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

From equation (C) on page 397, $H^E = aT + c$. 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, then calculate the desired properties.

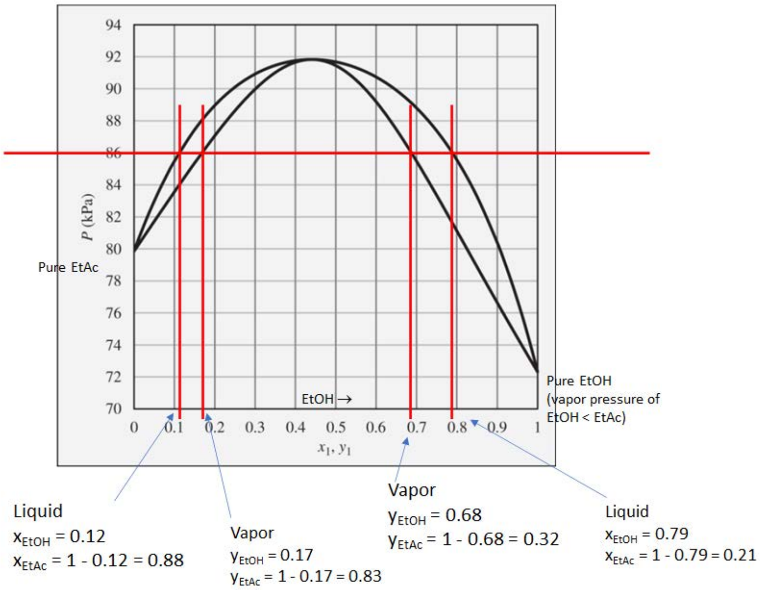
```
In[1]:= (*excess enthalpy regression*)
data1 = {{283.15, 932.1}, {303.15, 893.4}, {323.15, 845.9}};
model1 = a * x + c;
fit1 = FindFit[data1, model1, {a, c}, x]

Out[3]= {a → -2.155, c → 1543.75491667}

In[4]:= 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]

Out[8]= {b → -13.548828616}

In[9]:= b = b /. fit2;

(*At 25 deg C*)

In[10]:= (*excess enthalpy calculation from regression function*)
HE = a * (298.15) + c

Out[10]=
901.241666667

In[11]:= (*excess Gibbs energy calculation from regression function*)
GE = -a * (298.15 * Log[298.15] - 298.15) + b * 298.15 + c

Out[11]=
522.439797714
```

In[12]:=
```
(*excess entropy calculation from regression function*)
(*calculated as T*SE*)
TSE = 298.15 * (a * Log[298.15] - b) (*Equation B on p. 388*)
```
Out[12]=
```
378.801868953
```
```
(*//ANS, all units are J/mol *)
```

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

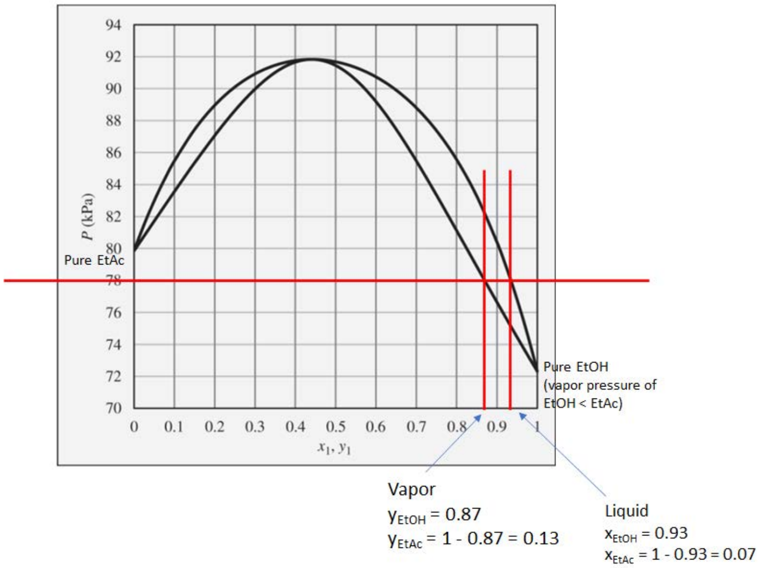


(*//ANS, all units are dimensionless *)

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.
(e) Given T=105 degC and P=120 kPa, find x_1 and y_1

Common Information for parts (a) through (e):

In[ ]:=
```
a = {13.7819, 13.9320};
b = {2726.81, 3056.96};
c = {217.572, 217.625};
```
$$\text{Psat} = \text{Exp}\left[a - \frac{b}{T + c}\right];$$

Solution to Part (a):

In[ ]:=
```
T = 100;
K = Psat / P
```
Out[ ]=
$$\left\{\frac{180.452792533}{P}, \frac{74.2597196691}{P}\right\}$$

In[ ]:=
```
x = {0.33, 0.67};
y = K * x
```
Out[ ]=
$$\left\{\frac{59.5494215359}{P}, \frac{49.7540121783}{P}\right\}$$

In[ ]:=
```
eq1 = Plus @@ y == 1
```
Out[ ]=
$$\frac{109.303433714}{P} == 1$$

In[ ]:=
```
ans1 = Quiet[Solve[eq1, P]]
```
Out[ ]=
```
{{P → 109.303433714}}
```

In[ ]:=
```
P = P /. ans1[[1]] (*//ANS in kPA*)
```
Out[ ]=
```
109.303433714
```

In[ ]:=
```
y (*//ANS dimensionless*)
```
Out[ ]=
```
{0.544808333209, 0.455191666791}
```

Solution to Part (c):

In[ ]:=
```
Clear[T, P, y];
```

In[ ]:=
```
P = 120; (*kPa*)
K = Psat / P
```

Out[ ]=

$$\left\{\frac{1}{120}\, e^{13.7819-\frac{2726.81}{217.572+T}},\ \frac{1}{120}\, e^{13.932-\frac{3056.96}{217.625+T}}\right\}$$

In[ ]:=
```
x = {0.33, 0.67};
y = K * x
```

Out[ ]=

$$\left\{0.00275\, e^{13.7819-\frac{2726.81}{217.572+T}},\ 0.00558333333333\, e^{13.932-\frac{3056.96}{217.625+T}}\right\}$$

In[ ]:=
```
eq3 = Plus @@ y == 1
```

Out[ ]=

$$0.00275\, e^{13.7819-\frac{2726.81}{217.572+T}} + 0.00558333333333\, e^{13.932-\frac{3056.96}{217.625+T}} == 1$$

In[ ]:=
```
ans3 = Quiet[Solve[eq3, T, Reals]] (*Reals helps MMA*)
```

Out[ ]=

$\{\{T \to 103.306835928\}\}$

In[ ]:=
```
T = T /. ans3[[1]] (*//ANS in degrees C*)
```

Out[ ]=

103.306835928

In[ ]:=
```
y (*//ANS dimensionless*)
```

Out[ ]=

{0.542158335809, 0.457841664191}

Solution to Part (b):

```
In[ ]:= Clear[T, P, y];

In[ ]:= T = 100;(*deg C*)
        K = Psat / P

Out[ ]= {180.452792533/P, 74.2597196691/P}

In[ ]:= y = {0.33, 0.67};(*given*)
        x = y / K

Out[ ]= {0.00182873312941 P, 0.00902238795117 P}

In[ ]:= eq2 = Plus @@ x == 1

Out[ ]= 0.0108511210806 P == 1

In[ ]:= ans2 = Quiet[Solve[eq2, P]]

Out[ ]= {{P → 92.1563765231}}

In[ ]:= P = P /. ans2[[1]] (*//ANS in kPA*)

Out[ ]= 92.1563765231

In[ ]:= x (*//ANS dimensionless*)

Out[ ]= {0.168529418834, 0.831470581166}
```

Solution to Part (d):

In[ ]:=
```
Clear[T, P, x];
```

In[ ]:=
```
P = 120;(*kPa*)
K = Psat / P
```

Out[ ]=

$$\left\{\frac{1}{120}\, e^{13.7819-\frac{2726.81}{217.572+T}},\ \frac{1}{120}\, e^{13.932-\frac{3056.96}{217.625+T}}\right\}$$

In[ ]:=
```
y = {0.33, 0.67};
x = y / K
```

Out[ ]=

$$\left\{39.6\, e^{-13.7819+\frac{2726.81}{217.572+T}},\ 80.4\, e^{-13.932+\frac{3056.96}{217.625+T}}\right\}$$

In[ ]:=
```
eq4 = Plus @@ x == 1
```

Out[ ]=

$$39.6\, e^{-13.7819+\frac{2726.81}{217.572+T}} + 80.4\, e^{-13.932+\frac{3056.96}{217.625+T}} == 1$$

In[ ]:=
```
ans4 = Quiet[Solve[eq4, T, Reals]] (*Reals helps MMA*)
```

Out[ ]=

$\{\{T \to 109.13089106\}\}$

In[ ]:=
```
T = T /. ans4[[1]] (*//ANS in degrees C*)
```

Out[ ]=

109.13089106

In[ ]:=
```
x (*//ANS dimensionless*)
```

Out[ ]=

{0.172627553166, 0.827372446834}

Solution to Part (e):

In[ ]:=
```
Clear[T, P, x];
```

In[ ]:=
```
T = 105;(*deg C*)
P = 120;(*kPa*)
K = Psat / P
```

Out[ ]=
```
{1.71784518805, 0.718374044153}
```

In[ ]:=
```
x = {x1, 1 - x1};
y = K * x
```

Out[ ]=
```
{1.71784518805 x1, 0.718374044153 (1 - x1)}
```

In[ ]:=
```
eq5 = Plus @@ y == 1
```

Out[ ]=
```
0.718374044153 (1 - x1) + 1.71784518805 x1 == 1
```

In[ ]:=
```
ans5 = Quiet[Solve[eq5, x1]]
```

Out[ ]=
```
{{x1 → 0.281774974263}}
```

In[ ]:=
```
x1 = x1 /. ans5[[1]]
```

Out[ ]=
```
0.281774974263
```

In[ ]:=
```
x (*//ANS*)
```

Out[ ]=
```
{0.281774974263, 0.718225025737}
```

In[ ]:=
```
y (*//ANS*)
```

Out[ ]=
```
{0.484045783649, 0.515954216351}
```

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 screen shot below provides the answers but reasons are not provided here.

		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 too close to the critical pressure of the molecules, meaning they will behave non-ideally.

For hydrogen and proane at 200K, hydrogen is above the critical temperature and cannot condense to the liquid phase.

For water and n-decane at1 bar, again this looks do-able, but the molecules are insoluble and two liquid phases are likely to form.