CH 302 – Unit 1

PHASE CHANGES, BASICS OF SOLUTIONS

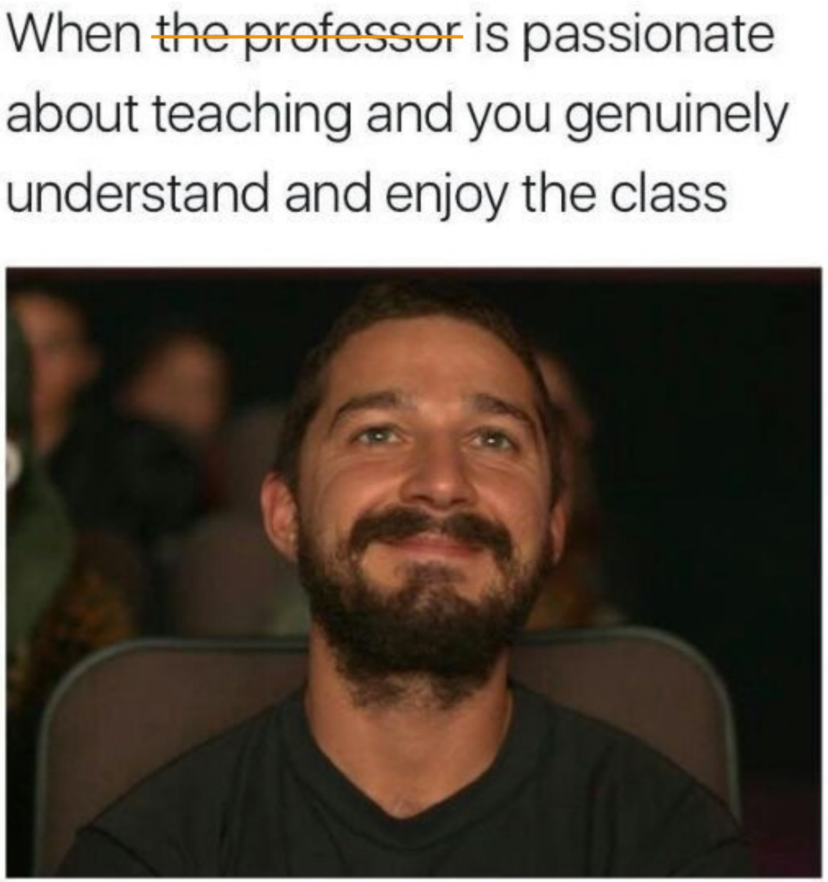
Outline

1. Free energy, equilibrium (CH301 Review)
2. Phase Changes
   - Equilibrium calculations, heating curves, and phase diagrams
3. Vapor Pressure
   - Concepts, calculations, and boiling

New Material:

4. Solutions
   - Terminology, miscibility, and free energy implications (maybe)

*Jimmy



When ~~the professor~~ is passionate about teaching and you genuinely understand and enjoy the class

Phase Changes

EQUILIBRIUM CALCULATIONS, HEATING CURVES, PHASE DIAGRAMS

Free Energy and Spontaneity

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

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

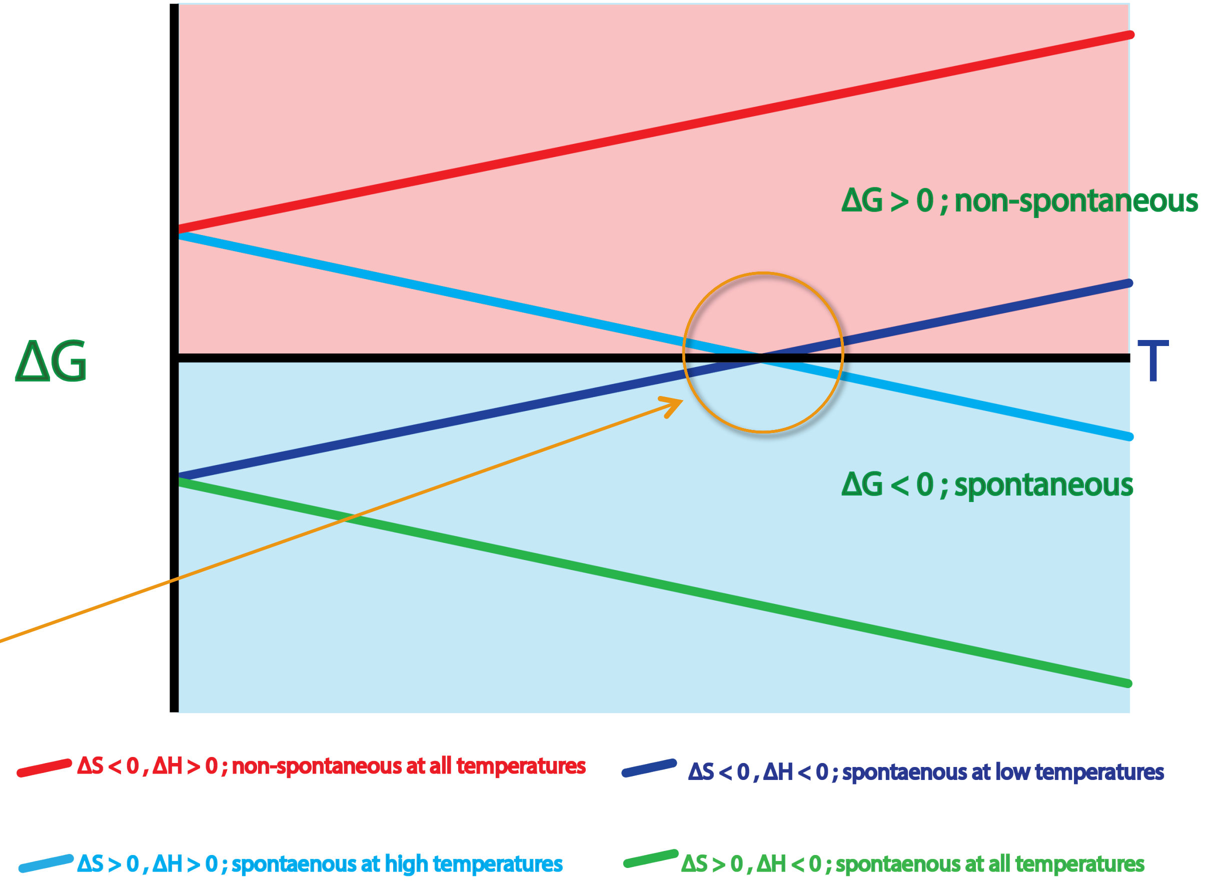
- This law gives us three conditions for **ΔG_{rxn}**:
  1. $\Delta G < 0$ (negative) ; your reaction is spontaneous
  2. $\Delta G = 0$ (zero) ; your reaction is at equilibrium
  3. $\Delta G > 0$ (positive) ; your reaction is nonspontaneous

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).

Free Energy: All Conditions Summary

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

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



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-	+	No	Always
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-	-	Yes	Low T
+	+	Yes	High T

Freezing, condensation, deposition

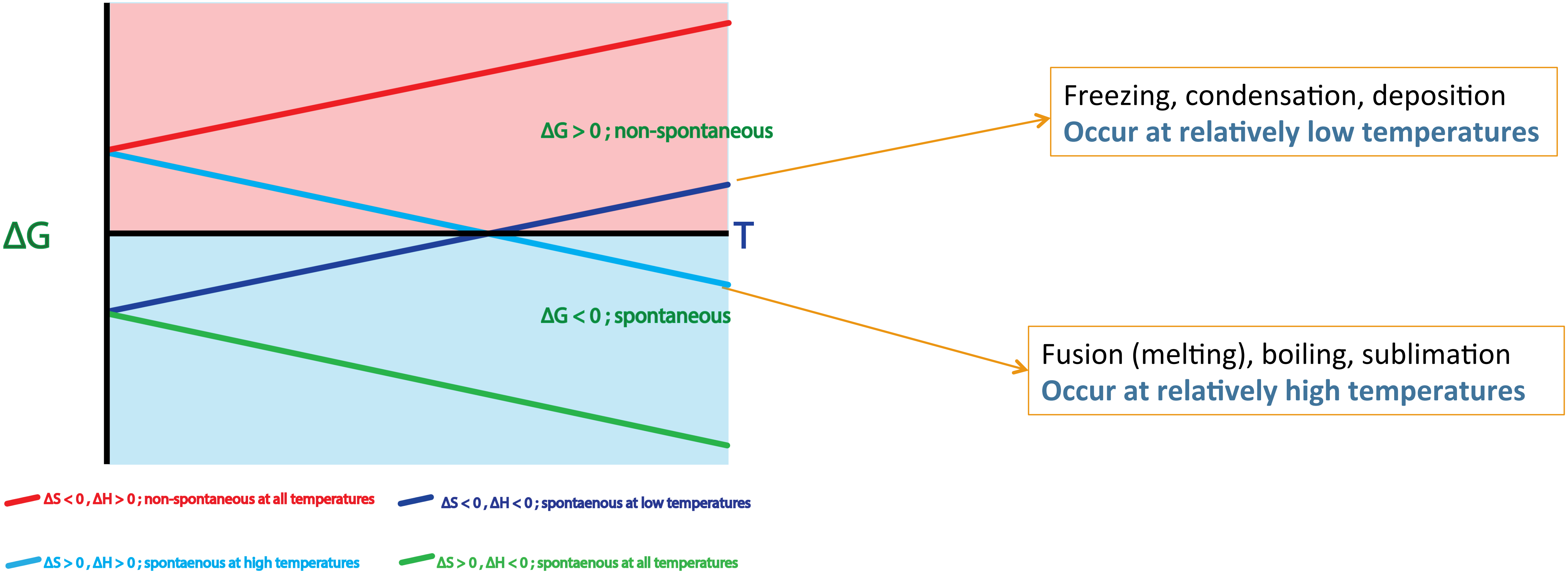
Energy OUT = lower entropy, energy state

Fusion (melting), boiling, sublimation

Energy IN = Higher entropy, energy state

Free Energy: All Conditions Summary

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



Freezing, condensation, deposition
Occur at relatively low temperatures

Fusion (melting), boiling, sublimation
Occur at relatively high temperatures

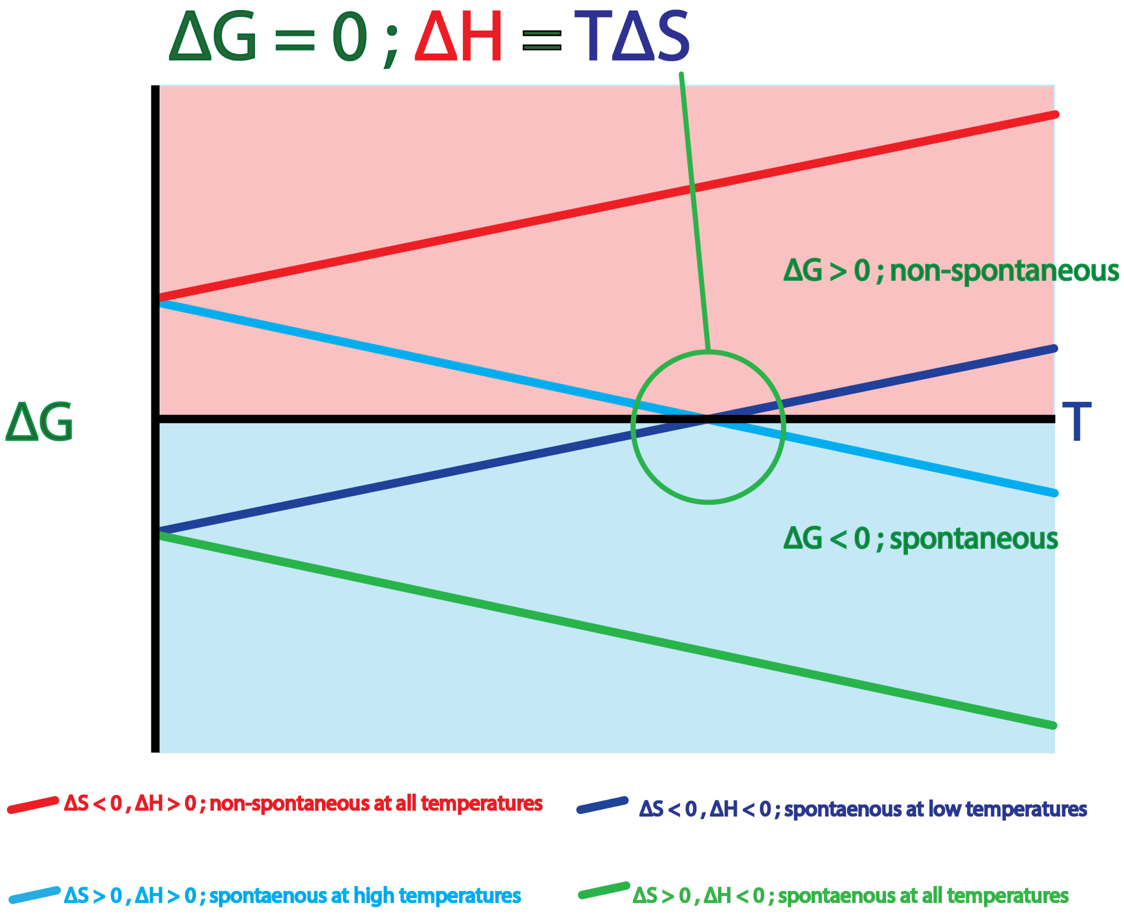
Free Energy: Equilibrium

For the conditions that are temperature dependent, it is possible to have a ΔG value equal to 0. This is, by definition, equilibrium.

It might be useful to remember that equilibrium can only occur when entropy and enthalpy have the same sign (both positive or both negative). The red and green lines cannot ever be in equilibrium.

In this class we are focused on one main equilibrium condition: phase change.

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



Free Energy: Physical Equilibrium Equations

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

$$\Delta G = 0$$

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

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

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

Homework Question

What is the change in entropy for the condensation of water (ΔH_{vap} = 2260 J / g) at its standard boiling temperature (100°C)? Answer in units of J / mol K.

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What is the change in entropy for the condensation of water (ΔH_{vap} = 2260 J / g) at its standard boiling temperature (100°C)? Answer in units of J / mol K.

Ans: -109.06 J / mol K

Homework Question

You are investigating the physical properties of an unknown liquid. You discover that the ΔH°_{vap} = 11 kJ / mol and the ΔS°_{vap} = 105 J / mol K. What is the boiling point of your unknown liquid? Answer in units of K.

Homework Question

You are investigating the physical properties of an unknown liquid. You discover that the $\Delta H°_{vap}$ = 11 kJ / mol and the $\Delta S°_{vap}$ = 105 J / mol K. What is the boiling point of your unknown liquid? Answer in units of K.

105K

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

$$0 = \Delta H - T\Delta S$$

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

↙ ↘

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

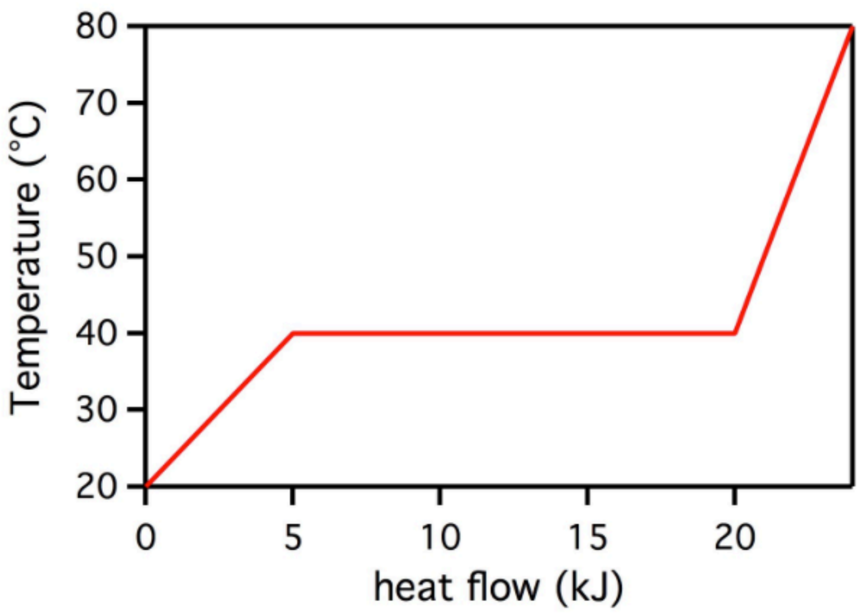
↙ ↓

$$\frac{11{,}000\ \text{J/mol}}{105\ \text{J/K mol}} \qquad \Delta S = \frac{-2260\,\frac{\text{J}}{\text{g}} \times \frac{18\text{g}}{\text{mol}}}{100°\text{C} + 273}$$

$$\boxed{= 105\text{K}} \qquad \boxed{= -109.06\ \text{J/K mol}}$$

Heating Curves Checklist

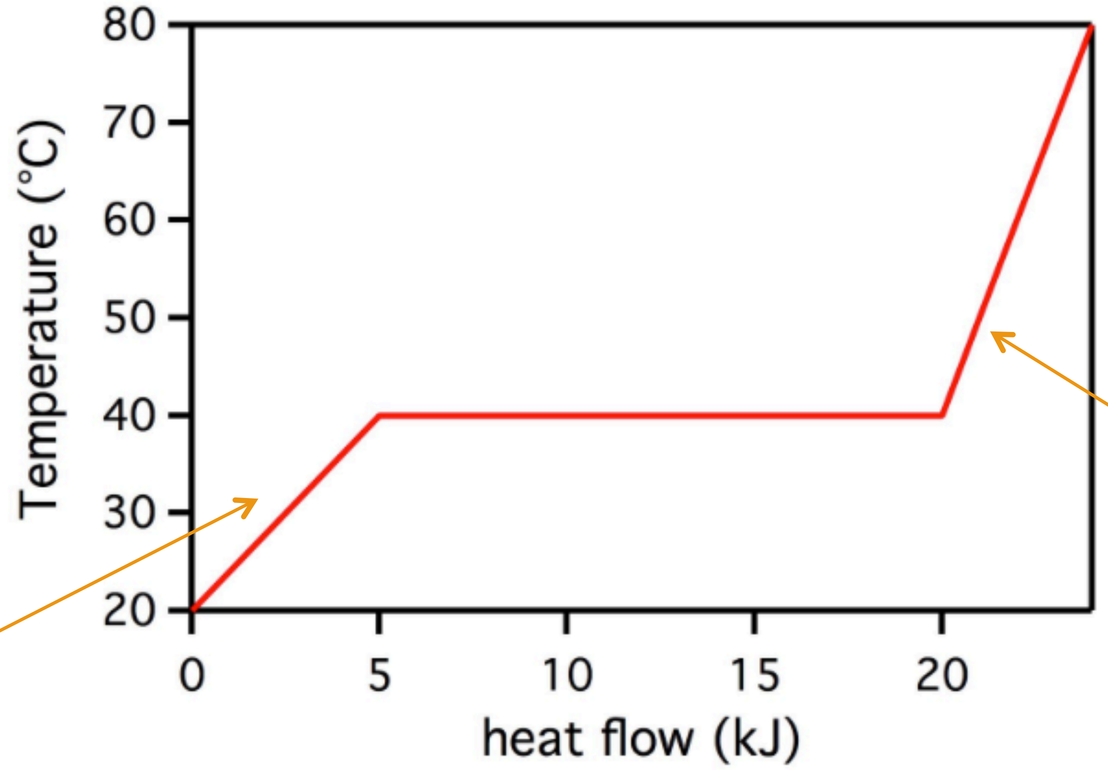
- Heating Curves are a 301 concept that show the two equations necessary to calculate the total heat of a single or multiple phase changes for a substance.



- 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

Heating Curves Checklist – Heat Capacity

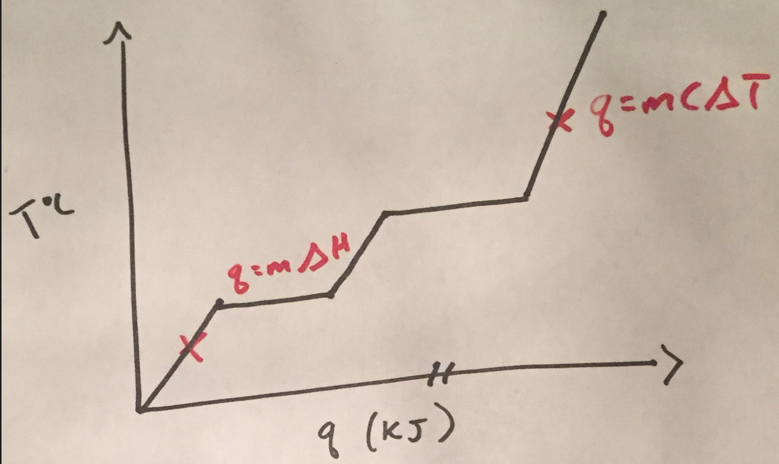
Heat capacity can be thought of as a substance's resistance to change in temperature. Consider the heating curve for a liquid being heated to the gas phase:

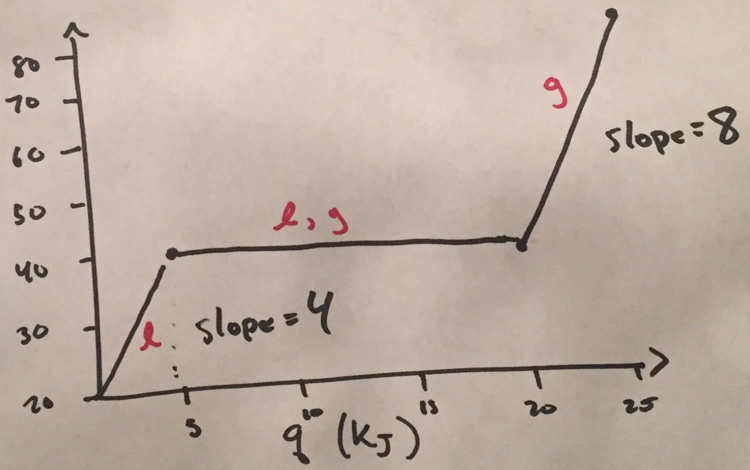


A high heat capacity results in a smaller slope on a heating curve (substance resists change in temperature when heat is applied)

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.


T°C
q=mΔH
q=mCΔT
q (KJ)

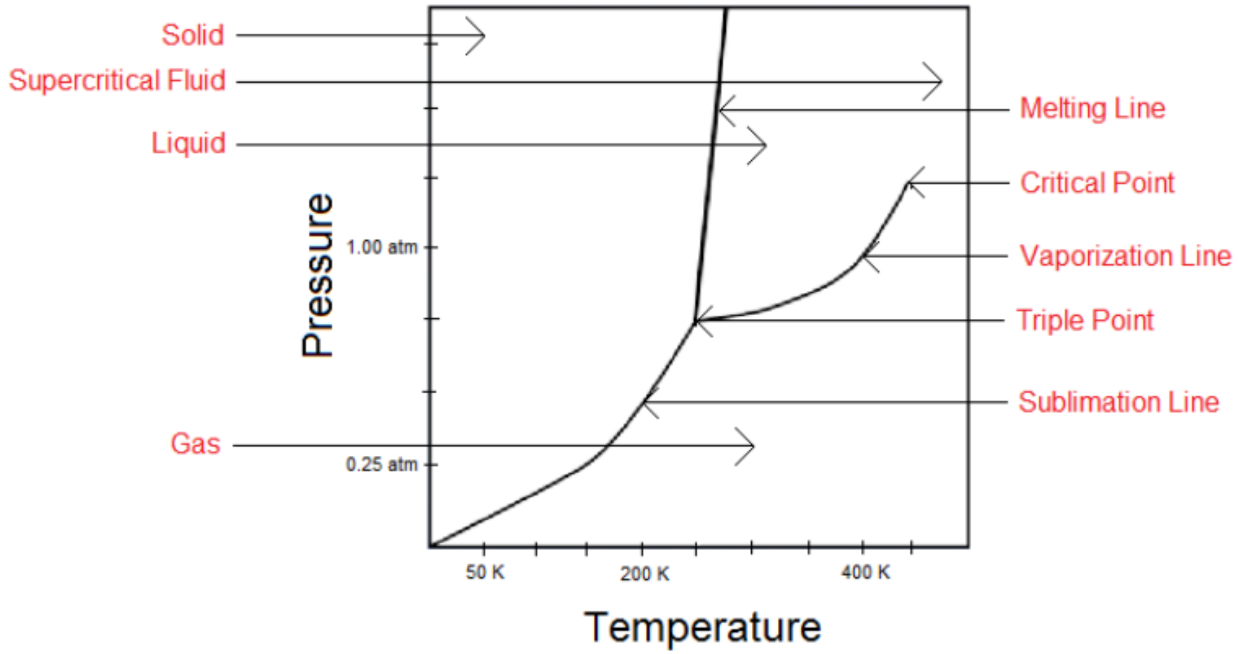

80
70
60
50
40
30
20
l
slope=4
l, g
g
slope=8
5
10
15
20
25
q (KJ)

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 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 Checklist

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

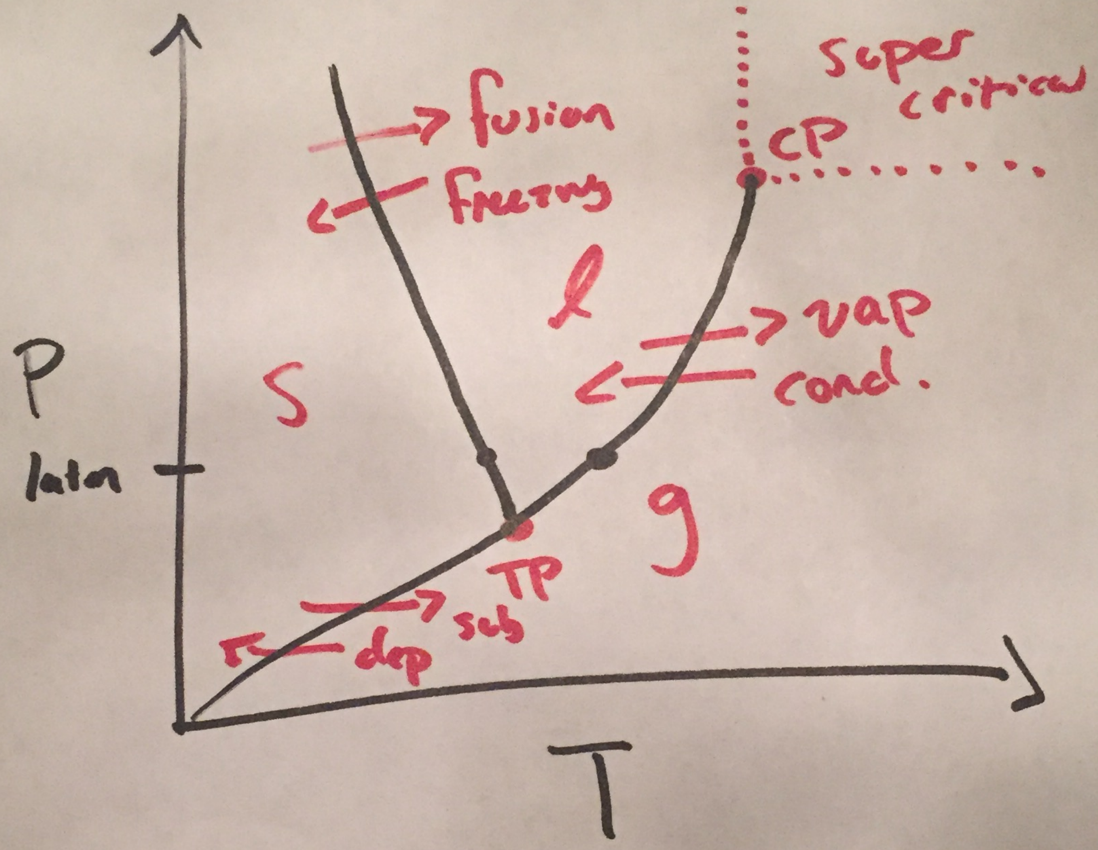


Identify the key features of the diagram:

- 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?



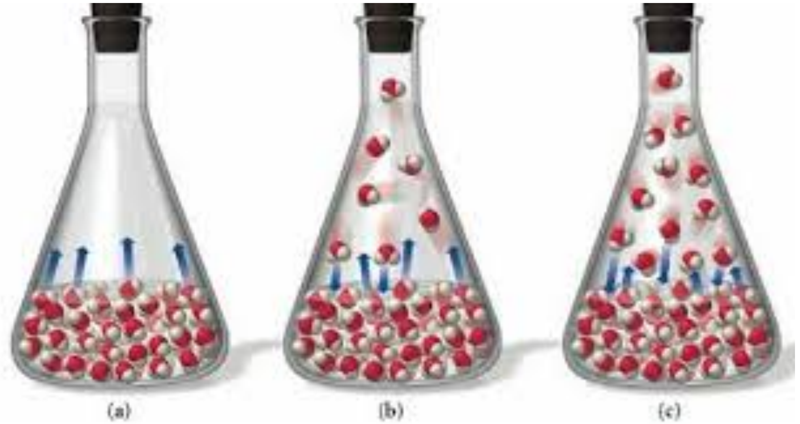
super critical
fusion
freezing
CP
l
vap
cond.
P
s
1atm
g
TP
sub
dep
T

Vapor Pressure

CONCEPTS, BOILING, CALCULATIONS

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.



- The Vapor Pressure is a function of **the IMF's of the liquid** and the temperature.

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)

Weak IMF -> high VP (and low boiling point)

IMF Review

Dispersion Forces < Dipole Forces < Hydrogen-Bonding

Vapor Pressure and Temperature

- 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

- Knowing that vapor pressure is the pressure exerted by a vapor above a liquid, **when the vapor pressure is equal to atmospheric pressure (1 atm), the temperature is equal to the boiling point.**
- If the vapor pressure is higher than atmospheric pressure, all of the liquid will dissolve.
- This is a very important relationship for conceptual questions
- This relationship is also useful when using the Clausius-Clapeyron equation.
  - Whenever a temperature value is equal to the boiling point of a liquid, the pressure is equal to 1 atm. That means the question does not have to give you a pressure value if one of your T – values is the boiling point.

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

If P_1 = 1 atm,
T_1 = normal boiling point

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

If P_{vap} = 1 atm,
T = normal boiling point

Vapor Pressure Conceptual Question

Rank the vapor pressures of the following compounds from least to greatest.

CH_3Cl , CH_3OH, CH_4

Which compound has the highest boiling point?

Vapor Pressure Conceptual Question

Which of the following has a higher VP at room temperature? (assume the 10mL container has space for air / vapor)

10mL water in a 10mL container

10mL water in a 20mL container

20mL water in a 10mL container

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

10mL water in a 10mL container

10mL water in a 20mL container

Vapor Pressure Conceptual Question

Which of the following has a higher VP at room temperature?

- 10mL water in a 10mL container
- 10mL water in a 20mL container
- 20mL water in a 10mL container

All the same

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

- 10mL water in a 10mL container
- 10mL water in a 20mL container

The 20mL container

Vapor Pressure Conceptual Question

Rank the vapor pressures of the following compounds from least to greatest.

$CH_3OH < CH_3Cl < CH_4$

Rank opposite of IMF strength.

H-bond > dipole-dipole > dispersion forces

Which compound has the highest boiling point?

CH_3OH ; contains hydrogen bonding

Vapor Pressure and Boiling Question

How many moles of gas moles will be formed if you place 20 moles of methanol liquid in an evacuated chamber at 150°C? Note: the boiling point of methanol is about 65°C.

Vapor Pressure and Boiling Question

How many moles of gas moles will be formed if you place 20 moles of methanol liquid in an evacuated chamber at 150°C? Note: the boiling point of methanol is about 65°C.

The temperature is significantly higher than the boiling point. The methanol will all boil. You will have 20 moles of gas. No calculation is needed.

Vapor Pressure and Boiling Question

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

Vapor Pressure and Boiling Question

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

Set up using C-C equation. Final answer is 333K

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

$P_2 = 0.63$ atm
$P_1 = 1$ atm (VP @ normal BP for any liquid)
$T_2 = 298K$
$\Delta H_{vap} = 30 \text{ kJ/mol}$, $R = 0.008314 \frac{\text{kJ}}{\text{mol}}$

$$\ln\left(\frac{0.63}{1}\right) = \frac{30 \text{kJ/mol}}{0.008314 \text{kJ/mol}}\left(\frac{1}{T_1} - \frac{1}{298}\right)$$

Set up whole problem 1st, or do step-wise

$$= A \quad = \quad B\left(\frac{1}{T_1} - \frac{1}{298}\right)$$

$$\left[\frac{A}{B} + \frac{1}{298} = \frac{1}{T_1}\right.$$

$$= C$$

$$\frac{1}{C} = T_1$$

$$\boxed{= 333.33K}$$

$A = \ln\left(\frac{0.63}{1}\right)$
$= -0.46$

$B = \frac{30}{0.008314}$
$= 3608$

$C = \frac{A}{B} + \frac{1}{298}$
$= 0.003$

Solutions

DEFINITIONS, CONCENTRATION UNITS, LIKE-DISSOLVES-LIKE, ENTHALPY OF A SOLUTION

Introduction to Solutions

- A solution is a homogenous mixture consisting of a solute (can be gas, liquid, or solid) dissolved in a liquid solvent.
- Solubility is a measurement of how much solute dissolves in a particular solvent
  - The most important term you will learn here is “like-dissolves-like”
  - Solubility is highest when the IMF’s of the solute match the IMF’s of the solvent
- Some basic rules:
  - Electrostatic interactions generally pair well with hydrogen bonding (example: salts in water)
  - Solvents with dominant hydrogen bonding don’t dissolve nonpolar solutes (and vice-versa)
  - Large organic molecules that are dominated by dispersion forces (example: fats) dissolve best in nonpolar solvents

Note: we will discuss more specific solubility rules later

Enthalpy of Solution

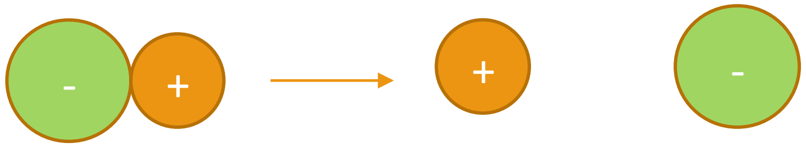
$$\Delta H_{solution} = \Delta H_{lattice} + \Delta H_{solvation}$$

Always +

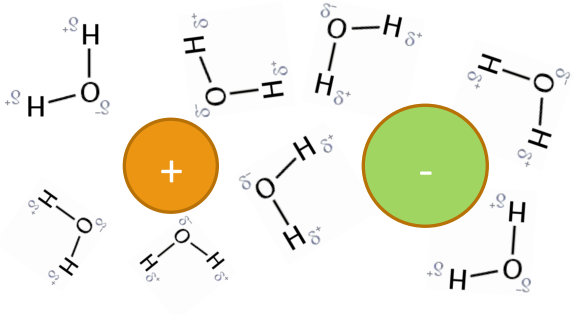
Always -

Step one: Lattice Energy breaks apart ionic compound

Step twp: Solvation Energy is released when solvent dissolves positive and negative charges

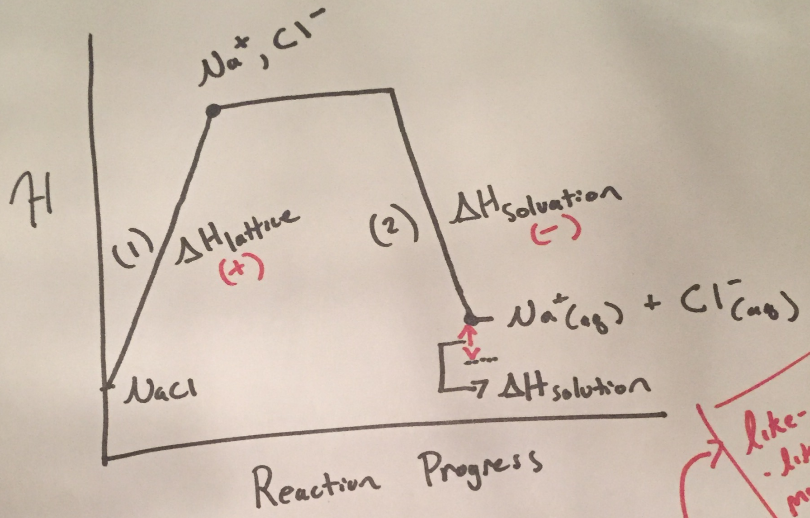


+



$+ \Delta H_{lattice}$ (positive value)

$+ \Delta H_{solvation}$ (negative value)



like-dissolves-like maximizes ΔHsolv

$$\underline{\Delta H_{solution}} = \underline{\Delta H_{lattice}} + \underline{\Delta H_{solvation}}$$

$$\Downarrow$$

$$\Delta G = \underset{(+/-)}{\Delta H} - T\underset{(+)}{\Delta S}$$

1) effect of T?
2) effect of ΔH?
3) effect of ΔS?

- solid → l
- liquid → l
- gas → l

Introduction to Solutions

- Some of the concentration units you should know for solutions are (gchem fundamentals chapter):
  - Molarity (M): moles of solute per liter solution (mol/L)
  - Molality: moles of solute per kilogram solvent (mol / kg)
  - Mole Fraction: moles of a particular species per total moles of solution / mixture (dimensionless)

$$M = \frac{mol}{L}$$

$$m = \frac{mol}{kg}$$

$$X_A = \frac{mol_A}{mol_{total}}$$

Fundamentals Question

Suppose you dissolve 0.5 moles of sodium sulfate into 500mL of water (assume sodium sulfate is completely soluble in water). Answer all of the following in molarity.

a. Before your salt dissolves, what is the concentration of sodium sulfate?
b. What is the final concentration of sodium ions?
c. What is the final concentration of sulfate ions?

Fundamentals Question

Suppose you dissolve 0.5 moles of sodium sulfate into 500mL of water (assume sodium sulfate is completely soluble in water). Answer all of the following in molarity.

a. Before your salt dissolves, what is the concentration of sodium sulfate? 1M
b. What is the final concentration of sodium ions? 1M
c. What is the final concentration of sulfate ions? 2M

$$\begin{tikzcd}[column sep=small] & \overset{0.5\,\text{mol}}{\boxed{Na_2SO_{4(s)}}} \arrow[r] \arrow[dl] \arrow[d] & \overset{1\,\text{mol}}{2Na^+_{(aq)}} + \overset{0.5\,\text{mol}}{\underline{SO_4^{2-}{}_{(aq)}}} \\ \underline{2Na^+} & 1SO_4^{2-} & \end{tikzcd}$$

$$\boxed{\begin{array}{l} \dfrac{0.5\,\text{mol}}{0.5\,\text{L}} = 1\,\text{M} \\[2ex] \dfrac{0.5\,\text{mol}}{0.5\,\text{L}} = 1\,\text{M} \\[2ex] \dfrac{1\,\text{mol}}{0.5\,\text{L}} = 2\,\text{M} \end{array}}$$

Coming Up

- Favoring solubility: there is a thermodynamic relationship between free energy and solubility that depends on the change in entropy and enthalpy of solution.
  - These relationships are different depending on the phase of your solute (for example, solids dissolve better at higher T, gases dissolve better at lower T)
- Adding solute to a solvent changes the physical properties. We call these colligative properties.
  - This is where our concentration units become useful
- We will calculate the exact amount of solute that dissolves in a solvent (usually water) based on the ion product (K_{sp}).

These last two topics are the most difficult. Work ahead to avoid getting lost right before the exam. We will cover these topics next week!

Free Energy of a Solution (salt dissolved in water)

$$\Delta G_{solution} = \Delta H_{solution} - T\Delta S_{solution}$$

- If you want to choose a solvent, you should find a liquid with IMF's similar to you solute. What does this have to do with free energy?
- Putting the pieces together:
    1. For the dissolution of a salt, the entropy change is always positive and the enthalpy change is also positive.
    2. This means the dissolution is driven by the enthalpy.
    3. We can minimize the $\Delta H_{solution}$ term by making the $-\Delta H_{solvation}$ very close to $\Delta H_{lattice}$
- Hopefully you can also see that increasing the temperature for this process will lower the free energy as well.