CH 302 – Unit 1

PHASE CHANGES, BASICS OF SOLUTIONS

Unit One 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: showing the most stable phase of a substance at a given temperature and pressure
4. Thermodynamics associated with creating a solution
    - Does it dissolve?
    - Temperature dependence
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

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:**

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

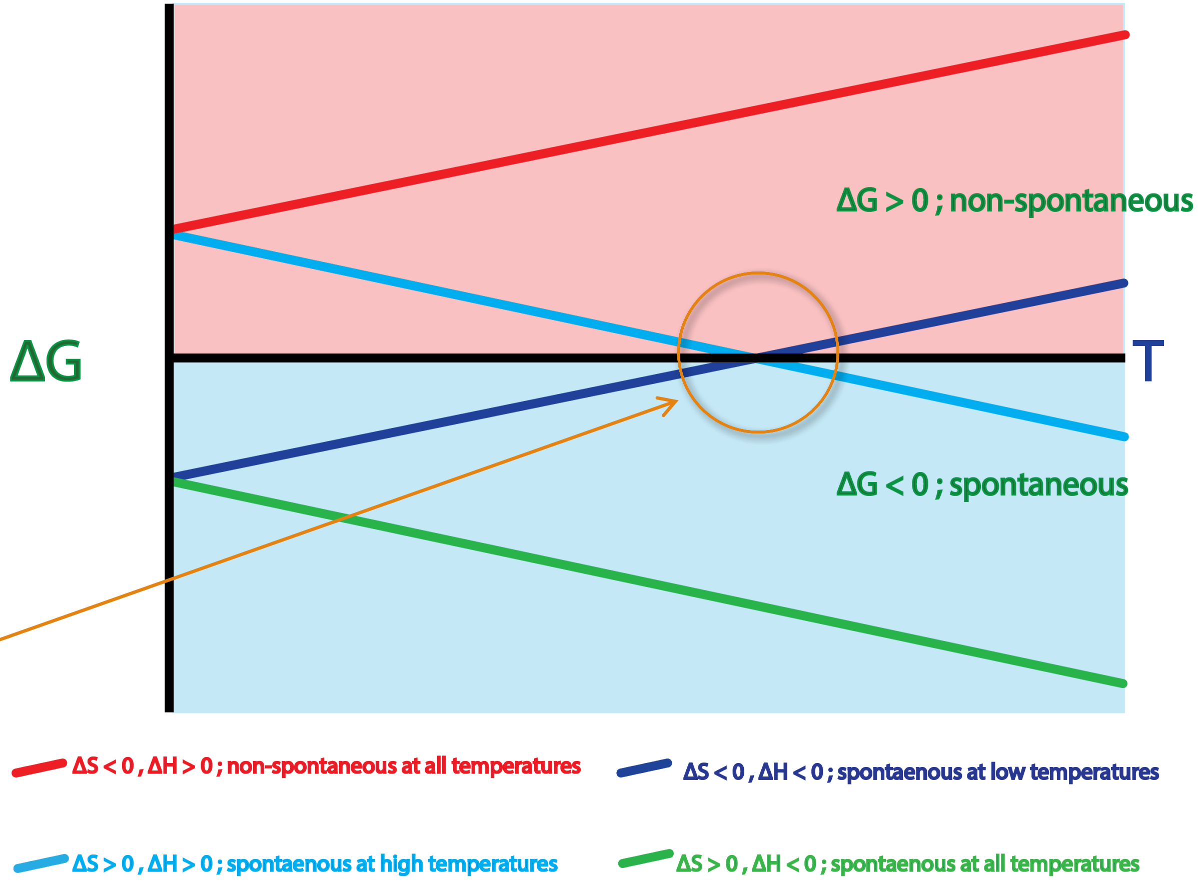
- This law gives us three conditions for **ΔG_{rxn}**:
  1. $\Delta G < 0$ (negative) ; your reaction is spontaneous
  2. $\Delta G = 0$ (zero) ; your reaction is at equilibrium
  3. $\Delta G > 0$ (positive) ; your reaction is nonspontaneous

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

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



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

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.

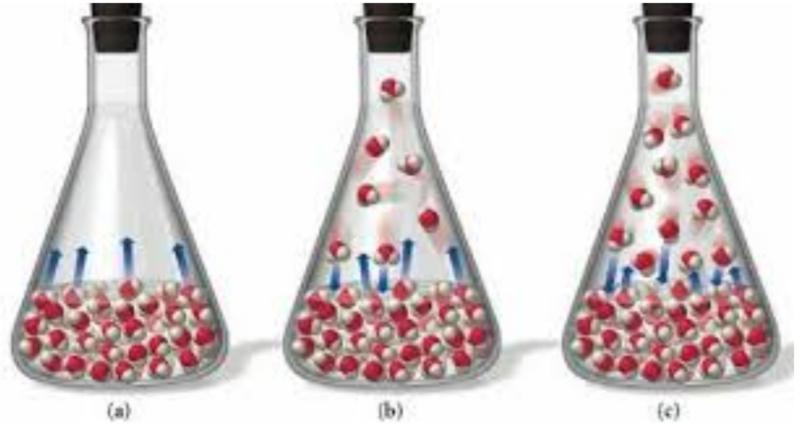
$$\Delta G = \Delta H - T\Delta S$$

Vapor Pressure

CONCEPTS, BOILING, CALCULATIONS

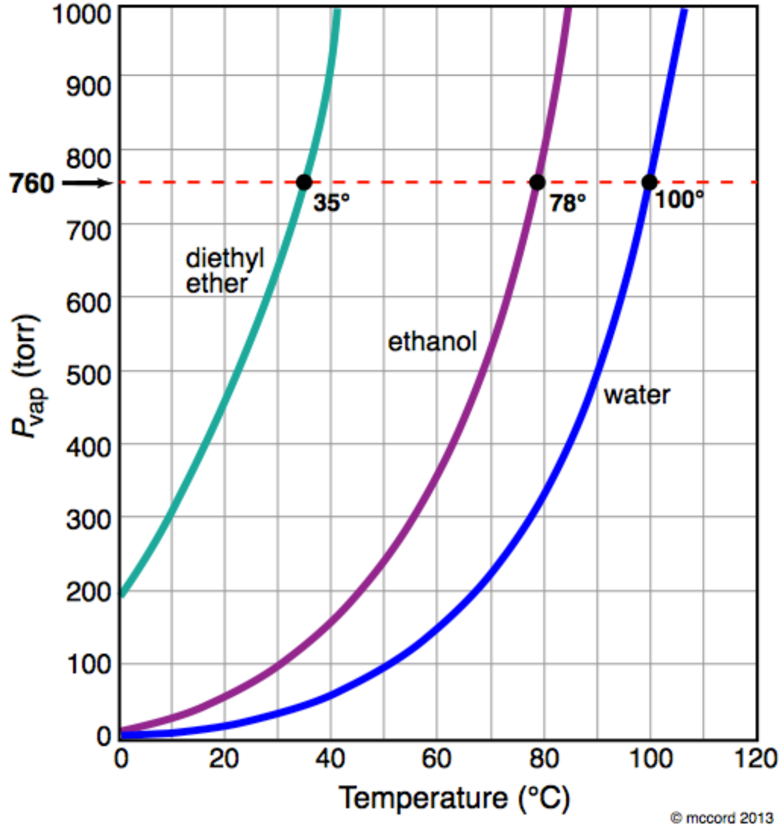
Vapor Pressure

- 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.



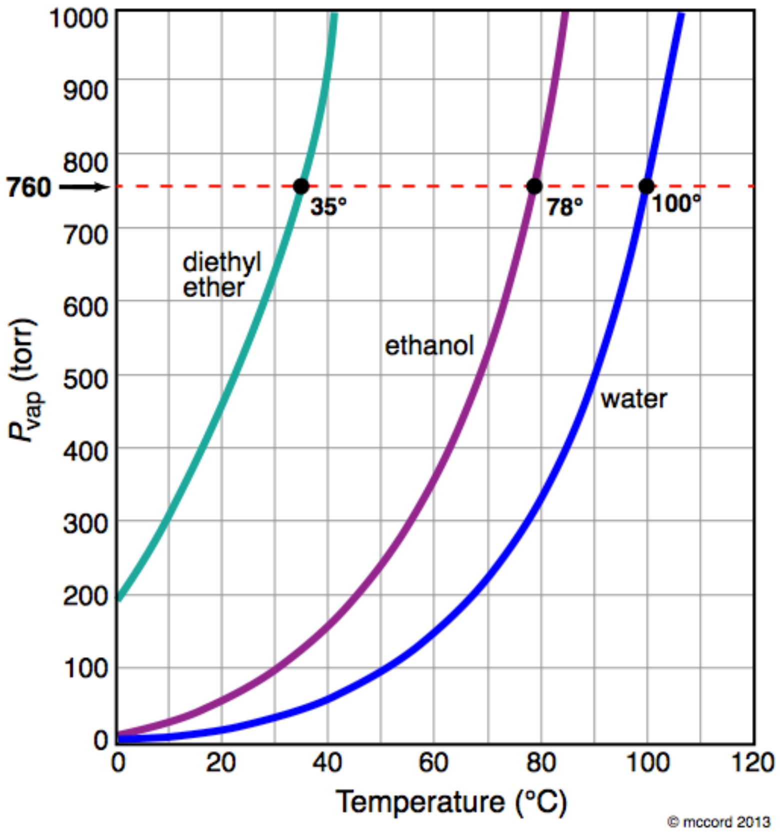
- The Vapor Pressure is a function of **the IMF's of the liquid** and the temperature.

Vapor Pressure Exam Question



Based on what I just explained about vapor pressure, which of these substances has the highest vapor pressure?

Vapor Pressure Exam Question



Based on what I just explained about vapor pressure, which of these substances has the highest vapor pressure?

Diethyl ether vapor will have the highest pressure at any given 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, 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, $C0_2$, F_2 etc.

Dipole-Dipole:

CH_2O, CH_3COCH_3, $AsCl_3$, etc.

H-bonding:

CH_3OH, H_2O, HF, NH_3, etc.

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?

CH_3Cl, CH_3OH, CH_4

Dipole-Dipole H-bond dispersion

$CH_3OH < CH_3Cl < CH_4$

——— VP ———→

←—— IMF, T_B, ΔH_{vap} ——

CH_3OH has highest T_b

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 Conceptual Question

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

10mL water in a 20mL container

10mL water in a 50mL container

20mL water in a 10mL container

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

10mL water in a 20mL container

10mL water in a 50mL container

Vapor Pressure Conceptual Question

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

10mL water in a 20mL container

10mL water in a 50mL container

20mL water in a 10mL container

All the same

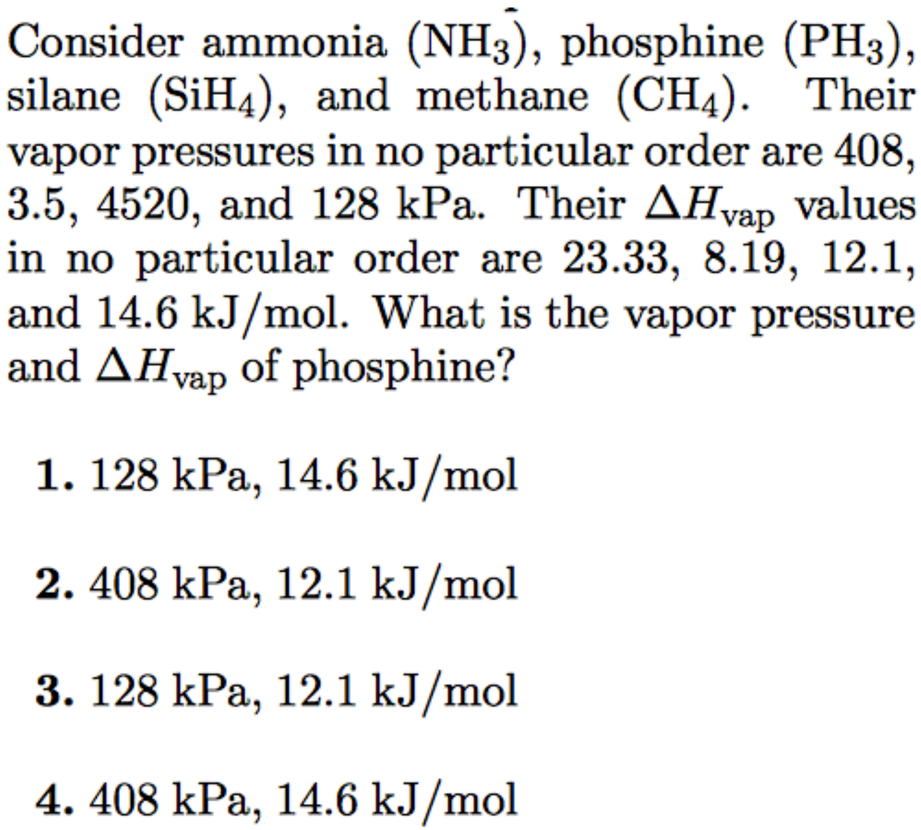
Which of the following has the highest number of gas moles?

10mL water in a 20mL container

10mL water in a 50mL container

The 50 mL container

Vapor Pressure Exam Question



Consider ammonia (NH_3), phosphine (PH_3), silane (SiH_4), and methane (CH_4). Their vapor pressures in no particular order are 408, 3.5, 4520, and 128 kPa. Their ΔH_{vap} values in no particular order are 23.33, 8.19, 12.1, and 14.6 kJ/mol. What is the vapor pressure and ΔH_{vap} of phosphine?

1. 128 kPa, 14.6 kJ/mol

2. 408 kPa, 12.1 kJ/mol

3. 128 kPa, 12.1 kJ/mol

4. 408 kPa, 14.6 kJ/mol

$:NH_3$, $:PH_3$, SiH_4, CH_4

H-bond, dipole-dipole, dispersion (big), dispersion

VP 408, 3.5, 4520, 128 Kpa

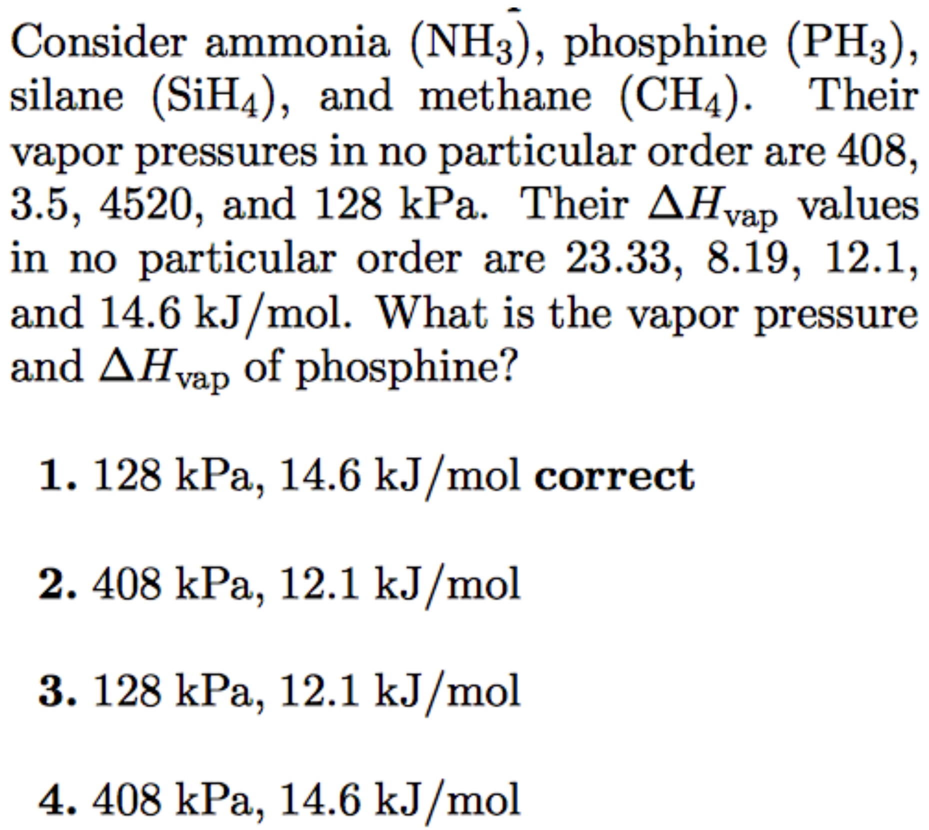
ΔH_{vap} 23.33, 8.19, 12.1, 14.6 KJ/mol

← ΔH_{vap} —

— VP →

3.5,	128,	408,	4520
23.33,	14.6,	12.1,	8.19
NH_3,	PH_3,	SiH_4,	CH_4

Vapor Pressure Exam Question



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1. 128 kPa, 14.6 kJ/mol **correct**

2. 408 kPa, 12.1 kJ/mol

3. 128 kPa, 12.1 kJ/mol

4. 408 kPa, 14.6 kJ/mol

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 a liquid solvent that has a vapor pressure of 0.63 atm at room temperature? The enthalpy of vaporization of this solvent is 30 kJ/mol. Answer in Celsius.

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

$T_2 = RT = 298.15K$

$P_2 = 0.63$ atm

normal BP = Temperature at which VP = 1atm
760 torr

$P_1 = 1$ atm

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

$$\underset{\underset{A}{\Downarrow}}{\ln\left(\frac{0.63}{1}\right)} = \underset{\underset{B}{\Downarrow}}{\frac{30}{0.008314}}\left(\frac{1}{T_1} - \frac{1}{298.15}\right)$$

$$\underbrace{\frac{A}{B} + \frac{1}{298.15}}_{C^{-1} = T_1} = \frac{1}{T_1}$$

37°C

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.

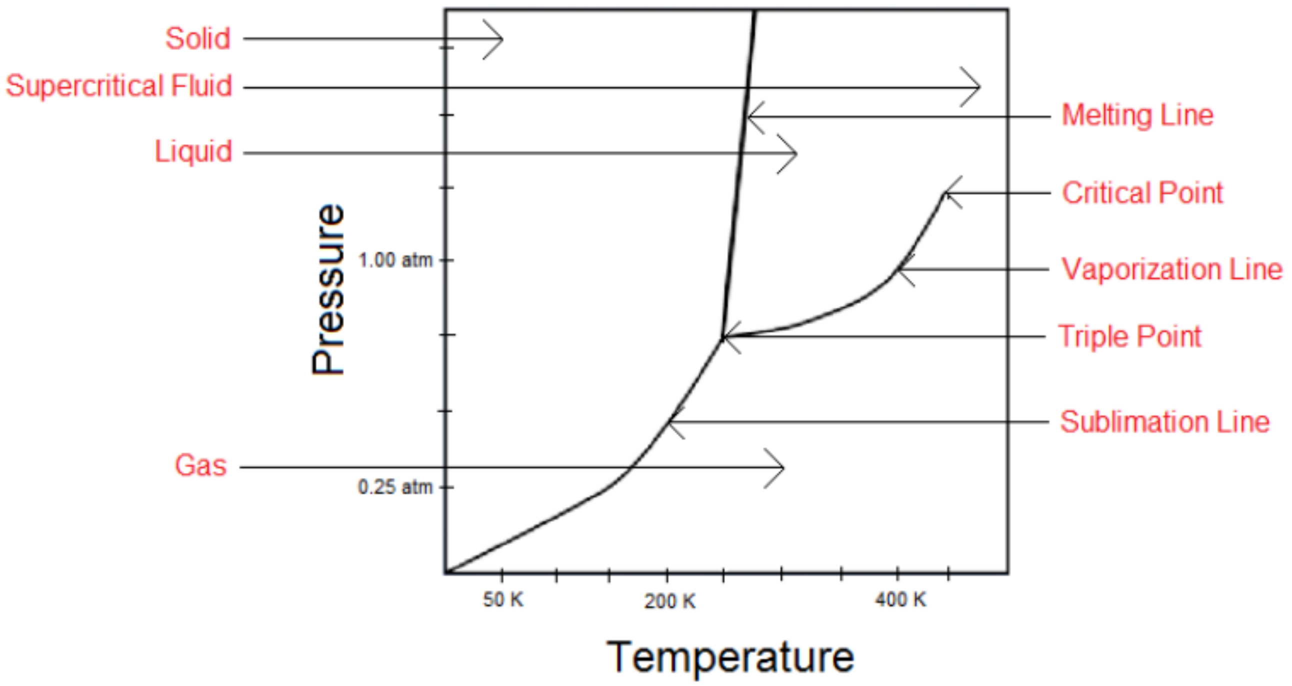
Set up using C-C equation. Final answer is 37˚C

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

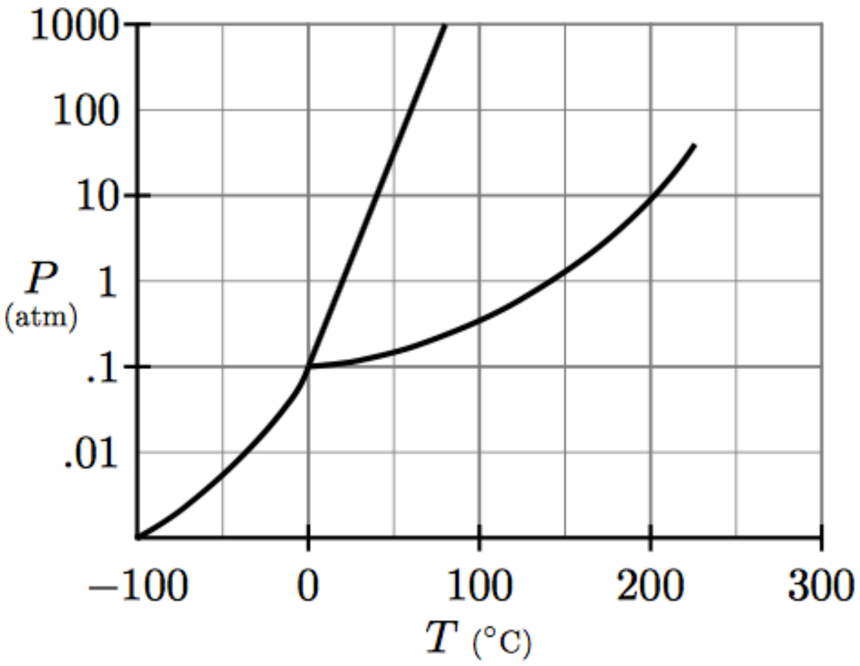
- Phase diagrams show the lowest free energy phase of a substance at a given temperature and pressure.



- 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



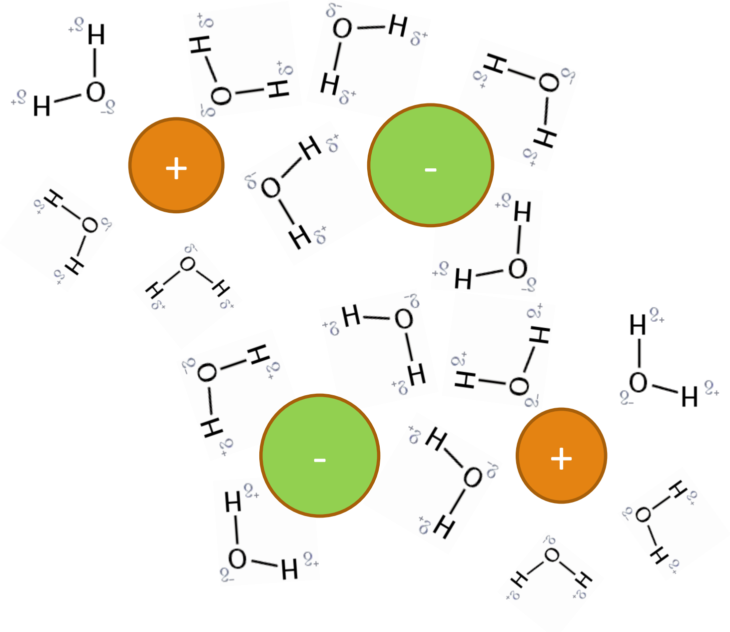
- What is the critical pressure of this substance?
  I. 35
  II. 100
  III. 90
  IV. 0.1
- What is the normal boiling point of this liquid ?
  I. 100˚C
  II. 0˚C
  III. 140 ˚C
  IV. 200 ˚C

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.
- **Whether a solute dissolves in a liquid solvent or not depends on basic thermodynamics: if the solution is more stable than the solute + solvent individually, the free energy of solution will be negative.**



- What does this mean? It means that if you dissolve a solute into a solvent, you are making a solution with a lower free energy.

Enthalpy of Solution

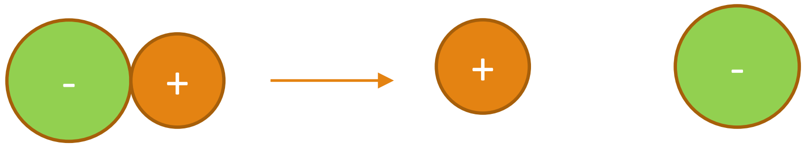
$$\Delta H_{solution} = \Delta H_{lattice} + \Delta H_{solvation}$$

Always +

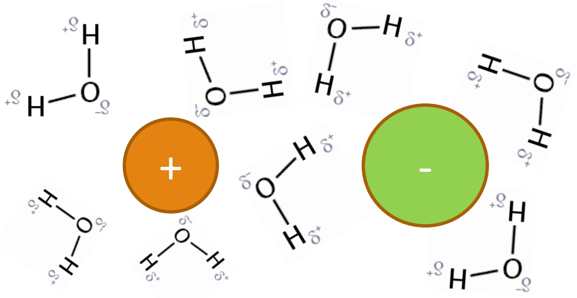
Always -

Step one: Lattice Energy breaks apart ionic compound

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



+

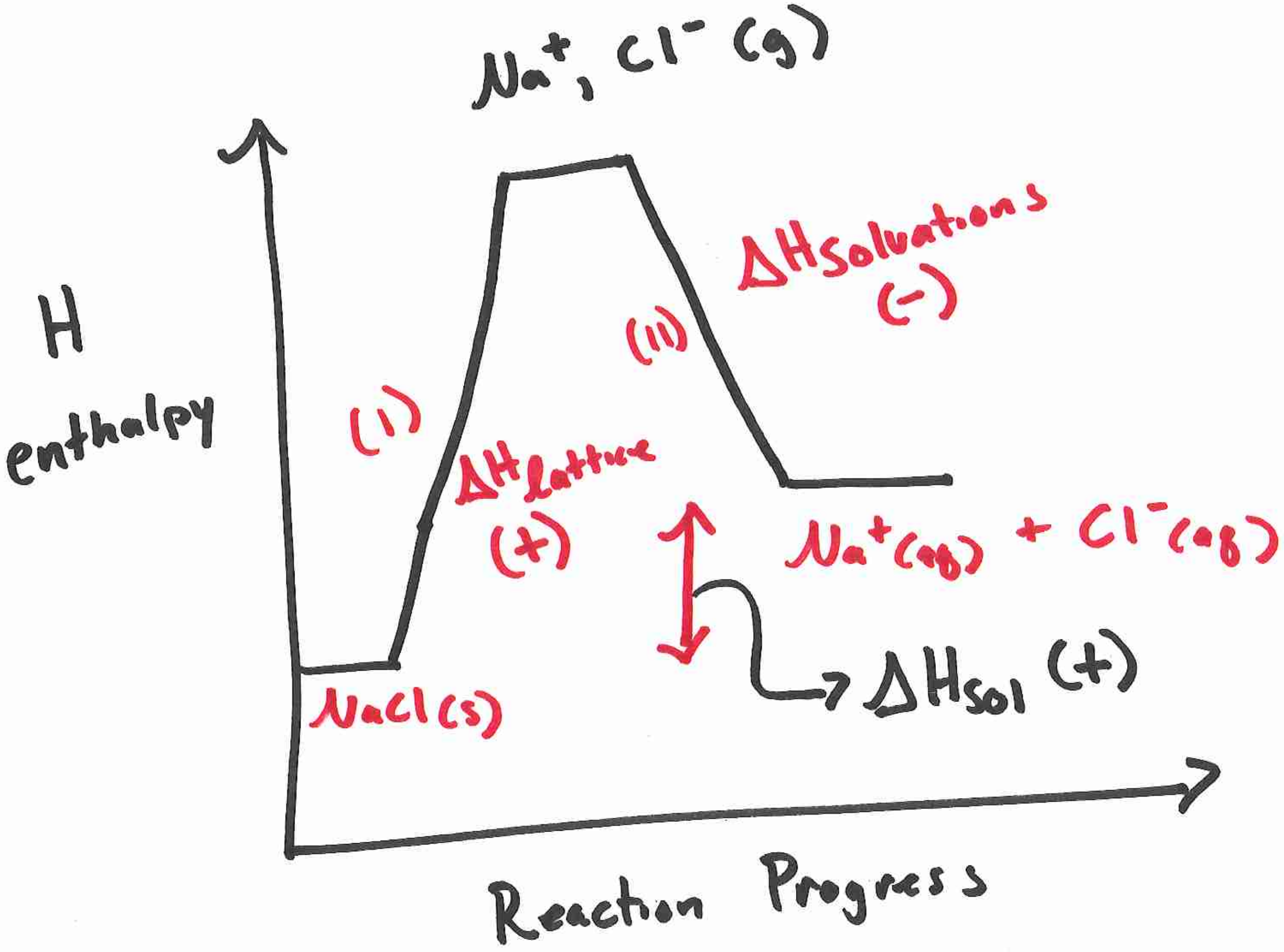


+ $\Delta H_{lattice}$ (positive value)

Bonds breaking = endothermic

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

Bonds forming = exothermic



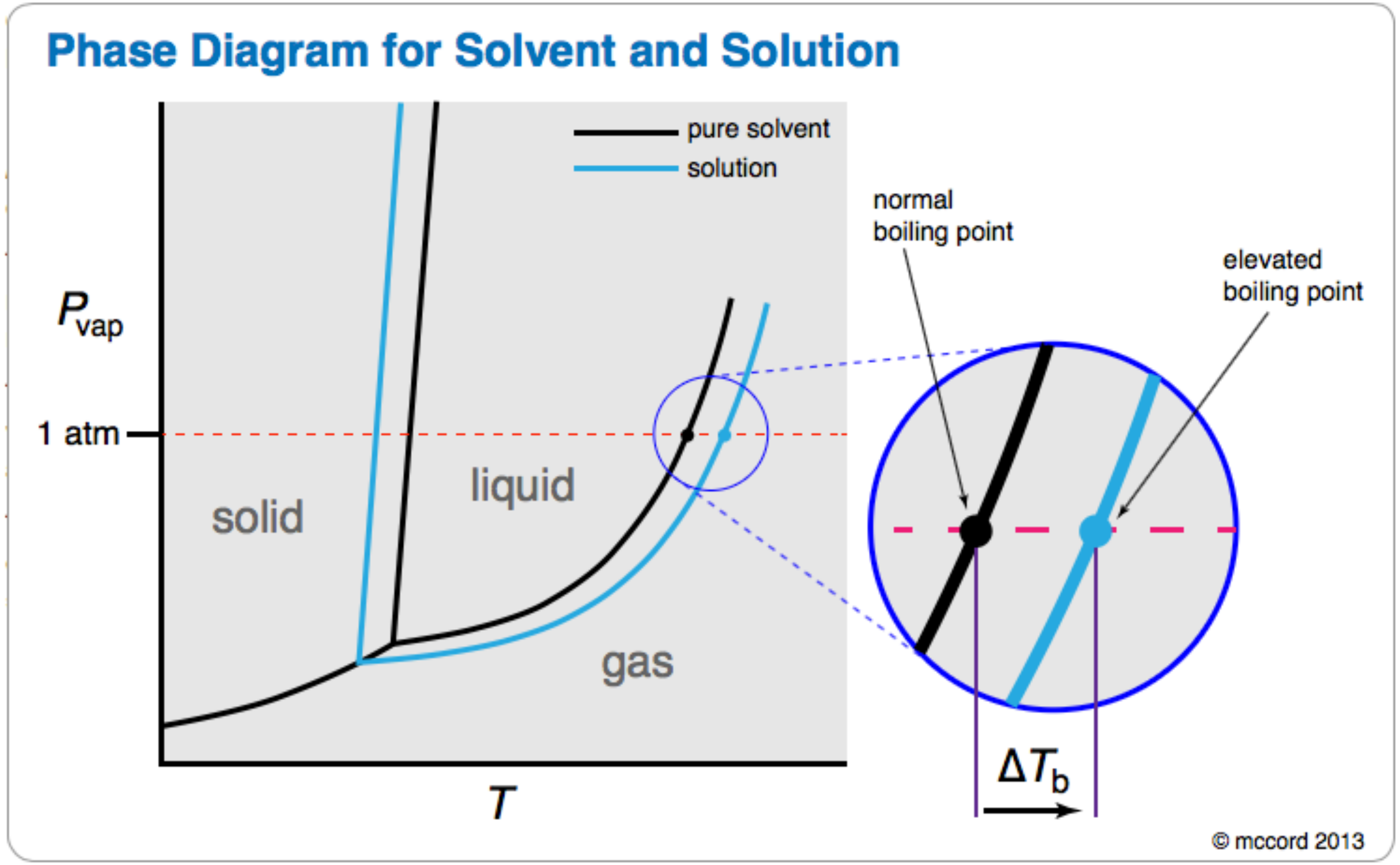
$\Delta H_{solution}$ is (+) for NaCl

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

$$\underline{\underline{(-)}} = (+) - \text{high}\,T\,(+)$$

Boiling Point Elevation, Freezing Point Depression

- Creating a solution from a pure solvent lowers the free energy of your substance in the liquid phase.
- This has two effects:
  1. **The freezing point decreases**
  2. **The boiling point increases**
- You can see in the diagram to the right that the liquid phase is favored in a larger range of temperatures



$\Delta T_f = i\, k_f\, m$

van’t Hoff Factor

- Colligative properties depend on the number of effective solute concentration, which can be more than just the given concentration.
- **Why? in the case of electrolytes (salts), colligative properties depend on the concentration of ions rather than the initial amount of the solid salt.**
- We make this “correction” by using the Van’t Hoff Factor (i) in our colligative properties calculations
- **The Van’t Hoff Factor is the total number of solute species in solution**

Which of the following solutions has the same boiling point as 0.6M Sucrose?

a. 0.6 M NaCl

b. 0.2 M Na_2SO_4

c. 0.12 M Fe_3SO_4

Colligative Property Summary

Vapor Pressure Lowering (Raoult's Law):

- Solves for **the *new* vapor pressure** (P_A) of a solution, based on the **mole fraction of the solvent** (X_A)
  - $P_A = X_A P°_A$

Freezing Point Depression:

- Solves for the ***negative change* in the freezing point** (ΔT_f), based on the **molality of the solute** (m)
  - $\Delta T_f = i\ k_f\ m$

Boiling Point Elevation:

- Solves for **the *positive change* in the boiling point** (ΔT_b), based on **the molality of the solute** (m)
  - $\Delta T_b = i\ k_b\ m$

Osmotic Pressure:

- Solves for the pressure exerted by a fluid to restore osmotic equilibrium, based on **the molarity of the solute** (M)
  - $\Pi = iMRT$

Boiling Point Elevation, Freezing Point Depression

- Using the following equations, you are solving for the change in the freezing point or boiling point. **Remember: you are solving for a change (ΔT_f is always negative, ΔT_b is always positive) and you are NOT solving for the final temperatures.**

Freezing Point Depression:

Solves for the ***negative change* in the freezing point** (ΔT_f), based on the **molality of the solute** (*m*)

$$\Delta T_f = i\ k_f\ m$$

Boiling Point Elevation:

Solves for **the *positive change* in the boiling point** (ΔT_b), based on **the molality of the solute** (*m*)

$$\Delta T_b = i\ k_b\ m$$

Vapor Pressure Lowering

- Vapor Pressure is **lower when a liquid is more stable**. Therefore, it should make sense that when you create a lower free energy solution from a pure solvent, the vapor pressure goes down.
- **Mathematically, vapor pressure looks like this:**

Vapor Pressure Lowering (Raoult's Law):

Solves for **the *new* vapor pressure** (P_A) of a solution, based on the **mole fraction of the solvent** (X_A) and the vapor pressure of the pure solvent ($P°_A$)

$$P_A = X_A P°_A$$

You WILL have to account for electrolytes in the "total moles" of this mole fraction term, even though you don't see a Van't Hoff Factor here.

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)

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

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

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

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 (usually) 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.