CH 302 Unit 1 Review 1

CH301 RECAP + CH302 PREVIEW

THERMODYNAMICS, PHASE CHANGES

Three Themes of Equilibrium So Far

- **Phase Changes:** Equilibrium is established when the temperature is equal to T_{trans}
  - Important: IMFs, ΔG, ΔH, ΔS, and T
- **Vapor Pressure:** Equilibrium is established between the vapor condensing into the liquid and the liquid vaporizing in a closed container
  - This is based on the distribution of kinetic energies in a sample
  - When $T = T_b$, VP = 1 atm
  - Important: IMFs, ΔH, and T
- **Stability**

Physical Equilibrium Road Map

The theme of Unit One is the thermodynamics of phase changes and how creating a solution increases the stability of the liquid phase

1. Quantifying phase changes using enthalpy, entropy, and free energy
2. Vapor Pressure: concepts, calculations, and its relationship to boiling and IMFs
3. Phase Diagrams: identifying the most stable phase of a substance at a given temperature and pressure

Foundation

4. Thermodynamics associated with creating a solution
   - Does it dissolve?
   - Temperature dependence of dissolution
5. Colligative Properties: the increased stability of a solution changes the physical properties accordingly
   - Vapor pressure lowering, freezing point depression, boiling point elevation, and osmotic pressure

Hard

Phase Changes

EQUILIBRIUM CALCULATIONS, HEATING CURVES, PHASE DIAGRAMS

Working Thermodynamics Definitions

- **Change in Enthalpy (ΔH, kJ):** Heat flow at constant pressure. We replace q (heat) with ΔH in almost all cases in CH 302.

  ← $-\Delta H$ —

  $s \rightarrow l \rightarrow g$

  $+\Delta H$

- **Entropy (S, J):** A measurement of energy dispersal. A positive ΔS means the products have more available microstates (more dispersed).

  $s \rightarrow l \rightarrow g$

  $+\Delta S$

- **Change in Free Energy (ΔG, kJ):** A measurement of spontaneity. A negative ΔG is a spontaneous reaction. A positive ΔG is a non-spontaneous reaction. **If ΔG = 0, you are at equilibrium.**

  $\Delta G < 0$

Free Energy and Spontaneity

The equation we will use to determine the spontaneity of a reaction is:

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

- This law gives us three conditions for **ΔG_{rxn}**:
  1. $\Delta G < 0$ (negative) ; your reaction is spontaneous ✓
  2. $\Delta G = 0$ (zero) ; your reaction is at equilibrium
  3. $\Delta G > 0$ (positive) ; your reaction is nonspontaneous

Summary: you have a finite energy in the universe. Any reaction that happens spontaneously will lower the amount of "free energy" in the universe (negative ΔG).

What Drives the Phase Change?

ΔH	ΔS	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T

Thermodynamically speaking, the term that **drives** the reaction is the one that is making the ΔG more negative.

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

$$(-) = (+) - T(+)$$

$$(-) = (-) - T(-)$$

Free Energy: All Conditions Summary

ΔH	ΔS	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T

Freezing, condensation, deposition

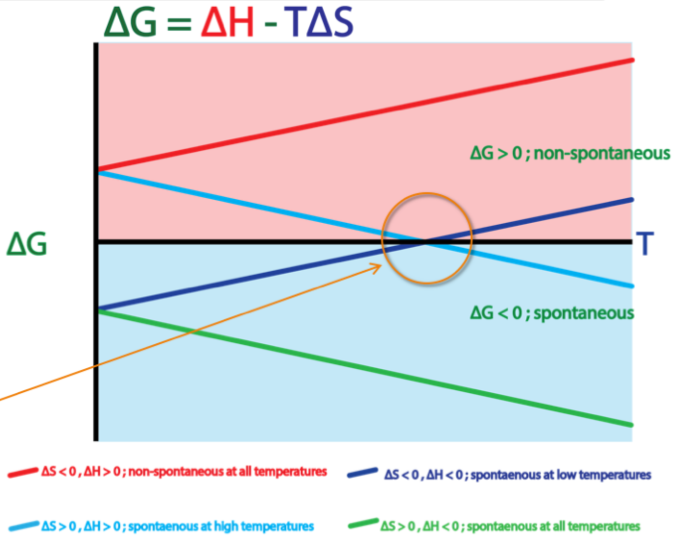
Energy OUT = lower entropy, energy state
Exothermic, so the phase change gives its energy to the surroudings

Fusion (melting), boiling, sublimation

Energy IN = Higher entropy, energy state
Endothermic, so we get the energy to do this phase change from the surroundings

Free Energy: All Conditions Summary

ΔH	ΔS	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T



Free Energy: Physical Equilibrium Equations

$$\Delta G = \Delta H_{trans} - T\Delta S_{trans}$$

$$\Delta G = 0$$

$$\Delta H_{trans} = T\Delta S_{trans}$$

$$T\Delta S = \Delta H$$

$$T = \frac{\Delta H}{\Delta S}$$

$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}}$$

The entropy change of a phase transition given an enthalpy and temperature value

$$T_{trans} = \frac{\Delta H_{trans}}{\Delta S_{trans}}$$

The temperature change of a phase transition (boiling point, freezing points, etc.) given the enthalpy and entropy

Thermodynamics Concepts

What is required for an endothermic reaction to be spontaneous?

1. A positive change in entropy and sufficiently high temperature

2. A negative change in entropy and a low enough temperature

3. A positive change in entropy at any temperature

4. An endothermic reaction is always spontaneous

5. A negative change in entropy at any temperature

What is the sign of ΔG for a reaction at equilibrium?

1. 0

2. +

3. -

Which of the following is true for any liquid that is currently in the act of freezing?

1. $\Delta S < 0$

~~**2.** $\Delta H > 0$~~

~~**3.** $\Delta T < 0$~~

~~**4.** $\Delta G > 0$~~

5. $\Delta H = 0$

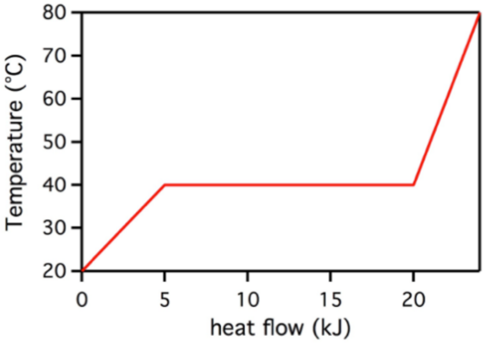
6. There is no change in energy during the process of freezing

~~**7.** $T = 0°C$~~

8. $T = 100°C$

Heating Curves Checklist

- Heating Curves are a 301 concept that show the two equations necessary to calculate the total heat of a single or multiple phase changes for a substance.



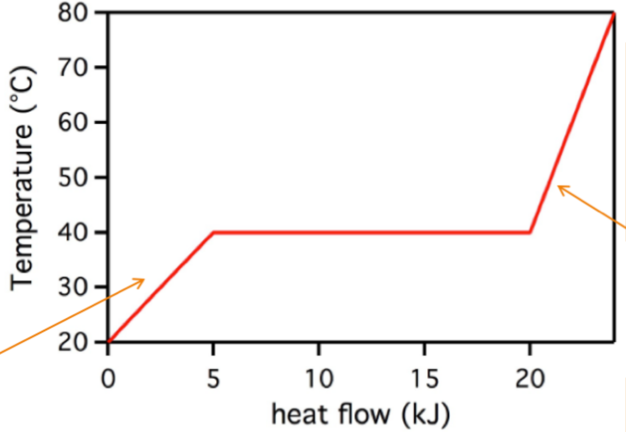
- Calculating Heat:
  - Use your two calculations ($q = mc\Delta T$ and $q = m\Delta H$)
  - **Be able to do this same calculation for cooling, even though we are used to doing it for heating (many mistakes on 301 exams)**
- Reading the graph:
  - Understanding heat capacity / slope of the heating curves
  - Determine the value of heat without making a calculation

$C = \frac{J}{°C}$ Slope $= \frac{\Delta T}{q} = \frac{°C}{J}$

Heating Curves Checklist – Heat Capacity

Heat capacity can be thought of as a substance's resistance to change in temperature. Consider the heating curve for a liquid being heated to the gas phase:

A high heat capacity results in a smaller slope on a heating curve (substance resists change in temperature when heat is applied)



A low heat capacity results in a steeper slope on a heating curve (substance does not do a good job resisting change in temperature when heat is applied)

Therefore, the gas of this substance has a lower heat capacity than the liquid.

Vapor Pressure

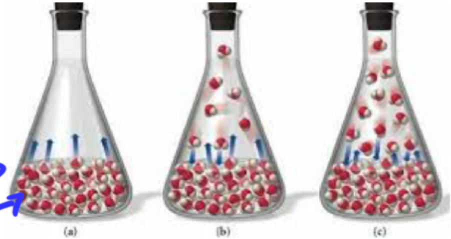
CONCEPTS, BOILING, CALCULATIONS

VP → ΔT
↳ Change the identity

Vapor Pressure

- For any given liquid sample in a closed container, a certain amount of that sample exists is the gas phase. This is what is known as the **vapor pressure**.
- **These molecules have enough kinetic energy to "escape" the attractions of other molecules on the surface.**
- Vapor pressure is a function of dynamic equilibrium between the gas and the surface molecules of a liquid.

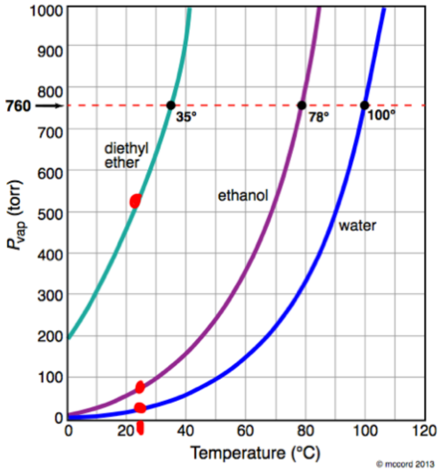
high E →
low E →



✓ The Vapor Pressure is a function of **the IMF's of the liquid (identity of liquid)** and the temperature.

✓ The normal boiling point of a liquid is where the VP = 1 atm

Vapor Pressure Exam Question



Based on the definition of vapor pressure, which of these substances has the highest vapor pressure at 25˚C?

→ diethyl ether

H_2O → lowest

H_2O, CH_3CH_2OH, $CH_3CH_2OCH_2CH_3$

Vapor Pressure and IMF’s

- If Vapor Pressure is the pressure of gas above a liquid in a closed container at a given temperature, we can easily determine that a sample with High IMF’s will have a Low VP (less molecules able to overcome the IMFs and be “lifted into the gas phase).

Strong IMF - > low VP (and high boiling point, high ΔH_{vap})

Weak IMF -> high VP (and low boiling point, low ΔH_{vap})

IMF Review

Dispersion Forces < Dipole Forces < Hydrogen-Bonding

Dispersion forces:

C_nH_{n+2}, CCl_4, CO_2, F_2 etc.

Dipole-Dipole:

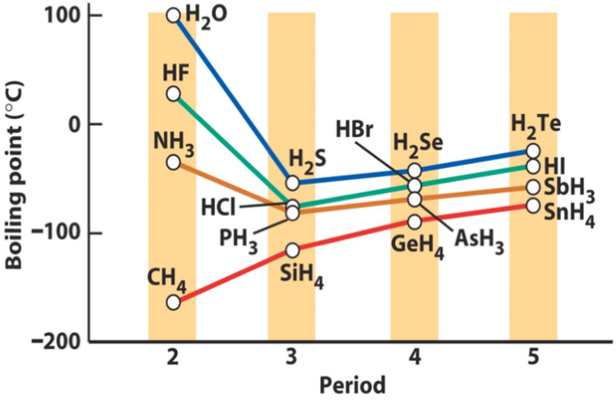
CH_2O, CH_3COCH_3, $AsCl_3$, etc.

H-bonding:

CH_3OH, H_2O, HF, NH_3, etc.

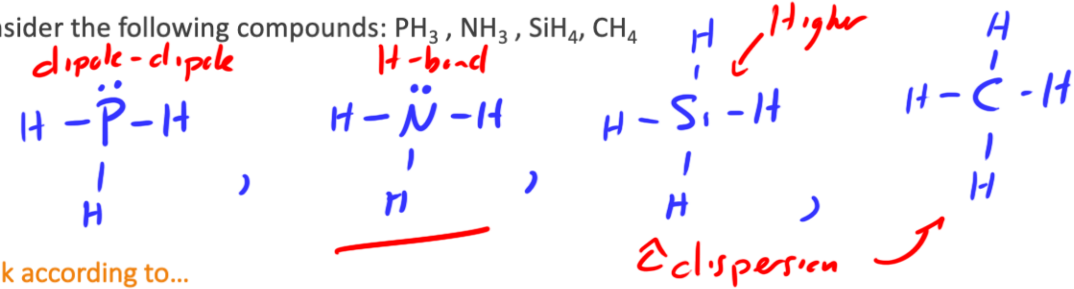
IMF Comparisons

- The key features of this graph are as follows:
  - **Polarizability increases down a group (left to right on this chart)**
  - Shape changes across a period, leading to different polarity across a group (down up on this chart)
  - **Ammonia, hydrofluoric acid, and water break the trend in polarizability because they form hydrogen bonds. The red line follows the trend the best (no hydrogen bond)**



Vapor Pressure Conceptual Question

Consider the following compounds: PH_3 , NH_3 , SiH_4, CH_4



Rank according to…

Stability as a liquid:

Boiling Point:

ΔH:

} $CH_4 < SiH_4 < PH_3 < NH_3$

Vapor Pressure: → $NH_3 < PH_3 < SiH_4 < CH_4$

Vapor Pressure Conceptual Question

Which of the following has a higher vapor pressure at room temperature?

10 mL water in a 20 mL container

10 mL water in a 50 mL container

20 mL water in a 10 mL container

10 mL water in an extra wide 50 mL container

all the same

$PV = nRT$

$P\uparrow = \uparrow RT$

@RT

Which of the following has the highest number of gas moles?

10 mL water in a 30 mL container

10 mL water in a 50 mL container ✓

Vapor Pressure Conceptual Question

Consider the vapor pressures from a data table shown below at 20°C:

Benzaldehyde, 1.27 mmHg

Formaldehyde, 3284 mmHg

Both substances are in identical closed containers. Compared to a one mole sample of formaldehyde, you can conclude that a one mole sample of benzaldehyde...

I. has a higher ΔH_{vap} ✓

II. has a higher boiling point ✓

III. has a lower ΔH_{vap}

IV. has a greater number of molecules in the condensed phase ✓

Vapor Pressure Calculations

- Mathematically, the vapor pressure for a given liquid is only dependent on a change in temperature.

Higher Temperature = Exponentially Higher Vapor Pressure

$$P_{vap} = K \cdot e^{\frac{-\Delta H^{\circ}_{vap}}{R \cdot T}}$$

- **Changing the surface area, size of the container, amount of water, and so on does not change the pressure.**
- Of all the derivations used to model this relationship, the most important equation to you will be the Clausius-Clapeyron Equation:

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

Note: the order of P_2 / P_1 and $(1 / T_1 - 1/T_2)$ is important. If you forget the order, remember that as you increase temperature, you are increasing vapor pressure. You are taking the difference of the inverse temperature, so you need to switch the order.

Vapor Pressure and Boiling Question

What is the normal boiling point of liquid X if it has a vapor pressure of 0.63 atm at room temperature? The enthalpy of vaporization of liquid X is 30 kJ/mol.

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$T_1 = T_B$, $P_1 = 1$ atm

$T_2 = 298.15$ K, $P_2 = 0.63$ atm

$\Delta H = 30$ kJ/mol, $R = 0.008314$ kJ/mol K

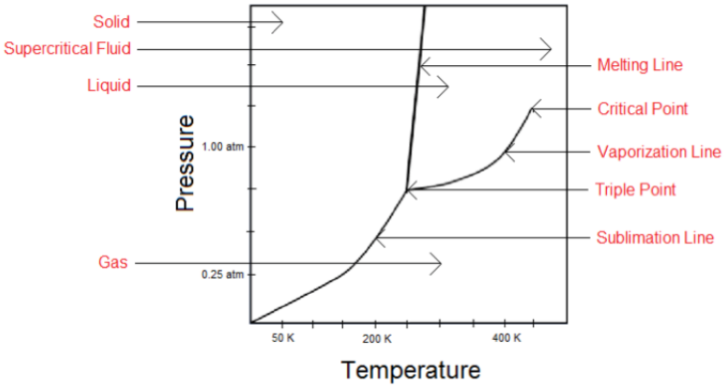
309.82 K

Phase Diagram Checklist

- Phase diagrams show the lowest free energy phase (most stable) of a substance at a given temperature and pressure.
- Identify the key features of the diagram:
    - What is the stable phase at a certain temperature and pressure?
    - Identify the triple point
    - Identify the critical point
    - What phase transition does a specific line represent?
    - What is the meaning of the solid-liquid line’s slope?
- Moving along the diagram:
    - What phase transitions do you go through if you go from point A to point B on the graph?

Phase Diagram Checklist

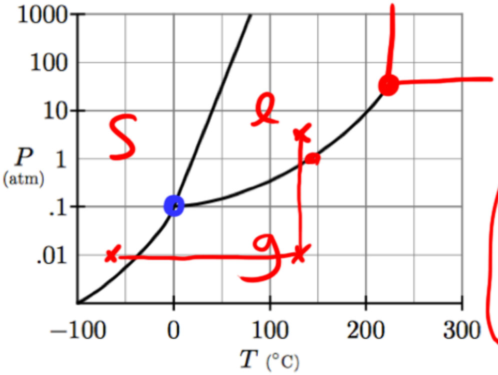
- Phase diagrams show the lowest free energy phase of a substance at a given temperature and pressure.



- Identify the key features of the diagram:
  - What is the stable phase at a certain temperature and pressure?
  - Identify the normal boiling point, melting point, etc.
  - Identify the triple point
  - Identify the critical point
  - What phase transition does a specific line represent?
- Moving along the diagram:
  - What phase transitions do you go through if you go from point A to point B on the graph?

Phase Diagram Exam Questions

On the exam, you will need to identify the specific temperature and/or pressure associated with the key features of the diagram. NOTE: the phase diagram is logarithmic



- What is the critical pressure of this substance?
  I. 35
  II. 100
  III. 90
  IV. 0.1
- What is the normal boiling point of this liquid ?
  I. 100˚C
  II. 0˚C
  III. 140 ˚C
  IV. 200 ˚C
- What phase transition(s) occur when you heat a solid at 0.01 atm and -60 ˚C to 120 ˚C, and then the pressure is increased to 3 atm.

1) Sub 2) Condensation