



Lecture #2 of 14

(3: TThF, 5: MTWThF, 4: MTWTh, 2: TW)

Prof. Shane Ardo

Department of Chemistry

University of California Irvine

PHYSICS/CHEM 207: Applied Physical Chemistry (<http://www.chem.uci.edu/~ardo/applpchem.html>)

Departments of Physics & Astronomy / Chemistry, UCI, Summer 2022 *Version Date: 2022.07.06*

Instructor Professor Shane Ardo (ardo@uci.edu); *Office Hours: By appointment only (via Zoom)*

Meetings *Class: M–F @ 9 am – noon PDT (FRH 4135) (video recordings may be available)*

Course Objectives

- To understand aspects of chemistry that are not often taught to, but are relevant to, physics students
- To instill thermodynamic and kinetic language that unites physics, chemistry, and engineering
- To quantitatively and qualitatively assess chemical systems, experimental data, and problems
- To summarize, explain, and critically evaluate seminal and recent chemistry peer-reviewed articles

Grading

50% *Synchronous Assignments* (~10 of them (*your lowest score will be dropped*); pre-lecture quizzes that will be worked on *individually* and then *in groups*, before being discussed)

20% *Synchronous Presentation* (~15 min per student; during penultimate class period (Th7/28))

30% *Synchronous Final Examination* (during the final class period (F7/29))

Course Policies

Late assignments are not accepted, and a make-up examination is not available.

UCI Add/Drop WebReg: <https://www.reg.uci.edu/calendars/quarterly/2021-2022/quarterly21-22.html>

UCI Chemistry Enrollment Inquiries: <https://www.chem.uci.edu/studentaffairs/>, or chemistry@uci.edu

UCI Physical Sciences COVID-19 Student Resources: <https://uci.edu/coronavirus/students/index.php>

UCI Policy on Academic Integrity and Student Conduct: <https://aisc.uci.edu/>

... given the number of students enrolled in our course, I updated the syllabus...

... I hope it's okay; yes?...

... I also put it on our course website:

<https://www.chem.uci.edu/~ardo/applpchem.html>

Discussion (*an hour-ish every-other-day-ish*) provides opportunities to discuss applied pchem research **35** ... of course, there are way too many topics to cover, but I decided on the following as the **FINAL** list:

- (1) Th7/7 (today!):** "Single-Molecule Lysozyme Dynamics Monitored by an Electronic Circuit", Y Choi, IS Moody, PC Sims, SR Hunt, BL Corso, I Perez, GA Weiss & PG Collins, *Science*, **2012**, 335, 319, DOI: [10.1126/science.1214824](https://doi.org/10.1126/science.1214824)
- (2) M7/11:** "Control of hierarchical polymer mechanics with bioinspired metal-coordination dynamics", SC Grindy, R Learsch, D Mozhdehi, J Cheng, DG Barrett, Z Guan, PB Messersmith & N Holten-Andersen, *Nature Materials*, **2015**, 14, 1210, DOI: [10.1038/nmat4401](https://doi.org/10.1038/nmat4401)
- (3) W7/13:** "Experiments and Simulations of Ion-Enhanced Interfacial Chemistry on Aqueous NaCl Aerosols", EM Knipping, MJ Lakin, KL Foster, P Jungwirth, DJ Tobias, RB Gerber, D Dabdub & BJ Finlayson-Pitts, *Science*, **2000**, 288, 301, DOI: [10.1126/science.288.5464.301](https://doi.org/10.1126/science.288.5464.301)
- (4) F7/15:** "Potentially Confusing: Potentials in Electrochemistry", SW Boettcher, SZ Oener, MC Lonergan, Y Surendranath, S Ardo, C Brozek & PA Kempler, *ACS Energy Letters*, **2021**, 6, 261, DOI: [10.1021/acseenergylett.0c02443](https://doi.org/10.1021/acseenergylett.0c02443)
- (5) T7/19:** "Solid-State Ionic Diodes Demonstrated in Conical Nanopores", TS Plett, W Cai, ML Thai, IV Vlassiuk, RM Penner & ZS Siwy, *Journal of Physical Chemistry C*, **2017**, 121, 6170, DOI: [10.1021/acs.jpcc.7b00258](https://doi.org/10.1021/acs.jpcc.7b00258)
- (6) Th7/21:** "Stable and Efficient Single-Atom Zn Catalyst for CO₂ Reduction to CH₄", L Han, S Song, M Liu, S Yao, Z Liang, H Cheng, Z Ren, W Liu, R Lin, G Qi, X Liu, Q Wu, J Luo & HL Xin, *Journal of the American Chemical Society*, **2020**, 142, 12563, DOI: [10.1021/jacs.9b12111](https://doi.org/10.1021/jacs.9b12111)
- (7) T7/26:** "Visualizing vibrational normal modes of a single molecule with atomically confined light", J Lee, KT Crampton, N Tallarida & VA Apkarian, *Nature*, **2019**, 568, 78, DOI: [10.1038/s41586-019-1059-9](https://doi.org/10.1038/s41586-019-1059-9)

... here is what I converged on... let's stick with these (for now)

okay, so that ends the introduction to the course...

... so the course format and grading scheme is now agreed upon...

... then let's agree that we should take a break somewhat soon...

... but before we do, let's take a **quick quiz** (Assignment) on the alphabet of physical chemistry (*for real this time*)!... it's on our Canvas website under Files... if need be, you can use the Internet to help you, but if you do, please indicate it on the quiz...

... when you are finished, upload your quiz in any format that you desire to our Canvas website under Assignment 1...

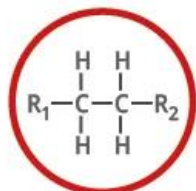
... then let's *get together as a class* to get on the same page... *and each of you present your results, at the board if applicable*...

... and finally *I'll give you full credit if you participated this activity; sound okay?*

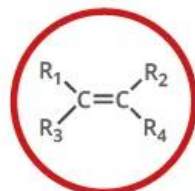
FUNCTIONAL GROUPS IN ORGANIC CHEMISTRY

FUNCTIONAL GROUPS ARE GROUPS OF ATOMS IN ORGANIC MOLECULES THAT ARE RESPONSIBLE FOR THE CHARACTERISTIC CHEMICAL REACTIONS OF THOSE MOLECULES. IN THE GENERAL FORMULAE SHOWN BELOW FOR EACH FUNCTIONAL GROUP, 'R' REPRESENTS THE REST OF THE MOLECULE, AND 'X' REPRESENTS ANY HALOGEN ATOM.

● HYDROCARBONS
 ● SIMPLE OXYGEN HETEROATOMICS
 ● HALOGEN HETEROATOMICS
 ● CARBONYL COMPOUNDS
 ● NITROGEN-BASED
 ● SULFUR-BASED
 ● AROMATIC



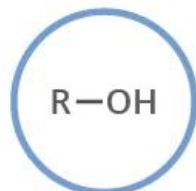
ALKANE
Naming: -ane
e.g. ethane



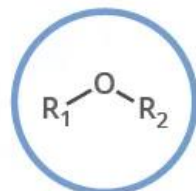
ALKENE
Naming: -ene
e.g. ethene



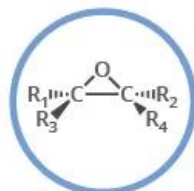
ALKYNE
Naming: -yne
e.g. ethyne



ALCOHOL
Naming: -ol
e.g. ethanol



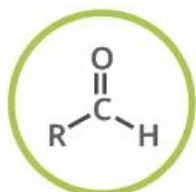
ETHER
Naming: -oxy-ane
e.g. methoxyethane



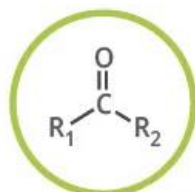
EPOXIDE
Naming: -ene oxide
e.g. ethene oxide



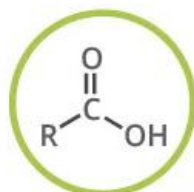
HALOALKANE
Naming: halo-
e.g. chloroethane



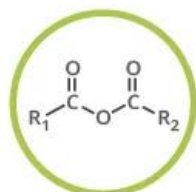
ALDEHYDE
Naming: -al
e.g. ethanal



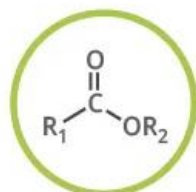
KETONE
Naming: -one
e.g. propanone



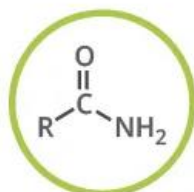
CARBOXYLIC ACID
Naming: -oic acid
e.g. ethanoic acid



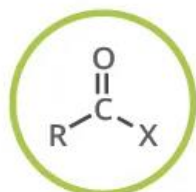
ACID ANHYDRIDE
Naming: -oic anhydride
e.g. ethanoic anhydride



ESTER
Naming: -yl -oate
e.g. ethyl ethanoate



AMIDE
Naming: -amide
e.g. ethanamide



ACYL HALIDE
Naming: -oyl halide
e.g. ethanoyl chloride



AMINE
Naming: -amine
e.g. ethanamine



NITRILE
Naming: -nitrile
e.g. ethanenitrile



IMINE
Naming: -imine
e.g. ethanimine



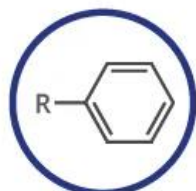
ISOCYANATE
Naming: -yl isocyanate
e.g. ethyl isocyanate



AZO COMPOUND
Naming: -azo-
e.g. azoethane



THIOL
Naming: -thiol
e.g. methanethiol



ARENE
Naming: -yl benzene
e.g. ethyl benzene

... so, if you want to impress the ChAMP Chemistry students and faculty, use some of these words at the next Friday pizza lunch talk...



Chemical Properties

Prof. Shane Ardo

Department of Chemistry

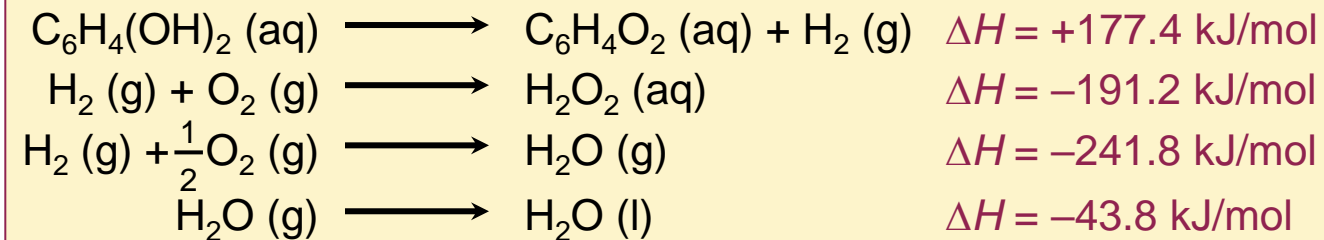
University of California Irvine

Chemical Properties

- Molecular nomenclature, Solutions, Balanced chemical reactions
- State functions, Standard states, Thermochemistry
- **Non-ideal gases, Intermolecular forces, Physical properties, Phase changes, Colligative properties, Water activity**
- Free energy, (X)Chemical potential, Chemical equilibrium, van't Hoff equation, Activity coefficients, Le Chatelier's principle
- Schrödinger equation, Internal energy, Atomic orbitals, Hybridization
- Valence bond theory, Molecular orbital theory, Band diagrams
- Crystal field theory, Ligand field theory

Balancing Reactions

Use measured reaction enthalpies to calculate ΔH for the following reaction:

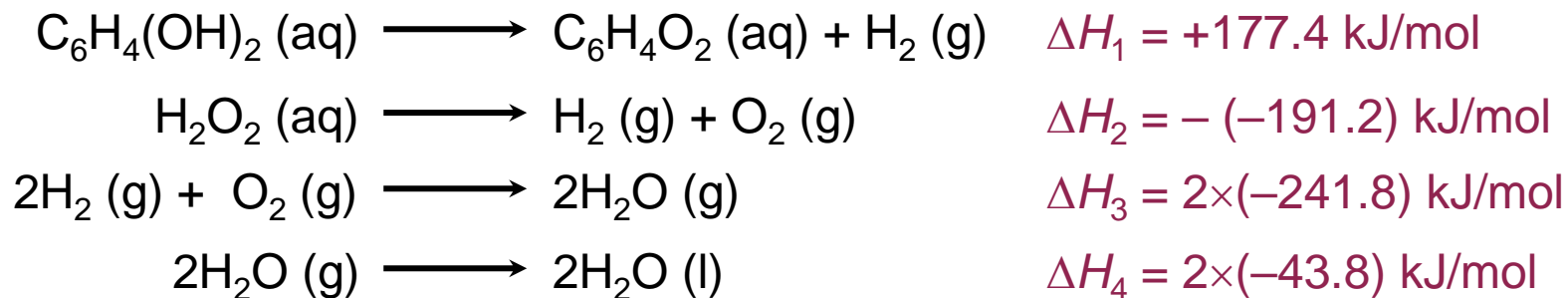


1. Balance the chemical equation.

What is this missing?

2. Reorder the sub-reactions with reactants to the left and products to the right, and correct for stoichiometries.

Assuming that this overall reaction is spontaneous ($\Delta G < 0$), and we had 1 mol of each species, which species is the limiting reagent?



What do I feel when I hold the beaker?

3. Do some arithmetic.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 = 177.4 + 191.2 - 483.6 - 87.6 = -202.6 \text{ kJ/mol}$$

Standard States

To define a thermochemical state of a (chemical) system, one needs boundary conditions!

For an element, standard *chemical* practice is to use:

The most stable state in which the element exists under conditions of $p = 1 \text{ atm}$ and $T = 25 \text{ }^\circ\text{C}$

For a compound, standard *chemical* practice is to use:

Gaseous substance: $p = 1 \text{ atm}$ and $T = 25 \text{ }^\circ\text{C}$

Liquid or solid substance: pure liquid or solid

Substance in solution: 1 M solution

If more than one form of the element exists under the standard conditions, use the most stable form

⇒ Oxygen (g) can exist as O_2 or as O_3 (ozone) at 1 atm and 298 K

Most stable form = O_2 (g)

$$\Delta H_f^\circ = 0 \text{ kJ/mol}$$

Less stable form = O_3 (g)

$$\Delta H_f^\circ = +142.7 \text{ kJ/mol}$$

⇒ Carbon (s) can exist as graphite or as diamond at 1 atm and 298 K

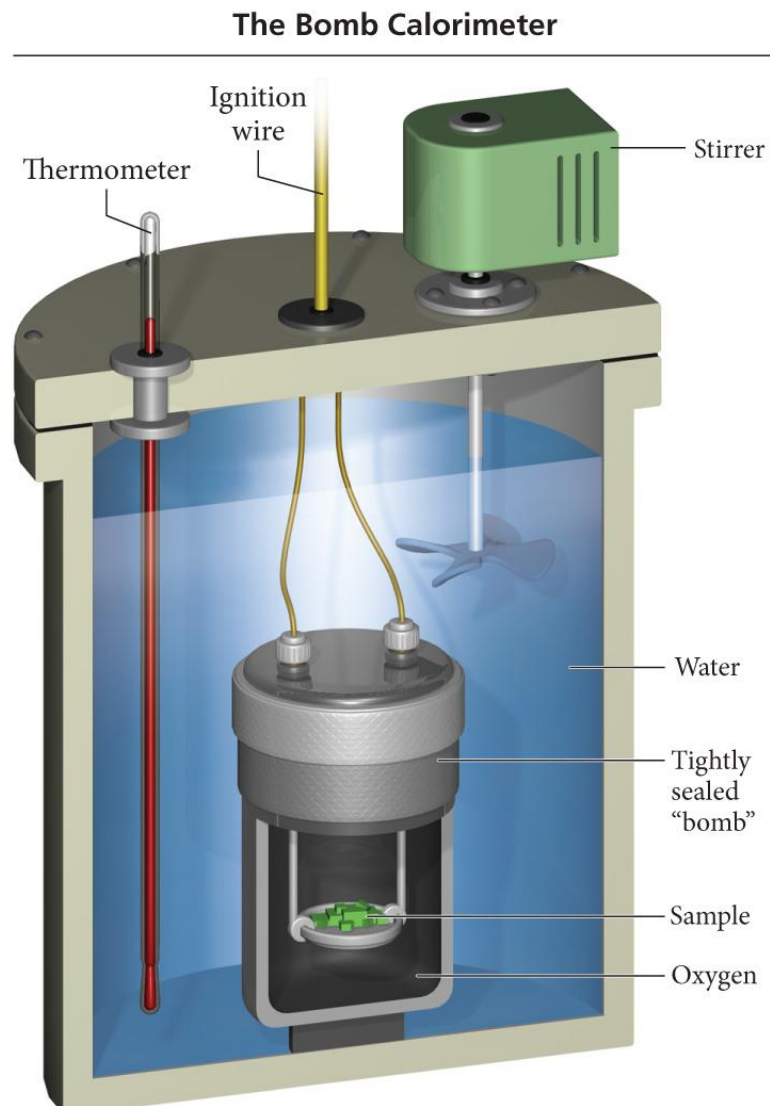
Most stable form = graphite

$$\Delta H_f^\circ = 0 \text{ kJ/mol}$$

Less stable form = diamond

$$\Delta H_f^\circ = +1.88 \text{ kJ/mol}$$

Measuring Changes in Internal Energy or Enthalpy

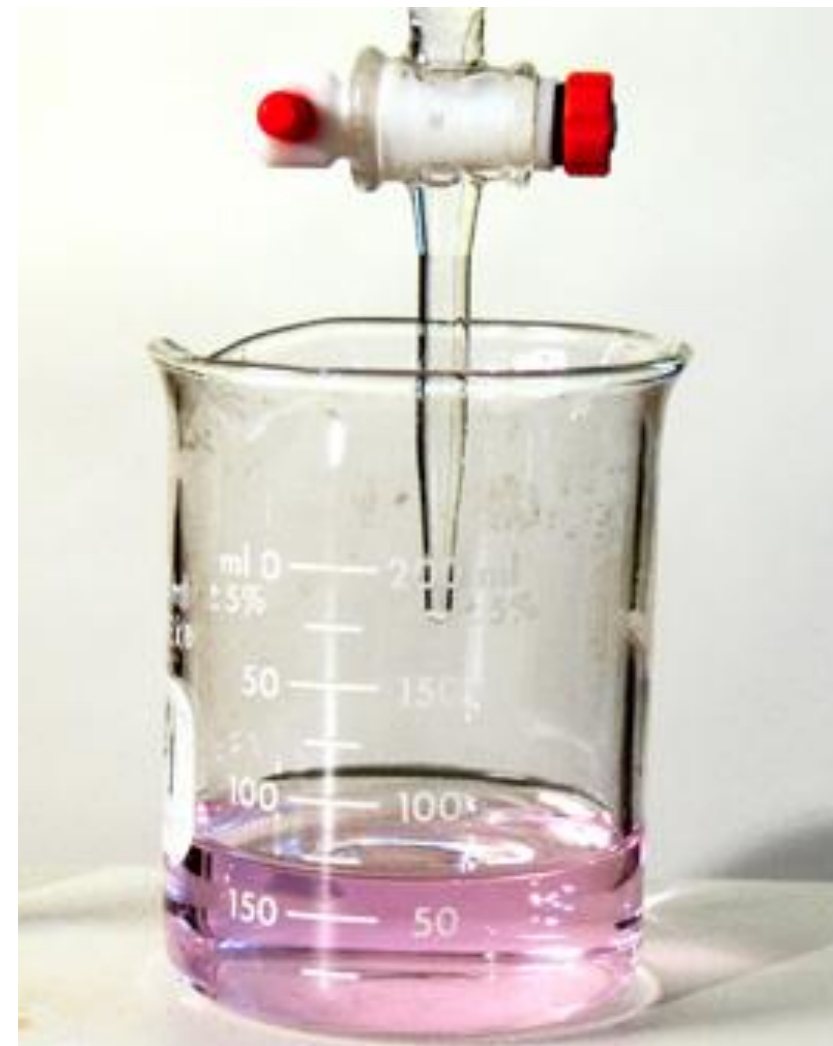


Which should we use to measure ΔE , and which to measure ΔH ?

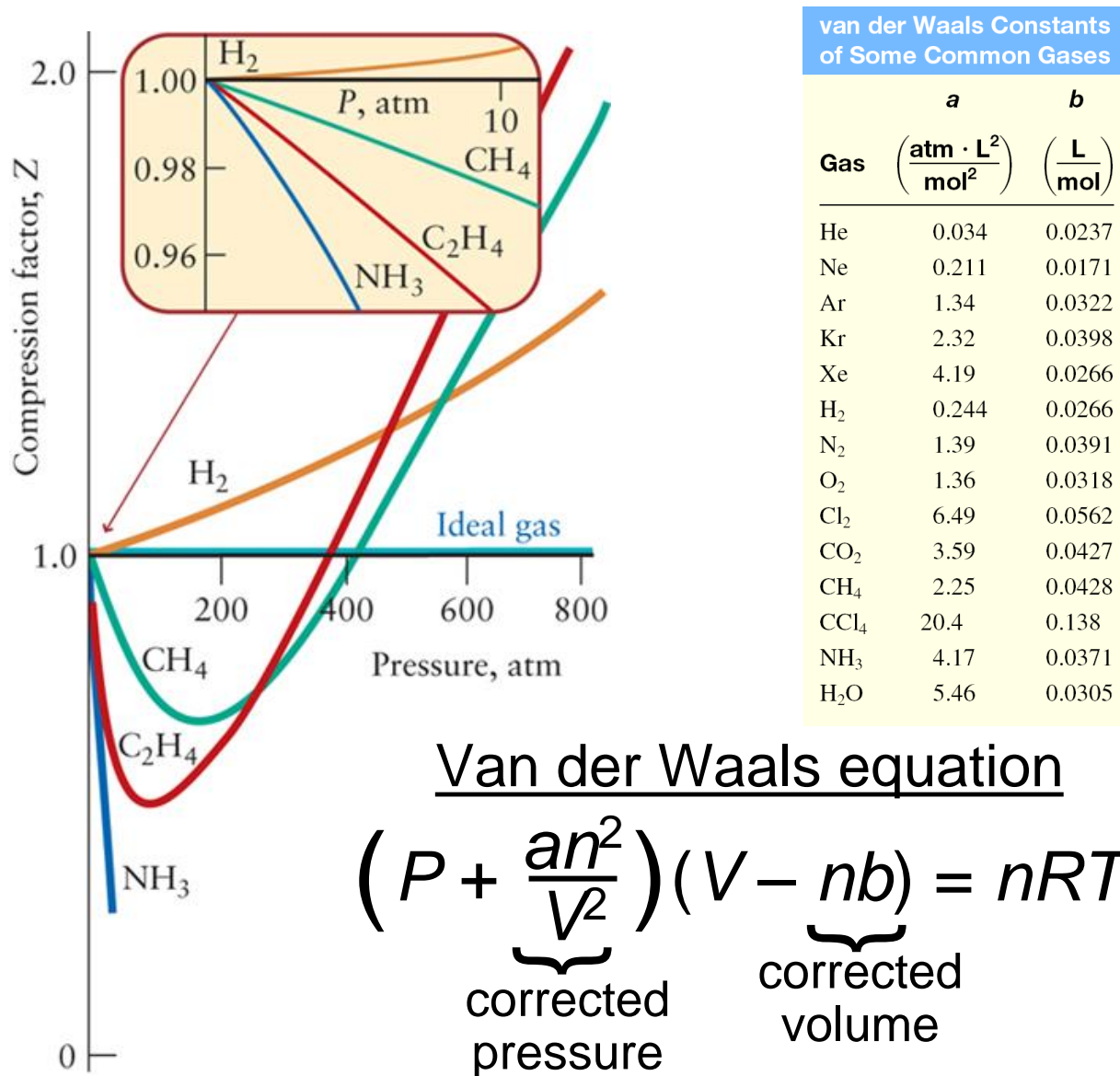
Does this help?

$$\Delta E = q_v = C_v \Delta T$$

$$\Delta H = q_p = C_p \Delta T$$



A Curious Observation under Extreme Conditions



One measure of non-ideality is the compression factor, Z

$$Z = \frac{V_{\text{molar}}}{V_{\text{molar}}^{\text{ideal}}}$$

$Z = 1$ under ideal conditions

For most gases, at low pressures, **attractive forces** (the effect of the a -parameter) are dominant and $Z < 1$.

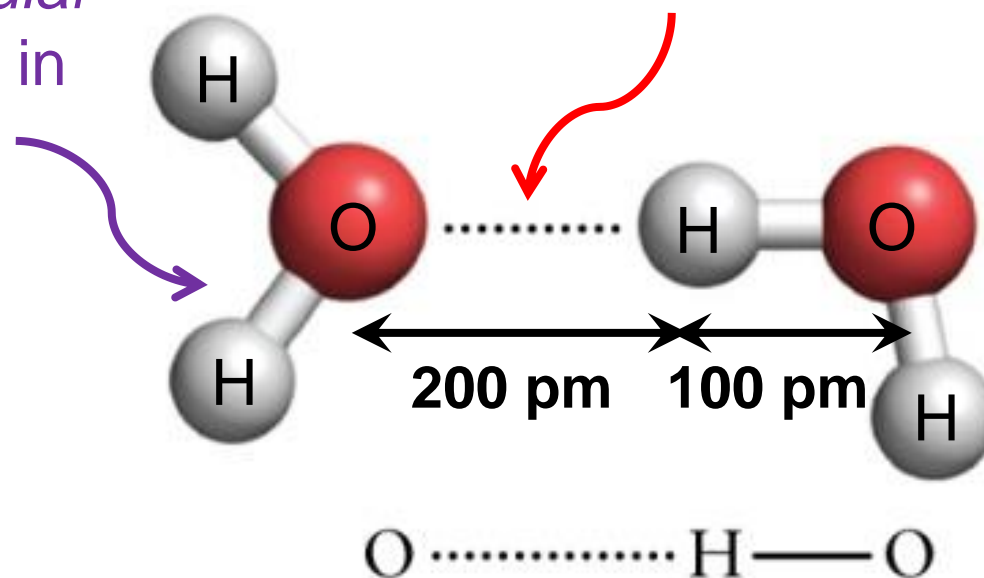
For all gases, at high pressures, **repulsive forces** (effect of the b -parameter) are dominant and $Z > 1$.

Coulombic Forces

It always seems to go back to electrostatics, and that is also critical to chemical bonding...

930 kJ to
break all
intramolecular
O-H bonds in
1 mole of
water

41 kJ to break all *intermolecular*
“Hydrogen Bonds” in 1 mole of liquid
water leading to its vaporization

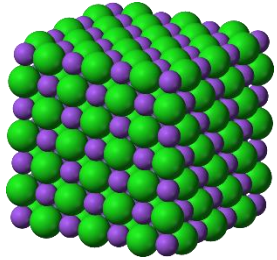


Larger bond
length =
weaker
attraction

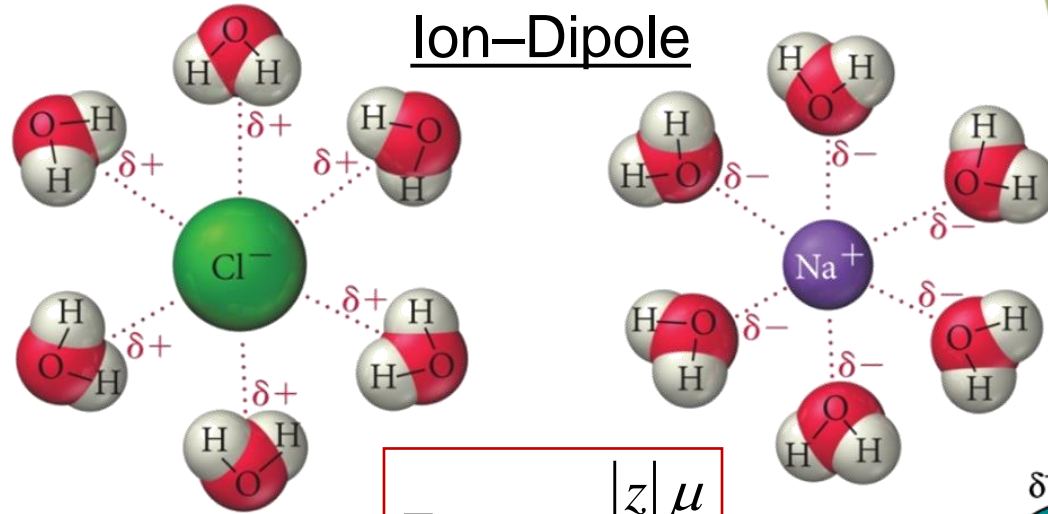
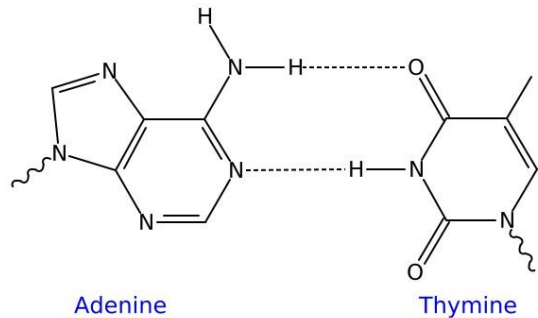
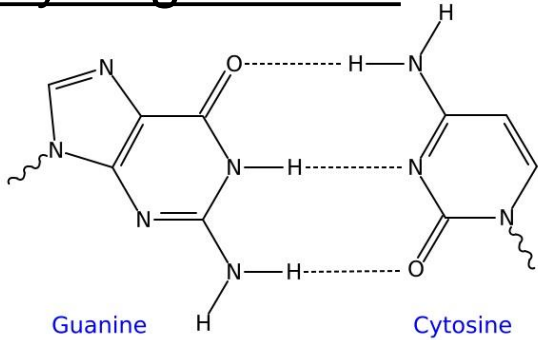
... for both intramolecular bonds, which we will discuss later, and intermolecular bonds...
... the latter of which we will discuss in more detail now...

Intermolecular Forces

What does salt (NaCl) look like in the Newport Beach ocean?



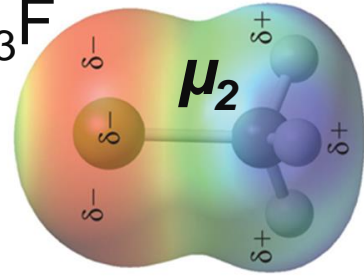
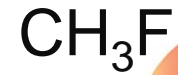
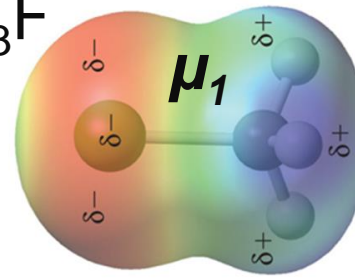
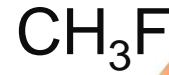
Hydrogen Bond



$$E_{binding} \propto \frac{|z|\mu}{r^2}$$

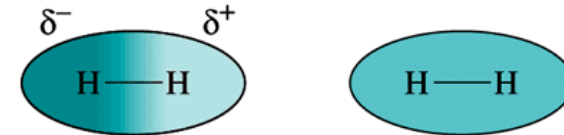
... like in DNA, proteins, water, ice, etc.

Dipole-Dipole

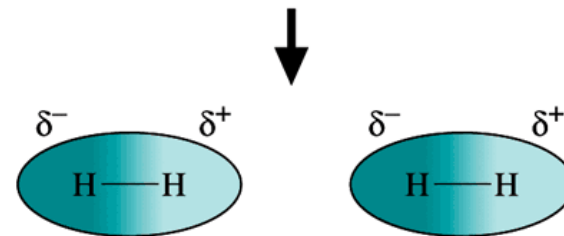


$$E_{binding} \propto \frac{\mu_1\mu_2}{r^3}$$

Induced Dipole-Induced Dipole



Molecule A
Instantaneous dipole on molecule A induces a dipole on molecule B

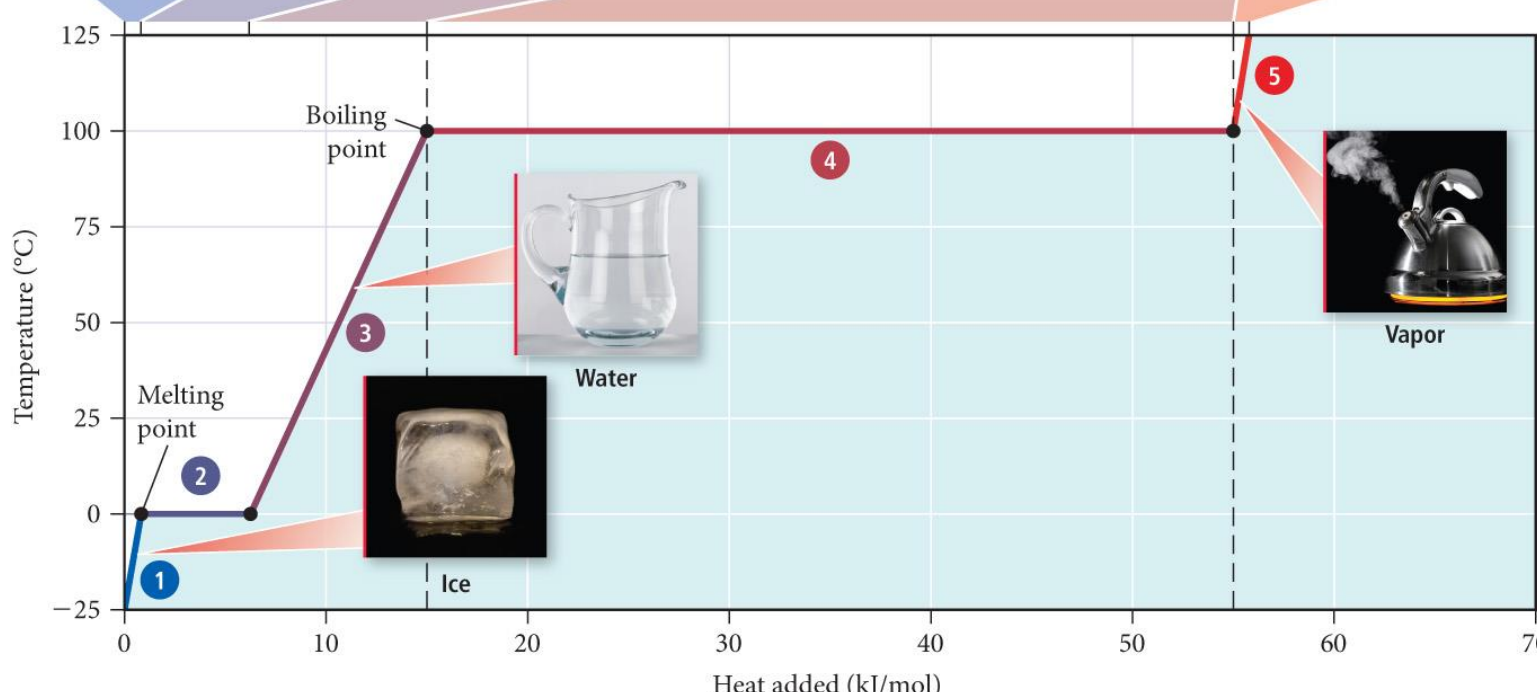
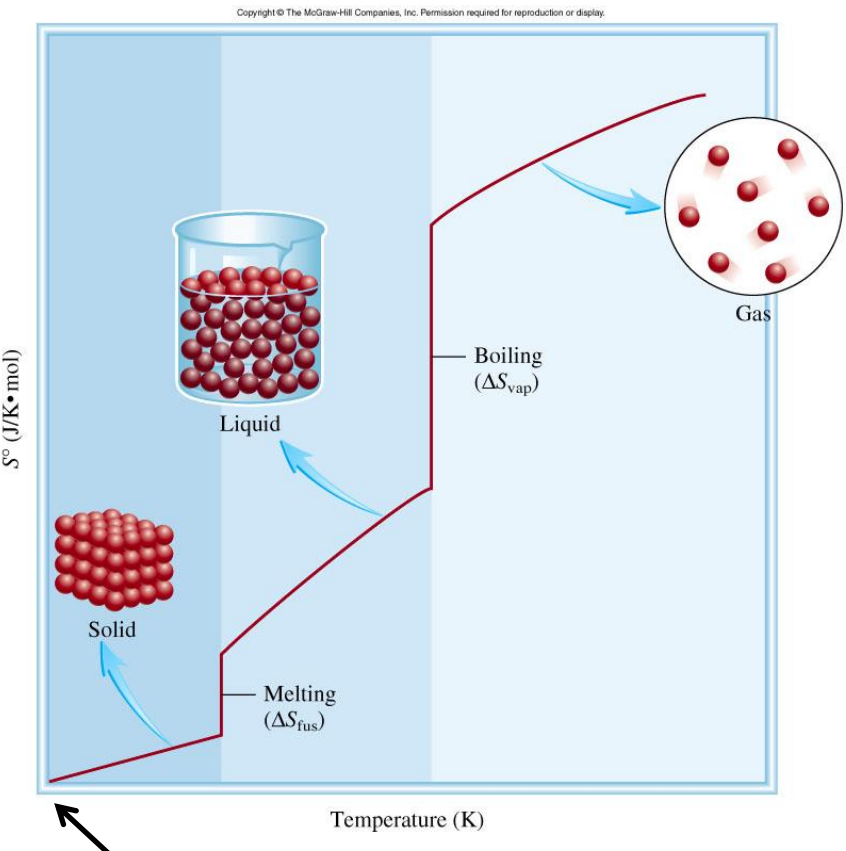
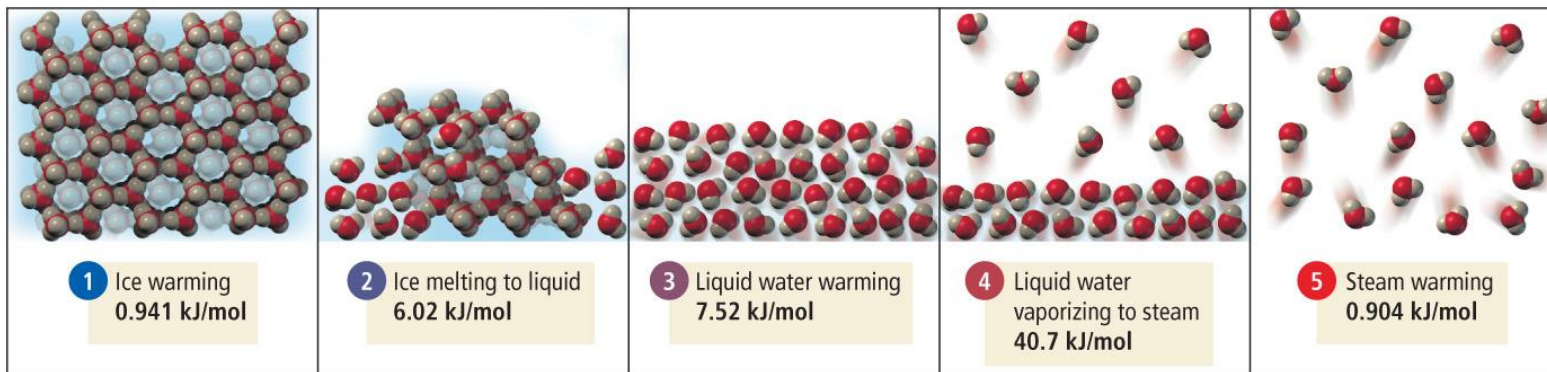


$$E_{binding} \propto \frac{\alpha_1\alpha_2}{r^6}$$

Explains viscosity, vapor pressure, capillary action, surface tension, osmotic pressure, boiling/freezing point

Phase Changes

$$q_1 = mC_{ice} \Delta T \quad q_2 = n\Delta H_{fus} \quad q_3 = mC_{liq} \Delta T \quad q_4 = n\Delta H_{vap} \quad q_5 = mC_{gas} \Delta T \quad 46$$



Perfect lattice, no rearrangements possible – only $W = 1$ microstate exists: $S = k_B \ln \Omega = 0$

(What is ΔG ?)

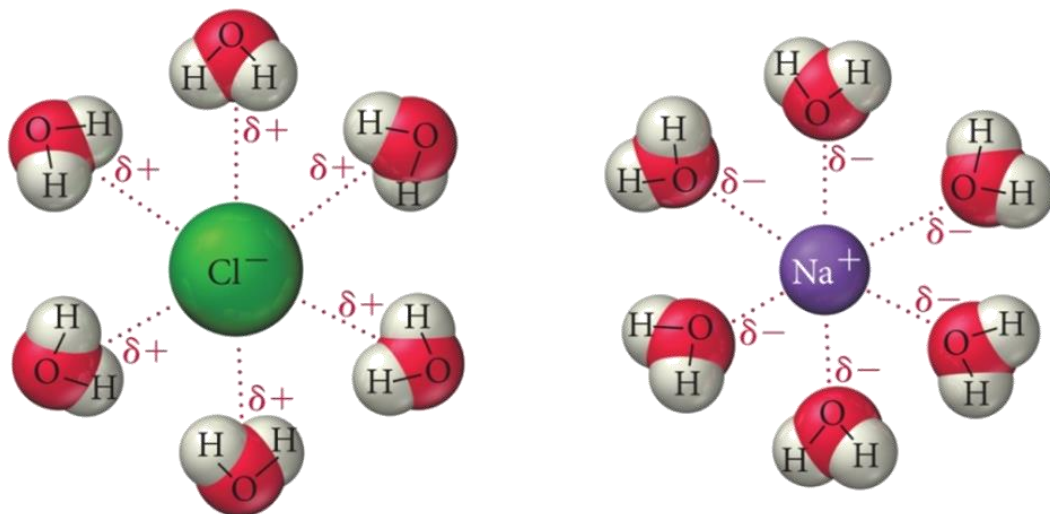
(Slow) phase-change processes are equilibrium transformations... and thus, $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$ $\Delta S_{fus} = \frac{\Delta H_{fus}}{T_m}$

Colligative Properties

Colligative properties depend on the number of particles present, **not** on the charge or chemical nature of the particle... **so how is this chemistry?**

This implies that substances that produce a pair of ions upon solvation (e.g., NaCl) contribute more than 1 particle: $\text{NaCl} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

The **van't Hoff factor** indicates the actual number of particles that contribute to the colligative properties.



$$i = \frac{\text{actual number of particles upon solvation}}{\text{number of units dissolved in solution}}$$

$$\text{Boiling-point elevation: } \Delta T_b = i K_b m$$

$$\text{Freezing-point depression: } \Delta T_f = i K_f m$$

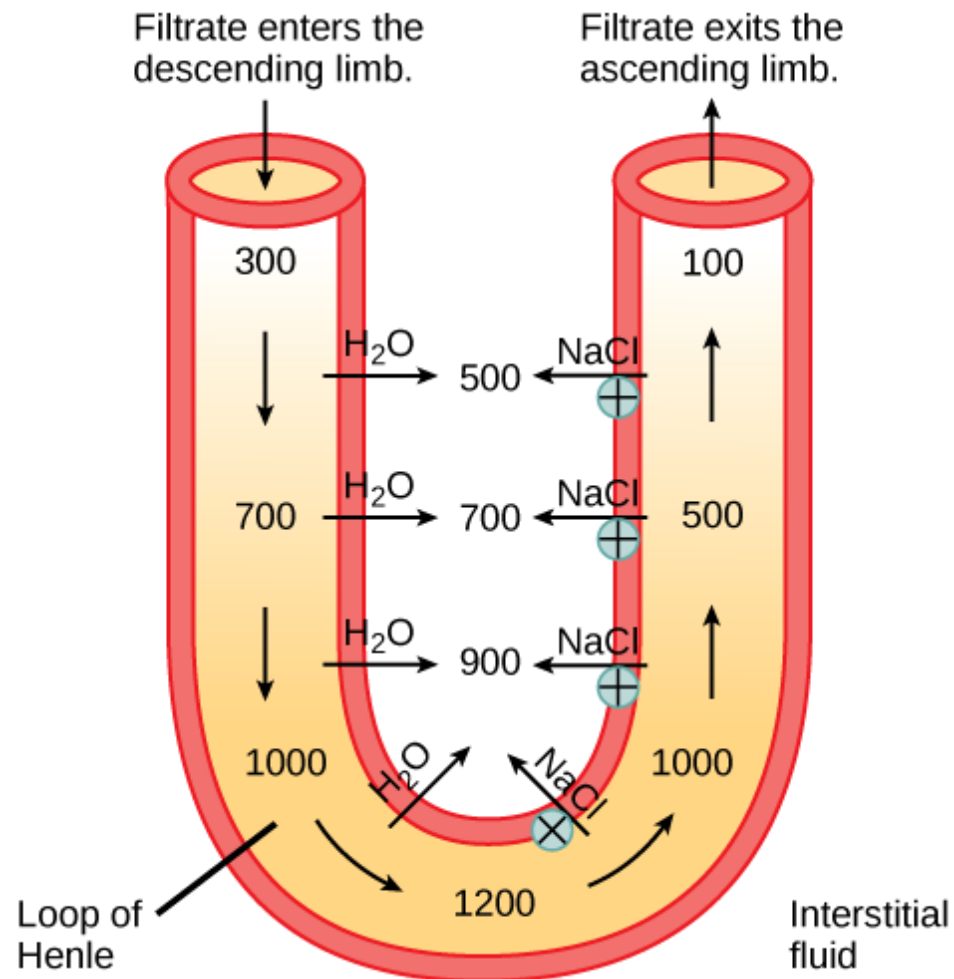
$$\text{Osmotic pressure: } \pi = i R T M$$

$$\text{Vapor-Pressure lowering: } P_1 \neq i P_1^\circ X_1$$

Does this cartoon possibly indicate why this is chemical?

Water Activity

My kidneys thank you, osmolyte, for influencing water activity and thus osmotic pressure...



The loop of Henle acts as a countercurrent multiplier that uses energy to create concentration gradients. The descending limb is water permeable. Water flows from the filtrate to the interstitial fluid, so osmolality inside the limb increases as it descends into the renal medulla. At the bottom, the osmolality is higher inside the loop than in the interstitial fluid. Thus, as filtrate enters the ascending limb, Na⁺ and Cl⁻ ions exit through ion channels present in the cell membrane. Further up, Na⁺ is actively transported out of the filtrate and Cl⁻ follows. Osmolarity is given in units of milliosmoles per liter (mOsm/L).

Chemical Properties (*summary for today*)

- Molecular nomenclature, Solutions, Balanced chemical reactions
- State functions, Standard states, Thermochemistry
- **Non-ideal gases, Intermolecular forces, Physical properties, Phase changes, Colligative properties, Water activity**
- Free energy, (X)Chemical potential, Chemical equilibrium, van't Hoff equation, Activity coefficients, Le Chatelier's principle
- Schrödinger equation, Internal energy, Atomic orbitals, Hybridization
- Valence bond theory, Molecular orbital theory, Band diagrams
- Crystal field theory, Ligand field theory