Chem 1038 Week 1

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Office Hour: Tues 4-5 This week in PSB 357. Stay tuned for longer Room location

Outline

- Chapter 1 definitions/basic concepts
  - Zeroth Law
  - Ideal gas
  - Real gas/Van der Waals
- Chapter 2
  - Internal Energy
  - Heat
  - Work
  - More definitions

Chapter 2 - Definition/basic concepts

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<table>
<thead>
<tr>
<th>Types of Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Open System</strong></td>
</tr>
<tr>
<td>Both energy and matter are exchanged freely.</td>
</tr>
</tbody>
</table>

| **Closed System** |
| Energy exchanged freely but matter does not go in or out. |

| **Isolated System** |
| Energy and matter do not exchange. |
```
Definition of State Variables - properties whose values are required to specify the state of a System

Types of State Variables

- Pressure
  - Collision of molecules / Change of linear momentum
  - Measured with a barometer
  $P = \frac{F}{A}$ Units of Pa, atm, bar, Torr, etc. (See Table 1)

- Temperature
  - Quantitative measurement of the average kinetic energy of a system
  - Thermodynamics uses an absolute temperature scale in units Kelvin
  $T(K) = T(°C) + 273.15$

- Volume
  - Spatial description of System
  - Measured with ruler, S.I. unit L or dm³

 Extensive and Intensive Properties/Variables

- Property does not depend on size or extent of system
  - e.g.) $P$ and $T$

- Property depends on size or extent of system
  - e.g.) $V$

Equilibrium

- When the system and surroundings have equal state variables
  - e.g.) $P, T, V$

  → Thermal Equilibrium - Equal Temperature

  → Thermodynamic Equilibrium - $P, T, V$ are in equilibrium
Zerotn Law of Thermodynamics

Two systems that are separately in equilibrium with a third system are also in thermal equilibrium with one another.

\[ A \iff B \iff C \]

i.e. Volume is zero

Ideal gas

- Assume all gases are the same point mass and are not interacting with each other. All collisions are assumed elastic.
- Ideal gas expression: \[ PV = nRT \] or \[ P \cdot V = n \cdot R \cdot T \] where \[ \Delta V = \frac{V}{n} \]
- Here \( R \) is a proportionality constant between the state variables.
  \[ R = 8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1} \]
- For a monatomic ideal gas \( KE = \frac{3}{2} nRT \) only depends on \( T \)

Real gases/Van der Waals

Van der Waals equation: \( (P + \frac{a}{V^2})(V - b) = nRT \)

- Corrects for actual volume/mass
- Corrects for attractive forces
- Corrects for repulsive forces

Conceptual Question

The parameter \( a \) in the Van der Waals equation is greater for \( H_2O \) than for \( He \). What does this say about the form of the potential function for the two gases?

A: If \( a_{H_2O} > a_{He} \) then \[ |\Delta V(r)_{H_2O}| > |\Delta V(r)_{He}| \]
Why (on the basis of electronic structure) is a in the van der Waals equation greater for H2O than for He?

A: H2O is a polar molecule. Dipole-Dipole Interactions will create attractions between H2O molecules. Hence "a" is greater for polar H2O than non-polar He.

Chapter 2

<table>
<thead>
<tr>
<th>State function VS. Path function</th>
</tr>
</thead>
<tbody>
<tr>
<td>differential symbol</td>
</tr>
<tr>
<td>Change of value dependent on form?</td>
</tr>
<tr>
<td>Value of cyclic integration</td>
</tr>
<tr>
<td>Calculate</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>dM (exact differential)</td>
</tr>
<tr>
<td>No</td>
</tr>
<tr>
<td>Path</td>
</tr>
<tr>
<td>∫M = 0</td>
</tr>
<tr>
<td>Final Initial</td>
</tr>
<tr>
<td>∫dM = M(final) - M(initial)</td>
</tr>
</tbody>
</table>

1st Law of Thermodynamics

\[ ΔU = q + w \]

U := Internal Energy state function
q := heat
w := work

If heat flows to surrounding, then q < 0
If heat flows to system, then q > 0

If work is done by the system, w < 0
If work is done to the system, w > 0
Heat

\[ dq_b = C_dT \Rightarrow q_b = C \Delta T = C(T_e - T_i) \]

- \( C \) is heat capacity
- \( \Delta \) is value change of a state function, always:
  \( \text{Value (final state)} - \text{Value (initial state)} \)
- \( q_b \) is heat, non-state function

For a monatomic ideal gas

at const. \( V \)

\[ q_V = C_v \Delta T = \frac{3}{2} nR \Delta T \Rightarrow C_v = \frac{3}{2} nR \text{ or } \overline{C_v} = \frac{3}{2} R \]

at const. \( P \)

\[ q_P = C_p \Delta T = \frac{5}{2} nR \Delta T \Rightarrow C_p = \frac{5}{2} nR \text{ or } \overline{C_p} = \frac{5}{2} R \]

Work

\[ W = - \int_{V_i}^{V_f} P_{ext} dV \]

Where \( P_{ext} = \) external pressure

Important key words from Chapter 2

Isochoric: \( \text{Const. } V \Rightarrow \Delta V = 0 \Rightarrow W = 0 \)

Isobaric: \( \text{Const. } P \Rightarrow \Delta P = 0 \)

Isothermal: \( \text{Const. } T \Rightarrow \Delta T = 0 \Rightarrow \Delta U = 0 \rightarrow q = w \)

Isolated: \( q = 0 \), \( W = 0 \)

Adiabatic: \( q = 0 \)

Reversible: \( P_{ext} = P_{int} \)

Free expansion or:

\( P_{ext} = 0 \Rightarrow W = 0 \)