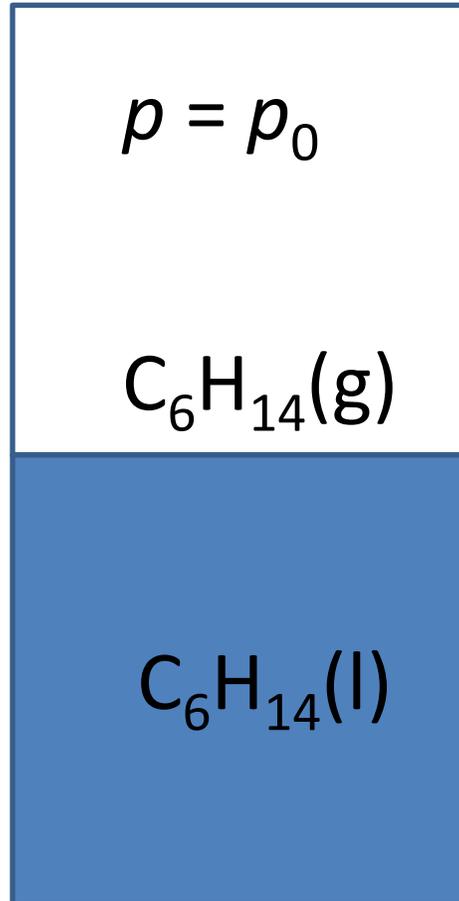


Thermodynamics tutorhour 5

Colligative properties

Elevation of boiling point



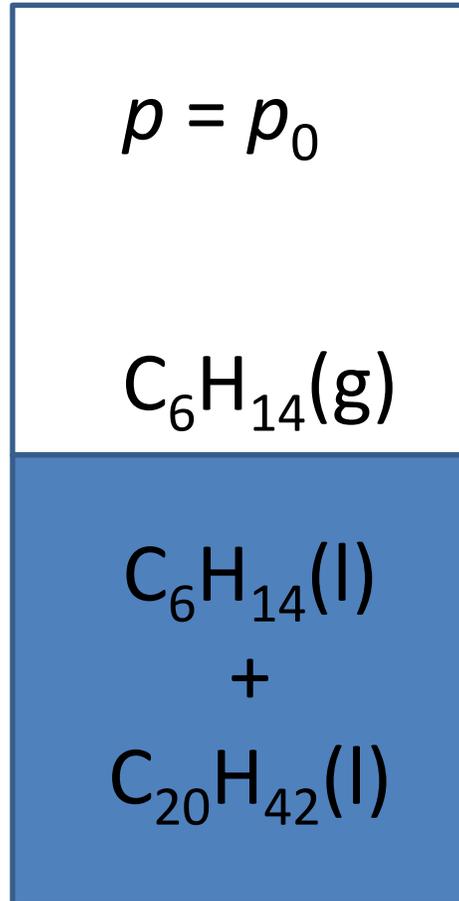
At equilibrium:

$$\mu_{\text{gas}} = \mu_{\text{liq}}$$

At $T = T_{\text{boil}}^*$ (69°C):

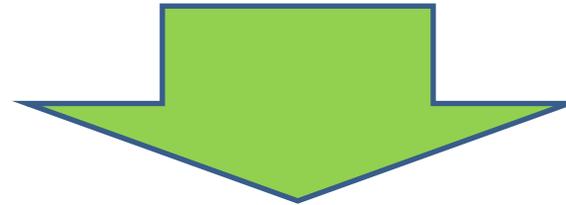
$$\mu_{\text{gas}}^* = \mu_{\text{liq}}^*$$

Elevation of boiling point



At equilibrium:

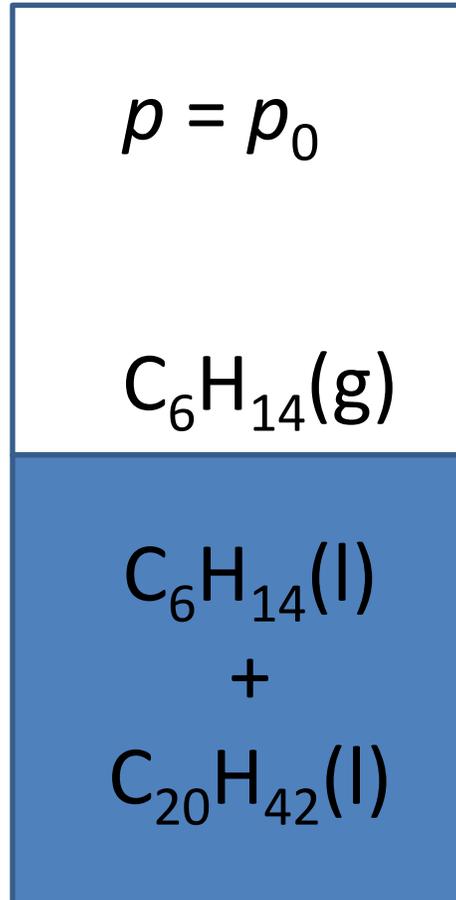
$$\mu_{\text{gas}} = \mu_{\text{liq}}$$
$$\mu_{\text{gas}}^* = \mu_{\text{liq}}^* + \text{correction for dissolving}$$



$$\Delta T = \left(\frac{RT_{\text{boil}}^{*2}}{\Delta_{\text{vap}} H} \right) x_B$$

$p = p_0$, ideal dilute solution (low concentration)

Elevation of boiling point



$$\Delta T = \left(\frac{RT_{boil}^{*2}}{\Delta_{vap}H} \right) x_B$$

ΔT : elevation of boiling point

T_{boil}^* : boiling point of pure **hexane**

$\Delta_{vap}H$: enthalpy of vaporization of **hexane**

x_B : mole fraction of **eicosane**

$$x_B = \frac{\# \text{ mol eicosane}}{\# \text{ mol hexane} + \# \text{ mol eicosane}}$$

$p = p_0$, ideal dilute solution

The depression of freezing point

$$\Delta T = \left(\frac{RT_{fus}^{*2}}{\Delta_{fus}H} \right) x_B$$

ΔT : depression of freezing point

T_{fus}^* : freezing point of the pure **solvent**

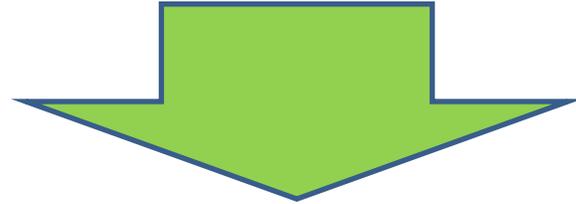
$\Delta_{fus}H$: enthalpy of fusion of the **solvent**

x_B : mole fraction of the dissolved **solute**

$p = p_0$, ideal dilute solution

Boiling point **elevation** and freezing point **depression**

$$\Delta T = \left(\frac{RT_{boil}^{*2}}{\Delta_{vap}H} \right) x_B \quad \Delta T = \left(\frac{RT_{fus}^{*2}}{\Delta_{fus}H} \right) x_B$$



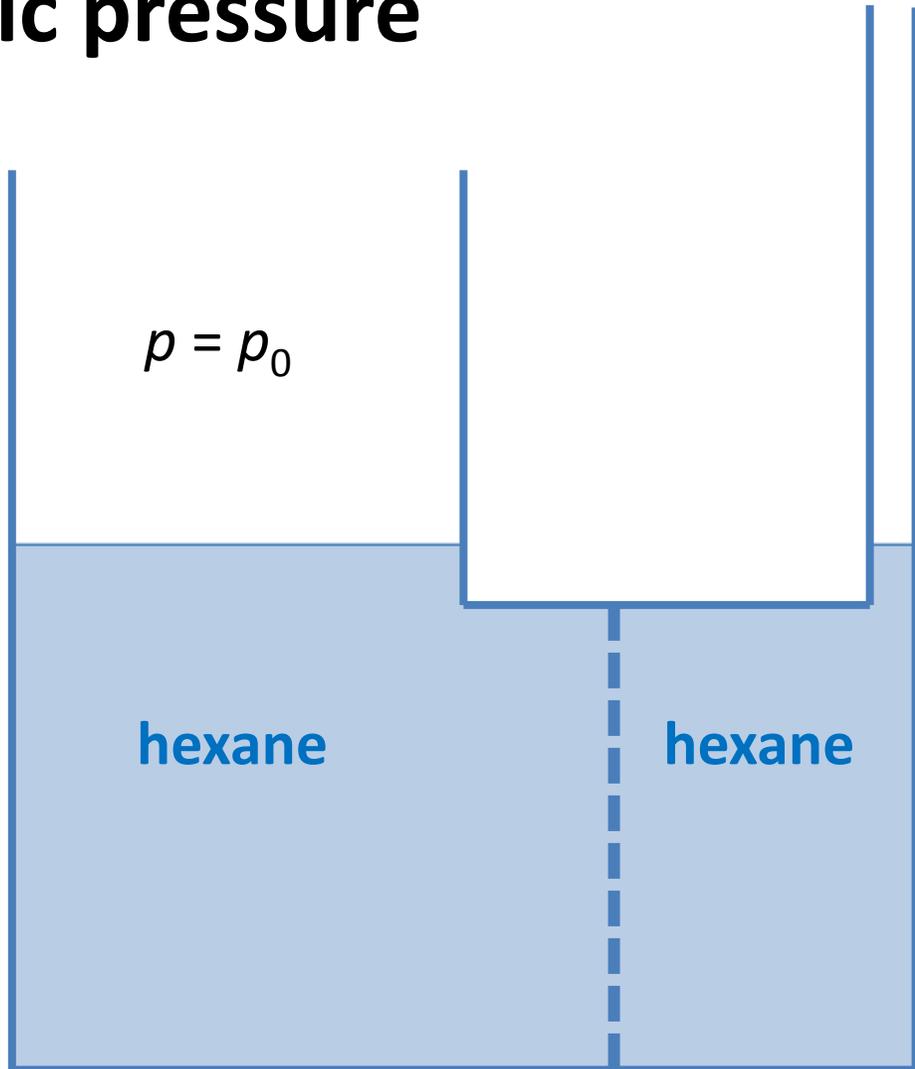
$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{trs}H} \right) x_B$$

See also the
checklist of
key equations

trs = transition

$p = p_0$, ideal dilute solution

Osmotic pressure

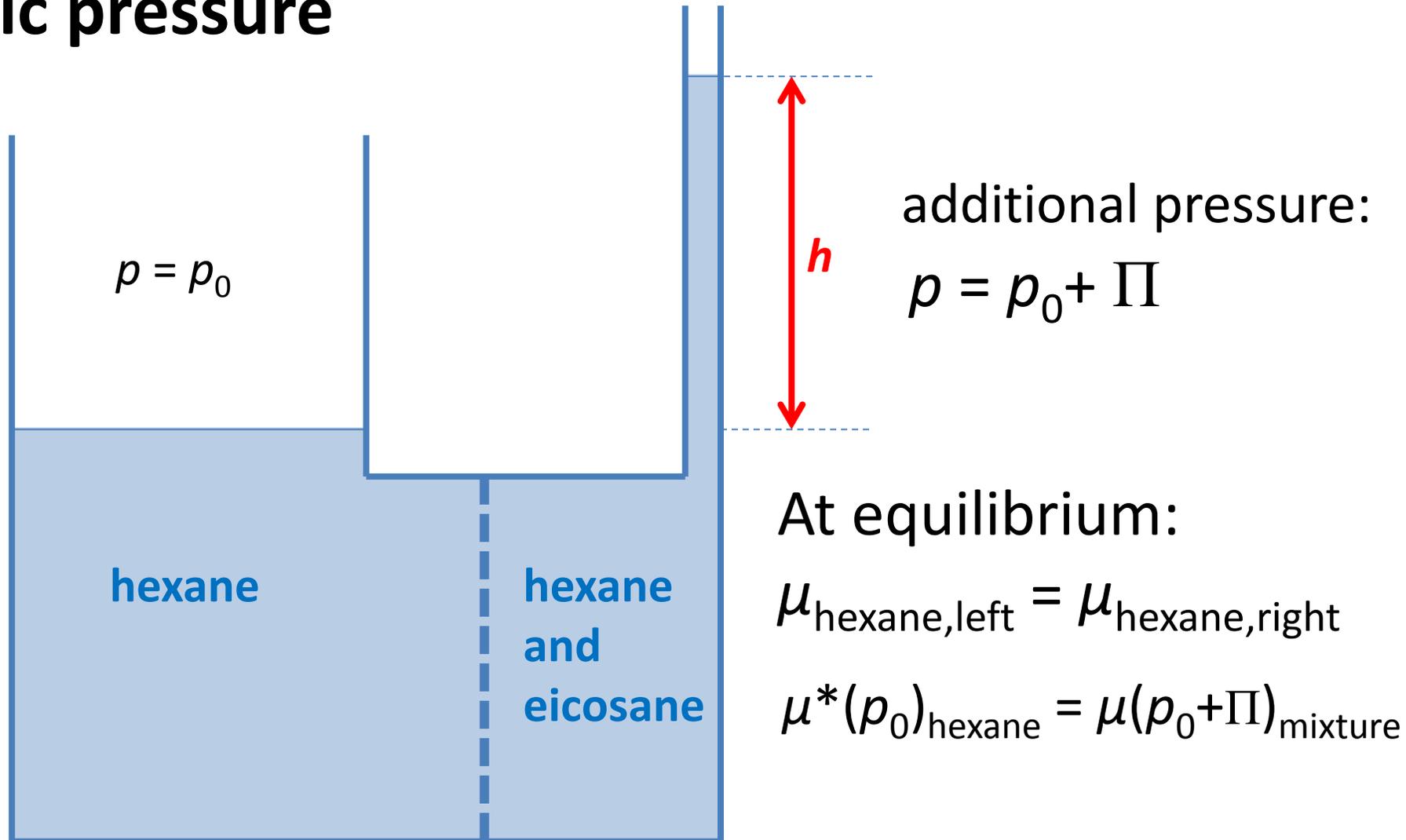


At equilibrium:

$$\mu_{\text{hexane, left}} = \mu_{\text{hexane, right}}$$

$$\mu^*_{\text{hexane}} = \mu^*_{\text{hexane}}$$

Osmotic pressure

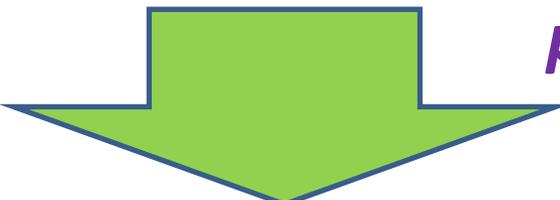


$$\mu^*(p_0)_{\text{hexane}} = \mu^*(p_0)_{\text{hexane}} + \text{correction for dissolving} + \text{additional pressure}$$

Osmotic pressure

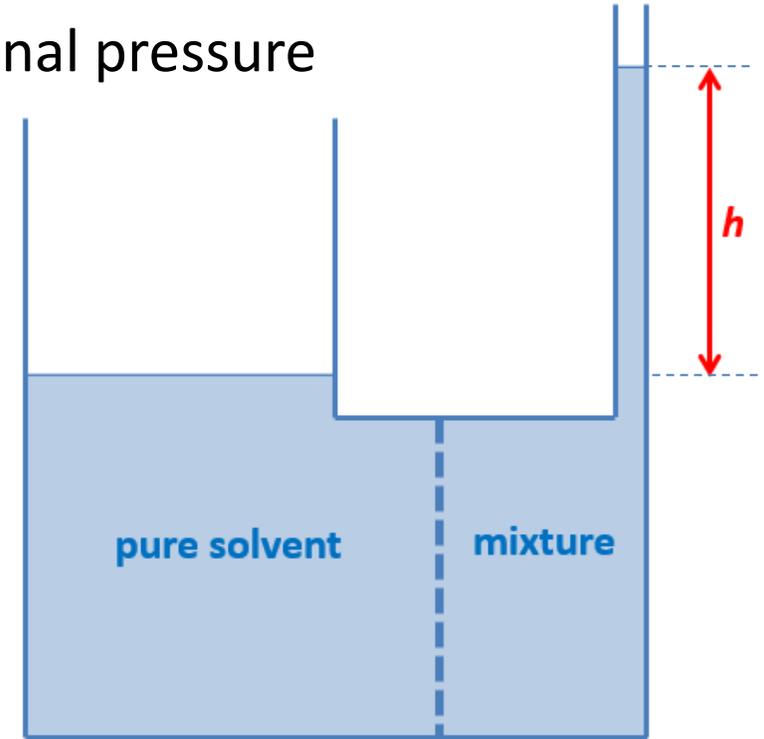
$$\mu^*(p_0)_{\text{hexane}} = \mu^*(p_0)_{\text{hexane}} + \text{correction for dissolving} + \text{additional pressure}$$

$p = p_0$, ideal dilute solution



$$\Pi = [B]RT = \frac{n_B}{V}RT$$

Note: [B] in mol/m³



Osmotic pressure can also be expressed as a function of height h :

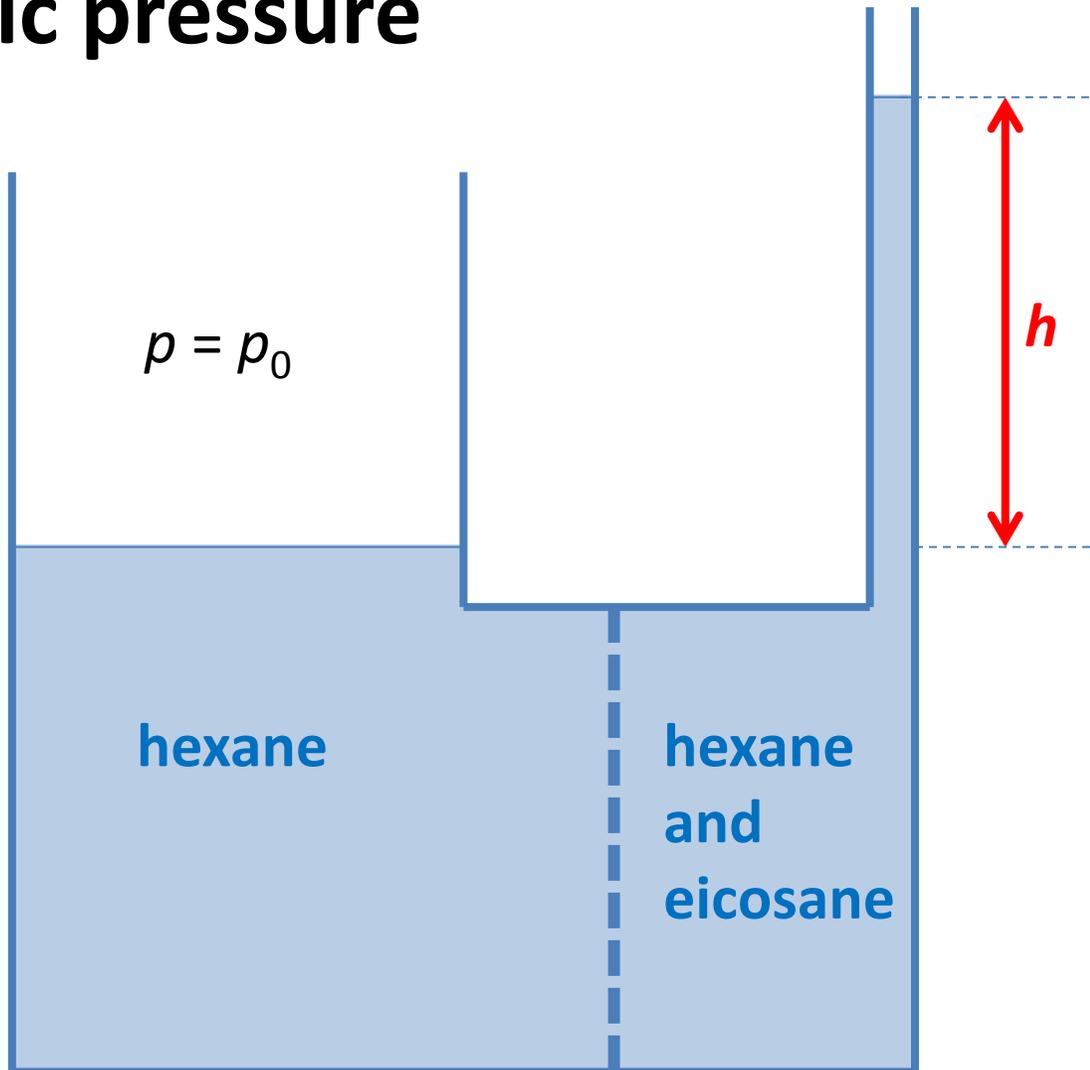
pressure: $p = F_z / A$

weight: $F_z = m \cdot g$

mass: $m = \rho \cdot V$

pressure: $p = F_z / A =$

Osmotic pressure



$$\Pi = \rho \cdot g \cdot h$$

At very low concentration:

$$\rho = \rho_{\text{solution}} \approx \rho_{\text{solvent}}$$

so in approximation:

$$\Pi = \rho_{\text{solvent}} \cdot g \cdot h$$

and earlier we saw:
$$\Pi = [B]RT = \frac{n_B}{V}RT$$

Answers:

Question 1

$$\begin{aligned} \text{a) } \Delta T &= \left(\frac{RT_{trs}^*2}{\Delta_{trs}H} \right) x_B \quad \text{and} \quad x_B = (\# \text{mole Ag}^+ + \# \text{mole Cl}^-) / (\# \text{mole H}_2\text{O} + \# \text{mole Ag}^+ + \# \text{mole Cl}^-) \\ &= (1.31 \cdot 10^{-5} \cdot 2) / (997/18.015 + 1.31 \cdot 10^{-5} \cdot 2) = 4.73 \cdot 10^{-7} \end{aligned}$$

$$\Delta T = (8.3145 \cdot 273.15^2 / 6.008 \cdot 10^3) \cdot 4.73 \cdot 10^{-7} = 4.89 \times 10^{-5} \text{ K}$$

the approximation: $x_B \approx (\# \text{mole Ag}^+ + \# \text{mole Cl}^-) / (\# \text{mole H}_2\text{O})$ also gives $\Delta T = 4.89 \times 10^{-5} \text{ K}$ as an answer

$$\begin{aligned} \text{b) } x_B &= \Delta T \left(\frac{\Delta_{trs}H}{RT_{trs}^*2} \right) \\ &= 1.00 \cdot (6.008 \cdot 10^3 / 8.3145 \cdot 273.15^2) = 9.68 \cdot 10^{-3} \end{aligned}$$

$$x_B = \# \text{mole DMSO} / (\# \text{mole H}_2\text{O} + \# \text{mole DMSO})$$

$$x_B = \# \text{mole DMSO} / (997/18.015 + \# \text{mole DMSO}) \Rightarrow$$

$$x_B (55.34 + \# \text{mole DMSO}) = \# \text{mole DMSO} \Rightarrow \# \text{mole DMSO} = 0.536 / (1 - x_B)$$

$$\# \text{mole DMSO} = 0.536 / (1 - 9.68 \cdot 10^{-3}) = 0.541$$

$$m_{\text{DMSO}} = 0.541 \cdot 78.13 = 42.3 \text{ g}$$

the approximation: $x_B \approx \# \text{mole DMSO} / \# \text{mole H}_2\text{O}$ gives $m_{\text{DMSO}} = 41.9 \text{ g}$ as an answer

Question 2

$$\Pi = \rho gh = [B]RT \quad \text{approximation: } \rho_{\text{solute}} \approx \rho_{\text{water}}$$

$$[B] = \rho gh / (RT) = 0.997 \cdot 10^3 \cdot 9.81 \cdot 5.746 \cdot 10^{-2} / (8.3145 \cdot 293) = 0.2307 \text{ mol/m}^3 \\ = 0.2307 \text{ } \mu\text{mol/cm}^3 = 0.2307 \cdot 10^{-6} \text{ mol/cm}^3$$

$$M_{\text{enzyme}} = m_{\text{enzyme}} / n_{\text{enzyme}} = 3.221 \cdot 10^{-3} \text{ g} / 0.2307 \cdot 10^{-6} \text{ mol} = 13.96 \times 10^3 \text{ g/mole}$$

Question 3

$$x_B = \Delta T \left(\frac{\Delta_{\text{trs}} H}{RT_{\text{trs}}^2} \right) = 0.780 \cdot (18.80 \cdot 10^3 / 8.3145 \cdot 354^2) = 1.407 \cdot 10^{-2}$$

$$x_B = \text{\#mole solute} / (\text{\#mole solute} + \text{\#mole solvent})$$

$$\text{\#mole solvent} = m_{\text{solvent}} / M_{\text{solvent}} = 250 / 128.18 = 1.95$$

$$x_B = \text{\#mole solute} / (\text{\#mole solute} + 1.95) \quad \Rightarrow$$

$$1.407 \cdot 10^{-2} (\text{\#mole solute} + 1.95) = \text{\#mole solute} \quad \Rightarrow$$

$$\text{\#mole solute} = 0.02745 / (1 - 1.407 \cdot 10^{-2}) = 0.02784$$

$$M_{\text{solute}} = m_{\text{solute}} / n_{\text{solute}} = 5.00 / 0.02784 = 179.6 = 180 \text{ g/mole}$$

the approximation: $x_B \approx \text{\#mole solute} / \text{\#mole solvent}$ gives $M_{\text{solute}} = 182 \text{ g/mole}$ as an answer