CHEM 331

Problem Set #1: Inter-molecular Forces and Vapour Pressure

Hand in all worked solutions in a neat and organized format. Not all questions will be graded.

Due: Friday, Feb 2nd.

1. The water solubility of several organic compounds are provided in the table below.

a) The solubility of straight chain aliphatic hydrocarbons decreases dramatically with chain length. With the information provided, show that there is roughly an inverse linear relationship between the *molar volume* and the logarithm of the aqueous solubility for these compounds.

b) Look up the water solubility's for *n*-nonane, cyclohexane and benzene in Appendix C of your text (Schwarzenbach, 2nd Ed) and fill in the missing information below. Is their solubility predicted by the relationship established in part a (above). Explain.

Substance	Molecular formula	C_w^{sat} (μM)	Density (g/mL) at 25°C
n-pentane	C_5H_{12}	560	0.626
n-hexane	C_6H_{14}	150	0.659
n-heptane	C_7H_{16}	30	0.684
n-octane	C_8H_{18}	6.3	0.70
n-nonane	C_9H_{20}	?	?
benzene	C_6H_6	?	?
cyclohexane	C_6H_{12}	?	?

Solution:

a) Using the molar mass and density of the liquids to estimate the molar volume, we can summarize the data given below.

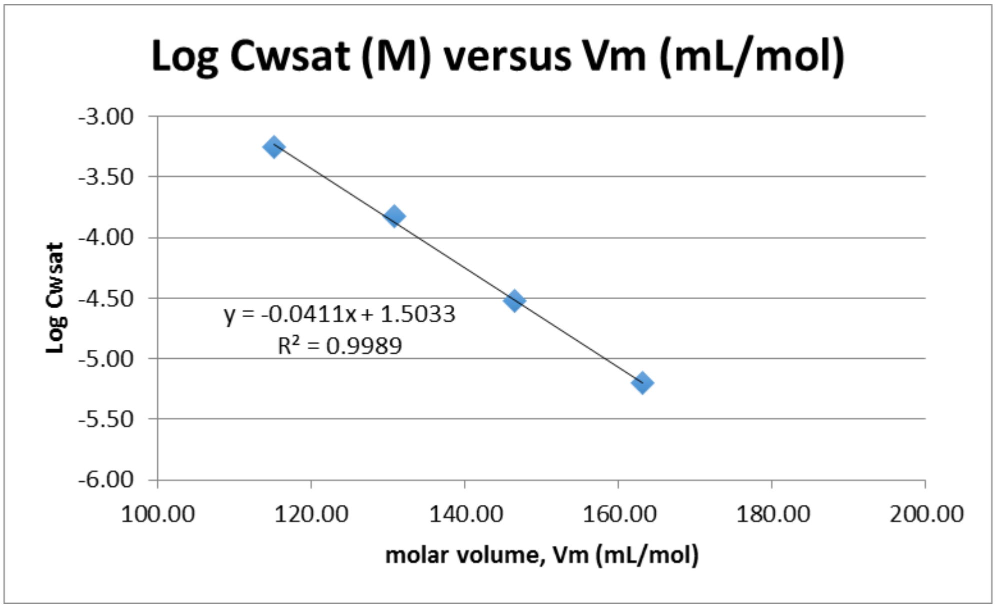
	MW (g/mol)	density (g/mL)	Vm (mL/mol)	Cwsat (uM)	log Cwsat
pentane	72.15	0.626	115.26	560	-3.25
hexane	86.18	0.659	130.77	150	-3.82
heptane	100.21	0.684	146.51	30	-4.52
octane	114.22	0.70	163.17	6.3	-5.20
Nonane*	128.3	0.72	178.19	1.7	-5.77
Cyclohexane*	84.16	0.778	108.17	676	-3.17
Benzene*	78.11	0.874	89.37	22,000	-1.66

* from Appendix C (p. 1198)

Plotting log C_w^{sat} versus molar volume for the series pentane through octane yields a straight line in the form;

log C_w^{sat} = -0.0411 log V_m + 1.503

with an $R^2 = 0.9989$ (see below)



b) Using this one parameter linear free energy relationship to predict the concentration of nonane, cyclohexane and benzene as follows,

Log C_w^{sat} (nonane) = -0.0411 (178.19) + 1.503 = -5.821 ➔ so, C_w^{sat} = 1.51 uM
Log C_w^{sat} (cyclohexane) = -0.0411 (108.17) + 1.503 = -2.943 ➔ so, C_w^{sat} = 1140 uM
Log C_w^{sat} (benzene) = -0.0411 (89.37) + 1.503 = -2.170 ➔ so, C_w^{sat} = 6760 uM

Comparing these numbers to the experimental values from Schwarzenbach (Appendix C), we see that this trend line works well for nonane, but not so well for cyclohexane and benzene. For cyclohexane this approach under predicts the water solubility by roughly a factor of two, probably as a result of the fact branched alkanes tend to have a smaller molar volume than that predicted by MW/ρ. The water solubility of benzene is under predicted by more than a factor of three times based on the trend established by aliphatic straight chain hydrocarbons. It is not structurally similar and will participate in additional solute:solvent intermolecular interactions, due mainly to it's increased polarizability resulting from the electrons in the π bonds.

2. The following compounds are listed in order of increasing refractive index as reported in Table 3.1 of your text (Schwarzenbach, 2nd Ed).

a) Classify each compound as *apolar*, *monopolar* or *bipolar* according to Schwarzenbach.

b) Rationalize the increase in refractive index in terms of molecular features that effect the *polarizability* of each compound.

c) How is the refractive index related to the polarizability and the magnitude of the dispersive free energy between a solute molecule '*i*' in a solvent molecule '1'.

d) Predict the order of increasing vapour pressures of these compounds at 25°C?

Substance	Molecular formula	n_D	BP (°C)	ΔH_{vap} (kJ/mol)
methanol	$\mathbf{CH_3OH}$	1.326	65	35
2-propanone	$\mathbf{CH_3(CO)CH_3}$	1.342	56	31
ethanol	$\mathbf{CH_3CH_2OH}$	1.359	78	39
n-hexane	$\mathbf{CH_3(CH_2)_4CH_3}$	1.372	69	29
1-octanol	$\mathbf{CH_3(CH_2)_6CH_2OH}$	1.427	195	70
1,2-ethandiol	$\mathbf{HOCH_2CH_2OH}$	1.429	197	66

Solution:

a) According to Schwarzenbach,

apolar: n-hexane
monopolar: 2-propanone
bipolar: methanol, ethanol, 1-octanol and 1,2-ethandiol

b) The refractive index of a molecular is related to it's polarizability which scales roughly with the size of the of molecule or more precisely it's corresponding electron cloud. All else being equal, the refractive index is expected to increase with the size of the molecule. In addition, other structural features that add to the polarizability of a molecule include lone pair electrons and electrons in pi bonds. The molecules in the Table are listed in order of increasing refractive index. Methanol is the smallest of these and hence has the smallest n_D, despite having two lone pairs of electrons on the oxygen. 2-propanone and ethanol are slightly larger in size and has a slightly higher n_D . Hexane does not have any lone pairs or pi bonds, is larger than methanol, 2-propanone and ethanol. 1-octanol is larger still and has the lone pair electrons associated with OH group and 1,2-ethandiol despite being smaller in size has two OH groups with their associated lone electrons.

c) The polarizability of a molecule is related to its ability to respond to electric fields through a distortion in its electron cloud. These temporary distortions are referred to as induced dipoles and occur on a femtosecond time scale. Since electromagnetic radiation (light) has an oscillating electric fields on a similar time scale, the refractive index of a molecule is a measure of its polarizability.

$$n_D = \frac{c}{v}$$

where c is speed of light in a vacuum and v is the speed of light in some medium (ie pure liquid phase of solute). D indicates that the wavelength is 589 nm (the ‘sodium D-line’).

The dispersive free energy term between a molecule ‘*i*’ and solvent ‘1’ can be expressed as,

$$\Delta G \approx -C(TSA_i)\left[\frac{n^2{}_{Di}-1}{n^2{}_{Di}+2}\right]\left[\frac{n^2{}_{D1}-1}{n^2{}_{D1}+2}\right]$$

where C is a constant, TSA_i is the total surface area of the solute.

d) The vapour pressure of a series of compounds at the same temperature will increase with the strength of the intermolecular interactions in the pure liquid state. The process can be written out as follows,

$$X_{(l)} \quad ==== \quad X_{(g)}$$

The vapour pressures will scale roughly with boiling points, with higher boiling compounds having lower vapour pressures. However, the enthalpy of vaporization is a direct measure of the temperature sensitivity of the vapourization process and will scale directly with vapour pressure.

$$\ln P^o = \frac{-\Delta H_{vap}}{T} + C$$

Hence, the vapour pressures will increase as follows;

1-octanol < 1,2-ethandiol < ethanol < methanol < 2-propanone < n-hexane

3. a) Referring to Figure 3.6 in your text (Schwarzenbach, 2nd Ed), explain why ln K_{iah} is inversely related to the dispersive vdW parameter for all compounds whereas ln K_{iaw} is positively correlated to the dispersive vdW parameter and only within a homologous series of structurally related compounds.

b) Referring to Table 3.6 in your text (Schwarzenbach, 2nd Ed), several one-parameter linear free energy relationships (LFERs) are given for predicting equilibrium partition constants. Why are these LFERs always based on logarithmic functions of equilibrium constants and what are the advantages and limitations of using these type of LFERs?

Solution:

a) K_{ah} is a partition constant for compound '*i*' in equilibrium between a hexadecane solvent and the gas phase; $i_{(\text{hexadecane})}$ ==== $i_{(\text{air})}$

$$K_{ah} = \frac{C_{air}}{C_{hexadecane}}$$

In the gas phase there are effectively no intermolecular forces, whereas in the hexadecane, the solvent:solvent and the solute:solvent interactions are non-specific dispersive vdW forces only for all compounds regardless of the functional groups present on the solute. All compounds show an inverse relationship between ln K_{iah} versus the dispersive vdW energy term. That is, the magnitude of ln K_{ah} decreases as the vdW dispersive parameter increases. Larger molecules will exhibit a smaller K_{ah}, because larger solute molecules will experience a greater solute:solute attractive dispersive force decreasing their vapour pressure and a greater solute:solvent attractive force increasing their solubility in hexadecane.

On the other hand, K_{aw} is a partition constant for compound 'i' in equilibrium between a water solvent and the gas phase; $i_{(\text{water})}$ ==== $i_{(\text{air})}$

$$K_{aw} = \frac{C_{air}}{C_{water}}$$

In water, the solute:solvent interactions include dispersive vdW as well as dipole and H-bonding for cmpds with appropriate functional groups. In this case, linear relationships exist only with structurally related series of cmpds where the intermolecular interactions are similar in nature. Since molecules with a larger vdW dispersion parameter are larger, they are less water soluble due to the greater energy costs associated with cavity formation. Consequently, the magnitude of K_{aw} increases with the vdW dispersive parameter as the solutes become larger.

b) One parameter linear free energy relationships involve log K since there is a fundamental thermodynamic relationship between Log K and ΔG^o (the Gibbs free energy change for a process at reference set of conditions). Table 3.6 lists several simple one-parameter linear free energy relationships that relate one type of partition constant (K_{12}) as a linear function of another type of partition constant (K_{34}). For example,

$$\log K_{12} = a \log K_{34} + b$$

or

$$\log K_{ow} = m \log k' + c$$

Since $\log K = \Delta G^o/2.3RT$, any linear relationship involving log K can be thought of as a LFER.

In general, these types of LFERs work best for a series of structurally related compounds when considering two similar systems (e.g., organic phase 1/water systems and organic phase 2/water).

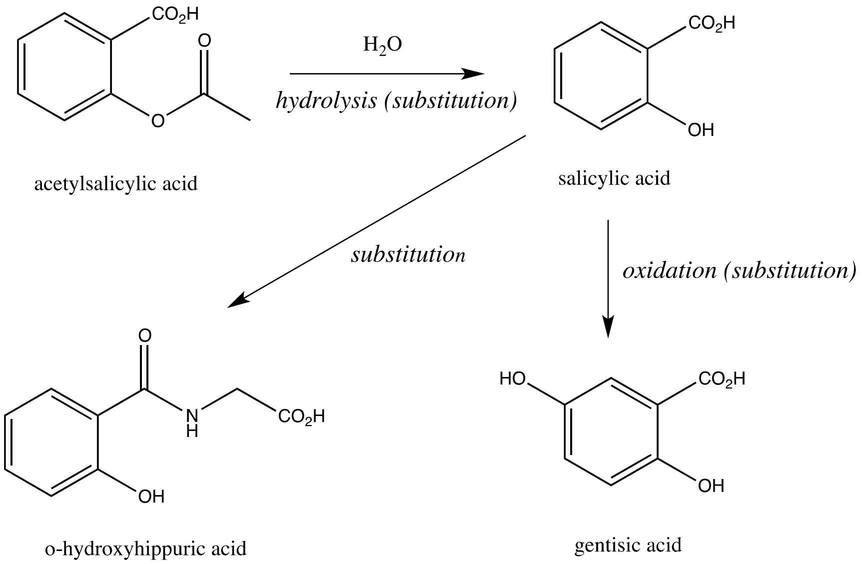
Advantages include a useful predictive tool when experimental results are difficult to obtain. They may also be useful in revealing special or unusual behaviour for specific compounds (e.g., intra-molecular interactions) by identifying ‘outliers’. Finally, when considering poorly defined phase systems (e.g., NOM/water, aerosol/air), the slope of the LFER can yield useful insight into these phases.

Disadvantages – these types of LFERs are limited to structurally related series of compounds which exhibit similar types of intermolecular interactions.

See further bottom of pg 89 – 91 (text).

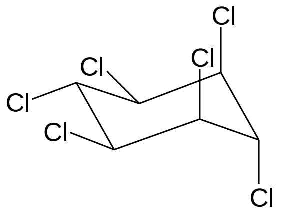
4. In an article by Ternes *et al*. (Environ. Sci. Technol., **2004**, *38*(20), 393A-399A) on the fate and distribution of pharmaceuticals and personal care products (PPCPs) in wastewater treatment facilities, he summarizes the fate of the painkiller acetylsalicylic acid (ASA). Three chemical compounds described as 'metabolites' are identified as salicylic acid, gentisic acid and o-hydroxyhippuric acid. Look up the chemical structures of each of these compounds and propose an overall reaction scheme classifying each reaction as *oxidation*, *reduction*, *addition*, *elimination, substitution, condensation* or *hydrolysis.*

Solution:



Note that all these reactions could be classified as 'substitutions', since in each case one atom (or group of atoms) is being replaced (or substituted) by another. However, a more specific description of the first step is hydrolysis (or an ester) with no net change in oxidation states. The conversion of salicylic acid to gentisic is more specifically referred to as an oxidation, since an H has been replaced by an OH and the oxidation state of the attached carbon has gone from -1 to +1 in the process.

5. One of the most widely used and frequently detected organochlorine pesticides is known commonly as *lindane* (γ-HCH). Using the information provided, estimate the upper limit of the vapour pressure of the *sub-cooled* liquid state at 25°C. Will the vapour pressure of solid *lindane* be higher or lower than that of the *sub-cooled* liquid state? Why?



MW = 291 g mol^{-1}
$C_w^{sat}(L) = 1.9 \times 10^{-4}$ M
T_m = 113 °C
T_b > 250 °C

Solution:

Lindane is a solid at 25 °C (T_m = 113 °C) and the boiling point is not known other than to say it is greater than 250 °C. We can estimate the vapour pressure (in atmospheres) of the sub-cooled liquid state using just the T_b as follows;

$$\ln P^o(L) \approx 19 \left(1-{}^{T_b}\!/_{T}\right) + 8.5 \left(\ln {}^{T_b}\!/_{T}\right)[\text{atm}]$$

using the T_b = 250 °C (523 K) as a lower limit on the boiling point, we have

$$\ln P^o(L) \approx 19 \left(1-{}^{523}\!/_{298}\right) + 8.5 \left(\ln {}^{523}\!/_{298}\right) = -14.34 + 4.78 = -9.56$$

Hence, $P^o(L) \sim e^{-9.56} = 7.1 \times 10^{-5}$ atm (or 7.1 Pa)

Since T_b > 523 K, the vapour pressure of the sub-cooled liquid state of lindane would actually be lower than this estimate, so the numbers above represent an upper limit.

Furthermore, lindane is a solid at 25 °C and the vapour pressure of a solid is always lower than that of the corresponding liquid, due to the additional energy costs associated with melting.

$$X(s) \overset{\text{DHmelt}}{\rightleftharpoons} X(l) \overset{\text{DHvap}}{\rightleftharpoons} X(g)$$

$$X(s) \rightleftharpoons X(g)$$

$$\text{DHsub} = \text{DHmelt} + \text{DHvap}$$

6. Pure 1,4-dichlorobenzene (DCB) is still used as a disinfectant and ‘air-refresher’ in some public urinals. You want to calculate the concentration of DCB in g per m^3 of air at 25 ^oC.

a) Estimate using only melting point (T_m = 53.0 ^oC) and boiling point (T_b = 173.9 ^oC) data.

b) Refine your answer using the vapour pressure data given below.

T (^oC)	29.1 s	44.4 s	54.8	84.8	108.4	150.2
P^o (mm Hg)	1	4	10	40	100	400

Solution:

a) Since T_m = 326.2 K and T_b = 447.1 K, DCB is a SOLID at 298 K (or 25 ^oC). We will need the vapour pressure of the solid, $P^o(s)$ at 298 K to solve this problem.

We can use the boiling point to estimate $P^o(L)$ from;

$$\ln P^o(L)\ (\text{atm}) \cong 19\left(1 - \frac{T_b}{T}\right) + 8.5\ln\left(\frac{T_b}{T}\right)$$

and then the melting point to estimate $P^o(s)$ from;

$$\ln\left(\frac{P^o(s)}{P^o(L)}\right) \cong 6.8\left(\frac{T_m}{T} - 1\right)$$

Therefore ln $P^o(L)$ = -9.506 + 3.448 = -6.058
and
$P^o(L) = e^{-6.058} = 2.338 \times 10^{-3}$ atm

and

ln {$P^o(s)/P^o(L)$} = 6.8 {(326.2/298.2)-1} = -0.6435

So, $P^o(s) = P^o(L) \times e^{-0.6435} = 1.228 \times 10^{-3}$ atm

The concentration in the gas phase in mol/L is given by;

$$\left(\frac{P^o(s)}{RT}\right) = \frac{1.228\text{x}10^{-3}\ \text{atm}}{(0.08206\ \text{L atm mol}^{-1}\text{K}^{-1})(298\ \text{K})} = 5.024 \times 10^{-5}\text{mol/L}$$

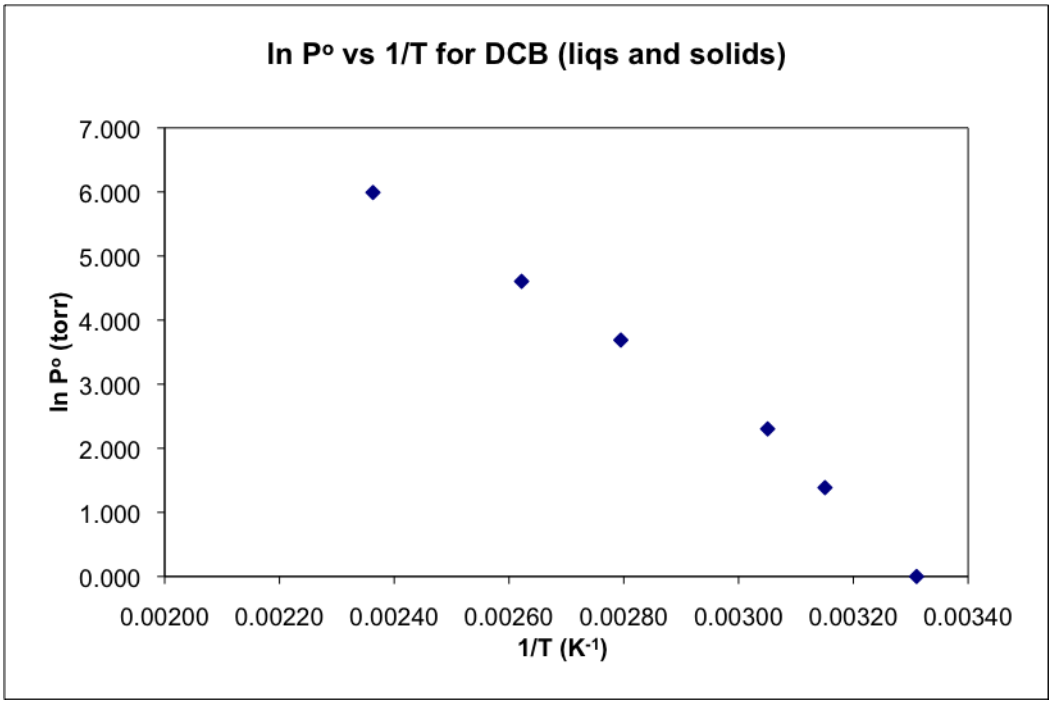
Converting this to g/m^3 yields;

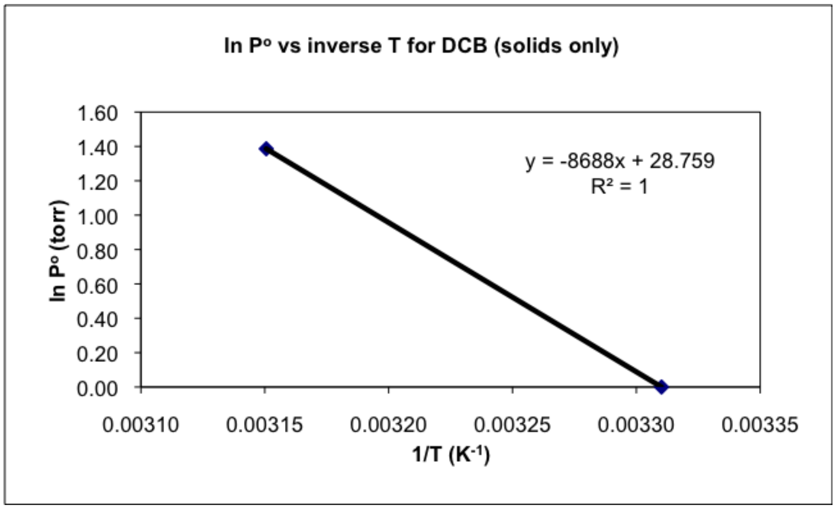
5.024×10^{-5} mol/L x 146.9 g/mol x 10^3 L/m^3 = 7.38 g/m^3

b) Using the data provided, plot *ln* P° versus inverse Temperature. The slope is equal to $-\Delta H_{vap}/R$ over temperatures where the DCB is a liquid and $-\Delta H_{sub}/R$ over temperatures for which it is a solid.

Data and Plots for Question 8

T(°C)	1/T (K^{-1})	P° (torr)	ln P°
29.1	0.00331	1	0.000
44.4	0.00315	4	1.386
54.8	0.00305	10	2.303
84.8	0.00279	40	3.689
108.4	0.00262	100	4.605
150.2	0.00236	400	5.991





Slope = $-\Delta H_{sub}/R = -8688\ K^{-1}$
(or $\Delta H_{sub} = 72232$ J/mol)

Since,

$$\ln\left(\frac{P_2^o}{P_1^o}\right) = \frac{-\Delta H_{sub}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

we can write;

$$\ln\left(\frac{P_2^o}{1\ \text{torr}}\right) = -8688 K^{-1}\left(\frac{1}{298.2} - \frac{1}{302.3}\right)$$

and therefore;

$P^o_2 = (e^{-0.4147})$ (1 torr) = 0.661 torr

Converting this to g/m^3 yields;

0.661 torr x 1 atm/760 torr x {1/(0.08206 L atm mol^{-1} K^{-1})(298.2 K)} x 146.9 g/mol x 10^3 L/m^3 = 5.22 g/m^3

7. The vapour pressure of 1,1,1,2-tetrafluoroethane (HFC-134a) is 132.9 kPa at -20°C and 292.9 kPa at 10°C. Estimate the normal boiling point of HFC-134a.

Solution:

Recall that

$$\ln P^{o} = \frac{-\Delta H_{vap}}{RT} + \text{Constant}$$

and therefore, at any two temperatures the vapour pressure ratio can be written as;

$$\ln\left(\frac{P^{o}_{2}}{P^{o}_{1}}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_{2}} - \frac{1}{T_{1}}\right)$$

where P^{o}_{1} = 132.9 kPa at T_1 = 253.2 K and P^{o}_{2} = 292.9 kPa at T_2 = 283.2 K

Therefore, we can write;

$$\Delta H_{vap} = \frac{-\ln\left(\frac{P^{o}_{2}}{P^{o}_{1}}\right)R}{\left(\frac{1}{T_{2}} - \frac{1}{T_{1}}\right)} = \frac{-(0.7902)(8.314 \text{ J mol}^{-1}\text{K}^{-1})}{(-4.1837\text{x}10^{-4}\ \text{K}^{-1})} = 15,700 \text{ J/mol}$$

The normal boiling point is the temperature at which P^{o} = 1.00 atm (or 101,300 kPa).

So, we can write;

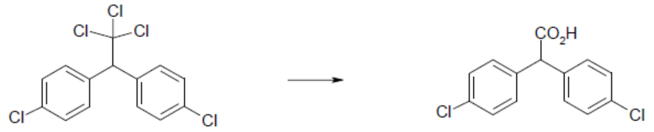
$$\ln\left(\frac{101.3 \text{ kPa}}{132.9 \text{ kPa}}\right) = \frac{-15,700 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{T_{b}} - \frac{1}{253.2 \text{ K}}\right)\left(\frac{1}{T_{b}} - \frac{1}{253.2 \text{ K}}\right) = 1.4375\text{x}10^{-4}\ \text{K}^{-1}$$

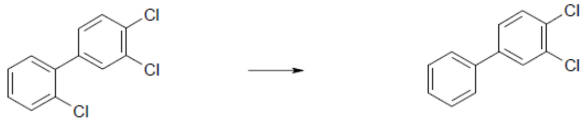
and therefore,

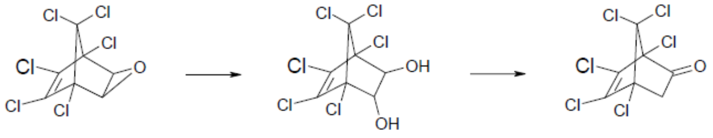
$$\left(\frac{1}{T_{b}} - \frac{1}{253.2 \text{ K}}\right) = 1.4375\text{x}10^{-4}\ \text{K}^{-1}$$

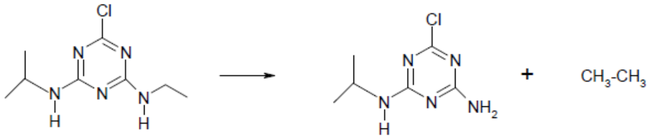
and T_b = 244.3 K or -28.9 ºC

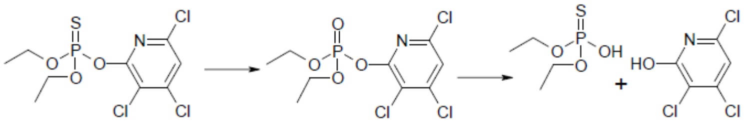
8. For each of the following;
a) identify the functional groups involved
b) the oxidation state changes and the number of moles of electrons transferred
c) if the reaction does not involve an overall change in oxidation state, classify the reaction as one of the following *addition*, *elimination*, *condensation* or *hydrolysis*.











1	oxidation	-2 mols e-
2	hydrolysis	+2 H_2O
3	reduction	+2 mols e-
4	oxidation	-2 mols e-
5	reduction	+6 mols e-
6	hydrolysis/condensation	+H_2O/-H_2O
7	reduction	+2 mols e-
8	hydrolysis/hydrolysis	+H_2O, -H_2S/ +H_2O