Problem Set 13 - Solutions

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 °C.

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

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

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

Solution - Excess Enthalpy

Equations are from Example 10.11 on page 397. From equation (C) on that page, $H^E = a\,T + c$. 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.

Excess enthalpy regression:

```
In[•]:= data1 = {{283.15, 932.1}, {303.15, 893.4}, {323.15, 845.9}};
       model1 = a * T + c;
       fit1 = FindFit[data1, model1, {a, c}, T];
```

```
In[•]:= HE = model1 /. fit1 /. T → 298.15
```

```
Out[•]=
       901.241666667
```

The excess enthalpy at 25 °C is 901.242 J/mol. //ANS

Solution - Excess Gibbs Energy

Excess Gibbs energy regression:

```
In[•]:= data2 = {{283.15, 544.0}, {303.15, 513.2}, {323.15, 494.2}};
       model2 = -a * (T * Log[T] - T) + b * T + c /. fit1;
       fit2 = FindFit[data2, model2, b, T];
```

```
In[•]:= model2 /. fit2 /. T → 298.15
```

```
Out[•]=
       522.439797714
```

The excess Gibbs energy at 25 °C is 522.440 J/mol. //ANS

Solution - Excess Entropy

The excess Gibbs energy at 25 °C is 522.440 J/mol. //ANS

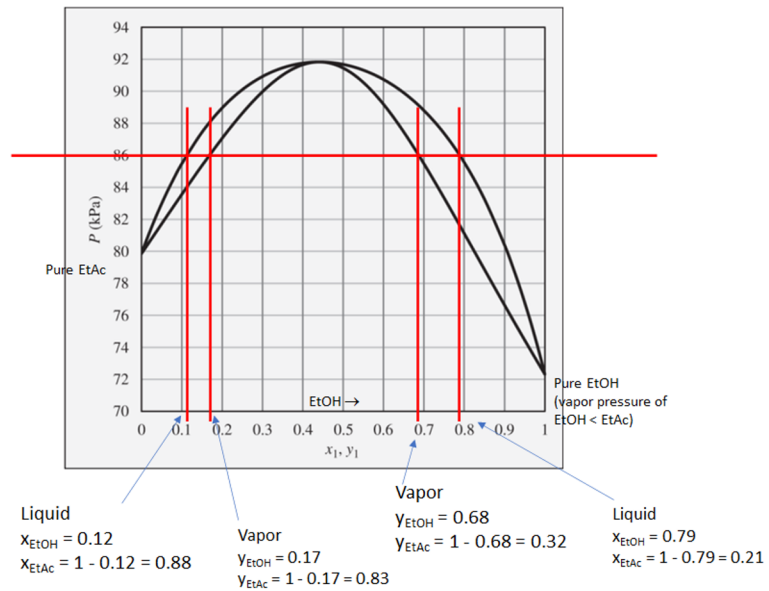Excess entropy (T*SE) calculation at 25 °C from regression function:

In[ ]:= `model3 = x * (a * Log[x] - b);`

In[ ]:= `model3 /. fit1 /. fit2 /. x → 298.15`

Out[ ]=

378.801868953

Excess entropy (T*SE) at 25 °C is 378.802 J/mol. //ANS

Problem 12.3

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

Solution

Liquid
$x_{EtOH} = 0.12$
$x_{EtAc} = 1 - 0.12 = 0.88$

Vapor
$y_{EtOH} = 0.17$
$y_{EtAc} = 1 - 0.17 = 0.83$

Vapor
$y_{EtOH} = 0.68$
$y_{EtAc} = 1 - 0.68 = 0.32$

Liquid
$x_{EtOH} = 0.79$
$x_{EtAc} = 1 - 0.79 = 0.21$

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

Problem 12.4

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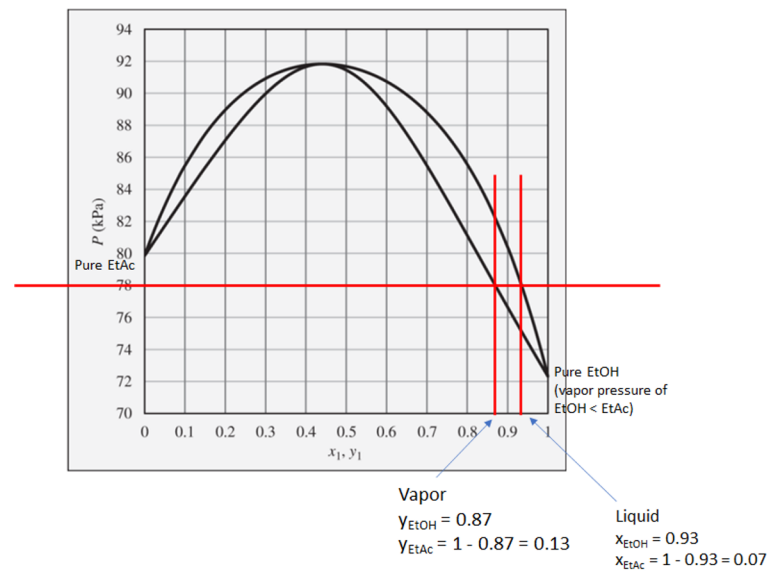
Solution

Vapor
$y_{EtOH} = 0.87$
$y_{EtAc} = 1 - 0.87 = 0.13$

Liquid
$x_{EtOH} = 0.93$
$x_{EtAc} = 1 - 0.93 = 0.07$

(*//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 °C, find y_1 and P.

(b) Given y_1=0.33 and T=100 °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.

Report temperature in °C and pressure in kPa.

Common Information

```
In[ ]:= (*benzene(1)/toluene(2)*)

(*feed concentrations*)
z1 = ξ;
z2 = 1 - z1;

(*vapor pressure*)
a = {13.7819, 13.9320};
b = {2726.81, 3056.96};
c = {217.572, 217.625};
Psat = Exp[a - b/(T + c)];

(*Activity Coefficients*)
γ1 = 1;
γ2 = 1;

(*Equilibrium Constants*)
K1 = γ1 * Psat[[1]] / P;
K2 = γ2 * Psat[[2]] / P;

(*Equilibrium Expressions*)
eq1 = x1 * K1 - y1 == 0;
eq2 = x2 * K2 - y2 == 0;

(*Species Mole Balances*)
eq3 = z1 == Ψ * y1 + (1 - Ψ) * x1;
eq4 = z2 == Ψ * y2 + (1 - Ψ) * x2;

(*Summation of Mole Fractions*)
eq5 = (x1 + x2) - (y1 + y2) == 0;

(*Equation and Variable Lists*)
eqns = {eq1, eq2, eq3, eq4, eq5};
var1 = {{x1, .5}, {x2, .5}, {y1, .5}, {y2, .5}, {T, 100}};
var2 = {{x1, .5}, {x2, .5}, {y1, .5}, {y2, .5}, {P, 100}};
```

Solution to Part (a)

```
In[ ]:= FindRoot[eqns /. {T → 100, Ψ → 0, ξ → .33}, var2]
```

Out[ ]=

$\{x1 \to 0.33, x2 \to 0.67, y1 \to 0.544808333209, y2 \to 0.455191666791, P \to 109.303433714\}$

P = 109.30 kPa and y_1 = 0.5448. //ANS

Solution to Part (b)

In[ ]:= **FindRoot[eqns /. {T → 100, Ψ → 1, ξ → .33}, var2]**

Out[ ]=

{x1 → 0.168529418834, x2 → 0.831470581166, y1 → 0.33, y2 → 0.67, P → 92.1563765231}

P = 92.156 kPa and x_1 = 0.1685. //ANS

Solution to Part (c)

In[ ]:= **FindRoot[eqns /. {P → 120, Ψ → 0, ξ → .33}, var1]**

Out[ ]=

{x1 → 0.33, x2 → 0.67, y1 → 0.542158335809, y2 → 0.457841664191, T → 103.306835928}

T = 103.31 °C and y_1 = 0.5422. //ANS

Solution to Part (d)

In[ ]:= **FindRoot[eqns /. {P → 120, Ψ → 1, ξ → .33}, var1]**

Out[ ]=

{x1 → 0.172627553166, x2 → 0.827372446834, y1 → 0.33, y2 → 0.67, T → 109.13089106}

T = 109.13 °C and x_1 = 0.1726. //ANS

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 °C.

(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 marks 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 close to the critical pressure, so fugacity will become important, but the molecules are very similar in terms of size, shape, and IMF's.

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.