

CHEM 20B Week 3

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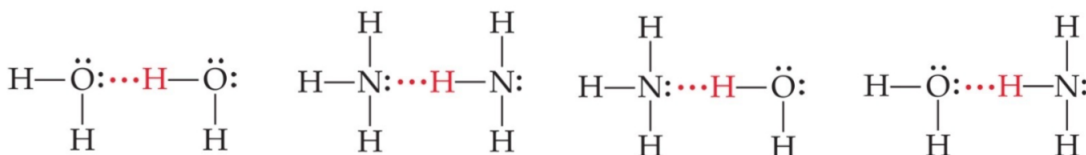
Intermolecular Forces (continued)

Repulsive Forces

- When two atoms or molecules are so close together that their respective core electrons repel each other, overwhelming the attractive forces.
- Very short range
- $\frac{1}{R^{12}}$

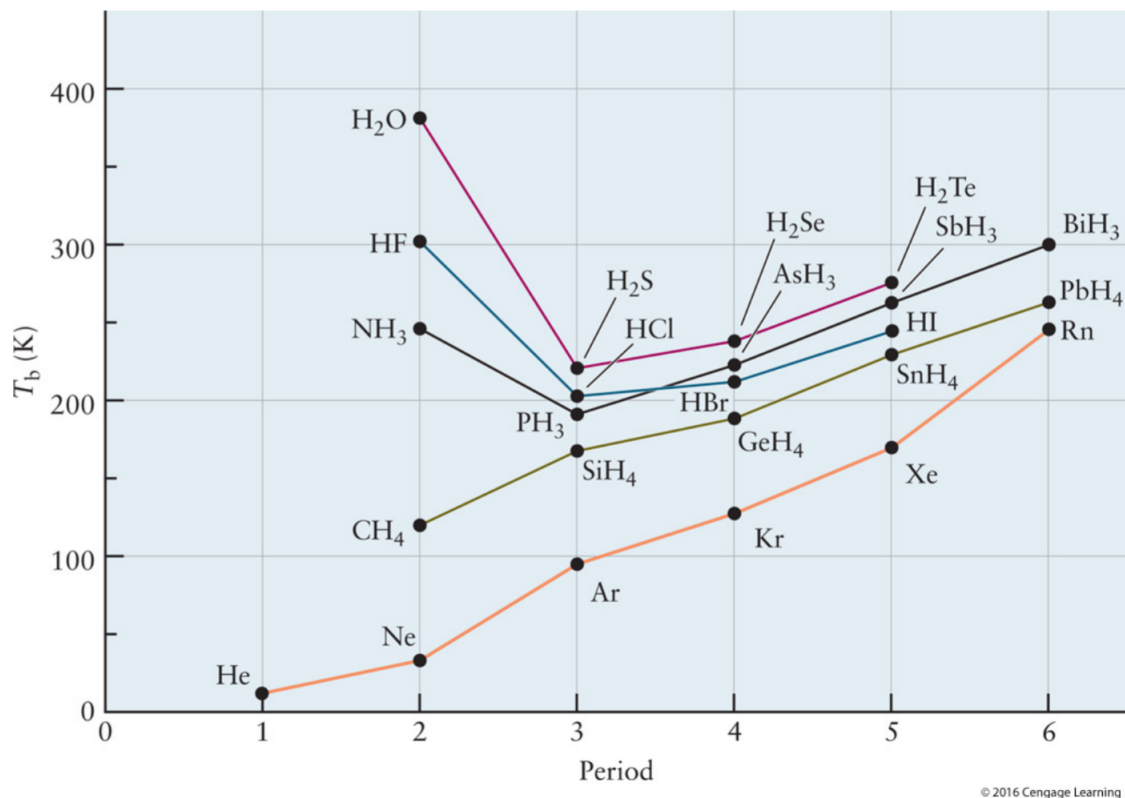
Hydrogen Bonding

- A special case of dipole-dipole
- Molecule with N-H, O-H, or F-H with polar molecule with lone pair on N, O, or F.
- N, O, and F are very electronegative and can almost steal electrons from hydrogen, leaving unshielded nucleus (p^+), which can interact with lone pairs of N, O, or F.
- It is weaker than ionic and covalent bonds but stronger than any intermolecular force.



Intermolecular Forces in Liquids

Trends in the boiling points of hydrides of some main group elements and the noble gases



Review: Types of Intermolecular Forces

Ion-Ion Interaction	ion + ion
Ion-Dipole Interaction	ion + polar molecule
Hydrogen Bonding	Molecule with N-H, O-H, or F-H + polar molecule with lone pair on N, O, or F
Dipole-Dipole Interaction	polar + polar molecule
Ion-Induced Dipole Interaction	ion + nonpolar molecule
Dipole-Induced Dipole Interaction	polar molecule + nonpolar molecule
London Dispersion Forces	nonpolar molecule + nonpolar molecule

Steps for comparing properties of molecules

1. Identify the compound: ion vs. polar vs. nonpolar
2. Identify the types of intermolecular forces
3. If two molecules have the same types of intermolecular forces, compare **size (molecular weight)**, then shape

Intermolecular Forces Affect Many Physical Properties

- **Melting point:** solid \rightarrow liquid
- **Boiling point:** liquid \rightarrow gas
- **Vapor pressure:** pressure caused by molecules that escape from liquid, (to escape from liquid, need to break all intermolecular forces)

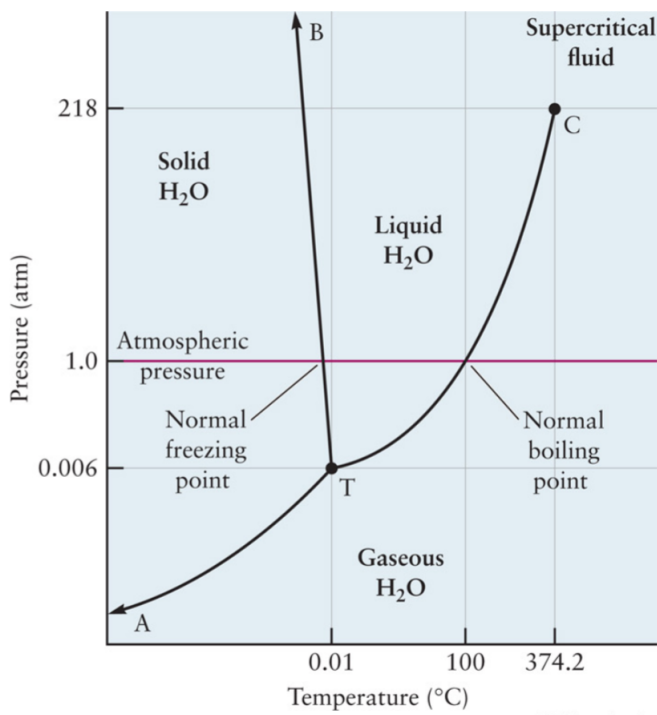
- Stronger intermolecular forces:
 - Higher boiling points (need higher temperature to break intermolecular forces)
 - Higher melting points (need higher temperature to break intermolecular forces)
 - Lower vapor pressure (harder for molecules to escape from liquid)

Phase Transition

- Boiling point: temperature in which the vapor pressure of a liquid equals the external pressure.
- Normal boiling point is the temperature at which the vapor pressure of the liquid equals 1 atm.

Phase Diagrams

- m.p. = normal melting point:
 - $T(\text{solid} \rightarrow \text{liquid})$ at 1atm
- b.p. = normal boiling point:
 - $T(\text{liquid} \rightarrow \text{gas})$ at 1atm, 373K (100° celsius)
- t.p. = triple point:
 - The pressure and temperature where the solid, liquid, and gas states coexist
 - (For H_2O : 0.01 Celsius, 0.006 atm)
- T_c , P_c : above which there are no liquid or gas phase transitions, just gradual transition; called "supercritical region"



Composition of Solutions

- Mole Fraction

$$X_1 = \frac{n_1}{n_1 + n_2}$$

- Concentration: number of moles per unit volume

– SI Unit: mol/m³ (large for chemical work)

- Molarity:

$$\text{molarity} = \frac{\text{moles solute}}{\text{liters solution}} = \text{molL}^{-1} = M = \text{molar}$$

- Molality:

$$\text{molality} = \frac{\text{moles solute}}{\text{kilograms solvent}} = \text{molkg}^{-1}$$

Solutions

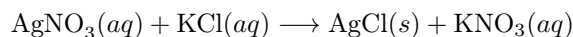
- Solute + Solvent
- Aqueous solution: solvent = water
- Species that dissolve in water:
 - Polar molecules:
 - * Glucose C₆H₁₂O₆
 - * Sucrose C₁₂H₂₂O₁₁
 - Ionic solic: NaCl(aq)
 - NaCl(aq) → Na⁺(aq) + Cl[−](aq)

Precipitation Reaction

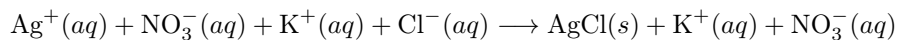
- A **precipitate** is an insoluble solid formed by a reaction in solution.

- Example:

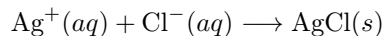
– Molecular Equation:



– Complete Ionic Equation:



– Net Ionic Equation:

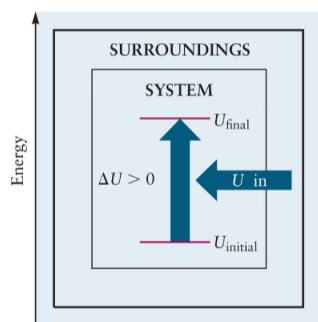


Systems, States, and Processes

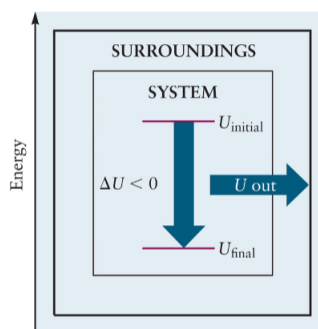
- **The system:** is that part of the universe we care about, for example, a chemical reaction, an engine, or a human being.
- **The surroundings:** the remainder of the universe
- **The thermodynamic universe** is the combination of the system and the surroundings for a particular process of interest, it is assumed to be closed and isolated.
 - An **open** system: matter and energy can be exchanged with the surroundings
 - A **closed** system: no exchange of matter between the system and surroundings.
 - An **isolated** system: no exchange of matter or energy

The Thermodynamics Universe

- Is the combination of the system and the surroundings for a particular process of interest. It can be closed or isolated.



(a) The system gains energy from the surroundings



(b) The system loses energy to the surroundings.

Reversible vs Irreversible Processes

Example: Start piston at P_2, V_2, T_2 and n ; End at P_1, V_1, T_1 , and same n . $P_2 > P_1, V_2 > V_1$.

If the transition between 1 and 2 is through gradual slow increase of pressure and compression of the volume, then the transition is *reversible*;

But, if the transition happens by placing a large mass on top of the piston and suddenly letting it go, then the process will be *irreversible* (the piston will compress and expand back and forth until eventually it will settle down at the new volume); i.e., throughout, P may not even be defined, only at the end.

- Reversible processes are a type of transition between states which proceeds through continuous series of thermodynamic states, and can be reversed at any stage.
- Irreversible processes are transitions that are not reversible.

State Functions

Definitions:

- A **state function** is a property whose value depends only on the current state of the system and not on the path taken.
- A **path-dependent quantity** is one in which the value does depend on the details of the path taken.
- Can be thought of like displacement (state function) vs. distance (path-dependent), but as some other measure (e.g., energy - E and ΔE) instead of length.

Energy Transfer

There are two different types of energy transfer

1. **Heat:** Energy transfer by thermal contact
2. **Work:** Ordered transfer (e.g., mechanical pushing or electron current).

Work

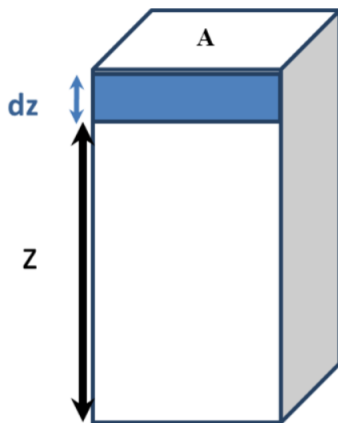
$$w = F \cdot d$$

- w = Work (Joules, Newton-Meters)
- F = Force (Newtons)
- d = displacement (meters)

Pressure-Volume Work:

- Mechanical work done by a system involving expanding gases.
- Perhaps the most important type of work in chemistry is **pressure-volume** work, in which a system either expands against or is compressed by external pressure

Derivation of Work



F = Force

P = Pressure

A = cross sectional area of piston

$$\text{Energy} = \text{Force} \cdot \text{distance}$$

$$dw = F \cdot dz$$

Pressure:

$$P = \frac{\text{Force}}{\text{Area}}$$

$$F = P \cdot A$$

$$= P_{ext} A$$

$$dw = -P_{ext} A \, dz$$

$$A \cdot dz = dV = \text{volume change}$$

Therefore,

$$dw = -F \, dz = -P_{ext} A \, dz$$

which implies:

$$dw = -P_{ext} \, dV$$