

# CHEM 20B Week 3

Aidan Jan

January 29, 2024

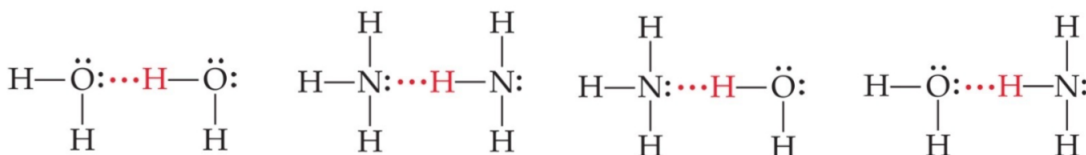
## Intermolecular Forces (continued)

### 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
- $\frac{1}{R^{12}}$

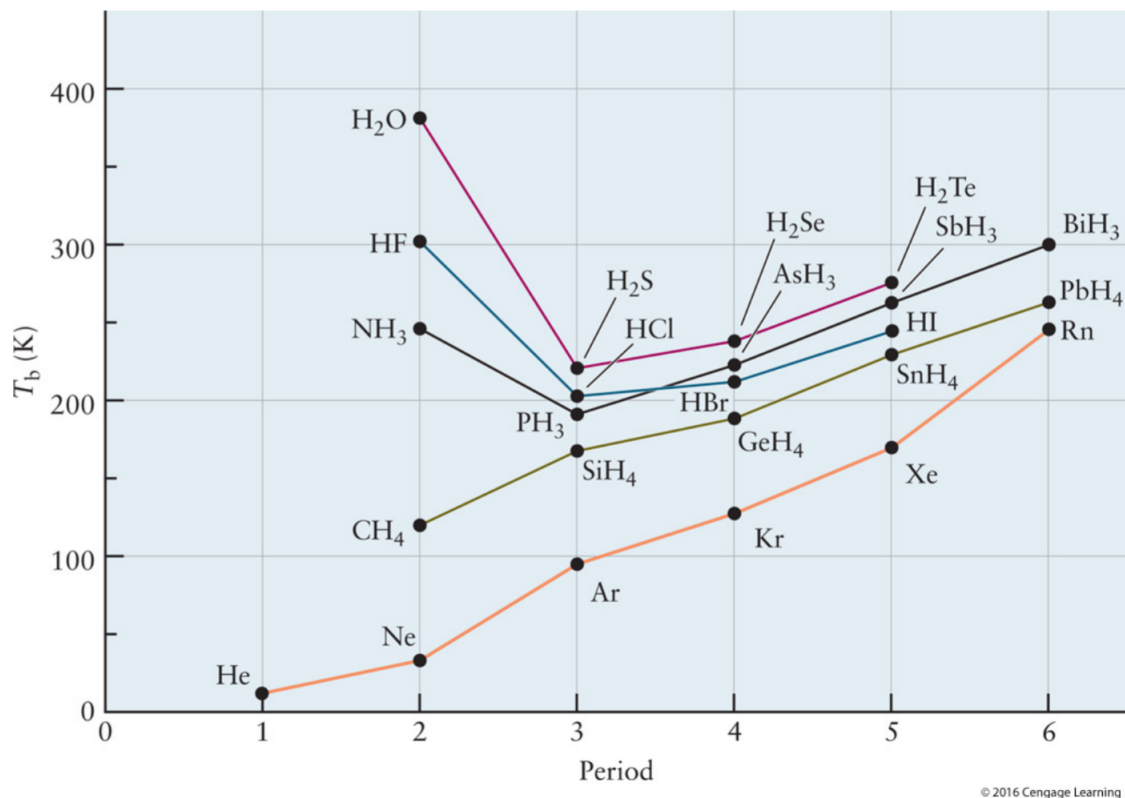
### Hydrogen Bonding

- 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)

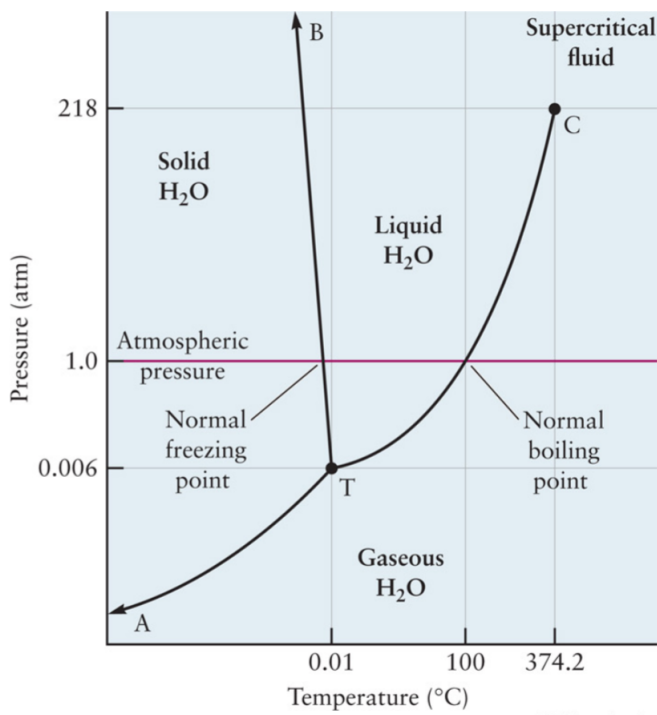
- Stronger intermolecular forces:
  - Higher boiling points (need higher temperature to break intermolecular forces)
  - Higher melting points (need higher temperature to break intermolecular forces)
  - Lower vapor pressure (harder for molecules to escape from liquid)

## 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  $\text{H}_2\text{O}$ : 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/m<sup>3</sup> (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

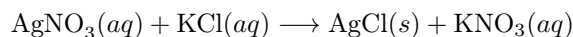
- Solute + Solvent
- Aqueous solution: solvent = water
- Species that dissolve in water:
  - Polar molecules:
    - \* Glucose C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>
    - \* Sucrose C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>
  - Ionic solic: NaCl(aq)
  - NaCl(aq) → Na<sup>+</sup>(aq) + Cl<sup>−</sup>(aq)

## Precipitation Reaction

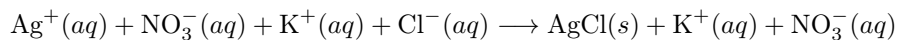
- A **precipitate** is an insoluble solid formed by a reaction in solution.

- Example:

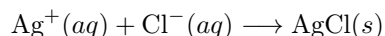
– Molecular Equation:



– Complete Ionic Equation:



– Net Ionic Equation:

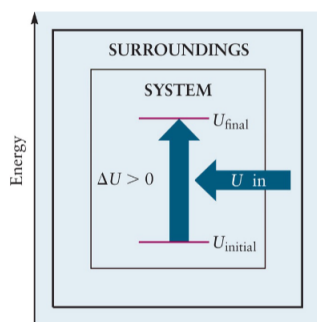


## Systems, States, and Processes

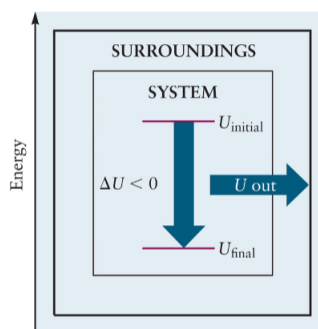
- **The system:** is that part of the universe we care about, for example, a chemical reaction, an engine, or a human being.
- **The surroundings:** the remainder of the universe
- **The thermodynamic universe** is the combination of the system and the surroundings for a particular process of interest, 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  $\Delta E$ ) 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

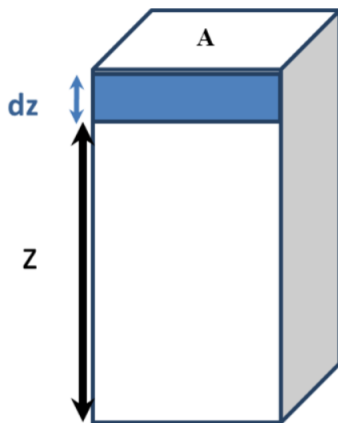
$$w = F \cdot d$$

- $w$  = 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:

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

## Heat

- Energy transfer by thermal contact
- Heat is transferred between two objects initially at different temperatures.
- Heat is transferred from the hotter object to the colder object

## The First Law of Thermodynamics

$$\Delta U = q + w$$

- $\Delta U$ : Internal energy change of system
- $q$ : heat involved in process
- $w$ : work involved in process
- The first law of thermodynamics is the law of conservation of energy.
- Energy can be neither created nor destroyed
- Any energy lost by a system must be gained by the surroundings, and vice versa.
- $\Delta U_{univ} = 0$ . The universe cannot gain or lose energy.

## Heat Capacity

- **Heat capacity** is the amount of energy required to raise the temperature of an object by  $1^\circ\text{C}$  (1 K).

$$c = \frac{q}{\Delta T}$$

- Constant P:
  - $C_p$  is the heat capacity at constant pressure.

$$C_p \equiv \frac{q_p}{\Delta T}$$

- Constant V:
  - $C_V$  is the heat capacity at constant volume.

$$C_v \equiv \frac{q_V}{\Delta T}$$

- The specific heat of water: 4.184 J/(kg K)

## Molar Heat and Specific Heat Capacity

**Molar heat capacity:** the heat capacity of one mole of a substance.

- $c_V = \frac{q_V}{n\Delta T}$  constant volume
- $c_P = \frac{q_P}{n\Delta T}$  constant pressure

**Specific Heat capacity:**  $c_S$ : The heat capacity of one gram of a substance.

- $c_S = \frac{q}{m\Delta T}$

## Specific Heat

$$q = C_s m \Delta T$$

mass is measured in grams.

### Example: Calorimetry

The heat  $q_2$  taken up by the cooler body is  $-q_1$ , the heat given up by the warmer body.

$$q_1 = -q_2$$

$$q_1 + q_2 = 0$$

$$m_1 c_{s1}(T_f - T_1) = -m_2 c_{s2}(T_f - T_2)$$

Solve for  $T_f$  to find the final temperature.

### Heat Transfer at Constant Pressure:

Work is **pressure-volume work** and the **external pressure is constant**.

$$\Delta U = q_p + w$$

$$\Delta U = q_p - P_{ext} \Delta V$$

If the external pressure is equal to the internal pressure of the system P, then:

$$\Delta U = q_p - P \Delta V$$

P is constant, then  $P \Delta V = \Delta(PV)$

$$q_p = \Delta U + \Delta(PV) = \Delta(U + PV)$$

Enthalpy,  $H$ , is defined as  $U + PV$ . Therefore, **at constant pressure**,

$$\Delta H = q_p = \Delta U + P \Delta V$$

### Enthalpy Change

$\Delta H = \Delta U + P \Delta V$  at constant pressure.

$\Delta U = q + w$  (always true.)

$w = -P \Delta V$  (work involved in expansion and compression of a gas at constant pressure) From the above formulas, we can derive the following:

$$\begin{aligned}\Delta H &= q + w + P \Delta V \\ &= q - P \Delta V + P \Delta V \\ &= q_p \text{ (heat gained or lost at constant pressure)}\end{aligned}$$

- $\Delta H(q_p > 0) \Rightarrow$  endothermic
- $\Delta H(q_p < 0) \Rightarrow$  exothermic

$$\Delta H = q_p$$

- H is a state function
- It depends on the initial and final states of the system, not on how the change occurs.
- Therefore,  $\Delta H = q_p$
- **Only P-V work is involved and the pressure is constant**



### Derivation of $\Delta H = nc_p\Delta T$

The average kinetic energy of  $N_A$  molecules (1 mole) is  $\bar{E} = \frac{3}{2}RT$

The average translational kinetic energy of  $n$  moles of an ideal gas =  $\frac{3}{2}nRT$  (kinetic theory)

$$\Delta U = \frac{3}{2}nR\Delta T$$

**Molar Heat capacities of monatomic ideal gases:**

$$c_V = \frac{3}{2}R$$

**Molar Heat capacities of any ideal gases:**  $c_p = c_v + R$ , where  $R = 8.3145 J K^{-1} mol^{-1}$

$$\Delta U = \frac{3}{2}nRT = n\left(\frac{3}{2}R\right)T = nc_v\Delta T \text{ (any ideal gas)}$$

$$\Delta U = nc_v\Delta T \text{ (any ideal gas)}$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = nc_v\Delta T + nR\Delta T$$

$$\Delta H = nc_p\Delta T \text{ (any ideal gas)}$$