CHEM1405 Worksheet 4: Intermolecular Forces and Introduction to Thermodynamics

**Information**

Intermolecular forces are the interactions between rather than inside molecules. They are responsible for many of the physical properties of substances, including their melting and boiling points.

In pure substances, there are 3 important intermolecular forces which may be present:

- **Dipole – dipole forces.** The dipole moment in a molecule will tend to align with those in its neighbours. This type of interaction is only possible if the molecule possesses a dipole.

- **Hydrogen bonds.** This is a particularly strong dipole – dipole interaction involving the interaction between the $\delta^+ \text{H}$ atoms in very polar bonds and lone pairs on very electronegative atoms. Hydrogen bonding therefore requires the presence of both $\delta^+ \text{H}$ atoms and electronegative atoms.

- **Dispersion forces.** These forces are present in all molecules and atoms. At any moment in time, the electron density in a molecule or atom may not be symmetrical and this leads to a dipole moment. This momentary or instantaneous dipole moment induces a matching dipole in neighbouring molecules or atoms by polarizing their electron density.

  Dispersion forces increase with the number of electrons in a molecule.

**Model 1: Boiling Points Change Down a Group of the Periodic Table**

Molecules are held in the liquid phase due to intermolecular forces so that boiling points are a good guide to their strength.

The figure opposite shows the boiling points of the Group 14 hydrides. All have the same shape but differ in the total number of electrons.

For example:

- C has 6 electrons and each H has 1 electron so CH$_4$ has $6 + 4 \times 1 = 10$.
- Sn has 50 electrons so SnH$_4$ has 54 electrons.

**Critical thinking questions**

1. What happens to the boiling point as the number of electrons increases?

2. What shape are the Group 14 hydrides?

3. Are dipole – dipole forces present in these molecules?

4. Is hydrogen bonding possible in these molecules?

5. What intermolecular force is present in these molecules?

6. Explain why the boiling points vary in the way you described in answer to Q1.
Model 2: Boiling Points Change Across a Row of the Periodic Table

On the graph opposite, the boiling points for the other hydrides have been added:

- Group 14 SiH₄, GeH₄ and SnH₄
- Group 15 PH₃, AsH₃ and SbH₃
- Group 16 H₂S, H₂Se and H₂Te
- Group 17 HCl, HBr and HI

Critical thinking questions

1. Use a Periodic Table to confirm that SiH₄, PH₃, H₂S and HCl all have 18 electrons.

2. What happens to the boiling point as the number of electrons increases? Why?

3. What is the molecular shape of PH₃, H₂S and HCl?

4. Do PH₃, H₂S and HCl have dipole moments?

5. Why is the boiling point of SiH₄ lower than that of PH₃, H₂S and HCl?

6. Is the boiling point of SnH₄ (54 electrons) higher or lower than the boiling point of PH₃ (18 electrons)?

7. Explain your answer to Q6, making sure that it is consistent with your answers to Q2 and Q5.

Model 3: Anomalous Boiling Points of NH₃, H₂O and HF

The graph opposite adds the boiling points of CH₄, NH₃, H₂O and HF to Model 3. N, O and F are very electronegative and N-H, O-H and H-F bonds are very polar.

Critical thinking questions

1. How do the boiling points of the Group 14 hydrides change down the group?

Re-read your answers to Model 1.
2. How many δ+ H atoms are there on the most electronegative element in the molecules below?
   (a) NH₃        (b) H₂O        (c) HF

3. How many lone pairs are there on the most electronegative element in these molecules?
   (a) NH₃        (b) H₂O        (c) HF

4. Explain why the boiling points of NH₃, H₂O and HF (10 electrons) are higher than those of PH₃, H₂S and HCl (18 electrons) Refer to the Information if you are unsure.

5. Given your answer to Q4, suggest why the boiling point of NH₃ (10 electrons) is lower than that of SbH₃ (54 electrons).


7. Predict the relative strength of the intermolecular forces between two NH₃ molecules, two H₂O and two HF molecules.

8. How many hydrogen bonds can each NH₃ molecule make on average in NH₃(l)? (Hint: re-read your answers to Q2 and Q3).

9. How many hydrogen bonds can each HF molecule make on average in HF(l)? (Hint: re-read your answers to Q2 and Q3).

10. How many hydrogen bonds can each H₂O molecule make on average in H₂O(l)? (Hint: re-read your answers to Q2 and Q3).

11. Use your answers to Q6 – Q10 to explain why the boiling points vary in the order NH₃ < HF < H₂O.
Model 4: Enthalpy ($\Delta_{\text{rxn}}H$) and Entropy ($\Delta_{\text{rxn}}S$) of Reaction

In Model 3 in week 10, you developed a way of working out the value of enthalpy change for any reaction from the values of the enthalpies of formation of the reactants and products:

$$\Delta_{\text{rxn}}H^\circ = \Delta_fH^\circ (\text{products}) - \Delta_fH^\circ (\text{reactants}) \quad (1)$$

The change in entropy in a reaction can similarly be calculated as the difference in the entropies of the reactants and products:

$$\Delta_{\text{rxn}}S^\circ = S^\circ (\text{products}) - S^\circ (\text{reactants}) \quad (2)$$

Nitrogen dioxide, NO$_2$, is a prominent air pollutant. At low temperatures, it is in equilibrium with its dimer, N$_2$O$_4$. Starting from NO$_2$, the formation of the dimer can be studied using one of the two equations below:

$$2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \quad (A)$$
$$\text{NO}_2(g) \rightleftharpoons \frac{1}{2} \text{N}_2\text{O}_4(g) \quad (B)$$

Starting from the dimer, the formation of NO$_2$ can be studied using one of the two equations below:

$$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \quad (C)$$
$$\frac{1}{2} \text{N}_2\text{O}_4(g) \rightleftharpoons \text{NO}_2(g) \quad (D)$$

**Critical thinking questions**

1. Using the data below, calculate $\Delta_{\text{rxn}}H^\circ$ and $\Delta_{\text{rxn}}S^\circ$ for reaction A.

   $\Delta_fH^\circ$: NO$_2$(g), 33 kJ mol$^{-1}$, N$_2$O$_4$(g) 9 kJ mol$^{-1}$. $S^\circ$: NO$_2$(g), 240 J K$^{-1}$ mol$^{-1}$, N$_2$O$_4$(g) 304 J K$^{-1}$ mol$^{-1}$

2. Explain in words the origin of the sign of $\Delta_{\text{rxn}}H^\circ$ and $\Delta_{\text{rxn}}S^\circ$ in terms of the chemical changes in the reaction.

3. Calculate $\Delta_{\text{rxn}}H^\circ$ and $\Delta_{\text{rxn}}S^\circ$ for reaction B. How are these values related to your answer to Q1?

4. Calculate $\Delta_{\text{rxn}}H^\circ$ and $\Delta_{\text{rxn}}S^\circ$ for reaction C and explain in words the origin of the sign of $\Delta_{\text{rxn}}H^\circ$ and $\Delta_{\text{rxn}}S^\circ$ in terms of the chemical changes in the reaction.

5. What are the values of $\Delta_{\text{rxn}}H^\circ$ and $\Delta_{\text{rxn}}S^\circ$ for reaction D?
Model 5: Free Energy of Reaction ($\Delta_{\text{rxn}} G$)

Reactions can be favoured if the products are more stable than the reactants. This occurs when the **enthalpy decreases**: $\Delta_{\text{rxn}} H < 0$. Reactions can also be favoured if the **entropy increases**: $\Delta_{\text{rxn}} S > 0$. Depending on the reaction, these factors can work together or in opposition. They are combined in the definition of the change in the **free energy**, $\Delta_{\text{rxn}} G$:

$$\Delta_{\text{rxn}} G^\circ = \Delta_{\text{rxn}} H^\circ - T \Delta_{\text{rxn}} S^\circ$$

Because a favourable reaction may have $\Delta_{\text{rxn}} H < 0$ and / or $\Delta_{\text{rxn}} S > 0$, a favourable reaction will have $\Delta_{\text{rxn}} G < 0$.

**Critical thinking questions**

1. Is reaction A in Model 1 favourable or unfavourable with respect to the **enthalpy** factor?
2. Is reaction A in Model 1 favourable or unfavourable with respect to the **entropy** factor?
3. Is reaction C in Model 1 favourable or unfavourable with respect to the **enthalpy** factor?
4. Is reaction C in Model 1 favourable or unfavourable with respect to the **entropy** factor?
5. Given your answers to Q1 – 4 and the equation for $\Delta_{\text{rxn}} G^\circ$ above, what additional factor needs to be considered to predict whether reaction A or C is favourable?
6. Calculate $\Delta_{\text{rxn}} G^\circ$ for reaction A at the two temperatures below and predict whether the reaction is favourable.
   (a) $T = 298$ K
   (b) $T = 398$ K
7. Calculate $\Delta_{\text{rxn}} G^\circ$ for reaction C at the two temperatures below and predict whether the reaction is favourable.
   (a) $T = 298$ K
   (b) $T = 398$ K
8. Using your answer to Q6, predict what happens to an **exothermic** reaction as the temperature is increased.
9. Using your answer to Q7, predict what happens to an **endothermic** reaction as the temperature is increased.
10. What combination of signs for $\Delta_{\text{rxn}} H$ and $\Delta_{\text{rxn}} S$ lead to a reaction that is never favourable?