

## Quiz II, Problem 3: Mixing Methanol (1) and Benzene (2)

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Start with an energy balance. Assume that the system is at a steady state, that the changes in potential and kinetic energy are negligible, and that there is no work. Similarly, there is no accumulation of mass in the calorimeter. Consequently, the energy balance reduces to:

$$\begin{aligned} 0 &= \dot{n}_1 h_1 + \dot{n}_2 h_2 - (\dot{n}_1 + \dot{n}_2) h_{mixture} + \dot{Q} \\ \text{or} \\ h_{mixture} &= \frac{\dot{n}_1}{\dot{n}_1 + \dot{n}_2} h_1 + \frac{\dot{n}_2}{\dot{n}_1 + \dot{n}_2} h_2 + \frac{1}{\dot{n}_1 + \dot{n}_2} \dot{Q} \end{aligned}$$

The enthalpy of the mixture is given by:

$$h_{mixture} = x_1 h_1 + x_2 h_2 + \Delta h_{mix}$$

Combining these two equations equates the change in enthalpy due to mixing with the heat removed from the calorimeter:

$$\begin{aligned} \Delta h_{mix} &= q \\ h_{mixture} &= x_1 h_1 + x_2 h_2 + q \end{aligned}$$

(a) A solution is ideal when  $\Delta h_{mix}^{ideal} = 0$ . Thus, the plot of  $h_{mixture}$  is a straight line:

$$\begin{aligned}
h_{mixture}^{ideal} &= x_1 h_1 + x_2 h_2 \\
&= h_2 + x_1 (h_1 - h_2) \\
&= 1400 + x_1 700 \text{ [J/mol]}
\end{aligned}$$

[ + 5 points ]

(b) To calculate the real solution, we must first quantify the heat of mixing. There are no data provided for the pure component systems. However, we know that for pure species,  $\Delta h_{mix} = 0$ , so these terms need to be included.

n <sub>MeOH</sub> [mol/min]	n <sub>benz</sub> [mol/min]	x <sub>MeOH</sub>	Q [J/min]	$\Delta h_{mix} = q$ [J/mol]	$h_{mixture}$ [J/mol]
		0		0	1400
0.27	1	0.21	-808.6	-636.69	912.1
0.61	1	0.38	-930.2	-577.76	1087.5
1.04	1	0.51	-1133.2	-555.49	1201.4
1.63	1	0.62	-1235.0	-469.58	1364.3
2.44	1	0.71	-1293.2	-375.93	1520.6
3.66	1	0.79	-1296.8	-278.28	1671.5
5.69	1	0.85	-1294.8	-193.54	1801.8
9.75	1	0.91	-1306.5	-121.53	1913.3
21.94	1	0.96	-1341.6	-58.48	2011.0
		1		0	2100.0

The real solution is given by the dashed line, which is the final column on the right, or simply the ideal case plus the values from the second column from the right.

$$\begin{aligned}
h_{mixture} &= x_1 h_1 + x_2 h_2 + \Delta h_{mix} \\
&= h_2 + x_1 (h_1 - h_2) + q
\end{aligned}$$

[+10 points]

(c) To solve for the partial molar enthalpies, we use the graphical method:

$$h_{mixture} = \underbrace{\bar{H}_2}_{\text{intercept}} + x_1 \underbrace{\frac{dh_{mixture}}{dx_1}}_{\text{slope}}$$

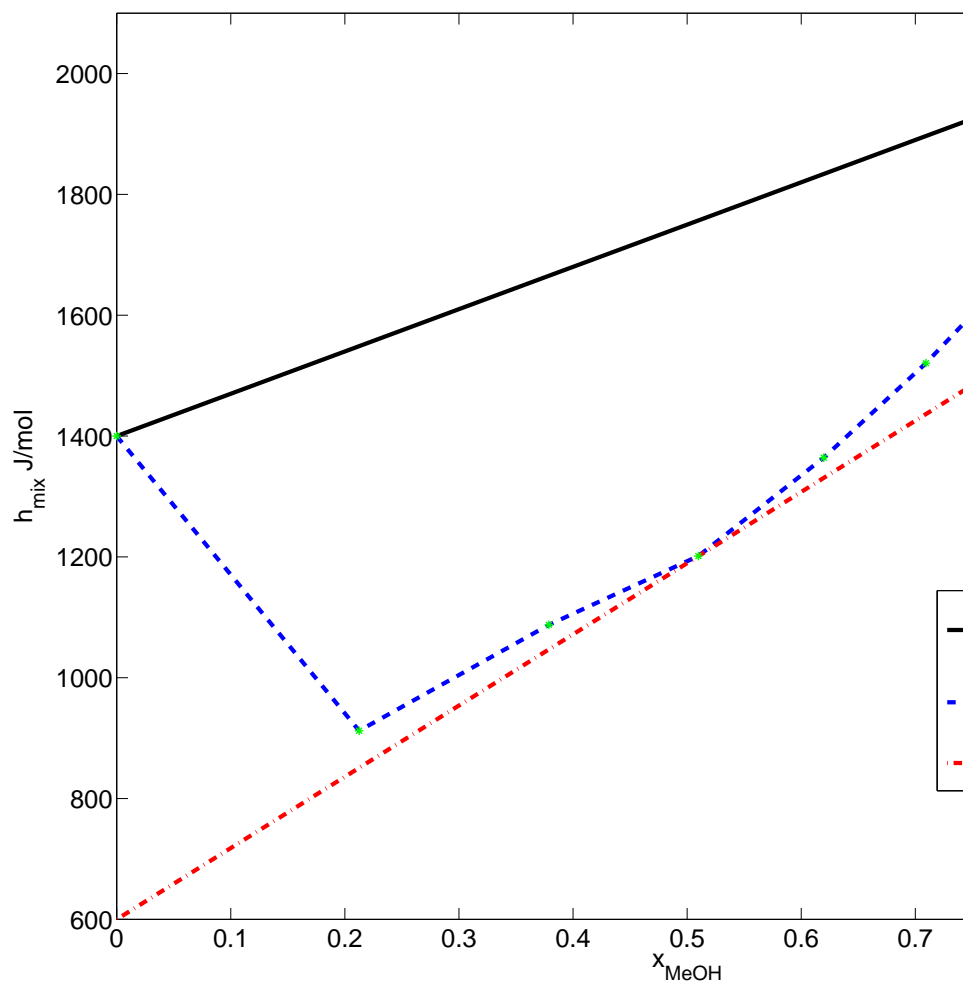
The partial molar enthalpies can be evaluated from the intercept of the tangent line at the point of interest. For simplicity, we will assume that the value of  $h_{mixture}$  does not change substantially between  $x_m = 0.5$  and  $x_m = 0.51$ .

$$\begin{aligned} h_{mixture}|_{x_m=0.5} &\approx h_{mixture}|_{x_m=0.51} \\ &= 1201.4 \text{ [J/mol]} \end{aligned}$$

The advantage with this assumption is that it is easier to evaluate the tangent at the “kink” in  $h_{mixture}$  at  $x_m = 0.51$ . Drawing the line tangent to this kink and reading off the intercepts allows us to approximate the partial molar enthalpies as follows:

$$\begin{aligned} \bar{H}_{benzene} &= 600 \text{ [J/mol]} \\ \bar{H}_{methanol} &= 1780 \text{ [J/mol]} \end{aligned}$$

[ +15 points ]



## Comments

This problem tested two things: (i) your ability to use an energy balance to calculate the enthalpy of the mixture, and (ii) your ability to apply graphical methods to predict partial molar properties. If you botched either of these components, you should not expect to get more than half credit.

For part (a):

if you got the slope wrong for some reason, you lost 3 points.

If you plotted  $h_{mixture}$  vs  $x_{benz}$ , that is incorrect. If you made this mistake but correctly labeled the x-axis, we gave you full credit; if you did not label your axes, you lost 2 points.

For part (b):

If you got the right shape but had no numbers, you got 1 point; if you had the correct shape, but your numbers were off for some reason, you got 2 points.

If your plot for (b) did not reflect the fact that  $\Delta h_{mix} = 0$  for pure components, (i.e. it did not join the plot from (a) at  $x_{MeOH} = 0$ , and  $x_{MeOH} = 1$ ), you lost 2 points.

If you made a sign error in your energy balance (e.g.  $\Delta h_{mix} = -q$ ), you lost 7 points.

For part (c):

If you wrote down that you would use the slope-intercept method and graphically determine the answer, you got 5 points; if you also included the tangent line with intercepts on your plot, it is an additional 2 points. Just writing the equation without specifying that you would use it with the plot doesn't get you more than a point. If you wrote the equation and followed it by a bunch of algebra, sorry.

If you did not write down the graphical method equation, but you did draw the tangent line to the curve from (b) and noted that the intercepts were the partial molar enthalpies, you got 5 points.

If you mixed up the intercepts (e.g.  $\bar{H}_1$  at  $x_1 = 0$ ), you lost 2 points.

Each correct value was worth 4 points – *provided* you answered part (b) correctly. If you botched part (b) but your answers for part (c) were close due to luck, sorry.

Finally, accuracy counts. If your tangent line does not look tangent to the curve from part (b) at  $x_1 = 0.5$ , you don't get credit for it.