The $\mathscr{B}$ and $\mathscr{T}$ indices indicate something related to benzene and toluene respectively. x_i, y_i indicate the molar fraction in the liquid (vapor) phase respectively.

A. Equation of the binary diagram

The equations used for the construction of the binary diagram are :
— The fact that at the equilibrium, the chemical potential in the vapor phase is equal to the one in the liquid phase :

$$\mu_i^g = \mu_i^l \tag{1}$$

— The expression of the potential for the solid and liquid phases (valid for an ideal system only) :

$$\mu_i^l = \mu_i^{l,\circ}(T) + RT \ln (x_i) \tag{2}$$

$$\mu_i^g = \mu_i^{g,\circ}(T) + RT \ln \left(\frac{p_i}{p^\circ} \right) = \mu_i^{g,\circ}(T) + RT \ln \left(y_i \frac{p^\circ}{p^\circ} \right) = \mu_i^{g,\circ}(T) + RT \ln (y_i) \tag{3}$$

— Then, we apply the Gibbs-Helmholtz relationship :

$$H - TS = G \tag{4}$$

$$dG = VdP - SdT \tag{5}$$

$$H = G + TS = G - T \left. \frac{\partial G}{\partial T} \right|_p \Leftrightarrow \frac{H}{T^2} = \frac{G}{T^2} - \frac{1}{T} \left. \frac{\partial G}{\partial T} \right|_p = - \left. \frac{\partial \frac{G}{T}}{\partial T} \right|_p \tag{6}$$

— By combining the relations (1), (2) et (3) :

$$\ln \left(\frac{y_i}{x_i} \right) = \frac{\mu_i^{l,\circ}(T) - \mu_i^{g,\circ}(T)}{RT} = - \frac{\Delta_{\text{vap}} G^\circ(T)}{RT} \tag{7}$$

And then deriving this relation with respect to temperature (after separation of the variables) :

$$d \ln \left(\frac{y_i}{x_i} \right) = \frac{\Delta_{\text{vap}} H^\circ(T)}{RT^2} dT \tag{8}$$

With the Ellingham approximation (the enthalpy of vaporization is constant with temperature) we can integrate the relationship between the pure compound ($x_i = y_i = 1$, $T = T_{\text{éb},i}$) and the wanted composition (x_i, y_i, T) :

$$\ln \left(\frac{y_i}{x_i} \right) - \underbrace{\ln \left(\frac{1}{1} \right)}_{=0} = \frac{\Delta_{\text{vap}} H_i^\circ(T)}{R} \left(-\frac{1}{T} + \frac{1}{T_{\text{éb},i}} \right) \tag{9}$$

— Then we have the following relationships for the toluene and the benzene in the liquid and vapor phase respectively :

$$x_{\mathscr{B}} + x_{\mathscr{T}} = 1 \tag{10}$$

$$y_{\mathscr{B}} + y_{\mathscr{T}} = 1 \tag{11}$$

We thus have a set of four equations with four unknowns $(x_{\mathscr{B}}, x_{\mathscr{T}}, y_{\mathscr{B}}, y_{\mathscr{T}})$ Where all the unknowns are a function of temperature. Those equations are enterd in the function `Equations`.

$$\ln\left(\frac{y_{\mathscr{B}}}{x_{\mathscr{B}}}\right) = \frac{\Delta_{\text{vap}}H_{\mathscr{B}}^{\circ}(T)}{R}\left(-\frac{1}{T} + \frac{1}{T_{\text{éb},\mathscr{B}}}\right) \tag{12}$$

$$\ln\left(\frac{y_{\mathscr{T}}}{x_{\mathscr{T}}}\right) = \frac{\Delta_{\text{vap}}H_{\mathscr{T}}^{\circ}(T)}{R}\left(-\frac{1}{T} + \frac{1}{T_{\text{éb},\mathscr{T}}}\right) \tag{13}$$

$$x_{\mathscr{B}} + x_{\mathscr{T}} = 1 \tag{14}$$

$$y_{\mathscr{B}} + y_{\mathscr{T}} = 1 \tag{15}$$

$$\tag{16}$$

By setting the temperature between the ebullition temperature of the toluene and the benzene, we can now solve this set of equation to find all the unknowns.

This is what is done with the line

```
sol = optimize.root(Equations, [0, 1,0,1,383.8],args=(T0,Teb,Hvap), jac=False
    , method='hybr')
```

The values returned are : $(x_{\mathscr{B}}, x_{\mathscr{T}}, y_{\mathscr{B}}, y_{\mathscr{T}}, T)$
And `arrsol` contains all the values with one row per temperature.

B.   Equation of the cooling curves

First, the molar enthalpies of the liquid and gases are computed at all temperatures with the function `molarEnthalpy` with :

$$H_i(T) = H_i(T = 298, 15) + C_p(T - 298.15) \tag{17}$$

Then, for a given value of composition (the one set with the blue bar), the temperatures of the ebullition and dew points are found in the `arrsol` array thanks to the function `FindTdewTeb`.

Once those temperatures are knwown, the composition of the system is determined at all temperatures for a system of one mole with the given composition.

Below the ebullition point, the system is liquid with the given composition $n_l = 1$. Above the dew point, the system is in a vapor phase $n_l = 0$. In between, we apply the baricentric rule and the conservation of matter :

$$x_{\mathscr{B},0} \times n_{\text{tot}} = x_{\mathscr{B}}(T)n_l(T) + y_{\mathscr{B}}(T) \times n_v(T) \tag{18}$$

$$n_l(T) + n_v(T) = 1 \tag{19}$$

Where everything is known except $n_l(T)$ and $n_v(T)$. We can the extract those two unknows from those equations (this is done with the function `SysComposition`).

Know, we fully know the composition of the system `nBl`, `nTl`, `nBg` and `nTg` :

$$n_{\mathscr{B}}^l(T) = x_{\mathscr{B}}(T) \times n_l(T) \tag{20}$$

$$n_{\mathscr{T}}^l(T) = x_{\mathscr{T}}(T) \times n_l(T) \tag{21}$$

$$n_{\mathscr{B}}^g(T) = y_{\mathscr{B}}(T) \times n_v(T) \tag{22}$$

$$n_{\mathscr{T}}^g(T) = y_{\mathscr{T}}(T) \times n_v(T) \tag{23}$$

and can determine the enthalpy of the system as a function of temperature (this is valid because the system is ideal but is not otherwise) :

$$H(T) = \sum_i n_i^{l,g} \times H_i^{l,g} \tag{24}$$

which is done with :

```
H = nBl*Hm[0][:,0]+nBg*Hm[1][:,0]+nTl*Hm[0][:,1]+nTg*Hm[1][:,1]
```

Now, we have $H(T)$.

If we assume that during the cooling, the system is always in equilibrium. We also usually assume that $\dfrac{\mathrm{d}\,H}{\mathrm{d}\,t}$, where t is the time, is nearly constant.

This is equivalent to stating that H decreases linearly with time. Or that $H = b - a \times t$. As we want the equation of $T(t)$, the previous equation states that it is equivalent to plotting $T(H)$. While inverting a function can be tricky, here, we just have to change the x axis with the y axis. A transformation to H is done such that the curve is always plotted between 0 and 1.

And *voilà*, we have both the binary diagram and the cooling curve for a system of given composition.