = \frac{p x_j}{p_o}$$

This assumption implies that the fugacity coefficient of each pure constituent $(\alpha_j = 1)$ is equal to unity. It is thus absolutely unsuitable for mixtures of real gases. In this case, more or less complex mixture rules are used.

The simplest rule (Kay, [5]) is only valid for mixtures of substances with similar properties. It consists of applying the principle of corresponding states on the basis of a pseudo critical point with coordinates depending on the mixture composition and the critical data of the constituents j :

$$p_c = \sum_j x_j p_{c_j}, \quad T_c = \sum_j x_j T_{c_j} \quad (27)$$

Then, it is sufficient to choose a real gas law, such as one of those presented in see § "Real gases", to write it in reduced coordinates and to apply it to the mixture:

$$Z = Z\left(\frac{p}{p_c}, \frac{T}{T_c}, \omega\right) \quad \text{where} \quad \omega = \sum_j x_j \omega_j \quad (28)$$

A less elementary model consists of writing that the molar volume of the mixture obeys a cubic state law of type (22) where the constant

(covolume) and product $a\alpha$ (function of temperature) are calculated from the data for pure constituents, or:

$$b_j = b_r \frac{RT_{c_j}}{p_{c_j}}, \quad a_j = a_r \frac{(RT_{c_j})^2}{p_{c_j}} \text{ and } \alpha_j = \alpha\left(\frac{T}{T_{c_j}}, \omega_j\right)$$

Applied to the Van der Waals equation $(\alpha_j = 1)$, the rule of the same name states that:

$$b = \sum_i x_i b_i \text{ and } a = \sum_{i,j} x_i x_j a_{ij} \text{ where } a_{ij} = \sqrt{a_i a_j}$$

To extend this to all the equations 22, it is sufficient to substitute the products $a\alpha$ and $a_{ij}\alpha_{ij}$ for the above constants a and a_{ij}.

This is the model used by the CEDRE code to calculate the properties of mixtures of real gases with cubic state equations ("GCUB1" type species, see following section). In [8] the reader can find a more complete presentation of this fluid model.

Finally, we note that, although the models presented here only need a minimum of information in the species databases, they are far too elementary to be reasonably applicable to complex systems like hydrocarbon mixtures (see [19]) or liquid solutions.

The CEDRE ThermoLib library

The *ThermoLib* library combines all the thermo-physical model related procedures in the CEDRE chain, from loading data into an internal model to calculating the properties of any phase (homogeneous mixture of chemical species) defined during loading. This independent set of FORTRAN 90 procedures can be used by all the components in the calculation chain, including those whose source is written in C++.

Uploading data, the first operation that the user code must start with, consists of reading the fluid model data and storing it in an internal static structure (F90 derived type). It continues by reading two XML files:
 • *thermog.xml* is a portable database (i.e. available on the delivery CD), which contains the pure substance data (see § "Properties species") for about sixty chemical species;
 • *epicea.xml*, produced by collecting the CEDRE calculation data via the EPICEA graphic interface, brings together all the physical-chemical model parameters set by the operator, including the fluid definition data.

From the THERMOLIB service viewpoint, any "fluid" defined by the user is any set of chemical species chosen from among the items available in the database and able to form a homogeneous mixture whose properties can be calculated as a function of pressure, temperature and composition. Since this concept can be extended to solid material, we prefer to speak of a mixture (current terminology) or phase.

As for the species themselves, they are identified by their name $(\text{exemples} : N_2, \; O_2, \; CH_4, \; CO_2, \; H_2O, \text{ etc...})$, which allows the up-

loading procedure to read their data from the file thermog.xml. At the same time, each species is characterized by the type that the operator has assigned to it from the graphic interface: perfect gas with single polynomial representation (GP1), compressible liquid (LC1), real gas whose state equation takes on the form of a Viriel expression (GR1), real gas with cubic state equation (GCUB1), etc. Of course, the choice of type depends on the type of data in the database. Thus, a gas for which only the standard state is known can only be of the "perfect gas" type, whereas if the coordinates of the critical point and the acentric factor appear in its data, it can be allocated either to the "perfect gas" type, or to one of the "real gas" types.

We note that it is possible to allocate different types of species to the same mixture, with the exception of the GCUB1 type, which has its own mixture model. Thus, some users combine a gaseous mixture of air and water vapor (type GP1) with liquid water (type LC1), in the same "fluid" treated by the CHARME solver, by considering that the two phases would be able to maintain themselves in mechanical and thermal equilibrium (same pressure and temperature), without the equality of the chemical potentials, etc., being ensured.

The data collected during the uploading phase is classified and stored in an internal ThermoLib model. This provides management of all its internal data, so that the user does not need to be concerned with this, and can just recover the content through the extraction procedures. Examples: number of mixture of a given name, number of species defined in this mixture, names of these species, molar masses, etc.

The procedures for calculating the properties operate on a mixture with number set by the calling program. For example: calculate, for the mixture $i_{me} = 1$, the enthalpy (H) and its partial derivatives with respect to pressure (H_p), temperature (H_T) and the mass fractions (H_y), from the state data (P, T, Y). To simplify vectorization and optimize the calculation time, each operation is performed on a set of n_s independent states (treatment by packets). Thus, the arguments that appear in the calling interface are real tables whose first dimension has a size equal to the size of the packet to be processed, for example:

$$
\begin{aligned}
&INTEGER, \quad Intent(in) \quad : i_{mel} \\
&INTEGER, \quad Intent(in) \quad : n_s, n_{esp} \\
&REAL, \qquad Intent(out) : P(n_s), T(n_s), Y(n_s, n_{esp}) \\
&RGAL, \qquad Intent(out) : H(n_s), H_P(n_s), H_T(n_s), H_y(n_s, n_{esp}) \\
&INTEGER, \quad Intent(out) \quad : error \\
&OPTIONAL, \qquad\qquad : H, H_p, H_T, H_y
\end{aligned}
$$

Of course, the size n_{esp} of the second dimension of the table of compositions (Y) must be equal to the number of species in the mixture considered: any ThermoLib calculation function verifies this first.

Conclusion

The CEDRE thermo-physical model has allowed the field of application of the code to be extended beyond the perfect gas domain. For the moment, the modeling remains fairly elementary, in particular at the level of mixture rules, but the fact that they are encapsulated in an independent library will allow progressive enrichment and without the risk of overlapping other developments ■

References

[1] M.M. ABBOTT, H.C. VAN NESS - *Theory and Applications of Thermodynamics*. Schaum series, 225 solved exercises, McGraw-Hill, 1987, 342 pages. (ISBN 2 7042 1001 2).

[2] B. COURBET, C. BENOIT, V. COUAILLIER, F. HAIDER, M.-C. LE PAPE and S. PÉRON - *Space Discretization Methods.* Aerospace Lab Issue 2 March 2011.

[3] D. DUTOYA, M.P. ERRERA - *A formal Decomposition of the Jacobian of the Euler Equations*. Rech.Aérosp.1992-1.

[4] D. DUTOYA - *Manuel théorique de la chaîne de calculs CEDRE.* CEDRE-MT-001-I-420x.

[5] W.B. KAY - *Density of Hydrocarbon Gases and Vapours at High Temperatures and Pressures*. Ind. Eng. Chem., 28, 1014-1019, 1964.

[6] B.I. LEE, M.G. KESLER - *A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding State.* AIChE J., 21, 510-527, 1975.

[7] G.N. LEWIS, M. RANDALL - *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill, New York, 1923.

[8] L. MATUSZEWSKI - *Modélisation et simulation numérique des phénomènes de combustion en régime supercritique, thèse pour l'obtention du titre de docteur de l'Université Pierre et Marie Curie* (to be published) 2011.

[9] D.Y. PENG, D.B. ROBINSON - *A New Two-Constant Equation of State*. Ind. Eng. Chem., Fundam., 15, 59-64, 1976.

[10] P. PERROT - *A to Z of Thermodynamics.* Oxford University *Press*. ISBN 0-19-856552-6, 1998.

[11] O. REDLICH, J.N.S. KWONG - *On the Thermodynamics of Solutions.* V. an Equation of State Fugacities of Gaseous Solutions. Chem. Rev., 44, 233-244, 1949.

[12] A. REFLOCH, B. COURBET, A. MURRONE, P. VILLEDIEU, C. LAURENT, P. GILBANK, J. TROYES, L. TESSÉ, G. CHAINERAY, J.B. DARGAUD, E. QUÉMERAIS and F. VUILLOT - *CEDRE Software.* Aerospace Lab Issue 2 March 2011.

[13] R.C. REID, J.M. PRAUSNITZ and B.E. POLING. *The properties of Gases and Liquids*. 4th édition, McGraw-Hill , 1986.

[14] D. SCHERRER, F. CHEDEVERGNE, P. GRENARD, J. TROYES, A. MURRONE, E. MONTREUIL, F. VUILLOT, N. LUPOGLAZOFF, M. HUET, B. SAINTE-ROSE, P. THORIGNY, N. BERTIER, J.M. LAMET, T. LE PICHON, E. RADENAC, A. NICOLE, L. MATUSZEWSKI and M. ERRERA - *Recent CEDRE Applications*. Aerospace Lab Issue 2 March 2011.

[15] G. SCHMIDT and H. WENZEL - *A Modified Van der Waals Type Equation of State*. Chemical Engineering Science, Volume 35, Issue 7, 1980, pl503-1512.

[16] G.S. SOAVE - *Equilibrium Constants from Modified Redlich-Kwong Equation of State*. Chem. Eng. Sci, 27, 6, 1197, 1972.

[17] C.H. TWU, J.E. COON and D. BLUCK - *Comparison of the Peng-Robinson and Soave-Redlich-Kwong Equations of State Using a New Zero-Pressure-Based Mixing Rule for the Prediction of High-Pressure and High-Temperature Phase Equilibria*. Industrial & engineering chemistry research, ISSN 0888-5885.

[18] J.D. VAN DER WAALS - T*he Equation of State for Gases and Liquids*. Nobel lectures in Physics, 1.254-265, Elsevier, Amsterdam (1967).

[19] J. VIDAL - *Thermodynamique, application au génie chimique et à l'industrie pétrolière*. éditions Technip. 21.

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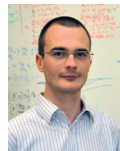
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