

Problem 10.44

Following are data for G^E and H^E (both in J/mol) for equimolar mixtures of the same organic liquids. Use all of the data to estimate values of G^E , H^E , and TS^E for the equimolar mixture at 25 deg C.

At T = 10 deg C, $G^E = 544.0$ and $H^E = 932.1$

At T = 30 deg C, $G^E = 513.2$ and $H^E = 893.4$

At T = 50 deg C, $G^E = 494.2$ and $H^E = 845.9$

Solution

Equations are from Example 10.11 on page 397. From equation (C) on that page, $H^E = aT + c$. From equation (A), $G^E = -a(T \ln T - T) + bT + c$. From equation (B), $S^E = a \ln T - b$. Use regression analysis to determine the constants a, b, and c, then calculate the desired properties.

```
In[1]:= (*Excess enthalpy regression*)
data1 = {{283.15, 932.1}, {303.15, 893.4}, {323.15, 845.9}};
model1 = a * x + c;
fit1 = FindFit[data1, model1, {a, c}, x];
a = a /. fit1;
c = c /. fit1;

In[6]:= (*Excess Gibbs energy regression*)
data2 = {{283.15, 544.0}, {303.15, 513.2}, {323.15, 494.2}};
model2 = -a * (x * Log[x] - x) + b * x + c;
fit2 = FindFit[data2, model2, b, x];
b = b /. fit2;

(*Excess enthalpy calculation at 25 deg C from regression function*)
HE = a * (298.15) + c

Out[8]=
901.242

(*HE=901.242 J/mol //ANS*)

(*Excess Gibbs energy calculation at 25 deg C from regression function*)
GE = -a * (298.15 * Log[298.15] - 298.15) + b * 298.15 + c

Out[9]=
522.44

(*GE=522.440 J/mol //ANS*)

(*Excess entropy (T*SE) calculation at 25 deg C from regression function*)
TSE = 298.15 * (a * Log[298.15] - b) (*Equation B on p. 388*)

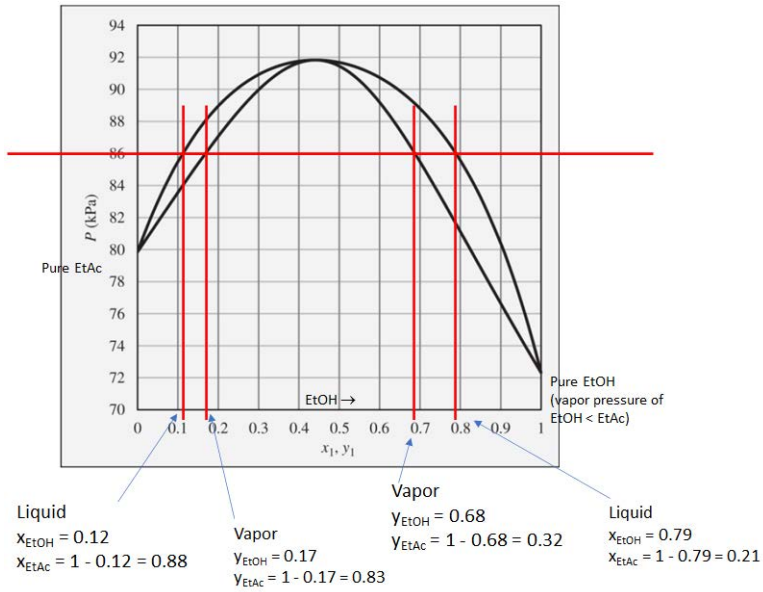
Out[10]=
378.802

(*TSE=378.802 J/mol //ANS*)
```

Problem 12.3

The pressure above a mixture of ethanol and ethyl acetate at 70 deg C is measured to be 86 kPa. What are the possible compositions of the liquid and vapor phases?

Solution

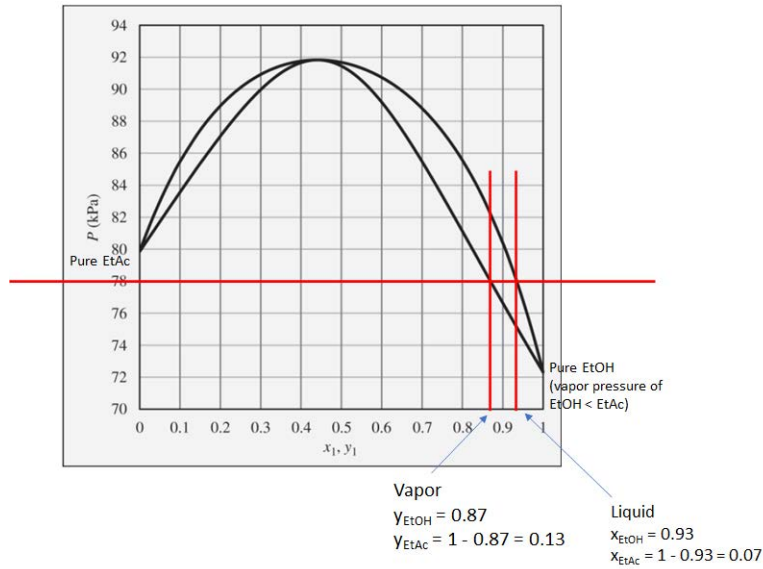


(*//ANS, all units are dimensionless *)

Problem 12.4

The pressure above a mixture of ethanol and ethyl acetate at 70 deg C is measured to be 78 kPa. What are the possible compositions of the liquid and vapor phases?

Solution



(*//ANS, all units are dimensionless *)

Problem 13.1

Assuming the validity of Raoult's Law, do the following calculations for the benzene(1)/toluene(2) system:

- (a) Given $x_1=0.33$ and $T=100$ deg C, find y_1 and P.
- (b) Given $y_1=0.33$ and $T=100$ deg C, find x_1 and P.
- (c) Given $x_1=0.33$ and $P=120$ kPa, find y_1 and T.
- (d) Given $y_1=0.33$ and $P=120$ kPa, find x_1 and T.

(*Common information for parts (a) through (d)*)
(*benzene(1)/toluene(2)*)

```
In[1]:= a = {13.7819, 13.9320};  
b = {2726.81, 3056.96};  
c = {217.572, 217.625};  
Psat = Exp[a -  $\frac{b}{t + c}$ ];  
K[t_, p_] = Psat / p;
```

Solution to Part (c):

```
In[6]:= xb = {ξ, 1 - ξ};  
yb[t_, p_, ξ_] = xb * K[t, p];  
f[t_, p_, ξ_] = Plus @@ (yb[t, p, ξ]) == 1;  
Tb[p_, ξ_] := t /. FindRoot[f[t, p, ξ], {t, 90}];  
  
In[10]:= Tb[120, .33]  
Out[10]=  
103.307  
  
In[11]:= yb[103.307, 120, .33]  
Out[11]=  
{0.542161, 0.457844}  
  
(*T=103.307 deg C and y1=0.542161 //ANS*)
```

Solution to Part (d):

```
In[12]:= yd = {ξ, 1 - ξ};  
xd[t_, p_, ξ_] = yd / K[t, p];  
g[t_, p_, ξ_] = Plus @@ (xd[t, p, ξ]) == 1;  
Td[p_, ξ_] := t /. FindRoot[g[t, p, ξ], {t, 90}];  
  
In[16]:= Td[120, .33]  
Out[16]=  
109.131  
  
In[17]:= xd[109.131, 120, .33]  
Out[17]=  
{0.172627, 0.82737}  
  
(*T=109.131 deg C and x1=0.172627 //ANS*)
```

Solution to Part (a):

```
In[18]:= Pb[t_, ξ_] := p /. FindRoot[f[t, p, ξ], {p, 90}];
```

```
In[19]:= Pb[100, .33]
```

```
Out[19]=
```

```
109.303
```

```
In[20]:= yb[100, 109.303, .33]
```

```
Out[20]=
```

```
{0.54481, 0.455193}
```

(*P=109.303 kPa and $y_1=0.544810$ //ANS*)

Solution to Part (b):

```
In[21]:= Pd[t_, ξ_] := p /. FindRoot[g[t, p, ξ], {p, 90}]
```

```
In[22]:= Pd[100, .33]
```

```
Out[22]=
```

```
92.1564
```

```
In[23]:= xd[100, 92.1564, .33]
```

```
Out[23]=
```

```
{0.168529, 0.831471}
```

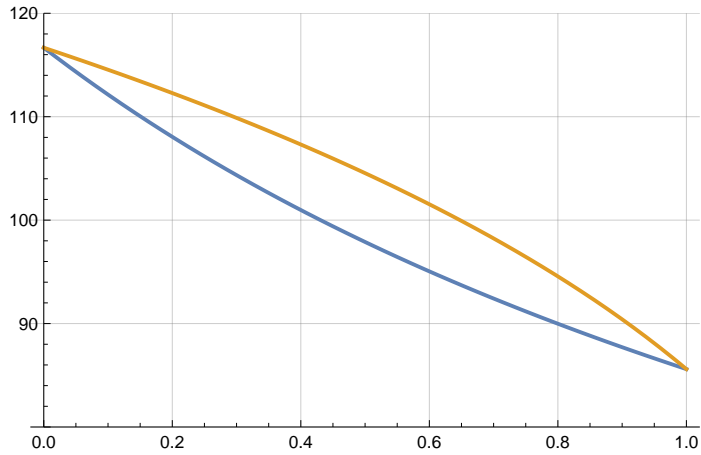
(*P=92.1564 kPa and $x_1=0.168529$ //ANS*)

Comparing Results to CHEMCAD:

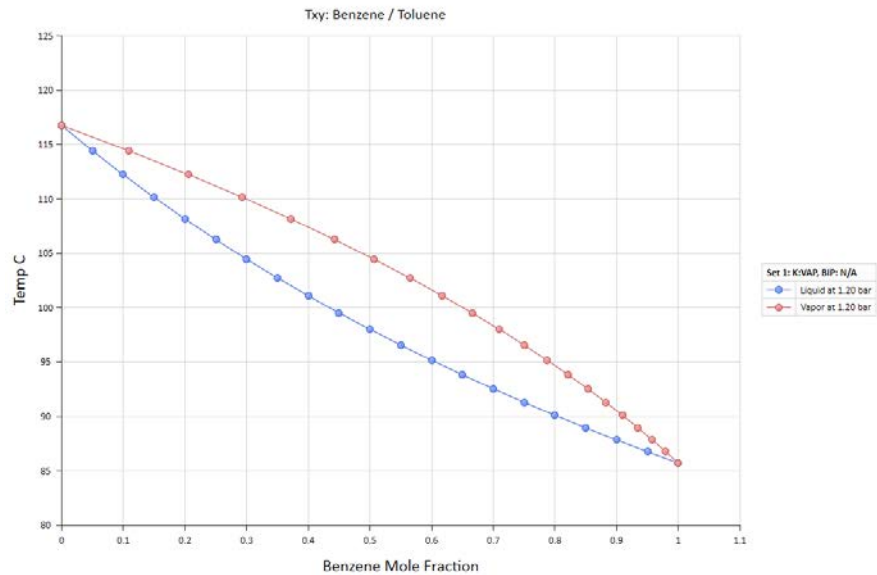
(*Txy plots from MMA (dew-point/bubble-point curves for parts c and d) *)

```
In[24]:= Plot[{Tb[120,  $\xi$ ], Td[120,  $\xi$ ]}, { $\xi$ , 0, 1},
  PlotRange -> {80, 120}, AxesOrigin -> 0, GridLines -> Automatic]
```

Out[24]=



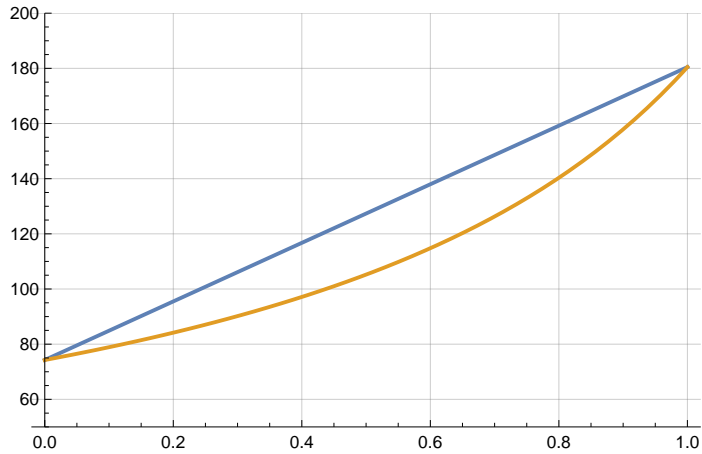
(*Txy plots from CHEMCAD *)



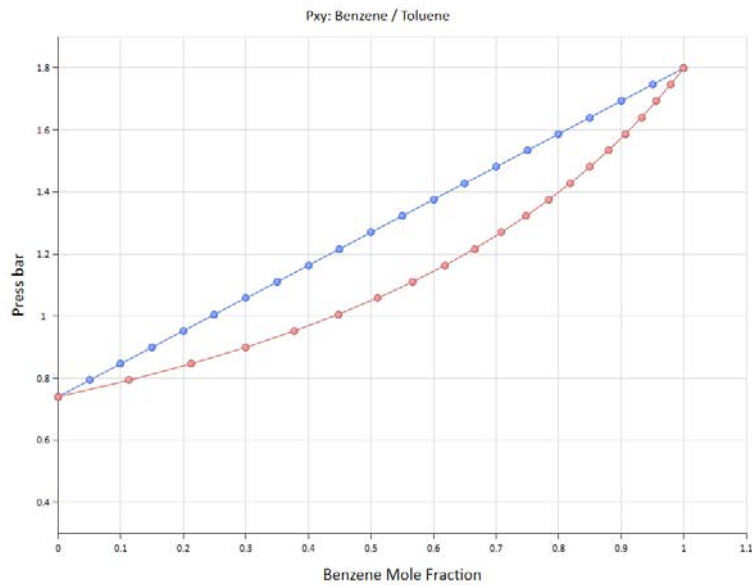
(*Pxy plots from MMA (dew-point/bubble-point curves for parts a and b) *)

```
In[25]:= Plot[{Pb[100,  $\xi$ ], Pd[100,  $\xi$ ]}, { $\xi$ , 0, 1},
  PlotRange -> {50, 200}, AxesOrigin -> 0, GridLines -> Automatic]
```

Out[25]=



(*CHEMCAD*)



Problem 13.6

Of the following liquid/vapor systems, which can be approximately modeled by Raoult's Law? For those which cannot, why? Table B.1 in Appendix B may be useful.

- (a) Benzene/toluene at 1 atm.
- (b) n-Hexane/n-heptane at 25 bar.
- (c) Hydrogen/propane at 200 K.
- (d) Isooctane/n-octane at 100 degC.
- (e) Water/n-decane at 1 bar.

Solution

This problem was discussed in class. The check marks designate the systems that follow Raoult's Law and the x's designate those that do not.

		ω	T_c / K	P_c / bar	
1 atm 1.013 bar	benzene	.210	562.2	48.98	✓
	toluene	.262	591.8	41.06	
25 bar	n-hexane	.301	507.6	30.25	✓
	n-heptane	.350	540.2	27.40	
200 K	hydrogen	-.216	33.19	13.13	✗
	propane	.152	369.8	42.48	
100 C 373.15 K	isooctane	.302	544.0	25.68	✓
	n-octane	.400	568.7	24.90	
1 bar	water	.345	647.1	220.55	✗
	n-decane	.492	617.7	21.10	

For n-hexane and n-heptane at 25 bar, this looks do-able, but the pressure is close to the critical pressure of both molecules, so we checked this in CHEMCAD and it does appear to be ideal.

For hydrogen and propane at 200K, hydrogen is above the critical temperature so hydrogen gas can dissolve in the liquid (following Henry's Law), but it cannot condense into a liquid.

For water and n-decane at 1 bar, the IMFs between W-W, D-D, and W-W are very different, meaning Raoult's Law is not applicable and we expect two liquid phases to form.