

# CH 302 Exam Review

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PHYSICAL EQUILIBRIUM, INTRO TO CHEMICAL EQUILIBRIUM

# Thermodynamics of Phase Changes

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STATE FUNCTIONS, PHASE DIAGRAMS, VAPOR PRESSURE

$$\Delta G^{(-)} = \Delta H - T\Delta S$$

## Free Energy - Phase Changes

$\Delta H$	$\Delta S$	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T

$g \rightarrow l \rightarrow s$

Freezing, condensation, deposition

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

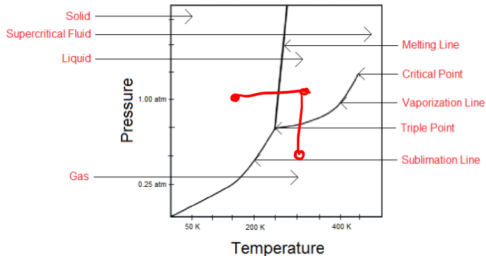
$s \rightarrow l \rightarrow g$

Fusion (melting), boiling, sublimation

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

# Phase Diagram Checklist

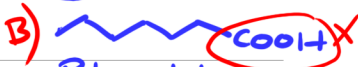
- Phase diagrams show the lowest free energy phase of a substance at a given temperature and pressure.



- 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?

Temperature, identity of the liquid

# Vapor Pressure and IMF's



## Polarizability

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:

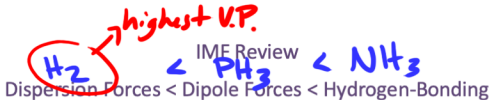
$CH_3OH$ ,  $H_2O$ ,  $HF$ ,  $NH_3$ , etc.

- 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 IMF's and be "lifted into the gas phase").



Strong IMF -> low VP (and high boiling point, high  $\Delta H_{vap}$ )

Weak IMF -> high VP (and low boiling point, low  $\Delta H_{vap}$ )



# Vapor Pressure Conceptual Question

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

Benzaldehyde, 1.27 mmHg

Formaldehyde, 3284 mmHg

↓VP ↑ $\Delta H_{vap}$   
↑BP?

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  $\Delta H_{vap}$
- II. has a higher boiling point
- III. has a lower  $\Delta H_{vap}$
- IV. has a greater number of molecules in the condensed phase

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

SAME!

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 Calculations

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

**Higher Temperature = Exponentially Higher Vapor Pressure**

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

- 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:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

*Handwritten notes in red and blue:*  $\Delta H < 0, \uparrow T \downarrow K$  and  $\Delta H > 0, \uparrow T \uparrow K$ . Red checkmarks are placed above  $\Delta H_{vap}$  and below  $R$  in the final equation.

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.

# Solutions

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



$\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$   
 Enthalpy of Salt Solution

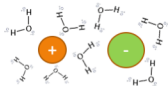
$\Delta G = \Delta H - T\Delta S$   
 (-) = (+) - T (+) (+)

$\Delta H_{\text{solution}} = \Delta H_{\text{lattice}} + \Delta H_{\text{solvation}}$   
 Always +      Always -

Step one: Lattice Energy breaks apart ionic solute-solute attractions (bonds breaking, endothermic)



+ Step two: Solvation Energy is released when solute-solvent attractions are formed (bonds forming, exothermic)



Theoretically, the value of  $\Delta H_{\text{solution}}$  should be 0. But what if...

1.  $\Delta H_{\text{lattice}} > \Delta H_{\text{solvation}}$

$\Delta H_{\text{sol}} > 0$

2.  $\Delta H_{\text{solvation}} > \Delta H_{\text{lattice}}$

$\Delta H_{\text{sol}} < 0$



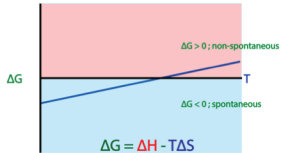
$$\Delta G = \Delta H - T\Delta S$$

(-) - T(-)

↓

## Gas Dissolving in Water - Details

- For a gas dissolving in liquid, the reaction is exothermic ( $\Delta H_{\text{solution}} < 0$ ) because there is **no lattice energy** and a negative solvation energy.
- There is a negative change in entropy ( $\Delta S < 0$ ) because you are going from gas to aqueous
- Therefore, dissolution is favored at low temperatures. Why? Dissolution of a gas is an enthalpy driven process!
- Henry's Law also states that gas dissolution is favored at high pressures.

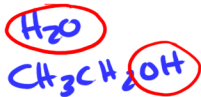


—  $\Delta S < 0, \Delta H < 0$ ; spontaneous at low temperatures

$$\checkmark P_{\text{gas,above}} = KX_{\text{gas,dissolved}}$$
$$\checkmark C_{\text{gas,dissolved}} = KP_{\text{gas,above}}$$

# Miscibility of Liquids - Like-Dissolves-Like

Like the dissolution of a solid, liquids mixing is typically an entropy-driven process, favored at high temperatures:



$$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} = \text{Negative}$$
$$\Delta G_{\text{solution}} = (+) - T(+)$$



Like the dissolution of a solid, liquids mixing is typically an entropy-driven process. There are two important points here:


1. Enthalpy is important when mixing two liquids. Matching the IMF's of two liquids MINIMIZES the  $\Delta H$  term.
2. Increasing temperature increases solubility

$\Delta H_{\text{solution}}$  is ~0  
when similar IMFs

# Colligative Properties

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DECREASING THE FREE ENERGY RESULTS IN A MORE STABLE LIQUID SOLUTION

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


## Colligative Property Summary

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### ✓ 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** ( $X_A$ )
- $P_A = X_A P_A^\circ$

### ✓ Freezing Point Depression:

- Solves for the **negative change in the freezing point** ( $\Delta T_f$ ), 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** ( $\Delta T_b$ ), 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** ( $M$ )
- $\Pi = iMRT$

van't Hoff Factor,  $\Delta T_f = i k_f m$

$i \cdot m$

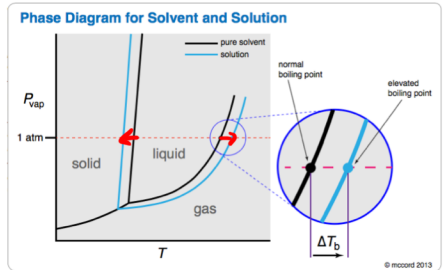
Colligative properties depend on the **identity of the solvent** and the **effective solute concentration**, which can be more than just the given concentration.

Compound	van't Hoff Factor
CaCO <sub>3</sub>	2
→ Glucosamine	1
Ca(NO <sub>3</sub> ) <sub>2</sub>	3
Fe <sub>2</sub> O <sub>3</sub>	5
CO <sub>2</sub>	1



# Stabilizing the Solution - Colligative Properties

- Creating a solution from a pure solvent lowers the free energy of your substance in the liquid phase.
- This has four effects that we call the **colligative properties**
- You can see in the diagram to the right that the liquid phase is favored in a larger range of temperatures
- The point: Colligative properties are a package deal



# Boiling Point Elevation, Freezing Point Depression

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

## Freezing Point Depression:

Solves for the **negative change in the freezing point** ( $\Delta T_f$ ), 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** ( $\Delta T_b$ ), based on the **molality of the solute** ( $m$ )

$$\Delta T_b = i k_b m$$



## Effective Concentration Comparisons

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Which of the following aqueous solutions have the same boiling point as 0.6 M sucrose?

a. 0.6 M NaCl  $\times 2 = 1.2 M$

b. 0.6 M glucosamine

c. 0.3 M KOH  $\times 2 = 0.6 M$

d. 0.2 M Na<sub>2</sub>SO<sub>4</sub>  $\times 3 = 0.6 M$

Which of the following aqueous solutions has the highest boiling point?

a. 0.6 M NaCl  $\times 2 = 1.2$   
 $\rightarrow 2Na^+ + SO_4^{2-}$

b. 0.2 M Na<sub>2</sub>SO<sub>4</sub>  $\times 3 = 0.6$

c. 0.6 M Sucrose  $\times 1 = 0.6$

Follow-up: Which of those solutions has the lowest freezing point? **a.**

# 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 lowering 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 ( $P_A^\circ$ )

$$P_A = X_A P_A^\circ$$

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.

mol Solvent  
mol Solvent +  $i \times$  mol Solute

## Vapor Pressure Lowering - Mixing Volatile Liquids

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- The vapor pressure of a binary liquid (A + B) must take into account the vapor pressure of both liquids.
- **Mathematically, this follows Dalton's Law of Partial Pressures:**

Vapor Pressure Lowering (Raoult's Law) + Dalton's Law:

$$P_A = \underline{X_A} P_A^\circ$$

$$P_B = \underline{X_B} P_B^\circ$$

$$P_{\text{total}} = P_A + P_B$$

# Vapor Pressure Lowering - Mixing Liquids

Consider two liquids, A and B. Liquid A has a vapor pressure of 200 Torr. Liquid B has a vapor pressure of 400 Torr. Calculate the vapor pressure when the concentrations of A and B are equal.

$$1 = \chi_A + \chi_B$$
$$\chi_A = \chi_B$$

$$\chi_A = 0.5, \chi_B = 0.5$$

Vapor Pressure Lowering (Raoult's Law):

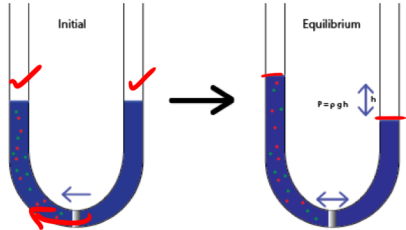
Solves for the total vapor pressure

$$\begin{aligned} P_A &= \chi_A P_A^\circ \\ P_B &= \chi_B P_B^\circ \\ P_{\text{total}} &= P_A + P_B \end{aligned}$$
$$\begin{aligned} (0.5)(200) &= 100 \\ (0.5)(400) &= 200 \\ \hline &= 300 \text{ Torr} \end{aligned}$$

Dalton's Law (CH301)

# Osmotic Pressure

- **Osmotic pressure is the pressure exerted by a fluid to restore osmotic equilibrium.**
- The basic idea is that fluid will flow from the less concentrated to the high concentrated side of a semipermeable membrane (only allows the flow of the solvent; blocks solute).
- The result is a more dilute solution on the left, but an equilibrium is established where there is still pure water left
- Again, this property is due to the fact that the solution is lower in energy. **This is why water flows toward the solution (going from high to low free energy).**



$$\Pi = iMRT$$

$\downarrow$   
mol  
 $\downarrow$

# Chemical Equilibrium

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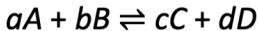
MASS ACTION EXPRESSION, EQUILIBRIUM CONSTANT

# Introduction to Chemical Equilibrium

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A working definition for equilibrium is the state of a chemical reaction when the rate of the forward reaction and the reverse reaction are equal.

- At this point, there is no net change in the concentrations of your reaction ( $\Delta G = 0$ )
- We use the equilibrium constant,  $K$ , to calculate these exact amounts at equilibrium:



$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

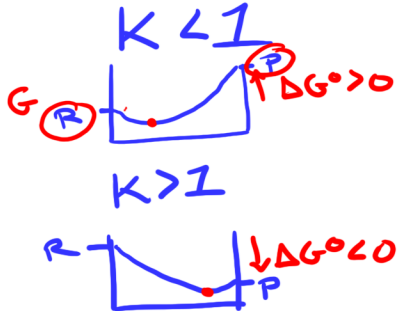
Mathematically,  $K$  is equal to the ratio of the action of the products raised to the power of their coefficients divided by the action of the reactants raised to the power of their coefficients.

Conceptually,  $K$  is a description of the equilibrium state. Not that a reaction is "spontaneous"/"non-spontaneous", but what the actual concentrations of the products/reactants are at equilibrium

Key point: Non-spontaneous reactions still can occur to a certain extent. Spontaneous reactions don't always go to 100% products

## Interpreting K

- When  $K$  is small (less than 1), your reaction is reactant-preferred. A reaction with a small  $K$  reacts to a small extent.
- When  $K$  is large (greater than 1), your reaction is product-favored. A reaction with a large  $K$  reacts to a large extent.





# Introduction to Chemical Equilibrium

- We can directly correlate activity to pressure and concentration to create a more sensible relationship.

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

*(Note: The above equation is heavily scribbled over with red ink in the original image. Arrows point from the activity terms to the corresponding concentration and pressure terms below.)*

$$a_i = \frac{[i]}{[i]^0}$$
$$a_i = \frac{P_i}{P^0}$$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

REMEMBER: Assume for this example that all species in the  $K_c$  example are aqueous. All the species in the  $K_p$  example are gases. Remember: the action of any LIQUID or SOLID is 1. These terms will drop out of the mass action expression.

# Brief overview of Equilibrium Terminology

- We use the relationship between  $Q$  and  $K$  to explain which way a reaction will progress toward equilibrium
- If the starting point of a reaction is  $Q < K$ , the reaction moves forward toward equilibrium
- If the starting point of a reaction is  $Q > K$ , the reaction moves backward toward equilibrium.
- We stress a system at equilibrium to examine how a reaction will “shift” to oppose the stress

$Q < K$   
rxn moves forward

$Q > K$   
rxn moves backward



# Anatomy of a RICE Table

$Q < K$

$$K = 50$$

$$K = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}}$$

R	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$		
I	0.1	0.1	$\emptyset$
C	-x	-x	+2x
E	0.1-x	0.1-x	2x

$$\sqrt{50} = \frac{(2x)^2}{(0.1-x)^2}$$