ME 3007 – HW 4 Solutions

1.

The van der Waals EOS is

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (*)$$

Using the critical state inflection points, a + b can be found:

$$\left(\frac{\partial P_c}{\partial V_c}\right)_{T_c} = 0, \quad \left(\frac{\partial^2 P_c}{\partial V_c^2}\right)_{T_c} = 0$$

$$a = \frac{9}{8} R T_c V_c \qquad b = \frac{1}{3} V_c$$

Substituting a + b into (*) yields

$$P_c = \frac{3}{8} R T_c / V_c$$

The vdW can now be written in reduced coordinates:

$$\left(T_r \equiv \frac{T}{T_c} \ldots \right)$$

$$P = \frac{RT}{V - \frac{V_c}{3}} - \frac{\frac{9}{8} R T_c V_c}{V^2} \quad \frac{RT_c}{V_c}\left[\frac{\frac{T}{T_c}}{\frac{V}{V_c} - \frac{1}{3}} - \frac{9}{8(V/V_c)^2}\right]$$

$$P = \frac{3}{8}\frac{RT_c}{V_c}\,\frac{8}{3}\left[\frac{T_r}{V_r - 1/3} - \frac{9}{8V_r^2}\right]$$

$$\boxed{P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}} \quad (\bigstar)$$

Now the process to find the vapor pressure data can begin. The steps outlined below will be demonstrated on the attached printout for $T_r = 0.9$, and the roman numerals corresponding to each step are shown on each of the T_r printouts (Mathematica was used for all of the calculations).

I) Specify T_r ($T_r = 0.4, 0.7, 0.9$)

II) Find $P_{r\,min}$ and $P_{r\,max}$. This can be done either graphically or mathematically. For the first method, the given value of T_r is substituted into ($\bigstar$), and P_r is plotted vs. V_r. The minimum & maximum points are then approximated from the graph.

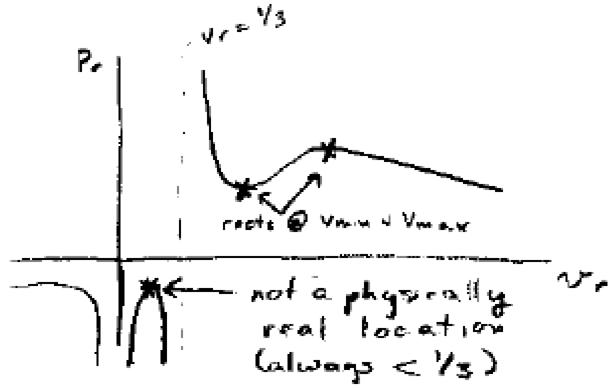
Mathematically, these points correspond to $\left(\frac{\partial P_r}{\partial V_r}\right)_{T_r} = 0$ locations.

$$\left(\frac{\partial P_r}{\partial V_r}\right)_{T_r} = \frac{6}{V_r^3} - \frac{24T_r}{(3V_r - 1)^2} = 0$$

$$6(3V_r - 1)^2 - 24T_rV_r^3 = 0$$

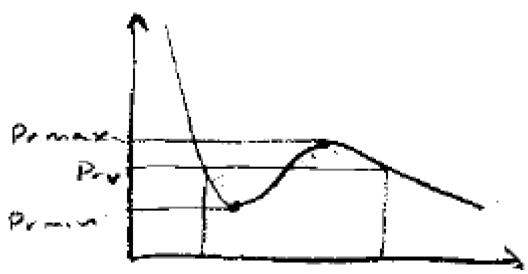
The roots to this can then be found using the cubic approximation discussed in class (see IV) or using Mathematica's "Roots" command.

3 Values of V_r will be returned, but only the higher 2 should be used, and the lowest value corresponds to a non-physical location:



Once $V_{r\,min}$ and $V_{r\,max}$ are known, they are substituted back into (★) to find $P_{r\,min}$ and $P_{r\,max}$.

III) $P_{r\,min}$ and $P_{r\,max}$ provide the bounds for the region where P_{rv} is found. If $P_{r\,min} < 0$, then 0 is the lower bound.



The first guess for P_{rv} will be the average (or midpoint) of $P_{r\,min}$ and $P_{r\,max}$.

IV) Using the guess value of P_{rv}, V_{rf} and V_{rg} can be found. To do this, (★) is converted into a cubic eqn in terms of V_r.

$$P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$

$$(P_r)\underbrace{(3V_r - 1)(V_r^2)}_{3V_r^3 - V_r^2} = 8T_r V_r^2 - 9V_r + 3$$

$$3P_r V_r^3 - P_r V_r^2 = 8T_r V_r^2 - 9V_r + 3$$

$$(3P_r)V_r^3 - (8T_r + P_r)V_r^2 + 9V_r - 3 = 0$$

$$V_r^3 - \left(\frac{8T_r + P_r}{3P_r}\right)V_r^2 + \left(\frac{3}{P_r}\right)V_r - \frac{1}{P_r} = 0 \qquad (P_r = P_{rv})$$

This cubic can be solved using

$c_0 = -\frac{1}{P_r}$

$c_1 = \frac{3}{P_r}$

$c_2 = -\frac{P_r + 8T_r}{3P_r}$

$Q = \frac{c_2^2 - 3c_1}{9}$

$R = \frac{2c_2^3 - 9c_1c_2 + 27c_0}{54}$

if $Q^3 - R^2 \geq 0$ there are 3 roots

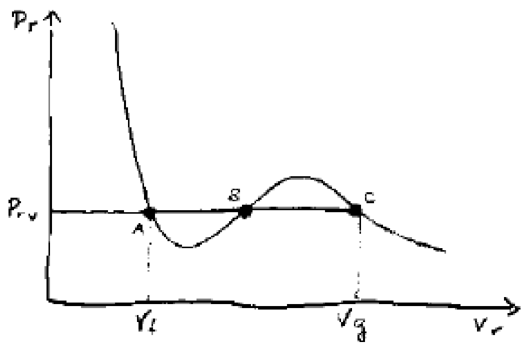
$$\theta = \cos^{-1}\left(R \cdot Q^{-3/2}\right)$$

$$V_{r1} = -2\sqrt{Q}\cos\left(\frac{\theta}{3}\right) - c_2/3$$

$$V_{r2} = -2\sqrt{Q}\cos\left(\frac{\theta+2\pi}{3}\right) - c_2/3$$

$$V_{r3} = -2\sqrt{Q}\cos\left(\frac{\theta+4\pi}{3}\right) - c_2/3$$

V_{r1-3} designate the points that P_{rv} crosses the $P_r - V_r$ curve.



Point A = V_{rf} = smallest root
Point C = V_{rg} = largest root

Point B = Physically unstable

V) The values of P_r, T_r, V_{rf}, and V_{rg} can be used to test Maxwell's construction:

$$\int_{V_f}^{V_g} p\,dv = P_V(V_g - V_f)$$

$$\int_{V_f}^{V_g}\left(\frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}\right)dV_r = P_{rv}(V_{rg} - V_{rf})$$

$$\frac{8}{3}T_r\ln(3V_{rg}-1) - \frac{8}{3}T_r\ln(3V_{rf}-1) + \frac{3}{V_{rg}} - \frac{3}{V_{rf}} = P_{rv}(V_{rg} - V_{rf})$$

Note: This can also be solved as 2 simultaneous eqns, where $P_r^v = \frac{8T_r}{3V_{r\,f \text{ or } g} - 1} - \frac{3}{V_{r\,f \text{ or } g}^2}$

If the calculated variables are correct,

$$f(P,V,T) = \frac{8}{3}T_r\ln\left(\frac{3V_{rg}-1}{3V_{rf}-1}\right) + \frac{3}{V_{rg}} - \frac{3}{V_{rf}} - P_{rv}(V_{rg} - V_{rf}) = 0$$

If they are not correct, and $f \neq 0$, then a new guess for P_{rv} is made, and steps IV + V are repeated. For my new guess, I used

$$P_{rv} = \frac{\frac{8}{3}T_r\ln\left(\frac{3V_{rg}-1}{3V_{rf}-1}\right) + \frac{3}{V_{rg}} - \frac{3}{V_{rf}}}{V_{rg} - V_{rf}}$$

And my convergence criterion was $f(P,V,T) \leq .001$

In[507]:=

```
I)  Tr=0.9;
II) Roots[6*(3*Vr-1)^2-24*Tr*Vr^3==0,Vr]
    Plot[8*Tr/(3*Vr-1) - 3/(Vr^2),{Vr,0.33,5}, Frame->True, PlotRange ->{0,2},
           GridLines->Automatic, FrameLabel-> {"vr","Pr","Tr=0.9"," "}]
```

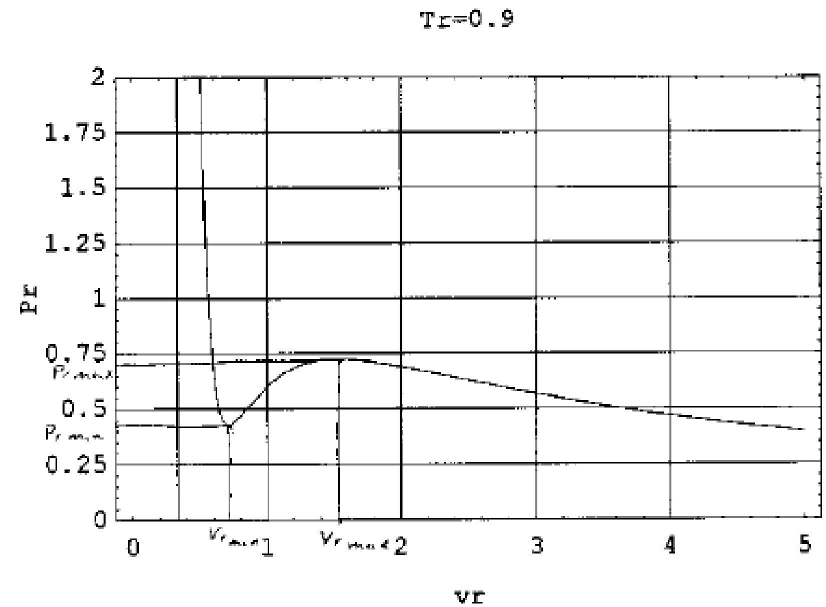
Mathematical way to find inflection points

Graphical "check" that roots are in right location

Out[508]=

```
Vr == 0.252898 || Vr == 0.718597 || Vr == 1.5285
```

V_{min} V_{max}



Out[509]=

```
-Graphics-
```

In[510]:=

```
Vmin=0.718597;
Pmn=8*Tr/(3*Vmin-1) - 3/(Vmin^2)
Vmax=1.5285;
Pmx=8*Tr/(3*Vmax-1) - 3/(Vmax^2)
```

Calculating $P_{r\,max}$ + $P_{r\,min}$ from V_r roots.

Out[511]=

0.419843 = $P_{r\,min}$

Out[513]=

0.724013 = $P_{r\,max}$

In[514]:=

III)

```
Pavg=(Pmn+Pmx)/2
```

Initial guess value for P_{V_r}. If $P_{mn} < 0$, $P_{avg} = \frac{0 + P_{r\,max}}{2}$

Out[514]=

0.571928

In[515]:=

(IV)

```
Pv=0.647;
c0=-1/Pv;
c1=3/Pv;
c2=-(Pv+8*Tr)/(3*Pv);
Q=((c2)^2-3*c1)/9
R=(2*(c2)^3 - 9*(c2)*(c1) +27*c0)/54
ineq=Simplify[Q^3-R^2]
```

← P_{rv}. This value is initially set to P_{avg}, and then altered (see below) if $f(P_r V_r T_r) > .001$ to a new guesss value

Calculation of the c_0, c_1, c_2, Q, and R values used to solve the cubic.

ineq = $Q^3 - R^2$ and is a check to make sure that $Q^3 - R^2 \geq 0$

Out[519]=

0.270396 = Q

Out[520]=

-0.0957678 = R

Out[521]=

0.0105983 = ineq

```
theta=ArcCos[R*Q^(-1.5)];
v1=-2*Q^(0.5)*Cos[theta/3]-(c2)/3
v2=Simplify[-2*Q^(0.5)*((Cos[theta/3])*(Cos[2*Pi/3])-(Sin[theta/3])*(0.866025403))
        -(c2)/3]
v3=Simplify[-2*Q^(0.5)*((Cos[theta/3])*(Cos[4*Pi/3])-(Sin[theta/3])*(-0.866025403))
        -(c2)/3]
```

Calculation of the roots: V_{rf}, V_{rg}, and the midpoint value.

Out[523]=
0.603402 $= v_1$

Out[524]=
2.34883 $= v_2$

Out[525]=
1.09053 $= v_3$

consistently, V_3 was found to be the midpoint value, $V_1 = V_{rf}$, and $V_2 = V_{rg}$.

In[526]:=

V)

```
Igral=Integrate[8*Tr/(3*Vi-1) - 3/(Vi^2),{Vi,v1,v2}]
Pfn=Pv*(v2-v1)
Eqlty=Igral-Pfn
corr=Igral/(v2-v1)
```

$\boxed{\frac{8T_r}{3V_r-1} - \frac{3}{V_r^2}} = P_r$

Testing of the Maxwell construction.

$Igral = \int_{V_{rf}}^{V_{rg}} P_r dV_r$; $Pfn = P_{rv}(V_{rg} - V_{rf})$

$Eqlty = \int_{V_{rf}}^{V_{rg}} P_r dV_r - P_{rv}(V_{rg} - V_{rf}) = f(P_r, T_r, V_r)$

If $Eqlty \geq .001$, new guess value for P_{rv} (symbol "Pv" within this program) is

$$P_{rv} = \frac{\int_{V_{rf}}^{V_{rg}} P_r dV_r}{(V_{rg} - V_{rf})} = corr.$$

Out[526]=
Igral = 1.12929 + 0. I

Out[527]=
Pfn = 1.12929

Out[528]=
Eqlty = $-2.8767\ 10^{-6}$ + 0. I

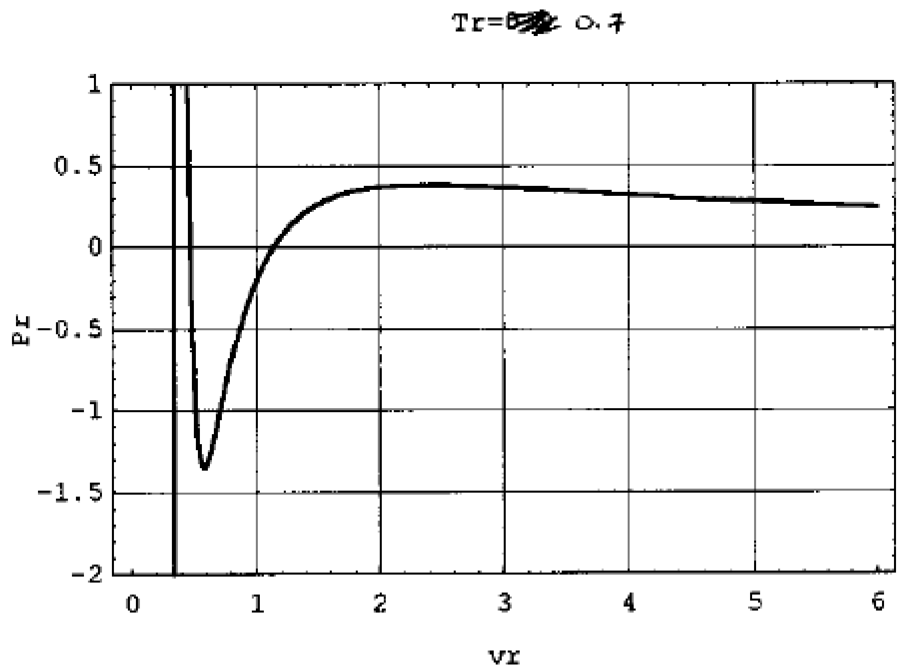
Out[529]=
corr = 0.646998 + 0. I

(I believe that the 0 I values are being returned because I set Mathematica to high accuracy.)

```
I)  Tr=0.7;
II) Roots[6*(3*Vr-1)^2-24*Tr*Vr^3==0,Vr]
    Plot[8*Tr/(3*Vr-1) - 3/(Vr^2),{Vr,0.33,6}, Frame->True, PlotRange ->{-2,1},
          GridLines->Automatic, FrameLabel-> {"vr","Pr","Tr=0.7"," "}]
```

Out[342]=

```
Vr == 0.25957 || Vr == 0.579201 || Vr == 2.37551
```



Out[343]=

```
-Graphics-
```

In[344]:=

```
Vmin=0.579201;
Pmn=8*Tr/(3*Vmin-1) - 3/(Vmin^2)
Vmax=2.37551;
Pmx=8*Tr/(3*Vmax-1) - 3/(Vmax^2)
```

Out[345]=

```
-1.35042
```

Out[347]=

```
0.38243
```

In[348]:=

III)

```
Pavg=(0+Pmx)/2
```

Out[348]=

```
0.191215
```

In[394]:=

IV

```
Pv=.2006;
c0=-1/Pv;
c1=3/Pv;
c2=-(Pv+8*Tr)/(3*Pv);
Q=((c2)^2-3*c1)/9
R=(2*(c2)^3 - 9*(c2)*(c1) +27*c0)/54
ineq=Simplify[Q^3-R^2]
```

Out[398]=

```
5.33779
```

Out[399]=

```
-11.6341
```

Out[400]=

```
16.7313
```

```
theta=ArcCos[R*Q^(-1.5)];
v1=-2*Q^(0.5)*Cos[theta/3]-(c2)/3
v2=Simplify[-2*Q^(0.5)*((Cos[theta/3])*(Cos[2*Pi/3])-(Sin[theta/3])*(0.866025403))
        -(c2)/3]
v3=Simplify[-2*Q^(0.5)*((Cos[theta/3])*(Cos[4*Pi/3])-(Sin[theta/3])*(-0.866025403))
        -(c2)/3]
```

Out[402]=

```
0.46719
```

V_{rl}

Out[403]=

```
7.80434
```

V_{rg}

Out[404]=

```
1.36722
```

In[405]:=

V)

```
Igral=Integrate[8*Tr/(3*Vi-1) - 3/(Vi^2),{Vi,v1,v2}]
Pfn=Pv*(v2-v1)
Eqlty=Igral-Pfn
corr=Igral/(v2-v1)
```

Out[405]=

```
1.47079 + 0. I
```

Out[406]=

```
1.47183
```

Out[407]=

```
-0.00103893 + 0. I
```

Out[408]=

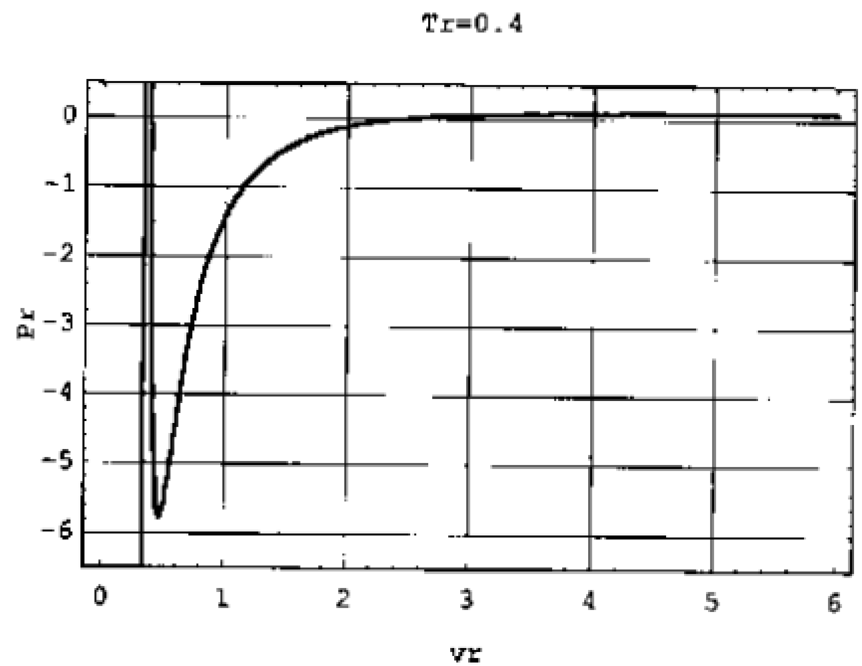
```
0.200458 + 0. I
```

In[1]:=

I)
```
Tr=0.4;
```
II)
```
Roots[6*(3*Vr-1)^2-24*Tr*Vr^3==0,Vr]
Plot[8*Tr/(3*Vr-1) - 3/(Vr^2),{Vr,0.33,6}, Frame->True, PlotRange ->{-6.5,0.5},
        GridLines->Automatic, FrameLabel-> {"vr","Pr","Tr=0.4"," "}]
```

Out[2]=

```
Vr == 0.273143 || Vr == 0.468573 || Vr == 4.88328
```



Out[3]=

```
-Graphics-
```

In[4]:=

```
Vmin=0.46853;
Pmn=8*Tr/(3*Vmin-1) - 3/(Vmin^2)
Vmax=4.88328;
Pmx=8*Tr/(3*Vmax-1) - 3/(Vmax^2)
```

Out[5]=

```
-5.77642
```

Out[7]=

```
0.10863
```

In[8]:=

III)

```
Pavg=(0+Pmx)/2
```

Out[8]=

```
0.054315
```

In[9]:=

IV)

```
Pv=0.00517;
c0=-1/Pv;
c1=3/Pv;
c2=-(Pv+8*Tr)/(3*Pv);
Q=((c2)^2-3*c1)/9;
R=(2*(c2)^3 - 9*(c2)*(c1) +27*c0)/54;
ineq=Simplify[Q^3-R^2]
```

Out[15]=

$6.65409 \; 10^{7}$

In[16]:=

```
theta=ArcCos[R*Q^(-1.5)];
v1=-2*Q^(0.5)*Cos[theta/3]-(c2)/3
v2=Simplify[-2*Q^(0.5)*((Cos[theta/3])*(Cos[2*Pi/3])-(Sin[theta/3])*(0.866025403))
        -(c2)/3]
v3=Simplify[-2*Q^(0.5)*((Cos[theta/3])*(Cos[4*Pi/3])-(Sin[theta/3])*(-0.866025403))
        -(c2)/3]
```

Out[17]=

0.386408 V_{rl}

Out[18]=

203.809 V_{rg}

Out[19]=

2.45606

In[20]:=

V)

```
Igral=Integrate[8*Tr/(3*Vi-1) - 3/(Vi^2),{Vi,v1,v2}]
Pfn=Pv*(v2-v1)
Eqlty=Igral-Pfn
corr=Igral/(v2-v1)
```

Out[20]=

1.05262 + 0. I

Out[21]=

1.0517

Out[22]=

0.000919223 + 0. I

Out[23]=

0.00517452 + 0. I

Tr	Pvr	vfr	vgr
0.4	0.00517	0.3864	203.809
0.6	0.08686	0.4326	16.7305
0.7	0.2006	0.4672	7.8043
0.8	0.3833	0.5174	4.17345
0.9	0.647	0.6034	2.3488

Pitzer's acentric factor (ω) is found for $T_r = 0.7$:

$$\omega = -1 - \log_{10}(P_r^{sat})_{T_r=0.7}$$

$$\omega = -1 - \log_{10}(0.2006)$$

$$\boxed{\omega = -.3024}$$

In[20]:=

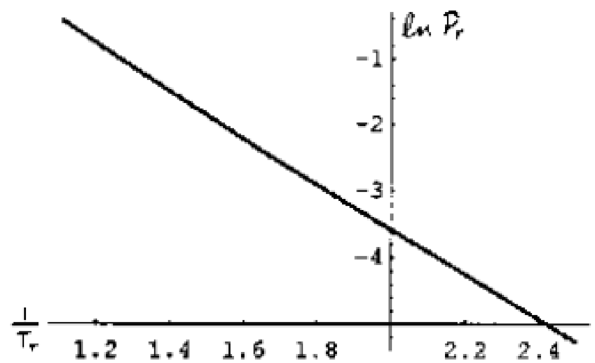
(1)
```
Fit[{{1/0.4,Log[0.00517]},{1/0.6,Log[0.08686]},{1/0.7,Log[0.2006]},
        {1/0.8,Log[0.3833]},{1/0.9,Log[0.647]}},{1,-tf},tf]
```

Out[20]=

(2)
```
3.36625 - 3.46143 tf
```

In[21]:=

(3)
```
g1=ListPlot[{{1/0.4,Log[0.00517]},{1/0.6,Log[0.08686]},{1/0.7,Log[0.2006]},
        {1/0.8,Log[0.3833]},{1/0.9,Log[0.647]}},PlotJoined->True]
```



Out[21]=

-Graphics-

The Clausius - Clapeyron Eqn. is of the form: $\boxed{\ln P_r = A - \frac{B}{T_r}}$, where A and B are constants. To find these constants, I entered the data found from the vdW eqn in the form $\{\underbrace{\frac{1}{T_r}}_{tf}, \underbrace{\ln(P_r)}_{pf}\}$, and then fit that data to a curve following the eqn:

$Pf = Const_1 - (Const_2)tf$ (see (1))

The result was (see (2)) $\boxed{\ln P_r = 3.36625 - \frac{3.46143}{T_r}}$

2.

Prove that, simultaneously,

$$F_1 = f_1^L(x_1) - f_1^V(y_1) = 0$$
$$F_2 = f_2^L(x_1) - f_2^V(y_1) = 0$$

for

① $T_c = 300\,K$ $P_c = 1000\,kPa$ at $T = 250\,K$ $z_1^V = .751$
② $T_c = 400\,K$ $P_c = 2000\,kPa$ $P = 400\,kPa$ $z_1^L = .665$

General form of the fugacity eqn.:

$$\ln \phi_i = \ln \frac{v_{mix}}{v_{mix} - b_{mix}} + \frac{b_i}{v_{mix} - b_{mix}} - \frac{2\sqrt{a_i}\sum_k z_k \sqrt{a_k}}{v_{mix} R_u T} - \ln Z_{mix} \qquad (\bigstar)$$

where $f_i = \phi_i x_i P_{mix}$

$\boxed{\text{Liquid Phase, pt. 1}}$ (where no subscript is appended, property is of the mixture; additionally, a_k, b_k, x_k, etc., are all assumed to have an L subscript in this eqn.)

$$\ln \frac{f_1^L}{x_1^L P} = \ln \frac{v}{v-b} + \frac{b_1}{v-b} - \frac{2\sqrt{a_1}\{x_1\sqrt{a_1} + x_2\sqrt{a_2}\}}{vRT} - \ln Z$$

$x_1^L = .665$
$x_2^L = 1 - .665 = .335$

vdW: $a = \frac{27}{64}\frac{R^2 T_c^2}{P_c}$, $b = \frac{1}{8}\frac{RT_c}{P_c}$

$a_1^L = \frac{27}{64}\frac{R^2 (T_{c_1})^2}{P_{c_1}} = \frac{27}{64}\frac{(8.314)^2}{1000\times10^3}(300)^2 = \underline{2.6245 \frac{N m^4}{mol^2}}$ | $b_1^L = \frac{1}{8}\frac{RT_{c_1}}{P_{c_1}} = \underline{3.11\times10^{-4}} \frac{m^3}{mol}$

$a_2^L = \frac{27}{64}\frac{R^2 T_{c_2}^2}{P_{c_2}} = \underline{2.33289}$ | $b_2^L = \frac{1}{8}\frac{RT_{c2}}{P_{c_2}} = \underline{2.079\times10^{-4}}$

Ⓐ

$$a_{mix}^L = \sum_i\sum_j z_i z_j a_{ij} = x_1^2 a_1 + 2x_1x_2\sqrt{a_1 a_2} + x_2^2 a_2$$
$$= (.665)^2(2.62) + 2(.665)(.335)\sqrt{(2.62)(2.33)} + (.335)(2.3329)$$
$$= 2.5249$$

$$b_{mix}^L = \sum_i z_i b_i = x_1 b_1 + x_2 b_2 = (.665)(3.11e{-4}) + (.335)(2.08e{-4})$$
$$= 2.77\times10^{-4}$$

We now need to find v_{mix}^L:

vdW: $P = \frac{RT}{V - b_m^L} - \frac{a_m^L}{V^2} \Rightarrow V^3 - \left(b_m^L + \frac{RT}{P}\right)V^2 + \frac{a_m^L}{P}V - \frac{ab_m^L}{P} = 0$

Ⓑ using cubic solver with $c_0 = -\frac{ab}{P}$, $c_1 = \frac{a}{P}$ and $c_2 = -b - \frac{RT}{P}$

yields

$v = 4.149 \times 10^{-4}$, 4.0×10^{-3} , 1.05×10^{-3}

(C) so $v_{mix}^{L} = v_f = v_{min} = 4.15 \times 10^{-4}$ m³/mol

(D) $Z_{mix}^{L} = \dfrac{1}{1 - b_{mix}^{L}/v_{mix}^{L}} - \dfrac{a_{mix}^{L}}{RT v_{mix}^{L}} = 0.0798$

and, substituting into (★)

$\ln \dfrac{f_1^L}{x_1^L P} = \ln \dfrac{4.15\times10^{-4}}{4.15\times10^{-4} - 1.77\times10^{-4}} + \dfrac{3.11\times10^{-4}}{(4.15-2.77)\times10^{-4}} - \dfrac{2\sqrt{2.62}\{(.665)(\sqrt{2.62}) + (.335)(\sqrt{2.33})\}}{(8.314)(250K)(4.15\times10^{-4})} - \ln(.0798)$

$= -0.0811$

(E) $\dfrac{f_1^L}{x_1^L P} = 0.922052$

$\boxed{f_1^L = 245{,}266 \text{ Pa}}$ ✓

$\boxed{\text{Vapor Phase, pt. 1}}$ $x_1^v = .751$ $x_2^v = 1 - .751 = .249$

(all subscripts not explicitly noted are v in this sxn.)

$a_1^v = a_1^L$, $a_2^v = a_2^L$, $b_1^v = b_1^L$, $b_2^v = b_2^L$

(F) $b_{mix}^{v} = x_1 b_1 + x_2 b_2 = (.751)(3.11\times10^{-4}) + (.249)(2.08\times10^{-4})$
$= 2.859 \times 10^{-4}$

$a_{mix}^{v} = x_1^2 a_1 + 2x_1 x_2 \sqrt{a_1 a_2} + x_2^2 a_2$

$= (.751)^2(2.62) + 2(.751)(.249)\sqrt{(2.62)(2.333)} + (.249)^2(2.333)$

$= 2.55$

(G) Find v again using cubic eqn solver $v = 4.37\times10^{-4}$
$v = 4.0\times10^{-3}$
$v = 1.04\times10^{-3}$

$v_{mix}^{v} = v_g = v_{max} = 4.003 \times 10^{-3}$

(H) $Z_{mix}^{v} = \dfrac{1}{1 - b_{mix}^{v}/v_{mix}^{v}} - \dfrac{a_{mix}^{v}}{RT v_{mix}^{v}} = 0.770413$

Substitute into (★) ⇒ $\ln \dfrac{f_1^v}{x_1^v P} = \ln \dfrac{v}{v-b} + \dfrac{b_1}{v-b} - \dfrac{2\sqrt{a_1}\{x_1\sqrt{a_1} + x_2\sqrt{a_2}\}}{vRT} - \ln Z$

(J)

$\ln \dfrac{f_1^v}{x_1^v P} = -0.203054$

$\dfrac{f_1^v}{x_1^v P} = 0.8162$

$\boxed{f_1^v = 245{,}197 \text{ Pa}}$ ✓

Liquid Phase, pt. 2

$x_1, x_2, a_1, a_2, b_1, b_2, v_{mix}$, etc. all the same as those found in Liquid Phase, pt. 1

(K)

Substitute into

$$\ln \phi_2^L = \ln \frac{v_m}{v_m - b_m} + \frac{b_2}{v_m - b_m} - \frac{2\sqrt{a_2}\,(x_1\sqrt{a_1} + x_2\sqrt{a_2})}{v_m RT} - \ln Z$$

$$\ln \frac{f_2^L}{x_2^L P} = -0.493049$$

$$\boxed{f_2^L = 81{,}842 \text{ Pa}}$$

Vapor Phase, pt. 2

x_1, x_2, etc. are all the same as those found in Vapor Phase, pt. 1

(L)

$$\ln \phi_2^V = \ln \frac{v_m}{v_m - b_m} + \frac{b_2}{v_m - b_m} - \frac{2\sqrt{a_2}\,(x_1\sqrt{a_1} + x_2\sqrt{a_2})}{v_m RT} - \ln Z$$

$$\ln \frac{f_2^V}{x_2^V P} = -0.195446$$

$$\boxed{f_2^V = 81{,}917.8 \text{ Pa}}$$ ✓

Proof:

$F_1 = f_1^L - f_1^V = 245{,}266 - 245{,}197 \text{ Pa} = .067 \text{ kPa}$

$F_2 = f_2^L - f_2^V = 81{,}842 - 81{,}917.8 \text{ Pa} = -.0758 \text{ kPa}$

$\underline{F_1}$ and $\underline{F_2}$ should equal $\underline{\text{zero}}$, so the error for each is:

F_1: $\frac{67}{245{,}197} = .00027 = .027\%$ error

F_2: $\frac{75.8}{81{,}842} = .0009 = .093\%$ error

Both of these errors are very small (less than .1%), so we can say that $F_1 \approx 0$, $F_2 \approx 0$.

3.

$y_i P = x_i P_i^{sat}$

$\log_{10}(P_1^{sat}) = 4.72583 - \dfrac{1660.652}{T-1.461}$ $\quad$ P → bar, T → K,

$\log_{10}(P_2^{sat}) = 4.07827 - \dfrac{1343.943}{T-53.773}$

These eqns may vary slightly depending on the source you use

a) For $T=100°C$,

$P_1^{sat} = 1.811$ bar , $P_2^{sat} = 0.7417$ bar

$P = x_1 P_1^{sat} + (1-x_1) P_2^{sat}$

$x_1 = 0.33$

$\boxed{P = 1.095 \text{ bar}}$, $y_1 = \dfrac{x_1 P_1^{sat}}{P} = \boxed{0.546}$

b) $T=100°C$, $y_1 = 0.33$; P_1^{sat} + P_2^{sat} are the same

$x_1 = \dfrac{y_1 P}{P_1^{sat}}$ and $1-x_1 = \dfrac{(1-y_1)P_2^{sat}}{P}$ → solve simultaneously

$\boxed{x_1 = 0.1678 \text{ , } P = 0.9213 \text{ bar}}$

c) $x_1 = 0.33$, $P = 120$ kPa ; $y_1, T = ?$

$\overset{=1.2\text{ bar}}{P} = x_1 P_1^{sat} + (1-x_1) P_2^{sat}$ → P_1^{sat} + P_2^{sat} are solely fns of T,

so $\boxed{T = 376.4 \text{ K}}$

$P_1^{sat} = 1.978$ bar

$y_1 = \dfrac{x_1 P_1^{sat}}{P} = \boxed{0.544}$

d) $T=100°C$, $P = 120$ kPa

P_1^{sat}, P_2^{sat} same as in part (a)

$P = x_1 P_1^{sat} + (1-x_1) P_2^{sat} \rightarrow \boxed{x_1 = 0.429}$

$y_1 = x_1 P_1^{sat}/P \rightarrow \boxed{y_1 = 0.647}$

(e) $z_1 = 0.33 \rightarrow z_1 = x_1 L + y_1 V = x_1 (1-V) + y_1 V$

$V = \frac{z_1 - x_1}{y_1 - x_1} = \frac{-0.1}{0.22} = -0.46 \leftarrow$ less than zero $\rightarrow$ impossible,

so cannot have overall $z_1 = 0.33$ (as should be obvious for x_1, y_1 found in part d)

(f) Benzene (C_6H_6) + Toluene (C_7H_8) are chemically similar, and we are looking at low to moderate pressures, which satisfy both the ideal sol'n + ideal gas restrictions.