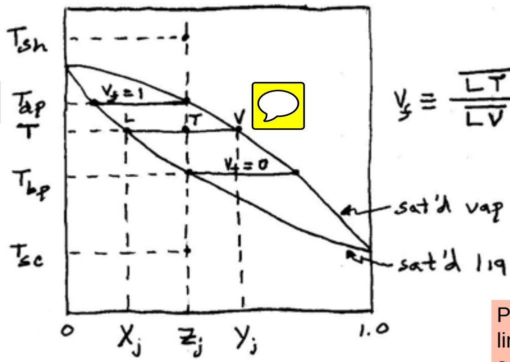
Raoult's Law Model
Multicomponent VLE

Diagram

constant P



$$V_f \equiv \frac{\overline{LT}}{\overline{LV}}$$

Assumptions

1. vapor-liquid equil.
2. Raoult's law; i.e., both liquid and vapor phases behave as ideal solutions.
3. Saturation pressure P_j^* is given by the Antoine equation.

Pictorially, the math model represents each horizontal line in the TXY diagram that can be drawn from the saturated liquid curve to the saturated vapor curve, and that line must cross or touch the vertical line somewhere from the dew-point temperature to the bubble-point temperature; that is, from a vapor fraction of one to zero for a given pressure P and any total composition (Z_j's) on the x-axis from zero to one.

Mathematical Model

total bal.	$1.0 = V_f + L_f$
comp. bal.	$Z_j = V_f Y_j + L_f X_j$
Raoult's Law	$Y_j = K_j X_j$
	$K_j = P_j^* / P$
Antoine eqn	$P_j^* = \text{PSAT}[T, \text{pure } j]$

end points of horizontal line connecting the sat'd liquid curve to the sat'd vapor curve.

for $j = 1, 2, \ldots, nc$

K_j is called the equilibrium distribution coefficient

$$\sum_{j=1}^{nc} X_j - \sum_{j=1}^{nc} Y_j = 0$$

# vars = 5 nc + 3
# eqns = 4 nc + 1
d.o.f. = nc + 2

Mathematical Algorithms

A. $[T, \bar{X}, \bar{Y}] = \text{vlet}[P, V_f, \bar{Z}]$

B. $[V_f, \bar{X}, \bar{Y}] = \text{vlevf}[T, P, \bar{Z}]$

C. $[P, \bar{X}, \bar{Y}] = \text{vlep}[T, V_f, \bar{Z}]$

where $\bar{X} \equiv X_1, X_2, \ldots, X_{nc}$; $\bar{Y} \equiv Y_1, Y_2, \ldots, Y_{nc}$; $\bar{Z} \equiv Z_1, Z_2, \ldots, Z_{nc}$

Raoult's Law Model
Multicomponent VLE

Find VLE Temperature

$[T, \bar{x}, \bar{y}] = \text{vlet}[P, V_f, \bar{z}]$

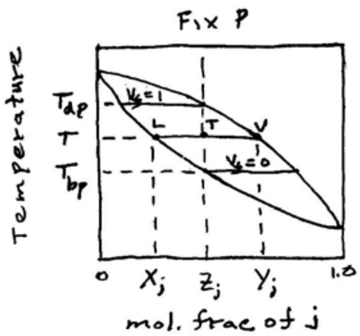
Click here to view info on the "EZ Setup" function for "vlet".

1. $L_f \leftarrow 1.0 - V_f$
2. Iterate on T in

$$\left.\begin{aligned} P_j^* &\leftarrow \text{psat}[T, \text{pure } j] \\ K_j &\leftarrow P_j^* / P \\ x_j &\leftarrow z_j / (V_f K_j + L_f) \\ y_j &\leftarrow K_j x_j \end{aligned}\right\} \text{for } j = 1, 2, \cdots, nc$$

$$f(T) \leftarrow \sum x_j - \sum y_j$$

Until $f(T)$ is 0.0



Find VLE Vapor Fraction

$[V_f, \bar{x}, \bar{y}] = \text{vlevf}[T, P, \bar{z}]$

Click here to view info on the "EZ Setup" function for "vlevf".

1. $P_j^* \leftarrow \text{psat}[T, \text{pure } j]$ for $j = 1, 2, \cdots, nc$
2. $K_j \leftarrow P_j^* / P$ for $j = 1, 2, \cdots, nc$
3. Iterate on V_f in

$$L_f \leftarrow 1.0 - V_f$$

$$x_j \leftarrow z_j / (V_f K_j + L_f) \quad \text{for } j = 1, 2, \cdots, nc$$

Click here for a tidbit.

$$y_j \leftarrow K_j x_j \quad \text{for } j = 1, 2, \cdots, nc$$

$$f(V_f) \leftarrow \sum x_j - \sum y_j$$

Until $f(V_f)$ is 0.0

Raoult's Law Model
Multicomponent VLE

Find VLE Pressure

Click here to view info on the "**EZ Setup**" function for "**vlep**".

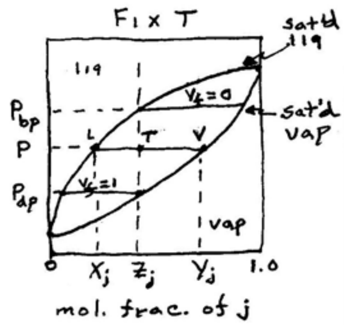
$[P, \bar{x}, \bar{y}] = \text{vlep}[T, V_f, \bar{z}]$ for $0 < V_f < 1.0$

1. $L_f \leftarrow 1.0 - V_f$
2. $P_j^* \leftarrow \text{psat}[T, \text{pure } j]$ for $j = 1, 2, \ldots, nc$
3. Iterate on P in

$$\left.\begin{aligned} K_j &\leftarrow P_j^*/P \\ x_j &\leftarrow z_j/(V_f K_j + L_f) \\ y_j &\leftarrow K_j\, x_j \end{aligned}\right\} \text{ for } j = 1, 2, \ldots, nc$$

$$f(P) \leftarrow \sum x_j - \sum y_j$$

Until $f(P)$ is 0.0



special solutions that do not have iteration

$[P_{bp}, \bar{x}, \bar{y}] = \text{vlep}[T, V_f = 0, \bar{z}]$

1. $L_f \leftarrow 1.0$
2. $P_j^* \leftarrow \text{psat}[T, \text{pure } j]$ for $j = 1, 2, \ldots, nc$
3. $x_j \leftarrow z_j$
4. $P_{bp} \leftarrow \sum_{j=1}^{nc} P_j^* x_j$ ← $\boxed{\sum_{j=1}^{nc} y_j = 1.0}$
5. $K_j \leftarrow P_j^*/P_{bp}$ for $j = 1, 2, \ldots, nc$
6. $y_j \leftarrow K_j\, x_j$

$[P_{dp}, \bar{x}, \bar{y}] = \text{vlep}[T, V_f = 1, \bar{z}]$

1. $L_f \leftarrow 0.0$
2. $P_j^* \leftarrow \text{psat}[T, \text{pure } j]$ for $j = 1, 2, \ldots, nc$
3. $y_j \leftarrow z_j$
4. $P_{dp} \leftarrow \left[\sum_{j=1}^{nc} y_j/P_j^*\right]^{-1}$ ← $\boxed{\sum_{j=1}^{nc} x_j = 1.0}$
5. $K_j \leftarrow P_j^*/P_{dp}$ for $j = 1, 2, \ldots, nc$
6. $x_j \leftarrow y_j/K_j$

Raoult's Law Model: Multicomponent VLE

Process of Heating Pentane-Hexane from 40°C to 75°C at 1 atm

Point F — subcooled
40°C
1 atm
all liq
n_T
$z_{PT} = 0.4$
$z_{HX} = 0.6$

Point B — bubble point
T_{bp}
51.64°C
1 atm
sat'd liq
$n_L \approx n_T$
$x_{PT} = z_{PT}$
$x_{HX} = z_{HX}$

$V_f = \frac{n_V}{n_T} = 0$

first bubble of vapor:
51.64°C
1 atm
sat'd vap
$n_V \lll n_T$
$y_{PT} = 0.661$
$y_{HX} = 0.339$

Point T — liq-vap
56.88°C
1 atm
sat'd vap
$y_{PT} = 0.496$
$y_{HX} = 0.504$
n_V

56.88°C
1 atm
sat'd liq
$x_{PT} = 0.257$
$x_{HX} = 0.743$
n_L

$n_T = n_V + n_L$

$V_f = \frac{n_V}{n_L} = \frac{\overline{LT}}{\overline{LV}} = 0.6$

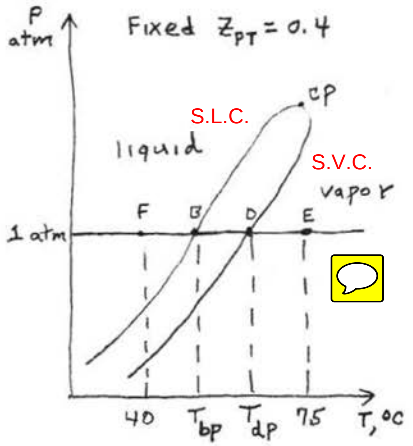
Point D — dew point
T_{dp}
59.55°C
1 atm
sat'd vap
$n_V \approx n_T$
$y_{PT} = z_{PT}$
$y_{HX} = z_{HX}$

$V_f = \frac{n_V}{n_T} = 1$

last drop of liquid:
59.55°C
1 atm
sat'd liq
$n_L \lll n_T$
$x_{PT} = 0.192$
$x_{HX} = 0.808$

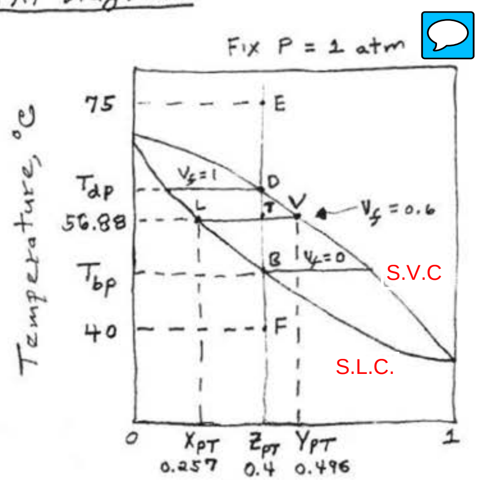
Point E — superheated
75°C
1 atm
all vap
n_T
$z_{PT} = 0.4$
$z_{HX} = 0.6$

PT Diagram



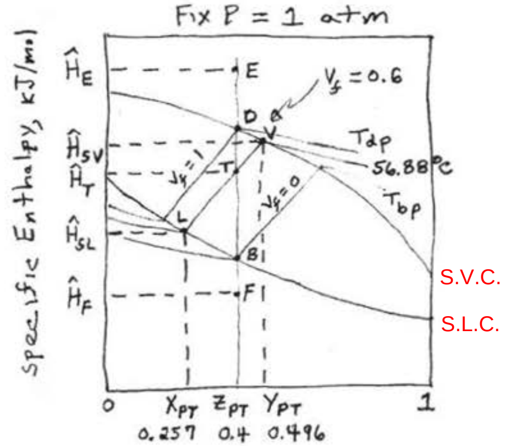
S.L.C. - Saturated Liquid Curve
S.V.C. - Saturated Vapor Curve

TXY Diagram



$z_{PT} = V_f\, y_{PT} + L_f\, x_{PT}$

HXY Diagram



$z_{PT} = V_f\, y_{PT} + L_f\, x_{PT}$
$\hat{H}_T = V_f\, \hat{H}_{SV} + L_f\, \hat{H}_{SL}$

Example Binary System for Vapor-Liquid Equilibrium

Click here to view this Excel "**EZ Setup**"/**Solver** formulation as Worksheet "**Raoult**".

```
/*  Raoult's Law applied to n-Pentane and n-Hexane System  */

//  Total and Two Component Material Balances
      1.0  =  Vf  +  Lf

      zPT  =   Vf * yPT  +  Lf * xPT
      zHX  =  Vf * yHX  +  Lf * xHX

//  Vapor-Liquid Equilibrium using Raoult's Law
      yPT  =  kPT * xPT
      yHX  =  kHX * xHX

      kPT  =  PsatPT / P
      kHX  =  PsatHX / P

//   Antoine Equations for the Two Components, F&R, 3rd Ed., Table B.4
      log(PsatPT)  =  6.84471  -  1060.793 / (T +  231.541)          //  range 13.3 to 36.8 C
      log(PsatHX)  =  6.88555  -  1175.817 / (T +  224.867)          //  range 13.0 to 69.5 C

//   Two mixture equations for the liquid and vapor phases
      xPT  +  xHX  -  yPT  -  yHX  =  0

//   Given Information
      Vf    =  0.0
      P     =  760
      zPT  =  0.40
      zHX  =  1.0  -  zPT
```

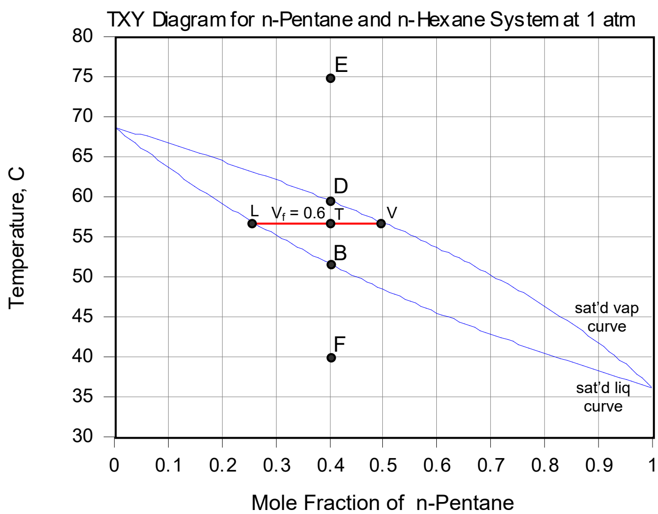
This Excel "**EZ Setup**"/**Solver** formulation is the VLE mathematical model given on "Page 1 of 6" above but written for a binary system.

The Excel **Solver** iterates on all of the equations simultaneously using the optimization technique of minimizing the sum of squares.

The "**EZ Setup**" formulation sets a value of 1.0 for all the unknowns to get the iteration started.

You solves this mathematical model three times using the Excel **Solver** by changing the value for vapor fraction (V_f). The results for vapor fractions of 1.0, 0.6, and 0.0 are shown below.

Excel SolverTable TXY Diagram



Excel Solver Solutions

[T_{dp}, X_{PT}, X_{HX}] = vlet [P, V_f, Z_{PT}]

P = 1 atm	T_{dp} = 59.55ºC
V_f = 1.0	X_{PT} = 0.1916
Z_{PT} = 0.4	X_{HX} = 0.8084

[T_{eq}, X_{PT}, Y_{PT}] = vlet [P, V_f, Z_{PT},]

P = 1 atm	T_{eq} = 56.88ºC
V_f = 0.6	X_{PT} = 0.2565
Z_{PT} = 0.4	Y_{PT} = 0.4956

[T_{bp}, Y_{PT}, Y_{HX}] = vlet [P, V_f, Z_{PT}]

P = 1 atm	T_{bp} = 51.64ºC
V_f = 0.0	Y_{PT} = 0.6607
Z_{PT} = 0.4	Y_{HX} = 0.3393

What would the equilibrium results for this pentane/hexane example look like if an equation of state was used to model the K-values instead of Raoult's Law? As an enhancement exercise, **click here** and do the equilibrium calculations for this example using the Peng-Robinson equation.

Alternate "EZ Setup" Solution for Example Binary System

Click here to view this Excel "**EZ Setup**"/**Solver** formulation as Worksheet "**fT-model**".

```
/*  Raoult's Law applied to n-Pentane and n-Hexane System  */

//  Total and Two Component Material Balances
      1.0  =  Vf  +  Lf

      zPT  =   Vf * yPT  +  Lf * xPT
      zHX  =  Vf * yHX  +  Lf * xHX

//  Vapor-Liquid Equilibrium using Raoult's Law
      yPT  =  kPT * xPT
      yHX  =  kHX * xHX

      kPT  =  PsatPT / P
      kHX  =  PsatHX / P

//   Antoine Equations for the Two Components, F&R, 3rd Ed., Table B.4
      log(PsatPT)  =  6.84471  -  1060.793 / (T +  231.541)        //  range 13.3 to 36.8 C
      log(PsatHX)  =  6.88555  -  1175.817 / (T +  224.867)        //  range 13.0 to 69.5 C

//   Two mixture equations for the liquid and vapor phases
      fT  =  xPT  +  xHX  -  yPT  -  yHX
       T  =  40

//   Given Information
      Vf    =  0.6
      P     =  760
      zPT  =  0.40
      zHX  =  1.0  -  zPT
```

This Excel "**EZ Setup**"/**Solver** formulation simulates the ITERATE loop for the scalar unknown of temperature found in the multicomponent "**vlet**" math algorithm given on "Page 2 of 6" above, but for a binary system.

The iteration variable **T** and the iteration function **fT** are written into the "**EZ Setup**" math model as shown by the two aqua-highlighted lines below.

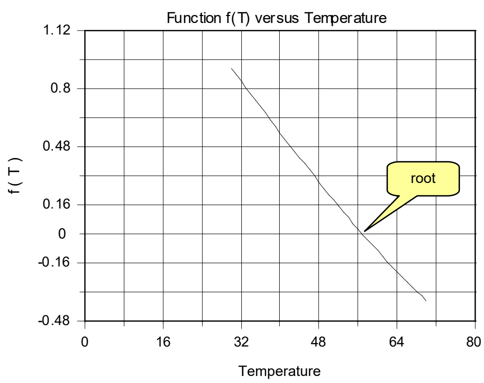
This technique of simulating an ITERATE loop can be used as a fallback whenever the "**EZ Setup**"/ **Solver** has difficulty solving the math model.

The simulation of an ITERATE loop is done by using the Excel **Solver** and **SolverTable** Add-Ins. A case study on temperature from 50 to 70°C was done, and the table of partial results is shown below. In this table, the function fT is close to zero near 57°C. Another case study could be done from 56 to 57°C to get the equilibrium temperature of 56.88°C for a vapor fraction of 0.60.

Excel SolverTable f(T) versus T Plot

T	fT	kHX	kPT	xPT	yPT
50	0.218885	0.533297	1.570680	0.297973	0.468018
51	0.186165	0.552683	1.619650	0.291590	0.472274
52	0.153740	0.572625	1.669800	0.285332	0.476446
53	0.121622	0.593136	1.721120	0.279198	0.480534
54	0.089823	0.614227	1.773650	0.273189	0.484541
55	0.058353	0.635908	1.827400	0.267301	0.488466
56	0.027221	0.658192	1.882380	0.261535	0.492310
57	-0.003562	0.681091	1.938620	0.255890	0.496074
58	-0.033989	0.704616	1.996140	0.250363	0.499758
59	-0.064051	0.728779	2.054950	0.244953	0.503365
60	-0.093741	0.753592	2.115070	0.239659	0.506894
61	-0.123052	0.779068	2.176520	0.234479	0.510347
62	-0.151979	0.805218	2.239310	0.229412	0.513725
63	-0.180515	0.832055	2.303480	0.224456	0.517029
64	-0.208656	0.859592	2.369030	0.219609	0.520261
65	-0.236398	0.887840	2.435980	0.214870	0.523420
66	-0.263737	0.916813	2.504360	0.210237	0.526509
67	-0.290671	0.946522	2.574180	0.205708	0.529528
68	-0.317195	0.976982	2.645460	0.201280	0.532480
69	-0.343309	1.008200	2.718220	0.196954	0.535364
70	-0.369011	1.040200	2.792480	0.192726	0.538183

The simulation of an ITERATE loop is depicted below by plotting f(T) versus T. The desired root is where the curve crosses the x-axis



To learn more about doing a manual iteration on a scalar quantity, see the "Development of a Math Algorithm" in the *CinChE* manual, Chapter 4, specifically Pages 4-16 to 4-17.

