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## 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  $T = 10\text{ °C}$ ,  $G^E = 544.0$  and  $H^E = 932.1$

At  $T = 30\text{ °C}$ ,  $G^E = 513.2$  and  $H^E = 893.4$

At  $T = 50\text{ °C}$ ,  $G^E = 494.2$  and  $H^E = 845.9$

### Solution - Excess Enthalpy

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

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];
HE = model1 /. fit1 /. T -> 298.15
```

```
Out[*]=
901.2417
```

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}];
model2 /. fit2 /. T -> 298.15
```

```
Out[*]=
522.4398
```

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 ( $T^*S^E$ ) calculation at 25 °C from regression function:

```
model3 = T * (a * Log[T] - b) ;
```

```
model3 /. fit1 /. fit2 /. T -> 298.15
```

```
Out[ ]=
```

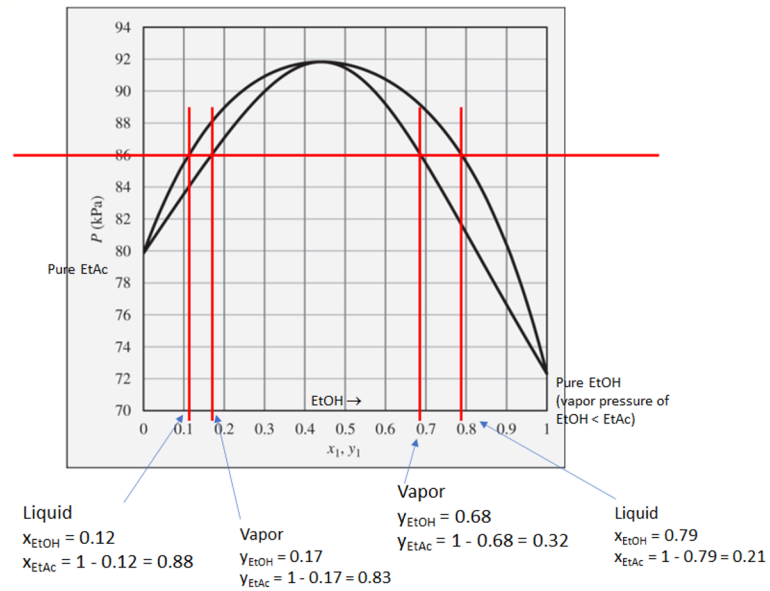
```
378.8019
```

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

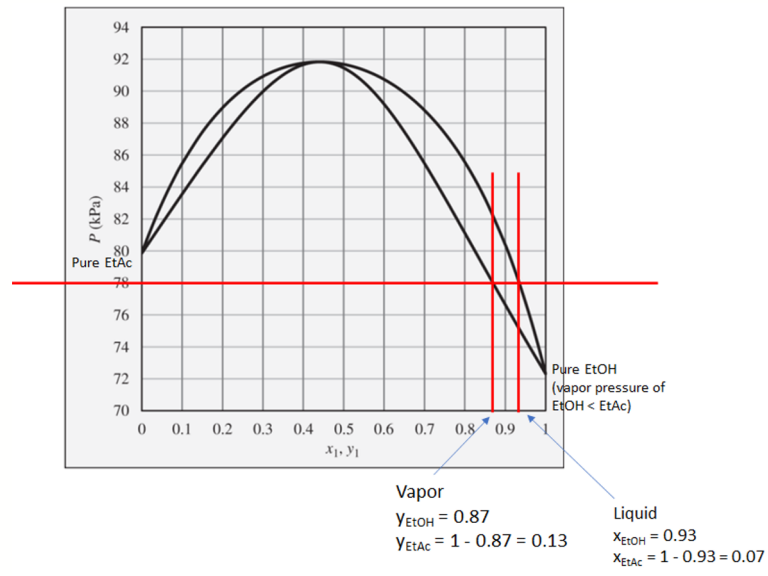


(\*//ANS, all units are dimensionless \*)

## 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



(\*//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  $T=100\text{ }^\circ\text{C}$ , find  $y_1$  and  $P$ .
- (b) Given  $y_1=0.33$  and  $T=100\text{ }^\circ\text{C}$ , find  $x_1$  and  $P$ .
- (c) Given  $x_1=0.33$  and  $P=120\text{ kPa}$ , find  $y_1$  and  $T$ .
- (d) Given  $y_1=0.33$  and  $P=120\text{ kPa}$ , find  $x_1$  and  $T$ .

Report temperature in  $^\circ\text{C}$  and pressure in kPa.

### Common Information

This solution follows slide 7 of lesson 38 - Application of the Duhem theorem. The five equations and five unknowns are indicated with bold red check marks in that slide.

```

(*benzene(1)/toluene(2)*)

(*feed mole fractions*)
z1 =  $\xi$ ;
z2 = 1 - z1;

(*Vapor pressure constants for benzene and toluene*)
a = {13.7819, 13.9320};
b = {2726.81, 3056.96};
c = {217.572, 217.625};
Psat = Exp[ $a - \frac{b}{T + c}$ ];

(*Activity coefficients for benzene and toluene*)
 $\gamma_1$  = 1;
 $\gamma_2$  = 1;

(*Equilibrium constants for benzene and toluene*)
K1 =  $\gamma_1$  * Psat[[1]] / P;
K2 =  $\gamma_2$  * Psat[[2]] / P;

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

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

(*Summation of Mole Fractions for benzene and toluene*)
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}, {P, 100}};
(*a and b - solve for P with T specified*)
var2 = {{x1, .5}, {x2, .5}, {y1, .5}, {y2, .5}, {T, 100}};
(*c and d - solve for T with P specified*)

```

## Part (a)

```

(*Specify T as required,  $\Psi=0$  to make  $x_i=z_i$ ,  $\xi=.33$  to make  $x_1=.33$ *)
FindRoot[eqns /. {T → 100,  $\Psi$  → 0,  $\xi$  → .33}, var1]

```

Out[ ]=

```
{x1 → 0.33, x2 → 0.67, y1 → 0.5448083, y2 → 0.4551917, P → 109.3034}
```

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

### Part (b)

(\*Specify T as required,  $\Psi=1$  to make  $y_i=z_i$ , and  $\xi=.33$  to make  $y_1=.33$ \*)  
**FindRoot**[eqns /. {T → 100,  $\Psi$  → 1,  $\xi$  → .33}, var1]

Out[ ]=

{x1 → 0.1685294, x2 → 0.8314706, y1 → 0.33, y2 → 0.67, P → 92.15638}

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

### Part (c)

(\*Specify P as required,  $\Psi=0$  to make  $x_i=z_i$ , and  $\xi=.33$  to make  $x_1=.33$ \*)  
**FindRoot**[eqns /. {P → 120,  $\Psi$  → 0,  $\xi$  → .33}, var2]

Out[ ]=

{x1 → 0.33, x2 → 0.67, y1 → 0.5421583, y2 → 0.4578417, T → 103.3068}

$y_1 = 0.5422$  and  $T = 103.31$  °C. //ANS

### Part (d)

(\*Specify P as required,  $\Psi=1$  to make  $y_i=z_i$ , and  $\xi=.33$  to make  $y_1=.33$ \*)  
**FindRoot**[eqns /. {P → 120,  $\Psi$  → 1,  $\xi$  → .33}, var2]

Out[ ]=

{x1 → 0.1726276, x2 → 0.8273724, y1 → 0.33, y2 → 0.67, T → 109.1309}

$x_1 = 0.1726$  and  $T = 109.13$  °C. //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.

		$\omega$	$T_c / K$	$P_c / \text{bar}$	
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 this was 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 (W) and n-decane (D) at 1 bar, the IMFs between W-W, D-D, and W-D are very different, with W-W having H-bonding IMFs and D-D having van der Waals IMFs. Since water and oil do not mix, we expect two liquid phases meaning Raoult's Law is not applicable.