Nuggets: Phase Diagrams and Phase Changes

PHASE DIAGRAMS: A diagram of Pressure (y-axis) versus Temperature (x-axis) that shows what phase (solid, liquid or gas) is present at a particular T and P.

**Triple Point:** All 3 phases coexist at this T and P.

**Along the lines:** Equilibrium or co-existence of 2 phases (solid+liquid, liquid+gas, and solid+gas)

**Critical Point:** The T and P at which there is an abrupt halt of the vapor pressure curve. Above this point, the liquid and gas phases no longer become distinguishable; *a supercritical fluid exists.*

**Critical Temperature:** The T at which the critical point occurs

**Critical Pressure:** The P at which the critical point occurs

**Supercritical fluid:** Density resembles a liquid and viscosity resembles a gas.

**Terms:**
- Solid $\rightarrow$ liquid: *melting*
- Liquid $\rightarrow$ solid: *freezing*
- Liquid $\rightarrow$ gas: *vaporization (or boiling)*
- Gas $\rightarrow$ liquid: *condensation*
- Solid $\rightarrow$ gas: *sublimation*
- Gas $\rightarrow$ solid: *deposition*

Most substances: $D_{\text{solid}} > D_{\text{liquid}}$; $\text{H}_2\text{O}$: $D_{\text{solid}} < D_{\text{liquid}}$ (ice floats)
HEATING CURVE: Phase changes: There is no temperature change during a phase change
Solid → Liquid: \( \Delta H_{\text{fusion}} = \Delta H_{\text{fus}} \); Liquid → Solid: \( -\Delta H_{\text{fus}} \)
Liquid → Gas: \( \Delta H_{\text{vaporization}} = \Delta H_{\text{vap}} \); Gas → Liquid: \( -\Delta H_{\text{vap}} \)

\[ s \rightarrow l: \quad \text{Heat} = \Delta H_{\text{fus}} x \text{mol} \quad \text{(if } \Delta H_{\text{fus}} = \text{J/mol}) \quad \text{or} \quad \text{Heat} = \Delta H_{\text{fus}} x \text{grams} \quad \text{(if } \Delta H_{\text{fus}} = \text{J/g}) \]

\[ l \rightarrow g: \quad \text{Heat} = \Delta H_{\text{vap}} x \text{mol} \quad \text{(if } \Delta H_{\text{vap}} = \text{J/mol}) \quad \text{or} \quad \text{Heat} = \Delta H_{\text{vap}} x \text{grams} \quad \text{(if } \Delta H_{\text{vap}} = \text{J/g}) \]

Example: How much heat is required to heat 25.0g H\(_2\)O(l) from 75.0˚C to 125˚C? \( (C_{\text{H}_2\text{O(l)}} = 4.184\text{J/g}^\circ\text{C}; C_{\text{H}_2\text{O(g)}} = 2.08\text{J/g}^\circ\text{C}; \Delta_{\text{vap-H}_2\text{O(l)}} = 2256\text{J/g}) \)

Answer: \( q_{\text{total}} = q_{\text{heat water to bp}} + q_{\text{boil water}} + q_{\text{heat H}_2\text{O(g)}} \)

\[ q_{75 \rightarrow 100} = (4.184\text{J/g}^\circ\text{C})(25\text{g})(100-75) = 2615\text{J}; q_{\text{boil}} = (2256\text{J/g})(25\text{g}) = 56400\text{J}; \]

\[ q_{100 \rightarrow 125} = (2.08\text{J/g}^\circ\text{C})(25\text{g})(125-100) = 1300\text{J}; q_{\text{total}} = q_{75 \rightarrow 125} = 2615 + 56400 + 1300 = 60315\text{J} = 60400\text{J} \]

Point on a HEATING CURVE aligned with points on a PHASE DIAGRAM
A heating curve (see below) has data collected at one pressure (in this case, \( P = 1.00\text{atm} \)); the values on a heating curve correspond to values found along one horizontal line of a phase diagram (in this case, the values are plotted at \( P = 1.00\text{atm} \) on the phase diagram); note how all the data points that occur during a phase change on the heating curve (B, C, D, E for melting and H, I, J, K for boiling) all land at one point on a phase diagram.
Water’s unique properties *(if covered)*:
- \( D_{\text{solid}} < D_{\text{liquid}} \) so ice floats (most substances have \( D_{\text{solid}} > D_{\text{liquid}} \))
- Very high \( C_{\text{liquid}}, \Delta H_{\text{fus}}, \) and \( \Delta H_{\text{vap}} \)
- Negative slope of solid-liquid co-existence phase line in a phase diagram

**CLAUSIUS-CLAPEYRON *(if covered)*:** \( \ln P = \frac{-\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} \right) + C \)

The above equation is an equation of a line \( (y = mx + b) \):

The \( \Delta H_{\text{vap}} \) can be determined from the slope of the line and \( R = 8.314 \text{ J/molK} \),
(units of \( \Delta H_{\text{vap}} \) in J/mol)

The Clausius-Clapeyron equation can be rearranged to yield:

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

where \( P_1 \) and \( P_2 \) are the vapor pressures (any units but must be the same units) of a liquid at two temperatures, \( T_1 \) and \( T_2 \) (T in K); \( \Delta H_{\text{vap}} \) must be in J/mol when \( R = 8.314 \text{ J/molK} \)

1. a. If a substance is at point B on the phase diagram, and the temperature is increased, what phase is entered?
   b. What phases exist at Point C?
   c. What is Point A called?
   d. What is the term for the phase change that would occur if the pressure on a substance at Point D increased until a new phase is entered?

2. In a phase diagram, what two phases typically exist in the lower T and lower P region?
3. Use the heating curve and phase diagram to answer the questions. 
(Note the y-axis scale on the phase diagram is logarithmic.)

I. Which point on the phase diagram would correspond best with Point I from the heating curve?

II. Which point on the phase diagram would correspond best with Point II from the heating curve?

III. Which point on the phase diagram would correspond best with Point III from the heating curve?

IV. Which point on the phase diagram would correspond best with Point IV from the heating curve?
4. Using the phase diagram below answer the following questions. (Note: The y-axis is logarithmic. If you divide the first section (1 bar to 10 bars) into 9 equal portions each segment will be 1 bar. In the next segment (10 bars to 100 bars), if that portion is divided into 9 equal portions each segment will be 10 bars.)

a. What are the temperature and pressure of the triple point?
b. What are the lowest temperature and lowest pressure when the supercritical fluid region starts?
c. Estimate what the normal boiling point is. (Note: It is not on the graph and you will need to extrapolate the curve a little bit.) To simplify, assume 1 bar = 1 atm.
d. If you start at a pressure of 100 bars and increase the temperature starting at 200 K, what phases does the chemical go through?
e. If you start at a pressure of 5 bars and increase the temperature starting at 200 K, what phases does the chemical go through? What is this change of phase called?

5. Carbon monoxide has a triple point at a temperature of -205°C and a pressure of 0.15 atm, and a critical point at a temperature of -140°C and a pressure of 35 atm. Its normal boiling point is -192°C. Draw a phase diagram using the above information. Label the triple, critical, and normal boiling points. Label the diagram region that represents gas, liquid, solid, and supercritical fluid. Label the axes and place markers on both axes where the triple, critical, and normal boiling points cross the axes (i.e., label where -205°C is and the other data points).

6. (Clausius-Clapeyron; skip if not covered) If the vapor pressure of water at 50.0°C is 92.6 torr, what is the temperature (in °C) at which the vapor pressure of water has doubled? The ΔH_vap of water is 4.10 x 10^4 J/mol.
   a. 36.0°C   b. 50.0°C   c. 65.3°C   d. 280.0°C   e. none of the above

7. (Clausius-Clapeyron; skip if not covered) The vapor pressure of benzene is 100.0 mmHg at 26.1°C and 400.0 mmHg at 60.6°C. What is the normal boiling point of benzene?
ANSWERS
1. a. gas  b. solid, liquid, gas (triple point)  c. critical point  d. freezing

2. gas and solid

3. I. b  {Point I on the heating curve corresponds to a phase change between a solid and liquid, e.g., melting/freezing. On the phase diagram, this occurs at Points B and C. However, Point C occurs at about 0°C while Point B occurs at about -20. From the heating curve, the melting occurs around -20°C so Point B is the correct point. In addition, since the pressure of a heating curve is constant, if Point C is chosen as the correct answer subsequent questions don’t have appropriate points marked on the phase diagram.}

II. e  {Point II on the heating curve corresponds to a liquid phase. On the phase diagram, the liquid region/liquid of a liquid occurs at Point E.}

III. f  {Point III on the heating curve corresponds to a liquid phase but hotter than Point II. On the phase diagram, the liquid region/liquid of a liquid occurs at Point F.}

IV. g  {Point IV on the heating curve corresponds to the phase change between a liquid and gas, e.g., boiling/condensation. On the phase diagram this occurs at Point G. It also occurs at Point I but this is not a valid choice because Point I occurs at ~140°C and from the heating curve it should occur at ~70°C which Point G does.}

4. a. ~215K and ~7bars
   b. ~300K and ~90bars
   c. ~190K
   d. solid to liquid to supercritical fluid
   e. solid to gas; this phase change is called sublimation

5.

6. c  {use } \ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right); P_1 = 92.6\text{torr}; T_1 = 50.0+273.15 = 323.15\text{K}; P_2 = 2 \times P_1 = 185.2\text{torr}; T_2 = x; 

\Delta H_{\text{vap}} = 4.10 \times 10^4\text{J}; R = 8.314\text{J/molK}; \ln \left( \frac{185.2\text{torr}}{92.6\text{torr}} \right) = \frac{4.10 \times 10^4\text{J}}{8.314\text{J/molK}} \left( \frac{1}{323.15} - \frac{1}{T_2} \right); 0.693 = 4931.4 \left( 0.003095 - \frac{1}{T_2} \right);

0.0001405 = 0.003095 - \frac{1}{T_2}; 0.002954 = \frac{1}{T_2}; T_2 = 338.47\text{K} - 273.15 = 65.32\text{°C}
79.4 °C \{\text{use } \ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \text{ two times; first find } \Delta H_{\text{vap}}; \}

\begin{align*}
P_1 &= 100.0 \text{mmHg}; T_1 = 26.1 + 273.15 = 299.25 \text{K}; P_2 = 400.0 \text{mmHg}; T_2 = 60.6 + 273.15 = 333.75; \\
\ln \left( \frac{400.0 \text{mmHg}}{100.0 \text{mmHg}} \right) &= \frac{\Delta H_{\text{vap}}}{8.314 \text{J/molK}} \left( \frac{1}{299.25 \text{K}} - \frac{1}{333.75 \text{K}} \right); 1.386 = \frac{\Delta H_{\text{vap}}}{8.314 \text{J/molK}} \left( 0.0003454 \right); \Delta H_{\text{vap}} = 33.362 \text{J/mol};
\end{align*}

Will use 100.0mmHg and 299.25K for $P_1$ and $T_1$; could also have used 400.0mmHg and 333.75K instead;

$P_1 = 100.0 \text{mmHg}; T_1 = 299.25 \text{K}; P_2 = 760.0 \text{mmHg}; T_2 = x$

now find $T_2$: \[ \ln \left( \frac{760.0 \text{mmHg}}{100.0 \text{mmHg}} \right) = \frac{33.362 \text{J/mol}}{8.314 \text{J/molK}} \left( \frac{1}{299.25 \text{K}} - \frac{1}{T_2} \right); \]

\begin{align*}
2.028 &= 4012 \left( 0.003342 - \frac{1}{T_2} \right); 0.0005055 &= 0.003342 - \frac{1}{T_2}; \\
0.002837 &= \frac{1}{T_2}; T_2 &= 352.55 \text{K}; °C = 352.55 - 273.15 = 79.40 \text{°C}
\end{align*}