1) At $90^{\circ} \mathrm{C}$, the vapour pressure of methylbenzene is 53.3 kPa and that of 1,3 -dimethylbenzene is 18.0 kPa . What is the composition of a liquid mixture that boils at $90^{\circ} \mathrm{C}$ when the pressure is 0.40 atm ? What is the composition of the vapour produced?
An expression for composition of the solution in terms of its vapour pressure is required. This is obtained from Dalton's law and Raoult's law as follows

$$
p=p_{\mathrm{A}}+p_{\mathrm{B}} \text { [Dalton's law] }=x_{\mathrm{A}} p_{\mathrm{A}}^{*}+\left(1-x_{\mathrm{A}}\right) p_{\mathrm{B}}^{*}
$$

Solving for $x_{\mathrm{A}}, x_{\mathrm{A}}=\frac{p-p_{\mathrm{B}}^{+}}{p_{\mathrm{A}}^{*}-p_{\mathrm{B}}^{*}}$
For boiling under $0.40 \mathrm{~atm}(40.5 \mathrm{kPa})$ pressure, the combined vapour pressure, $p$, must be 40.5 kPa;
hence $x_{\mathrm{A}}=\frac{40.5-18.0}{53.3-18.0}=0.637, x_{\mathrm{B}}=0.373$
The composition of the vapour is given by eqn 6.5

$$
y_{\mathrm{A}}=\frac{x_{\mathrm{A}} p_{\mathrm{A}}^{*}}{p_{\mathrm{B}}^{*}+\left(p_{\mathrm{A}}^{*}-\hat{p}_{\mathrm{B}}^{*}\right) x_{\mathrm{A}}}=\frac{0.637 \times 53.3}{18.0+(53.3-18.0) \times 0.637}=0.839
$$

and $y_{\mathrm{B}}=1-0.839=0.161$
2) The vapour pressure of pure liquid A at 293 K is 68.8 kPa and that of pure liquid $B$ is 82.1 kPa . These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of $A$ in the vapour is 0.612 . Calculate the total pressure of the vapour and the composition of the liquid mixture.
The vapour pressures of components A and B may be expressed in terms of both their composition in the vapour and in the liquid. The pressures are the same whatever the expression; hence the expressions can be set equal to each other and solved for the composition.

$$
\begin{aligned}
& p_{\mathrm{A}}=y_{\mathrm{A}} p=0.612 p=x_{\mathrm{A}} p_{\mathrm{A}}^{*}=x_{\mathrm{A}} \times(68.8 \mathrm{kPa}) \\
& p_{\mathrm{B}}=y_{\mathrm{B}} p=\left(1-y_{\mathrm{A}}\right) p=0.388 p=x_{\mathrm{B}} p_{\mathrm{B}}^{*}=\left(1-x_{\mathrm{A}}\right) \times(82.1 \mathrm{kPa})
\end{aligned}
$$

Therefore, $\frac{y_{\mathrm{A}} p}{y_{\mathrm{B}} p}=\frac{x_{\mathrm{A}} p_{\mathrm{A}}^{*}}{x_{\mathrm{B}} p_{\mathrm{B}}^{*}}$
Hence $\frac{0.612}{0.388}=\frac{68.8 x_{\mathrm{A}}}{82.1\left(1-x_{\mathrm{A}}\right)}$
which solves to $x_{\mathrm{A}}=0.653, x_{\mathrm{B}}=1-x_{\mathrm{A}}=0.347$
and, since $0.612 p=x_{\mathrm{A}} p_{\mathrm{A}}^{*}$
$p=\frac{x_{\mathrm{A}} p_{\mathrm{A}}^{*}}{0.612}=\frac{(0.653) \times(68.8 \mathrm{kPa})}{0.612}=73.4 \mathrm{kPa}$
3) It is found that the boiling point of a binary solution of $A$ and $B$ with $x_{\mathrm{A}}=0.479$ is $88^{\circ} \mathrm{C}$. At this temperature the vapour pressures of pure A and B are 130.1 kPa and 74.9 kPa , respectively. (a) Is this solution ideal? (b) What is the initial composition of the vapour above the solution?
(a) Check to see if Raoult's law holds; if it does the solution is ideal.

$$
\begin{aligned}
p_{\mathrm{A}} & =x_{\mathrm{A}} p_{\mathrm{A}}^{*}=(0.479) \times(130.1 \mathrm{kPa})=62.32 \mathrm{kPa} \\
p_{\mathrm{B}} & =x_{\mathrm{A}} p_{\mathrm{B}}^{*}=(0.521) \times(74.9 \mathrm{kPa})=39.0 \mathrm{kPa} \\
p & =p_{\mathrm{A}}+p_{\mathrm{B}}=101.3 \mathrm{kPa}=1 \mathrm{~atm}
\end{aligned}
$$

Since this is the pressure at which boiling occurs, Raoult's law holds and the solution is ideal.
(b) $y_{\mathrm{A}}=\frac{p_{\mathrm{A}}}{p}[6.4]=\frac{62.32 \mathrm{kPa}}{101.3 \mathrm{kPa}}=0.615 \quad y_{\mathrm{B}}=1-y_{\mathrm{A}}=1.000-0.615=0.385$

