

# AGENDA

## UC Davis General Chemistry II Winter 2018: Delmar Larsen

Unit I: Chemical Thermodynamics • Unit II: Physical Equilibria • Unit III: Chemical Equilibria  
Agenda • Homework Exercises • Worksheets

Unit I: Chemical Thermodynamics	Unit II: Physical Equilibria	Unit III: Chemical Equilibria
<ul style="list-style-type: none"> <li>Lecture 1: 1/8/2018 (Fundamentals of Thermochemistry)</li> <li>Lecture 2: 1/10/2018 (Fundamentals of Thermochemistry)</li> <li>Lecture 3: 1/12/2018 (Fundamentals of Thermochemistry)</li> <li>No Lecture: 1/15/2018 (Martin Luther King Holiday)</li> <li>Lecture 4: 1/18/2018 (Principles of Thermodynamics)</li> <li>Lecture 5: 1/19/2018 (Principles of Thermodynamics)</li> <li>Lecture 6: 1/22/2018 (Principles of Thermodynamics)</li> <li>Lecture 7: 1/24/2018 (Principles of Thermodynamics)</li> <li>Lecture 8: 1/26/2018 (Principles of Thermodynamics)</li> <li>Exam 1: 1/29/2018 (Lecture 1 - Lecture 8)</li> </ul>	<ul style="list-style-type: none"> <li>Lecture 9: 1/31/2018 (States of Matter)</li> <li>Lecture 10: 2/2/2018 (States of Matter)</li> <li>Lecture 11: 2/5/2018 (States of Matter)</li> <li>Lecture 12: 2/7/2018 (States of Matter)</li> <li>Lecture 13: 2/9/2018 (States of Matter)</li> <li>Lecture 14: 2/12/2018 (States of Matter)</li> <li>Lecture 15: 2/14/2018 (States of Matter)</li> <li>Lecture 16: 2/16/2018 (States of Matter)</li> <li>No Lecture: 1/19/2018 (Presidents' Day)</li> <li>Lecture 17: 2/21/2018 (States of Matter)</li> <li>Lecture 18: 2/23/2018 (States of Matter)</li> <li>Exam 2: 2/26/2018 (Lecture 9 - Lecture 18)</li> </ul>	<ul style="list-style-type: none"> <li>Lecture 19: 2/28/2018 (Chemical Equilibria)</li> <li>Lecture 20: 3/2/2018 (Distillation and Chemical Equilibria)</li> <li>Lecture 21: 3/5/2018 (Chemical Equilibria)</li> <li>Lecture 22: 3/7/2018 (Chemical Equilibria)</li> <li>Lecture 23: 3/9/2018 (Chemical Equilibria)</li> <li>Lecture 24: 3/12/2018 (Acids and Bases)</li> <li>Lecture 25: 3/14/2018 (Acids and Bases)</li> <li>Lecture 26: 3/16/2018 (pH Calculations, Common Ions, Buffers and Polyprotic Acids)</li> <li>Comprehensive Review: Cruess 107 @ 1:00 - 3:00 (Monday)</li> <li>Final Exam: 3/20/20 17 @ 6:00 p.m.-8:00 p.m. (Tuesday)</li> </ul>

## LECTURE 1: 1/8/2018 (FUNDAMENTALS OF THERMOCHEMISTRY)

Energy is the capacity to supply heat or do work. Two ways to transfer energy: Heat (Originate from difference in temperatures (i.e., average kinetic energy of molecules)) and Work (moving an object against a resistance (e.g., expansion work of a gas)). Mechanical work:  $w = Fd$ , Expansion (PV) Work:  $w = P\Delta V$  (under constant pressure). Energy is fluid (but not a real fluid) that can be converted where Kinetic energy can be interconverted with Potential Energy.

Readings	Homework	Worksheets
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Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>12.1: Systems, States and Processes</li> <li>12.2: Heat</li> <li>12.3: Work</li> <li>12.4: The First Law of Thermodynamics</li> </ul>	<ul style="list-style-type: none"> <li>Homework 1 (Due 1/12/2018 in class)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 1: Thermochemistry I</li> </ul>

### Assumed Knowledge

- Temperature Conversion and Dimensional Analysis

## LECTURE 2: 1/10/2018 (FUNDAMENTALS OF THERMOCHEMISTRY)

Both Heat and Work are path functions (depends on the path taken from point A to B). Energy (internal) is a state function (depends on the difference from point A to B). Internal Energy, Heat, and work are connected via the First Law of Thermodynamics (which is the really the law of conservation of energy)  $\Delta U = q + w$ . The universe can be cut up into either system or surrounding: (1) An open system is a system that freely exchanges energy and matter with its surroundings. (2) A closed system is a system that exchanges only energy with its surroundings, not matter. (3) An isolated system does not exchange energy or matter with its surroundings. Reactions can be exothermic ( $q_{sys} < 0$ ) or endothermic ( $q_{sys} > 0$ ). Also, Internal energy vs. External Energy. We introduce Heat Capacity (almost always positive). Internal Energy, Heat, and work are connected via the First Law of Thermodynamics (which is the really the law of conservation of energy). Many (most) real physical and chemistry reaction has an associated heats including: Heat of combustion ( $\Delta H_{comb}$ ), Heat of fusion ( $\Delta H_{fus}$ ), Heat of vaporization ( $\Delta H_{vap}$ ), Heat of solution ( $\Delta H_{soln}$ ).

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>12.5: Heat Capacity, Calorimetry and Enthalpy</li> <li>12.5B: Molecules as Energy Carriers and Converters</li> </ul>	<ul style="list-style-type: none"> <li>Extra Exercises (do not turn in)</li> <li>Extra Exercises (Even more Solutions)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 1: Thermochemistry I</li> </ul>

## LECTURE 3: 1/12/2018 (FUNDAMENTALS OF THERMOCHEMISTRY)

Path vs. State variables. Physical and chemistry process (changes) have associated "heats". Breaking a bond always require energy. Making a bond always gives energy. Hamburgers have a lot of energy (quantified by combustion). Heats of a process can be quantified via calorimetry – either constant volume or constant pressure (what is the difference between these?). Special situations that make problems "easier": Isochoric, Adiabatic, Isothermal, Isobaric. Introduce the Enthalpy potential:  $\Delta H = \Delta U + P\Delta V$ . Energy is the heat released or absorbed (at const. pressure) and is ONE of the "driving forces" behind a process (physical or chemical).

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>12.6: Heats of Reactions: <math>\Delta U</math> and <math>\Delta H</math></li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 2 (Due 1/19/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 1: Thermochemistry I</li> </ul>

## NO LECTURE: 1/15/2018 (MARTIN LUTHER KING HOLIDAY)

## LECTURE 4: 1/18/2018 (PRINCIPLES OF THERMODYNAMICS)

Enthalpy is a potential that is one driving force for pushing a reaction (chemical or physical). Since only differences of enthalpies matter, there is no absolute enthalpy values. There are differing kinds of enthalpies of physical change: (1) Vaporization and Condensation, (2) Freezing and Melting, (3) Deposition and Sublimation. Breaking intermolecular forces cost energy (whether covalent or not). Enthalpies are additive. Why? Can construct heating or cooling curves for a system (often with a phase change or two). Hess's "law of obvious properties of a State Function" can be used to combine rxn eqn's and rxn heats. And can use known rxn heats and combine to get rxn heats for other rxns.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>12.7: Indirect Determination of <math>\Delta H</math>: Hess's Law</li> <li>12.8: Standard Enthalpies of Formation</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 2 (Due 1/19/2018)</li> <li>Data-Driven Homework 1 (1/24/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 2: Thermochemistry II</li> </ul>

## LECTURE 5: 1/19/2018 (PRINCIPLES OF THERMODYNAMICS)

Definition of Standard States. Definition of Heat of Reaction. Hess's "Law of Obvious properties of a State Function." Defined in terms of Enthalpy. Definition: (Standard) Heat of Formation. Mathematical Application of Hess's Law:

$$\Delta H^{\circ}_{rxn} = \sum n \cdot \Delta H^{\circ}_f(\text{products}) - \sum n \cdot \Delta H^{\circ}_f(\text{reactants}) \quad (1)$$

Enthalpy can drive a reaction (chemical or physical) and so can entropy. Entropy works by a "desire" to be more probable. Not a desire to be more disordered. Gibbs "Free" energy combines both in one function:  $\Delta G = \Delta H - T\Delta S$ . Like Enthalpy, Entropy is extensive and a state variable.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>13.1: The Nature of Spontaneous Processes</li> <li>13.2: Entropy and Spontaneity: A Molecular Statistical Interpretation</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 2 (Due 1/19/2018)</li> <li>Comprehensive Homework 3 (Due 1/26/2018)</li> <li>Data-Driven Homework 1 (1/24/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 2: Thermochemistry II</li> </ul>

## LECTURE 6: 1/22/2018 (PRINCIPLES OF THERMODYNAMICS)

Macrostates: A configuration you can observed- not caring about distinguishability of components of the ensemble. Microstates: A configuration that addresses the distinguishability of components of the ensemble. Entropy can be defined in terms of the weight of microstates for a specific configuration:  $S = k_B \ln \Omega$ .

Readings	Homework	Worksheets
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Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>13.3: Entropy and Heat: Experimental Basis of the Second Law of Thermodynamics</li> <li>13.4: Entropy Changes and Spontaneity</li> <li>The Molecular Basis for Understanding Simple Entropy Change (Optional)</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 3 (Due 1/26/2018)</li> <li>Data-Driven Homework 1 (1/24/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 2: Thermochemistry II</li> <li>Worksheet 3: Entropy and Probability</li> </ul>

## LECTURE 7: 1/24/2018 (PRINCIPLES OF THERMODYNAMICS)

Entropy works by a “desire” to be more probable. Not a desire to be more random. Spontaneous reactions in isolated systems require entropy to increase. Gibbs “Free” energy combines both in one function. Can backtrack entropy to the increase of available states. Then the drive for entropy is just the drive to be more probable: Higher mass species have higher entropy (PIB), Species with more atoms have higher entropy (#vibrations), and species with more flexibility have higher entropy (weaker spring constant in HO). Third Law of thermodynamics assigns a zero to entropy. Can do Hess-like problems to identify entropies of reaction.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>13.4: Entropy Changes in Reversible Processes</li> <li>13.5: Entropy Changes and Spontaneity</li> <li>13.6: The Third Law of Thermodynamics</li> </ul>	<ul style="list-style-type: none"> <li>Data-Driven Homework 1 (1/24/2018)</li> <li>Data-Driven Homework 2 (1/31/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 2: Thermochemistry II</li> <li>Worksheet 3: Entropy and Probability</li> </ul>

- Example Midterm 1 Questions
- Example Midterm 1 Solutions

## LECTURE 8: 1/26/2018 (PRINCIPLES OF THERMODYNAMICS)

We can reconfigure the 2nd law:  $\Delta S_{\text{entire isolated system}} > 0$  into  $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$ . This is an applicable criterion for spontaneity under **constant pressure and constant temperature**: (1) Reactions can be enthalpically driven, (2) Reactions can be entropically driven, (3) Reactions can be both enthalpically and entropically driven (4) or neither. Reactions that are neither are not spontaneous. Increasing temperature, increased entropic contribution to Gibbs Energy. Spontaneous if  $|\Delta S| < |\Delta H|$  if enthalpically driven **only**. Spontaneous if  $\Delta S > \Delta H$  if entropically driven **only**.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>13.7: The Gibbs Free Energy</li> </ul>	<ul style="list-style-type: none"> <li>Data-Driven Homework 2 (1/31/2018)</li> <li>No Monday Homework - Study hard for exam</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 3: Entropy and Probability</li> </ul>

- [Example Midterm 1 Questions](#)
- [Example Midterm 1 Solutions](#)

## EXAM 1: 1/29/2018 (LECTURES 1 - 8)

- [Example Midterm 1 Questions](#)
- [Example Midterm 1 Solutions](#)

## LECTURE 9: 1/31/2018 (STATES OF MATTER)

Physical Phenomena are guided by thermodynamics too. There are four fundamental forces of Nature, but electrostatic is “the beast” for chemistry. Three common states of matter (to chemists). Properties of each state is directly a consequence of the intermolecular forces at play Solids are Resistant to deformation and condensed phase. Gases are Compressible, expandable and not-condensed phase. Liquids have Definite volume and indefinite shape and condensed phase and have Fluidity, Diffusion and Surface tension.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>• <a href="#">10.1: Bulk Properties of Gases, Liquids, and Solids: Molecular Interpretation</a></li> <li>• <a href="#">10.2: Intermolecular Forces: Origins in Molecular Structure</a></li> <li>• <a href="#">10.3: Intermolecular Forces in Liquids</a></li> <li>• <a href="#">Optional: Electric Potentials (Physics Libretext)</a></li> </ul>	<ul style="list-style-type: none"> <li>• <a href="#">Data-Driven Homework 3 (2/7/2018)</a></li> <li>• <a href="#">Comprehensive Homework 4 (Due 2/2/2018)</a></li> </ul>	<ul style="list-style-type: none"> <li>• <a href="#">Worksheet 3: Entropy and Probability</a></li> <li>• <a href="#">Worksheet 4: Intermolecular Forces and Interactions</a></li> </ul>

## LECTURE 10: 2/2/2018 (STATES OF MATTER)

Intermolecular Forces dictate Bulk properties. Liquids have definite volume and indefinite shape and condensed phase. Other properties of liquids include: fluidity, diffusion, and surface Tension. Introduce the concept of a Potential Energy Surface (curve). Discussed four types of IMFs: (1) Permanent - Permanent Charge Distribution IMFs, (2) Permanent - Induced Charge Distribution IMFs, (3) Instantaneous - Induced Charge Distribution IMFs, and (4) Repulsive Forces. The potentials of these IMFs typically depend on both distance and orientation of the interacting molecules.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>• <a href="#">A survey of intermolecular forces (optional, but recommended)</a></li> <li>• <a href="#">10.4: Phase Equilibrium</a></li> </ul>	<ul style="list-style-type: none"> <li>• <a href="#">Data-Driven Homework 3 (2/7/2018)</a></li> <li>• <a href="#">Comprehensive Homework 4 (Due 2/2/2018)</a></li> <li>• <a href="#">Monday Homework 2 (Due 2/5/2018)</a></li> </ul>	<ul style="list-style-type: none"> <li>• <a href="#">Worksheet 4: Intermolecular Forces and Interactions</a></li> </ul>

## LECTURE 11: 2/5/2018 (STATES OF MATTER)

Discussed four types of IMFs: (1) Permanent - Permanent Charge Distribution IMFs, (2) Permanent - Induced Charge Distribution IMFs, (3) Instantaneous - Induced Charge Distribution IMFs, and (4) Repulsive Forces. Potential is Typically depends on Distance and Orientation (except ion-ion). Introduced the “Squishy” factor, which is really polarizability for a molecules:  $\mu_{ind} = \alpha E$ . The bigger the molecule, the larger the polarizability. The less bound the electrons in the molecule,

the larger the polarizability (1) This is correlated with the number of electrons (2) This is correlated with charge (ions < neutral < anions). Why? Discussed the relative energies of these energies and which ones are applicable depends on the nature of the molecules.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>10.5: Phase Transitions (you already know this stuff)</li> <li>10.6: Phase Diagrams</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 5 (Due 2/9/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 4: Intermolecular Forces and Interactions</li> </ul>

## LECTURE 12: 2/7/2018 (STATES OF MATTER)

More discussion of polarizability and what alters it: (1) size, (2) anisotropy (orientation), (3) effective charge on electrons, (4) number of electrons (related to effective charge). Properties of metals result from IMFs: (1) Conduction – sea of electron picture of bonding, (2) Malleability of metals, (3) High Melting points. Three Types of (crystalline) solids (so we are ignoring glasses and most polymers): (1) Ionic Solids (held by monopole-monopole forces), (2) Molecular Solids (held by higher order electrostatics and other IMFs), (3) Molecular Covalent (network) Solids (held by covalent bonding). Introduced lattices and unit cells (largely for ionic solids where we are packing balls). There are different types depending on size of ions. Discussed Vapor Pressure as result of equilibrium between condensed phase and gas phase. Equilibrium (dynamic vs. static, stable vs. unstable)

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>10.7: Clausius-Clapeyron Equation</li> <li>10.8: The Solid State</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 5 (Due 2/9/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 4: Intermolecular Forces and Interactions</li> </ul>

## LECTURE 13: 2/9/2018 (STATES OF MATTER)

Dynamic Equilibria equations: solid- liquid, liquid-vapor, solid-vapor. (should include phase-phase equilibria too). These occurs when microscopic rates equal... so no macroscopic changes occur. Distribution of kinetic energies: Temperature - > Average kinetic energy; Probability of molecules having energy above threshold energy instead with temperatures, Evaporation is an endothermic process (require heat to overcome IMF). This is manifested in the boiling (and melting points): greater IMF -> more energy needed to escape and more energy needed to escape -> greater boiling point. Similar argument can be made for solid-liquid equilibria. Boiling point is when vapor pressure equation external pressure. Normal Boiling point is temperature under 1 atm of pressure. Triple point is where three phases exist.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>10.9: Bonding in Metals</li> <li>Types of Solutions: Some Terminology</li> <li>Composition of Solutions</li> <li>Nature of Dissolved Species</li> <li>Solution Concentration</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 6 (Due 2/16/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 5A: Pure Phases and their Transitions</li> <li>Worksheet 5B: Solutions and Vapor Pressures</li> </ul>

## LECTURE 14: 2/12/2018 (STATES OF MATTER)

Pure Phase Transitions have different Phases in three different States: (1) A coexistence of two phases occurs in a line, (2) A coexistence of three phases occurs in a point (triple point), (3) Never see a coexistence of four phases. The curve for two phases in equilibrium is dictated by the Clapeyron equation:  $\frac{dP}{dT} = \frac{\Delta H}{T\Delta\bar{V}}$ . The Clapeyron equations can be approximated to the Clausius-Clapeyron Equation to address condensed phase-Gas phase equilibria. The Clausius-Clapeyron can be used for solid-gas equilibria (sublimation) or liquid-gas equilibria (vaporization). Critical point is another special point on diagram where the difference between liquid and gas is blurred. Lots of cool phenomena occur (e.g., increased solubility). Introduction to Solutions.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>Types of Solutions: Some Terminology</li> <li>Composition of Solutions</li> <li>Nature of Dissolved Species</li> <li>Solution Concentration</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 6 (Due 2/16/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 5A: Pure Phases and their Transitions</li> <li>Worksheet 5B: Solutions and Vapor Pressures               <ul style="list-style-type: none"> <li>Non-Ideal Mixtures of Liquids (useful for worksheet)</li> </ul> </li> </ul>

## LECTURE 15: 2/14/2018 (STATES OF MATTER)

We continue our discussion about Solutions. There are different types depends on state of solute and state of solvent. There are different ways to characterize solubility: Molarity and Mole fractions are the most popular although you must be familiar with others. The solubility of the a substance depends on the nature of the solute and solvent; specifically on the nature of the IMFs at play: "Like dissolve like". We can review thermodynamics of dissolving from a cycle perspective: Entropy ALWAYS favors Dissolving ( $\Delta S_{\text{solution}} > 0$ ), but Enthalpy does not ALWAYS favors Dissolving ( $\Delta H_{\text{solution}} > 0$  or  $< 0$  or  $= 0$ ). If  $\Delta H_{\text{solution}} = 0$  then entropy is the only force to dissolve and this is called an ideal solution.. Similar (but not identical) to an ideal gas. Introduce concept of a lattice energy as a metric of IMF strength with higher IMF  $\rightarrow$  higher lattice energy. Lattice energy for ions can be rationalized in terms of Coulmbic equations (size and charge): Greater charge or smaller ion  $\rightarrow$  greater latter energy. Solvation (or Hydration) Energy: The energy of interactions between solute and solvent... Higher IMF  $\rightarrow$  greater Solvation energy (enthalpy).

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>Types of Solutions: Some Terminology</li> <li>Solution Concentration</li> <li>Factors Affecting Solubility</li> <li>Temperature Effects on the Solubility of Gases</li> <li>Lattice Energies of Crystals               <ul style="list-style-type: none"> <li>Lattice Enthalpies and Born Haber Cycles (optionl and repeat of above)</li> </ul> </li> <li>Hydration Enthalpy</li> <li>Solution Types and Energetics (This is purely optional reading, but ties together concepts nicely the above factors)</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 6 (Due 2/16/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 5A: Pure Phases and their Transitions</li> <li>Worksheet 5B: Solutions and Vapor Pressures               <ul style="list-style-type: none"> <li>Non-Ideal Mixtures of Liquids (useful for worksheet)</li> </ul> </li> </ul>

## LECTURE 16: 2/16/2018 (STATES OF MATTER)

We continue our discussion about Solutions. Solubility is driven by Gibbs Energy differences. This involves both Entropy and Enthalpy differences. Entropy always drive dissolving ( $\Delta S > 0$ ). Enthalpy does not ALWAYS favor dissolving ( $\Delta H_{\text{solution}} > 0$  or  $< 0$  or  $0$ ). Enthalpy contribution is a difference of two Enthalpies (Energies): (1) Lattice Enthalpy and (2) Solvation (hydration) enthalpy. Sometimes the Gibbs energy is minimized for inhomogeneous mixtures (not solutions): e.g. Micelles (normal and reverse), cell membranes (bilayers); this can be viewed within the adhesive/cohesive force arguments discussed previously.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>Types of Solutions: Some Terminology</li> <li>Composition of Solutions</li> <li>Nature of Dissolved Species               <ul style="list-style-type: none"> <li>Electrolytes</li> </ul> </li> <li>Colloidal Suspensions</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 6 (Due 2/16/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 5A: Pure Phases and their Transitions</li> <li>Worksheet 5B: Solutions and Vapor Pressures               <ul style="list-style-type: none"> <li>Non-Ideal Mixtures of Liquids (useful for worksheet)</li> </ul> </li> </ul>

## NO LECTURE: 1/19/2018 (PRESIDENTS' DAY)

## LECTURE 17: 2/21/2018 (STATES OF MATTER)

(AGAIN) Solubility is driven by Gibbs Energy differences. This involves both Entropy and Enthalpy differences. Lattice Enthalpy can be calculated via a thermodynamic cycle: Born-Haber Cycle. Colligative properties depend on the nature of the solvent and the amount of solute... but are ideal properties since the IMF between solute and solvent don't matter. Vapor Pressure Lowering (using Mole Fraction), Boiling Point Elevation (using Molality), Melting Point Depression (using Molality), Osmotic Pressure (using Molarity). Raoult's Law (ideal): Vapor pressure is proportional pure solvent vapor pressure via the mole fraction of solution. Deviations of Raoult's Law result from the IMFs ( $\Delta \text{solution} \neq 0$ ): (1) Strong solvent-solute (vs. pure system) IMFs decreases vapor pressure and results in negative deviations and (2) Weak solvent-solute (vs. pure system) IMFs increases vapor pressure and results in positive deviations.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>11.5: Phase Equilibrium in Solutions: Nonvolatile Solutes</li> <li>11.6: Phase Equilibrium in Solutions: Volatile Solutes</li> <li>Non-Ideal Mixtures of Liquids</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 7 (Due 2/26/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 6: Colligative Properties</li> </ul>

## LECTURE 18: 2/23/2018 (STATES OF MATTER)

Close out the Colligative properties discussion, which depend on the nature of the solvent and the amount of solute. These are ideal properties since the IMFs between solute and solvent don't matter. We specifically discussed Boiling Point Elevation (using Molality), Melting Point Depression (using Molality), Osmotic Pressure (using Molarity). Osmotic Pressure can be used to determine molecular weights, for desalination (reverse osmosis) and is critical for cell nutrient regulation (Hypertonic vs. Isotonic vs. Hypotonic). Volatile solutes modify Raoult's law slightly ( $P_{\text{total}} = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ$ ). But non-ideality rears its head and you can have positive or negative deviations depending on relative IMFs involved. When the solution is non-ideal, Raoult's Law cannot be applied, but we can use Henry's Law (Henry's Law: The amount of dissolved gas is proportional to its partial pressure in the gas phase):  $P_A = k P_A^\circ$ . Henry's constant is related to the solubility of gas in solution (soda water and bends): [https://www.youtube.com/watch?v=DNtOBD\\_pF4](https://www.youtube.com/watch?v=DNtOBD_pF4).



Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>21.5: A Deeper Look: Lattice Energies of Crystals</li> <li>Raoult's Law and Ideal Mixtures of Liquids</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 7 (Due 2/26/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 6: Colligative Properties</li> </ul>

## EXAM 2: 2/26/2018 (LECTURES 9 - 18)

All topics from Lecture 11 to Lecture 21 are fair game on the exam including the readings (unless noted as optional).

- Example Midterm 2 Topics

## LECTURE 19: 2/28/2018 (CHEMICAL EQUILIBRIA)

Henry's Law is a non-ideal result. Equations of state can be ideal or not ideal. We can deal with non-ideality by pretending the ideal EOS works, but we tweak it with effective concentrations or pressures - these are called activities and fugacities (Everything should be defined in terms of these). Again, an equilibrium state is one that no change of the "macrostate" (observable) is observed. This does not mean the microstates are not constantly changing -> dynamics vs. static. The Law of Mass Action derived from a kinetic argument -> introduces an equilibrium constant. Interestingly, an equilibrium is constant (at a specific temperature - more later). Back to activities... why  $K_{eq}$  are often written in terms of concentrations, they really should be written in terms of activities (relative to a standard): Activities = concentrations when dilute. Activities can be bigger or less than concentrations when concentrated.  $A(\text{Solvents}) \approx 1$  (when dilute) and  $A(\text{liquid}) = A(\text{Solid}) = 1$  (this is really nice).

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>14.1: The Nature of Chemical Equilibrium</li> <li>14.2: The Empirical Law of Mass Action</li> <li>Electrolytes</li> <li>Activities and their Effects on Equilibria</li> </ul>	<ul style="list-style-type: none"> <li>Monday (Friday this time) Homework 3 (Due 3/1/2018)</li> <li>Comprehensive Homework 8 (Due 3/5/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 6: Colligative Properties</li> </ul>

## LECTURE 20: 3/2/2018 (CHEMICAL EQUILIBRIA)

Introduced Fractional Distillation: Separation of liquid mixtures on basis of boiling point. Results from differing concentration of components in the vapor and solution: Vapor is richer in more volatile component. Can go in steps (fractions) to concentrate more volatile component. Important in petroleum refineries. Distillation does NOT mean the boiling of the volatile component from the other. Then things can real (via IMFs).. Introduce azeotropes (minimum or maximum boiling). Law of Mass Action = Equilibrium Constants can be formulated in terms of activities (so in heterogeneous systems - >2 phases, things get easier). Why? The drive toward equilibrium is the same drive toward minimizing Gibbs energy.  $K_c$  and  $K_p$  are two "flavors" of equilibrium constants. For gases, they can be expressed as  $K_p = K_c(RT)^{\Delta g}$ . Reaction Quotients (Q) dictate how non-equilibrium system -> equilibrium. Le Châtelier Principle: stress is applied to a system in dynamic eq., the eq. tends to adjust to relieve the stress

Readings	Homework	Worksheets
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Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>Fractional Distillation of Ideal Mixtures (carry over from Phase Equilibria)</li> <li>Fractional Distillation of Non-ideal Mixtures (Azeotropes) (carry over from Phase Equilibria)</li> <li>14.4: The Law of Mass Action for Related and Simultaneous Equilibria</li> <li>14.5: Gas-Phase and Heterogeneous Reaction Equilibria</li> <li>14.6: The Direction of Change in Chemical Reactions: Empirical Description               <ul style="list-style-type: none"> <li>10.2: Le Châtelier's Principle (optional)</li> <li>10.3: Reaction Quotient (optional)</li> <li>10.4: Equilibrium Expressions (optional)</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>Monday (Friday this time) Homework 3 (Due 3/1/2018)</li> <li>Comprehensive Homework 8 (Due 3/5/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 6: Colligative Properties</li> </ul>

## LECTURE 21: 3/5/2018 (CHEMICAL EQUILIBRIA)

Readdressing how the **van't Hoff factor** contributes to colligative properties with an emphasis on vapor pressure lowering (implicit vs. explicit). (incorrectly) Think of Energy as reactant (endothermic) or product (exothermic): (1) For endothermic rxns,  $K$  increases with increase in  $T$  and (2) For exothermic rxns,  $K$  decreases with increase in  $T$ . A more correct interpretation is that how equilibria change with temperature depends on the sign of the applicable heat of reaction. Can express Equilibrium const. in terms of partial pressures or concentrations. When there is an increase in pressure, the equilibrium will shift towards the side of the reaction with fewer moles of gas. When there is a decrease in pressure, the equilibrium will shift towards the side of the reaction with more moles of gas. When volume of container holding a gaseous system is reduced, the system acts to minimize its volume, as well. Equilibrium constant is a rule for equilibrium, but there are different ways to satisfy the Law of Mass Action

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>14.4: The Law of Mass Action for Related and Simultaneous Equilibria</li> <li>14.5: Gas-Phase and Heterogeneous Reaction Equilibria</li> <li>14.6: The Direction of Change in Chemical Reactions: Empirical Description</li> <li>10.5: Equilibrium Calculations</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 9 (Due 3/12/2018)</li> <li>Monday (Friday this time) Homework 4 (Due 3/9/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 8: Equilibria and Equilibrium Constants</li> </ul>

## LECTURE 22: 3/7/2018 (CHEMICAL EQUILIBRIA)

We did a recap on Le Chatelier in Action for changing pressure, volume, and temperature on a reaction. Equilibrium constant is a rule for equilibrium, but there are different ways to satisfy the Law of Mass Action. Gave two examples of equilibrium points that satisfy the Law of Mass Action with different absolute concentrations, but same relative. Introduced ICE table as a mechanism to describe which specific equilibrium point will be established for a specific

non-equilibrium starting point. This follows a Initial, Change, Equilibrium approach. (1) This often results in the need to solve for the roots of a polynomial. (2) This is quadratic most of the times in this class, but depends on the coefficients of the balanced equations (why?). What dictates the slope from the non-equilibrium point (e.g., 1 and 2 above) toward the equilibrium curve? Thermodynamics can be connected to equilibria via  $\Delta G_{rxn} = RT \ln(Q/K_{eq})$  and then via this equation, we can identify:  $\Delta G_{rxn}^o = -RT \ln K_{eq}$ . This is really cool since it connects equilibria properties to thermodynamics!

Readings	Homework	Worksheets
14.7: The Direction of Change in Chemical Reactions: Thermodynamic Explanation	<ul style="list-style-type: none"> <li>Comprehensive Homework 9 (Due 3/12/2018)</li> <li>Monday (Friday this time) Homework 4 (Due 3/9/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 8: Equilibria and Equilibrium Constants</li> </ul>

## LECTURE 23: 3/9/2018 (CHEMICAL EQUILIBRIA)

We continued our discussion of how equilibrium constants (that define a reaction under equilibrium conditions) is connected to thermodynamics (Gibbs energy differences) under different conditions (Either standard or otherwise).  $\Delta G_{rxn} = RT \ln(Q/K_{eq})$ . This equation can be simplified for equilibrium conditions since there is no driving force for a reaction under equilibrium,  $\Delta G_{rxn} = 0$  so  $\Delta G_{rxn}^o = -RT \ln K_{eq}$ . Another reminder that we should be working in effective concentrations (activities), rather than concentrations both for  $Q$  and  $K$ . We discussed the math that one can do with equilibrium constants rather than  $\Delta G$ , which is largely the math behind logs. We readdressed the temperature dependence of equilibrium constants (any) and connected it to the sign of  $\Delta H$ . While this can be qualitatively described in terms of Le Châtelier' Principle, it can be quantitatively described via the [van't Hoff equation](#). We transitions into acid/base chemistry, which is largely a flavor of chemical equilibria. There are three definitions of Acids/Base and we discussed the **Arrhenius definition**: Acids are proton donor and Base are proton acceptors. When mixed they "neutralize" each other. Strong acids dissociate fully. Weak do not and have a corresponding  $K_a$  to describe the incomplete dissociation.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>15.1: Classifications of Acids and Bases</li> <li>15.2: The Brønsted-Lowry Scheme</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 9 (Due 3/12/2018)</li> <li>Monday (Friday this time) Homework 4 (Due 3/9/2018)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 8: Equilibria and Equilibrium Constants</li> </ul>

## LECTURE 24: 3/12/2018 (ACIDS AND BASES)

The Arrhenius Theory of Acids and Bases in Water was reintroduced... Strong acids make weak bases and vice versa. Can view Neutralization as a competition between different species (water and conjugate base) for a proton? Which win? Reiterated that strong acids decompose 100% to general hydronium and conjugate base in solution. Weak Acids do not... Water is unstable (slightly) and autoionizes to general hydronium and hydroxide ions spontaneously with a  $K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$ . Leveling Effect: (1)  $H_3O^+$  is strongest acid in water,  $OH^-$  is strongest base in water. This limits the range of weak and strong acids. Change the solvent -> change the range.

Readings	Homework	Worksheets
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Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>15.3: Acid and Base Strength</li> <li>15.4: Equilibria Involving Weak Acids and Bases</li> <li>15.8: Organic Acids and Bases: Structure and Reactivity (optional)</li> <li>The Fall of the Proton - Viewing Acid/Base Chemistry from a Thermodynamic Perspective (optional)</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 9 (Due 3/12/2018)</li> <li>Comprehensive Homework 10 (Due 3/19/2018 @ noon)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 10: Acids/Bases, Common Ion Effect, and Buffers</li> </ul>

## LECTURE 25: 3/14/2018 (ACIDS AND BASES)

You can view an acid-base reaction as the "fall" of the proton from a higher potential energy to a lower potential energy. We readdressed the Leveling Effect: (1)  $H_3O^+$  is strongest acid in water,  $OH^-$  is strongest base in water. This limits the range of weak and strong acids. Change the solvent  $\rightarrow$  change the range. We discussed Brønsted-Lowry definition of acid/base compared to Arrhenius (famous example is ammonia in water). Water is amphoteric with both acidic and basic behavior. Autoionization of water was discussed again with  $K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$  at 25 °C. As with all equilibrium constant,  $K_w$  is temperature dependent. It increases at elevated temperature: We discussed the definition of an acidic, basic (alkaline) and neutral solution: (1) Acid solutions have excess hydronium concentration over hydroxide, (2) Basic solutions have excess hydroxide concentration over hydronium, and (3) Neutral solutions have equal hydroxide concentration over hydronium. Water at elevated temperatures is still neutral, but behaves with more acidic and more basic character in reactions that are sensitive to pH. pH is related to pOH and  $K_w$  via  $pH + pOH = pK_w = 14$ , but only at 25 °C.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>15.5: Buffer Solutions</li> <li>15.6: Acid-Base Titration Curves</li> <li>15.7: Polyprotic Acids</li> <li>15.10: Nucleophilicity vs. Basicity (optional)</li> <li>15.8: A Deeper Look: Exact Treatment of Acid-Base Equilibria (optional)</li> <li>16.1: The Nature of Solubility Equilibria (optional)</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 10 (Due 3/19/2018 @ noon)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 10: Acids/Bases, Common Ion Effect, and Buffers</li> </ul>

## LECTURE 26: 3/16/2018 (PH CALCULATIONS, COMMON IONS, BUFFERS AND POLYPROTIC ACIDS)

The final lecture addresses four concepts that have been touched upon several times in the past lectures/labs/worksheets: (1) Calculating pH of acid (or base) in water under dilute and concentrated conditions (2) Polyprotic systems, (3) Common Ion Effect (rehash from [Worksheet 10](#)) and (4) Buffers. The lecture was ICE heavy, but the point is the qualitative features of the trends discussed, not the specific equations (with one exception: the [Henderson-Hasselbalch equation](#)). The UPSHOT of topic (1) is that solving for the Acid dissociate in water with its own dissociation we get a cubic equation relating hydronium concentration to  $K_a$ ,  $K_w$  and amount of acid added ( $C_a$ ). For most practical applications, we can make approximations that eliminate the need to solve a cubic equation:

1. Dilute Weak acids/bases: We cannot ignore water  $\rightarrow$  ICE it

2. Concentrated Weak acids/bases: We **can** ignore water. But,  $[H^+]$  is dependent on how much acid added and  $K_a$  - > ICE TABLE it
3. Dilute Strong acids/bases: We **cannot** ignore water -> ICE it
4. Concentrated Strong acids/bases: We **can** ignore water.  $[H^+]$  is only dependent on how much acid added

We discussed these cases within titration curves (qualitatively). Buffers are the **Common Ion Effect** in action for acid/base equilibria. Need to know why one uses Henderson-Hasselbach approximation.

Readings	Homework	Worksheets
<ul style="list-style-type: none"> <li>16.2: Ionic Equilibria between Solids and Solutions (optional)</li> <li>16.3: Precipitation and the Solubility Product (optional)</li> <li>16.4: The Effects of pH on Solubility (optional)</li> <li>16.5: Complex Ions and Solubility (optional)</li> </ul>	<ul style="list-style-type: none"> <li>Comprehensive Homework 10 (Due 3/19/2018 @ noon)</li> </ul>	<ul style="list-style-type: none"> <li>Worksheet 10: Acids/Bases, Common Ion Effect, and Buffers</li> </ul>

## FINAL EXAM: 3/20/20 17 @ 6:00 P.M.-8:00 P.M. (TUESDAY)

- Example Midterm 1 Questions
- Example Midterm 2 Questions
- Example Final Conceptual Questions