

User Guide

of TEP Lib

fluid thermodynamic properties server

coupled with ThermoOptim

A Java tool for predicting the thermodynamic properties of fluids has been created from the libraries for calculating the thermodynamic properties of mixtures of the Laboratory of Thermodynamics of phase equilibria of the Ecole des Mines de Paris (Mines ParisTech). This tool has been coupled with the ThermoOptim software for simulation of energy systems by R. Gicquel and B. Liu.

This library called TEP lib is composed of a set of modules that determine the equilibrium between different phases of fluid mixtures or pure substances and quickly calculate the thermodynamic properties most required in the simulation of energy systems.

This manual is intended to document the program:

- Explicit models implemented and facilitate future improvements
- Explain how the libraries can be used with ThermoOptim

Only the section on pure substances is currently drafted, the mixture modules still being under development.

In what follows, we speak of fluid system to characterize the family of mixtures that can be generated by varying the overall composition, based on a set of pure components. A mixture is defined as a system whose overall composition is set. Obviously, the composition of the mixture varies in the area of liquid-vapor equilibrium.

1. Models implemented

Fluid models implemented are of the "cubic equation of state" type. They have the advantage that they can be solved analytically without using complex numerical methods. This significantly reduces the computation time.

The cubic equations implemented are:

- van der Waals (vdW) model

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}$$

$$b = \frac{1}{8} \frac{RT_c}{P_c}$$

$$Z_c = \frac{P_c v_c}{RT_c} = 0.375$$

- Soave-Redlich-Kwong (SRK) model

$$P = \frac{RT}{v - b} - \frac{a(T)}{(v + b)v}$$

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \text{ avec } \Omega_a = 0.42748$$

$$b = \Omega_b \frac{RT_c}{P_c} \text{ avec } \Omega_b = 0.086640$$

$$Z_c = \frac{P_c v_c}{RT_c} = \frac{1}{3}$$

- Peng-Robinson (PR) model

$$P = \frac{RT}{v - b} - \frac{a(T)}{v + 2bv - b^2}$$

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \text{ avec } \Omega_a = 0.457240$$

$$b = \Omega_b \frac{RT_c}{P_c} \text{ avec } \Omega_b = 0.07780$$

$$Z_c = \frac{P_c v_c}{RT_c} = 0.3074$$

- Patel-Téjà (PT) model

$$P = \frac{RT}{v - b} - \frac{a(T)}{v + (b + c)v - cb}$$

$$a = \Omega_a \frac{R^2 T_c^2}{P_c}$$

$$b = \Omega_b \frac{RT_c}{P_c}$$

$$c = \Omega_c \frac{RT_c}{P_c}$$

Values of Ω_a , Ω_b , Ω_c are calculated from the following system of equations when Z_c is known:

$$\begin{cases} u\Omega_b = 1 + \Omega_b - 3Z_c \\ \Omega_b^3 + [(1 - 3Z_c) + (u + w)]\Omega_b^2 + 3Z_c^2\Omega_b - Z_c^3 = 0 \\ \Omega_a = 1 - 3Z_c(1 - Z_c) + 3(1 - 2Z_c)\Omega_b + [2 - (u + w)]\Omega_b^2 \end{cases}$$

The $\alpha(T)$ functions implemented correspond to the cubic models described above

$$a(T) = a_c \alpha(T)$$

$$a_c = \Omega_a \frac{R^2 T_c^2}{P_c}$$

You can choose the functions α from the following:

- generalized α (SRK, PR and PT):

$$\alpha(T) = [1 + m(1 - T_r^{0.5})]^2$$

$$SRK \quad m = 0.47830 + 1.6337\omega - 0.3170\omega^2 + 0.760\omega^3$$

$$PR \quad m = 0.374640 + 1.542260\omega - 0.26992\omega^2$$

$$PT \quad m = 0.452413 + 1.30982\omega - 0.296937\omega^2$$

- Mathias-Copeman α (SRK, PR et PT):

$$T_r \leq 1, \alpha(T) = (1 + c_1(1 - T_r^{0.5}) + c_2(1 - T_r^{0.5})^2 + c_3(1 - T_r^{0.5})^3)^2$$

$$T_r > 1, \alpha(T) = (1 + c_1(1 - T_r^{0.5}))^2$$

c_1, c_2, c_3 are determined experimentally.

The α functions of Stryjeck / Vera (SRK, PR and PT), Daridon (SRK, PR) and Twu et al. are also available in the program. However, these modules are still being tested.

Calculations of state functions, enthalpy and entropy, are made by:

$$(h - h^0)_{T,P} = \frac{a(T) - a'(T)T}{b(r_1 - r_2)} \ln\left(\frac{v - br_1}{v - br_2}\right) + Pv - RT$$

$$(s - s^0)_{T,P} = R \ln\left(\frac{Pv - Pb}{RT}\right) - \frac{a'(T)}{b(r_1 - r_2)} \ln\left(\frac{v - br_1}{v - br_2}\right)$$

$$r_1 = \frac{-u + \sqrt{u^2 - 4w}}{2} \quad \text{et} \quad r_2 = \frac{-u - \sqrt{u^2 - 4w}}{2}$$

Equation of state	u	w
vdW	0	0
SRK	1	0
PR	2	-1
PT	$1+c/b$	c/b

h^0 and s^0 are the enthalpy and entropy of the fluid considered ideal. These ideal terms are calculated through the specific heat correlations C_p at can take different forms in different databases.

Polynomial form (by default in Thermoptim):

$$C_p = A + BT + CT^2 + DT^3 + ET^4 + \frac{G}{T^2} + \frac{K}{T}$$

Form in the DIPPR database:

$$C_p = A + B \left(\frac{\frac{C}{T}}{\sinh\left(\frac{C}{T}\right)} \right)^2 + D \left(\frac{\frac{E}{T}}{\cosh\left(\frac{E}{T}\right)} \right)^2$$

Other forms of correlations are also available. The choice of the correlation of C_p is necessary for the construction of .mel files containing the input data for models (see 3.Adding a pure substance).

The pressure and saturation temperature are calculated by seeking equal liquid and vapor fugacities. An iterative algorithm is used for that. Initialization of the desired size can be made by the following correlations:

- Saturation pressure (depending on the reduced temperature T_r):
 - o Exponential formulation (Thermoptim) :

$$P_0 = e^{A + \frac{B}{T_r} + C \ln(T_r) + D T_r^E}$$

- o Lee-Kesler formulation:

$$P_0 = P_c \exp\left(5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln(T_r) + 0.169347 T_r^6 + \omega (15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln(T_r) + 0.43577 T_r^6)\right)$$

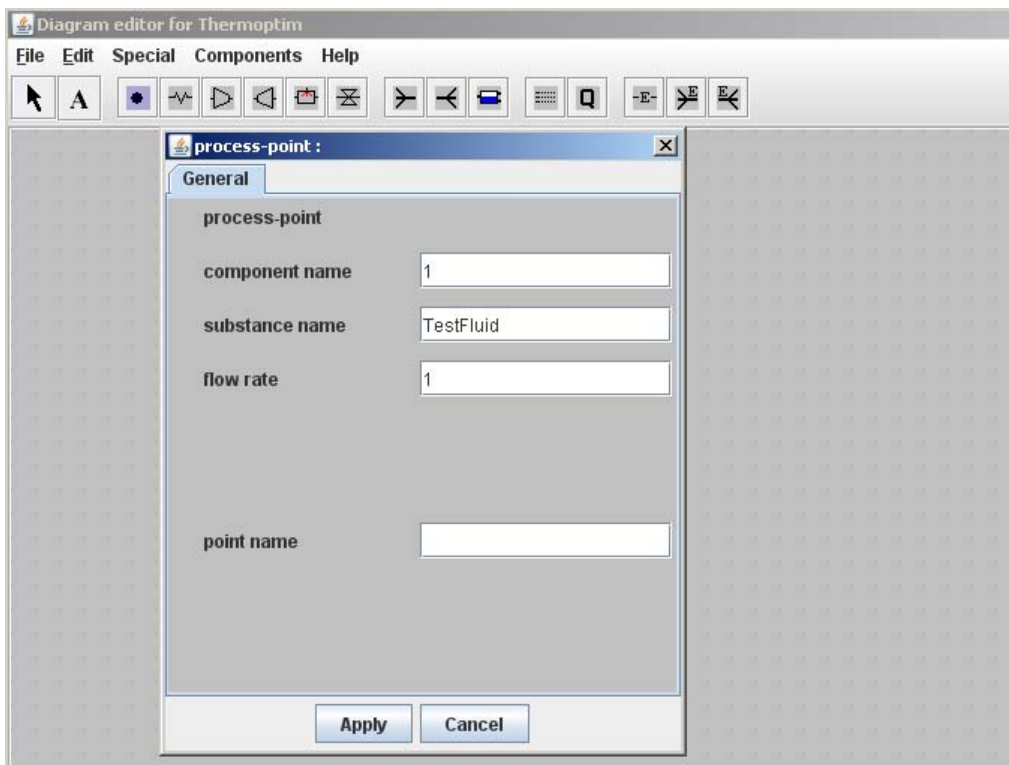
- Saturation temperature (depending on the pressure P)
 - o Logarithmic formulation in Thermoptim :

$$T_0 = A + B \ln(P) + C (\ln(P))^2 + D (\ln(P))^3 + E (\ln(P))^4$$

2. Operation of the server with ThermoOptim

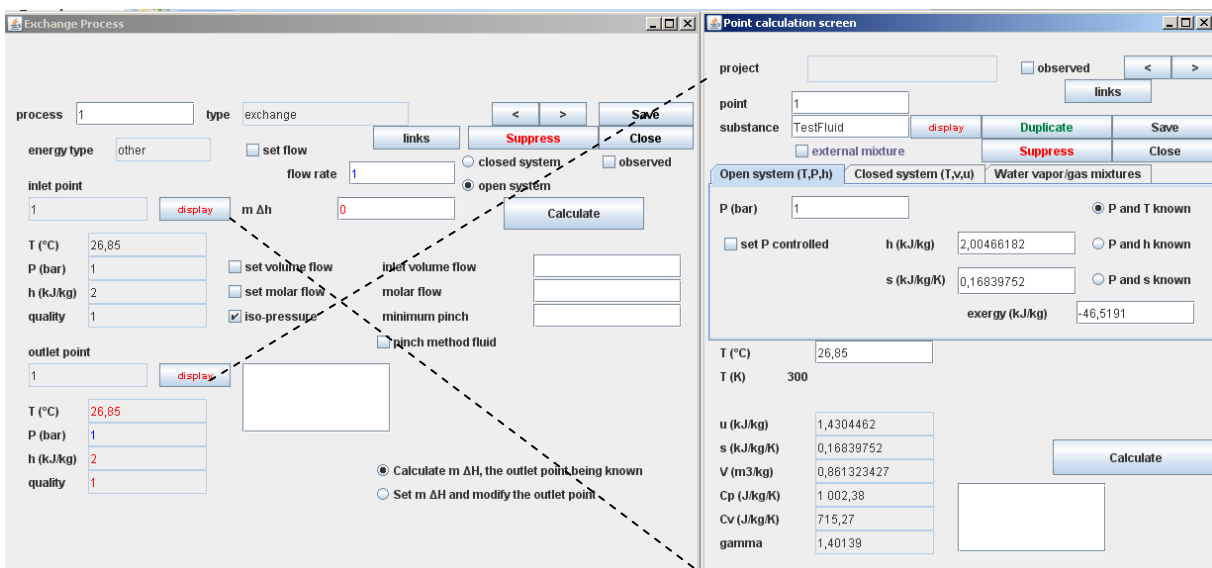
The use of the fluid thermodynamic properties server requires that the input data are given in a .mel file. We will see in Section 3 how to create these .mel files.

We start by creating a component. In this example, a point was chosen for simplicity. We choose here in particular the name of the external substance we wish to use.



Choice of the external substance:

Once the component is created in ThermoOptim, double-click it to display the process screen, then click "display" to open the upstream or downstream point. The window for calculating a point opens.



Check the "external mixture" control under the name of the substance chosen by "FluideTest1" and then hit enter.

The substance loading window appears with LiBr-H₂O system as default. Choose the system in the drop down menu at the bottom right of the window. Then click "load the mixture". It is also possible to save the name of the substance chosen for later use by clicking "Save". But the name of the new substance will only be taken into account after restarting Thermoptim. The data on the substance selected are then loaded.

component name	molar fraction	mass fraction
lithium bromide	0	0
water	0	0

For a pure substance, the mole and mass fractions are of course worth 1. For a mixture, enter the molar composition before saving the external substance.

Calculation options displayed when the substance is correctly loaded

The previous calculation options must appear in the point calculation window.

To calculate the thermodynamic properties of fluids, it is sufficient to define the two known quantities: (P, T), (P, h) or (P, s). Then enter the corresponding values. For pressure and saturation temperature, check "set the saturation pressure" or "set the saturation temperature" instead of "unconstrained", after entering the value of the quality.

3. Adding a pure substance

Although the use of the fluid thermodynamic properties server is simple and fairly intuitive, the preparation of files containing the input data of the fluid is much longer and complex.

Each pure substance has a .mel file stored in the \ mixtures \ TEPlib_MEL folder, and must be declared in the TEPlib.mix file at the root of the "mixtures" folder.

The TEPlib.mix file contains the list of proposed systems. Its standard format is:

external mixture file

```
butane-propane      butanePropane.mel    2      butane propane      MolMass=44
                    PC=200    TC=404.128    Tmaxi=1100    Tmini=216.7    T0=293.15    P0=1.
CO2 CO2.mel         1      CO2    MolMass=44    PC=73.77    TC=304.128    Tmaxi=1100
                    Tmini=216.7    T0=273.15    P0=36.59027
```

Fin
Fin

A single line

Each line includes:

- The name of the system as it will appear in the ThermoOptim screens (e.g. butane-propane)
- The definition file of the mixture, in the format of the properties server (e.g. butanePropane.mel)
- The number of components
- Component names as they appear on the ThermoOptim screens
- The molar mass, the pressure and critical temperature, maximum and minimum temperatures for the fluid and the pressure and the temperature reference values (where $h = u = s = 0$)

It is basically through the .mel mixture definition file that the system is initialized, ThermoOptim merely changes the composition and state variables. Examples of .mel files are provided in the archive containing the executables.

The .mel file structure is:

```
TEP Library mixture data file
1 [Components] 1
  [Models] 0:Van der Waals, 1:RSK, 2:PR, 3: Patel & Teja 4: Harmens & Knapp, 5 SRK controle
2 Model 2
  [Alpha]0:Soave(1972); 1:generalized SRK; 2:generalisee PR; 3:Daridon & al. 4:Twu & al. SRK 5:
  Twu & al. Peng-Robinson 6: Stryjeck & Vera 7: Mathias & Copeman 8: generalized with P&T
3 Alpha 2
4 [component 1]
  CO2
5 Tc 304.128
6 Pc 73.773e5
7 Vc 0.002143623
8 M 44.0098
9 omega 0.22394
10 Tref 298.15
11 Pref 100000
12 Tb 194.7
13 Tmini 250.
14 Tmaxi 800.
15 Pmaxi 1.e8
  C1 0.740714277155924
16 C2 -0.7212452909569848
  C3 1.1383410305472594
17 Cp 1 23.376644 46.703677 -30.079808 9.333596 -1.12343
  0.167658 -2.362244
18 Psat 1 25.89762677 -12.49477298 -10.56156879 2.409974844 2
19 Tsat 1 178.0475635 26.58894603 -4.327657677 1.615377903 -0.107082138
  h0 22301
  s0 120.7 } 20-22
```

A single line

23	u0	0			
	nbexp	21			
	exp	T(K)	Psat(Pa)	Vsat_L(m3/mol)	Hvap(J/mol)
	exp	260	2415604.7	4.40567E-05	11733
	exp	262	2559602.9	4.44998E-05	11519
	exp	264	2709804.7	4.4964E-05	11299
	exp	266	2866379.3	4.54504E-05	11073
	exp	268	3029499.6	4.59622E-05	10838
	exp	270	3199342.2	4.6503E-05	10595
	exp	272	3376088.6	4.70765E-05	10343
	exp	274	3559925.2	4.76826E-05	10080
	exp	276	3751045	4.83325E-05	9807
	exp	278	3949648.3	4.90244E-05	9522
	exp	280	4155944.9	4.97711E-05	9224
	exp	282	4370155.9	5.05766E-05	8911
	exp	284	4592516.8	5.14536E-05	8581
	exp	286	4823281.9	5.24109E-05	8231
	exp	288	5062729.4	5.34702E-05	7860
	exp	290	5311169.7	5.46538E-05	7462
	exp	292	5568957.1	5.5991E-05	7030
	exp	294	5836508.5	5.75341E-05	6557
	exp	296	6114333.1	5.93613E-05	6027
	exp	298	6403087.4	6.16181E-05	5416
	exp	300	6703688.9	6.46037E-05	4675
	[component 2]				

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This file contains the following information (in order of appearance):

1. Number of components: always 1 for pure substances
2. Equation of state chosen
3. Alpha function chosen *
4. Name of the fluid
5. Critical temperature of the fluid
6. Critical pressure of the fluid
7. Critical volume of the fluid
8. Molecular weight
9. Acentric factor
10. Reference temperature
11. Reference pressure
12. Boiling point
13. Minimum operating temperature
14. Maximum operating temperature
15. Maximum operating pressure
16. Three coefficients C1, C2, C3 for the Mathias-Copeman alpha function *
17. Correlation of Cp *
18. Correlation used to initialize the saturation pressure *
19. Correlation used to initialize the saturation temperature *
20. Reference enthalpy
21. Reference entropy
22. Internal energy reference
23. Number of experimental values*
24. Experimental values: temperature, saturation pressure, liquid saturation volume, latent heat of vaporization *

This writing must be strictly observed.

When writing the .mel file, we must take particular care data with a star. The explanations are as follows:

8 For the alpha function chosen, it is necessary to take the one corresponding to the equation of state selected in the previous line. If the Mathias-Copeman alpha function is chosen for prediction, one must have either parameter values C1, C2, C3 or reliable experimental data to adjust the 3 Mathias-Copeman parameters.

17 For the calculation of Cp, we have seen that there are several types of correlations. The current program allows for systematic calculations for the polynomial and DIPPR formulations. The first integer of the line, between 0 and 2, allows the choice of the correlation:

- 1 for the polynomial correlation
- 2 for the DIPPR correlation
- 0 for other forms of correlation

If you want to implement other more complex correlations, you then have to change the code of the fluids thermodynamic properties server. The classes concerned are, "fonctionCp (int, double)" and "numeroCas."

Depending on the correlation chosen, the coefficients A, B, C, D, E, F, G, K are different. The molar unit used is J/K/mol.

18-19 To initialize the saturation pressure, one can also choose the correlation used. The first integer of the line, between 0 and 1, allows you to choose respectively the method of Lee-Kesler or the exponential correlation used by default in ThermoOptim (cf. 1.Models implemented).

To initialize the saturation temperature, only the logarithmic correlation is introduced (see 1.Models implemented).

23-24 The experimental data are used to adjust the values of the Mathias-Copeman alpha function. If we have some and wish to determine the parameters C1, C2 and C3 from these data, we must specify the number of experimental values at different temperatures. Then enter in the following order: temperature, saturation pressure, volume of saturated liquid and latent heat of vaporization. It is important to note that: if the number of experimental data is not 0, then the parameters C1, C2, C3 will be calculated from the experimental data. The values of C1, C2, C3 written in the .mel file a few lines later are not used by the model in this case.

References :

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