

1, 2, 3, 4: please see the lecture note

$$5. \Delta S = nR \ln \frac{V_{\text{final}}}{V_{\text{initial}}} = nR \ln \frac{1}{4} = 1 \text{ mol} \cdot 8.314 \text{ (J/mol}\cdot\text{K)} \cdot \ln \frac{1}{4} \\ = -11.53 \text{ J/K}$$

$\Delta S < 0$, It's not a spontaneous process.

$$6. \Delta G^\circ = -RT \ln \frac{C_B}{C_A} = -8.314 \text{ (J/mol}\cdot\text{K)} \times (273+20) \text{ K} \times \ln \frac{7.2}{1} = -4.81 \times 10^3 \text{ (K}\cdot\text{mol}^{-1})$$

7. see lecture notes

8.

(a) Ethane, which has no dipole moment and no acid-base properties, can only have London force interaction between each other, thus resulting a low bp.

However, acetic acid does have both a dipole moment and acid properties.

This gives it the ability to have London force, induction interactions, dipole-dipole interactions, and hydrogen bonding (acid-base interaction) with itself.

Taken together, these interactions give acetic acid a higher bp than that of ethane.

$$(b). \Delta H_m = \bar{V}_i (\delta_1 - \delta_2)^2, \quad \Delta H_m: \text{change in enthalpy due to mixing} \\ \bar{V}_i: \text{molar volume of solute} \\ \delta_1 \text{ and } \delta_2: \text{Hildebrand Solubility parameters.}$$

This means that the energy due to the change in enthalpy is unfavorable. However, ΔH_m approaches 0 (i.e. becomes less disfavored) as δ_1 and δ_2 become closer in value. This is the mathematical basis of the saying "Like dissolves Like".

9.

$$\bar{V}_i = \frac{m.w}{\text{density}}, \quad (\alpha_i)_V = \left[\frac{3\pi N}{4} \right] \left[\frac{n^2 - 1}{n^2 + 2} \right]$$

$$\bar{E}_L = C_L \bar{V}_i (\alpha_i)_V \cdot (\alpha_j)_V, \quad C_L = \text{Dispersion constant (uniform for most compounds)}$$

(a)

Compound	\bar{V}_i (ml/mol)	$(\alpha_i)_V$	\bar{E}_L / C_L
ethane	52.57	3.54×10^{22}	6.6×10^{46}
propane	75.36	2.57×10^{22}	4.98×10^{48}
butane	96.67	2.92×10^{23}	8.22×10^{48}
Pentane	115.22	3.11×10^{23}	1.12×10^{49}
hexane	130.52	3.25×10^{23}	1.38×10^{49}
heptane	146.57	3.35×10^{23}	1.64×10^{49}
octane	162.60	3.42×10^{23}	1.9×10^{49}
CCl_4	96.94	3.89×10^{23}	1.47×10^{49}
Br_2	51.24	5.25×10^{23}	1.41×10^{49}
CS_2	60.28	5.06×10^{23}	1.54×10^{49}
H_2O	18.02	2.92×10^{23}	1.54×10^{48}
Methanol	40.49	2.89×10^{23}	3.37×10^{48}
Benzene	89.13	4.18×10^{23}	1.56×10^{49}

(b) : please plot use the data above.

Reason: \bar{E}_L increases with the number of atoms in n-alkanes

(c), (d) Reason: Boiling point of n-alkanes is determined by the \bar{E}_L between them.
The larger \bar{E}_L , the higher Boiling point.

(e)

	Actual Boiling point	estimated from (d) plot.
CCl_4	76.8	76.1
Br_2	58.8	69.7
CS_2	46.2	85.3
H_2O	100.1	-76.0
Methanol	65.0	-54.7
Benzene	80.1	87.0

CCl_4 and Benzene show good agreement, because their polarizability are to those of n-alkane.

H_2O and methanol show poor agreement, because besides London force, hydrogen exist between the molecules between them, these two compounds show higher

For Br_2 and CS_2 , the difference may be due to the change of C_L . Br_2 and CS_2 are quite different than n-alkanes.

10.

$$\ln(X_{i,j}) = - [\bar{V}_i (\delta_i - \delta_j)^2] / RT$$

	δ_j	$ \delta_j - \delta_i $
Water	23.4	11.4
methanol	14.5	2.5
Cyclohexane	8.6	3.8
Carbon tetrachloride	8.2	3.4

Solubility: methanol > carbon tetrachloride > cyclohexane > water.

11. Hint: $\ln(x_i) - [\bar{v}_i (\delta_i - \delta_j)^2] / RT$.

12. $k = \frac{0.15}{1.32 \times 10^3} \approx 87.1$ is approximate to the true value of 82.6.

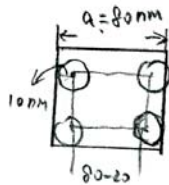
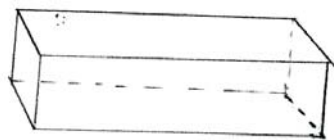
13. $I_h(k) = (-\bar{V}_A / RT) (\delta_{\text{cdq}} - \delta_{\text{tho}}) (\delta_{\text{cdq}} + \delta_{\text{tho}} - 2\delta_A)$

$$= -\left[\left(\frac{165}{1.32} \text{ mL/mol} \right) \left(\frac{1.987 \text{ cal/mol} \cdot \text{K}}{298 \text{ K}} \right) \right] [8.6 - 23.4] (8.6 + 23.4 - 2 \times 14.3) \text{ (cal/mL)}$$

$$= 11.22 \quad \text{unit!}$$

$k = 7.46 \times 10^4$

14.



$$\ln k = -(\Delta \bar{H} - T \Delta \bar{S}^\circ) / RT = \frac{\Delta S^\circ}{R} = \frac{R \ln \frac{V_1}{V_2}}{R} = \ln \frac{V_1}{V_2}$$

$$k = \frac{V_1}{V_2} = \frac{(a-d)^2}{a^2} = \frac{(80-20)^2}{80^2} = 0.75$$

$$C_{i, \text{pore}} = 1 \text{ mM} \times 0.75 = 0.75 \text{ nM}$$

$$V_{\text{pore}} = [(80 \times 10^{-8})^2 \times 20 \times 10^{-5}] \text{ L} = 1.28 \times 10^{-15} \text{ L}$$

$$\mu = C_{i, \text{pore}} \cdot V_{\text{pore}} = 0.75 \times 10^{-9} \text{ M} \times 1.28 \times 10^{-15} \text{ L}$$

$$= 9.6 \times 10^{-25} \text{ mol}$$

Less than one particle! The chance for a particle in the pore is 60%.

14.

$D \downarrow \rightarrow K \uparrow \rightarrow M \uparrow$

15.

$$K = \exp\left[-\frac{sL}{2}\right] = 0.123.$$