



Physical Equilibria Unit Activity – “Thinking Like a Chemist” KEY

A major goal for this class is for you to learn the concept of macro/micro thinking or “Thinking Like a Chemist”. Thinking like a chemist is the ability to look at the macroscopic properties of a static substance or a substance undergoing a change and be able to simultaneously account for those properties on a microscopic (molecular) level. This activity will walk you through some of these concepts you likely mastered in CH301. You should work with a couple of neighbors. You will be stopped periodically and we will check in to make sure the entire class is making progress. Since this is student centered learning environment, the check in may take one of many forms: a group of students might be asked to approach the board and write their answers to selected questions on the board, an individual might be asked to give an explanation while still seated speaking into a microphone, we might ask a clicker question to poll the entire class or one of the instructors might provide a mini lecture. The experience will be most beneficial if you fully engage your brain and participate in this process. One or more platinum stars will be on the line.

1. Please state to the best of your ability a macroscopic description of the substances below the chemical names.

Iso-Propanol

Acetone

Both are colorless liquids that are not very viscous. Iso-Propanol evaporates SLOWER than Acetone upon observation.

Given the condensed structural formulae, consider the microscopic properties.

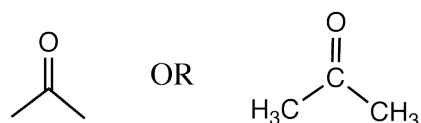
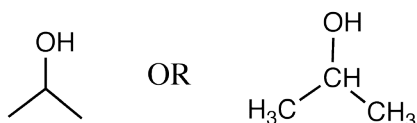
$\text{CH}_3\text{CHOHCH}_3$

CH_3COCH_3

2. Please draw the Lewis structure for each substance.

Iso-Propanol

Acetone



3. State the molecular geometry around each carbon.

All carbons are tetrahedral across the two substances except the central (second) carbon of acetone which is trigonal planar.

4. State if each molecule is polar or nonpolar.

Both molecules are polar.

5. Explain your answers for the polarity question (4).



The central carbon of iso-propanol has a tetrahedral geometry with dissimilar groups attached (CH_3 , CH_3 , H and OH). This lack of symmetry means that the individual dipole moments of the molecular do not cancel completely, leaving an overall NET dipole moment (aka polar).

The central carbon of acetone has a trigonal planar geometry with dissimilar groups attached (CH_3 , CH_3 , O). This lack of symmetry means that the individual dipole moments of the molecular do not cancel completely, leaving an overall NET dipole moment (aka polar).

6. What types of intermolecular forces (IMF) exist for each substance?

Iso-Propanol: London dispersion forces, dipole-dipole and hydrogen-bonding

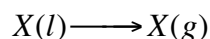
Acetone: London dispersion forces, dipole-dipole

7. Which substance do you think would have the higher boiling point?

We predict that iso-propanol would have the higher boiling point because its intermolecular forces are stronger than those of acetone (hydrogen-bonding is stronger than dipole-dipole and London dispersion forces).

CHECK IN – IF CALLED ON BE PREPARED TO SHARE YOUR ANSWERS WITH THE REST OF THE CLASS

Now we are ready to look at the energy changes associated with a phase change. We will assume that both liquids are at room temperature (298K) and room pressure (1 atm). Consider the process of the phase transition of going from a liquid to a gas (vaporization). Written generically as:



8. In general, which do you think would have the higher enthalpy, a substance in its liquid phase or the gas phase?

A substance in the gas phase generally has a higher enthalpy. The gas particles feel fewer IMFs than liquid particles. The attractive IMFs lower the energy of a substance and therefore the liquid phase has a lower enthalpy than the gas phase.

9. In general, what do you think the sign of the enthalpy of vaporization, $\Delta H^\circ_{\text{vaporization}}$, is for the process?

$$\Delta H^\circ_{\text{vaporization}} = H^\circ_{\text{gas}} - H^\circ_{\text{liquid}}$$

The enthalpy of the gas phase is generally greater than the enthalpy of the liquid. Therefore, we must add energy to break the IMFs between the liquid particles and move them into the gas phase. This is a positive ΔH process, or endothermic.

10. Now comparing the two liquids in question, isopropanol and acetone, do you think that the enthalpy of vaporization, $\Delta H^\circ_{\text{vaporization}}$, for isopropanol will be greater, less than or about the same as acetone? Why?

$\Delta H^\circ_{\text{vaporization}}$ for iso-propanol should be greater than that of acetone because the iso-propanol liquid molecules have greater attractive forces (IMF), which lower the enthalpy of the liquid. We must add more energy to break up these attractive forces between the iso-propanol molecules to move them from liquid into the gas phase than to break up the weaker attractive forces between acetone molecules. The $\Delta H^\circ_{\text{vaporization}}$ would therefore be greater for iso-propanol.

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11. In general, which do you think would have the higher entropy a substance in its liquid phase or the gas phase?

The gas phase of a substance generally has the higher absolute entropy. Particles in the gas phase have more possible microstates (arrangements) than substances in the liquid phase, which are given more structure due to IMFs.

12. In general, what do you think the sign of the entropy of vaporization, $\Delta S^\circ_{\text{vaporization}}$, is for the process?

$$\Delta S^\circ_{\text{vaporization}} = S^\circ_{\text{gas}} - S^\circ_{\text{liquid}}$$

The entropy of the gas phase is greater than the entropy of the liquid. So the change in entropy from liquid to gas is a positive change (+).

13. Now comparing the two liquids in question, isopropanol and acetone do you think that the entropy of vaporization, $\Delta S^\circ_{\text{vaporization}}$, for isopropanol will be greater, less than or about the same as acetone? Why?

$\Delta S^\circ_{\text{vaporization}}$ relates more to the nature of liquids and gasses in general rather than the specific IMFs that govern each substance. So the values for $\Delta S^\circ_{\text{vaporization}}$ for most substances are actually around the same value because the entropy of any gas is overwhelmingly larger than the entropy of any liquid. The $\Delta S^\circ_{\text{vaporization}}$ of iso-propanol and acetone are therefore close in value. Deviations from this may occur with substances containing very high IMFs that lower the entropy of the liquid significantly (the resulting $\Delta S^\circ_{\text{vaporization}}$ would be larger than usual).

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14. What is the equation that relates the change in Gibb's free energy to changes in enthalpy and entropy?

$$\Delta G = \Delta H - T\Delta S$$

15. What does the sign of change in free energy, ΔG° , tell you about a physical change?

The sign of ΔG indicates the spontaneity of a process (whether it will occur under given conditions).

+ ΔG = non-spontaneous (will not occur under the given conditions without added energy)

- ΔG = spontaneous (will occur under the given conditions)

16. How could one affect the sign of change in free energy, ΔG° ?

By changing the temperature (this sometimes works, but some processes are non-spontaneous at all temperatures).

The " $-T\Delta S$ " term can be varied with temperature.

17. What does it mean when $\Delta G^\circ = 0$?

When $\Delta G^\circ = 0$ the products and reactants have the same free energy. Therefore, neither the products nor the reactants side is a more stable state and the process is in **equilibrium**. During phase changes, the two phases are in equilibrium and $\Delta G^\circ = 0$.

18. Thinking back to isopropanol and acetone, is there a temperature at which $\Delta G^\circ_{\text{vaporization}} = 0$? If so, is it the same temperature for both substances or is one higher than the other?

If $\Delta G^\circ_{\text{vaporization}} = \Delta H^\circ_{\text{vaporization}} - T\Delta S^\circ_{\text{vaporization}} = 0$, then $\Delta H^\circ_{\text{vaporization}} = T\Delta S^\circ_{\text{vaporization}}$. This condition would occur at a particular temperature at which:

$$\frac{\Delta H^\circ_{\text{vaporization}}}{\Delta S^\circ_{\text{vaporization}}} = T$$

ΔH° and ΔS° are both positive for the vaporization process and therefore the calculated temperature will also be positive. This result is reasonable because temperature is measured in the Kelvin scale (always positive). So, there is a temperature at which $\Delta G^\circ_{\text{vaporization}} = 0$ and this is the boiling temperature of the substance (temperature of phase change between liquid to gas).

Since $\Delta S^\circ_{\text{vaporization}}$ is about the same for both substances, but $\Delta H^\circ_{\text{vaporization}}$ is higher for iso-propanol. We can predict that the boiling temperature (T_{boiling}) for iso-propanol will be higher.

$$\frac{\Delta H^\circ_{\text{vaporization}} (\text{iso-propanol})}{\Delta S^\circ_{\text{vaporization}}} > \frac{\Delta H^\circ_{\text{vaporization}} (\text{acetone})}{\Delta S^\circ_{\text{vaporization}}}$$



$T_{\text{boiling}}(\text{iso-propanol}) > T_{\text{boiling}}(\text{acetone})$

Such a conclusion can be predicted through the analysis of IMFs from questions #6 and #7 as well.