

Chapters 2-4 Outline Textbook Reading Notes

2.3: A Working Definition of Temperature

- Isotherm: range of values where $PV = T$, for some constant T

2.6: The Ideal Gas Equation

- Ideal gas law: $PV = nRT = \bar{R}T$
 - Proportionality of P-T, V-T, P-n, V-n, and inverse proportionality of P-V

2.7: Dalton's Law of Partial Pressures

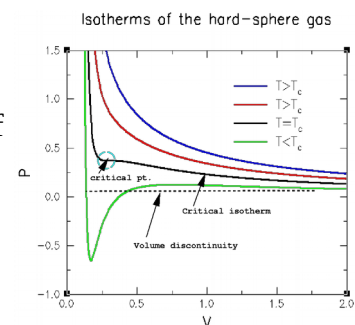
- Law of partial pressures: $P_{total} = \sum_{r=1}^i P_r$

2.8 Real Gases

- Compressibility factor: $Z = \frac{PV}{\bar{R}T}$
 - For ideal gases, $Z = 1$
 - For real gases: $\lim_{P \rightarrow 0} Z = 1$, $\lim_{P \rightarrow \infty} Z > 1$, b/c of non-negligible volume of particles
- Van der Waals equation: $(P + a\bar{V}^{-2})(\bar{V} - b) = RT$, $P = \frac{RT}{\bar{V} - b} - a\bar{V}^{-2}$,
 - a is related to IMFs, b is related to volume of particles
 - a proportional to speed and number of collisions, both of which are inversely proportional to the molar volume
- Virial equation of state: $Z = 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \frac{D}{\bar{V}^3} + \dots = 1 + B'P + C'P^2 + D'P^3 + \dots$
 - Uses empirical data (not VdW, which tries to account for physical properties)
 - Really only need first and second terms for reasonable accuracy, size of following terms is negligible for practical purposes

2.9: Condensation of Gases and the Critical State

- At high temperatures, P-V curves are roughly hyperbolic, not so for lower temperatures
- At lower temperatures, when compressing a gas (moving rtl on the P-V graph), pressure rises until a certain point, then change in volume without change in pressure (condensation), then rapid increase in pressure for small decreases in volume (compression of a liquid).
- Critical constants of a substance: P_c, T_c, V_c
 - T_c is the isotherm at which the gas cannot condense anymore
 - P_c and V_c are the points on the T_c isotherm at which the isotherm is tangent to the condensation curve
 - Critical constants are often used to estimate VdW constants:



$$\blacksquare a = \frac{27R^2T_c^2}{64P_c}, b = \frac{RT_c}{8P_c}$$

3.1: The Kinetic Theory of Gases Model

- Assumptions made:
 - Gases are many particles, size negligible compared to distances b/t them.
 - Molecules have mass but negligible volume.
 - Molecules are constantly in random motion.
 - Collisions between molecules are completely elastic.
 - There are no IMFs b/t particles.

3.2: Pressure of a Gas

$$\bullet P_{gas} = \frac{Nmv^2}{3V} = \frac{2N}{3V} \bar{E}_{trans}$$

Derivation:

$$\Delta_{collision}(mv_x) = 2mv_x$$

$$f_{collision} = \frac{2l}{v_x}$$

$$P_{gas} = \frac{F}{A} = \frac{Nma}{l^2} = \frac{Nmv_x^2 f}{l^2} = (2mv_x) \left(\frac{2l}{v_x} \right) = \frac{Nmv_x^2}{l^3} = \frac{Nmv_x^2}{V}$$

$$\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2 = 3\bar{v}_x^2, v_x \approx v_y \approx v_z$$

$$P_{gas} = \frac{Nmv^2}{3V} = \frac{2N}{3V} \bar{E}_{trans}$$

(this derivation assumes constant volume, will be used in constant volume heat capacity)

- $\bar{E}_{trans} = \frac{3}{2}k_B T$
- $v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_B T}{m}}$

3.8: Equipartition of Energy

- Each molecule has 3N DOFs
 - $\bar{E}_{trans} = \frac{3}{2}RT, \frac{1}{2}RT$ for each of three translational DOFs
 - For monatomic gases, only translational energy; for polyatomic gases, also rotational and vibrational energies
 - For linear molecules, 2 rotational DOFs with $\frac{1}{2}RT$ energy each; for nonlinear molecules, 3 rotational DOFs with $\frac{1}{2}RT$ energy each
 - For linear molecules, 3N-5 rotational DOFs with RT energy each ($\frac{1}{2}RT$ for both a kinetic and potential energy term); for nonlinear molecules, 3N-6 vibrational DOFs with RT energy each
 - Usually vibrational energy ignored at normal temperatures and pressures
 - $\bar{U} = \frac{3}{2}RT + \frac{1}{2}RT(\text{rotational DOFs}) + RT(\text{vibrational DOFs})$
 - $\bar{U}_{monatomic} = \frac{3}{2}RT$
 - $\bar{U}_{diatomic} = \frac{5}{2}RT$ (ignoring vibrational energy)

- $\bar{C}_V = \left(\frac{\partial \bar{U}}{\partial T} \right)_V$
 - Heat capacity is dependent on temperature, but can treat it like a constant in a small range of temperatures.

4.1: Work and Heat

- $w = -P_{ex}\Delta V$
Derivation:
 $P_{ex} = \frac{mg}{A}$
 $w = -mg\Delta h = -P_{ex}\Delta h = -P_{ex}(V_2 - V_1)$
- For a reversible process: $w = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}$
 - Reversible work is the maximum amount of work possible for this change in pressure and volume, but it is impossible to achieve in real life; reversibility is a measure of efficiency.
- Work is not a state function.
- Heat is also not a state function.

4.2: The First Law of Thermodynamics

- $dU = \bar{d}q + \bar{d}w$

4.3: Enthalpy

- In constant pressure: $\Delta U = q_p - P\Delta V \implies q_p = \Delta(U + PV)$
- Definition: $H = q_p = U + PV$
 - State function, because U, P, V are all state variables
 - When under constant pressure, is equal to q_p
- $\Delta H = \Delta U + P\Delta V + V\Delta P + \Delta P\Delta V$
 - Last term is not always non-negligible
 - If at constant pressure, then $\Delta H = \Delta U + P\Delta V$, $\Delta U = \Delta H - P\Delta V$
- ΔU doesn't have to equal ΔH for every equation
 - In chemical reactions involving evolution of gases (or reduction of moles of gases), the difference is $\Delta U - \Delta H = -P\Delta V = -RT\Delta n$, where n is the change in moles of gas, because some expansion work is done by gases and lowers the internal energy of the gas

4.4: A Closer Look at Heat Capacities

- $\bar{C}_V = \left(\frac{\partial \bar{U}}{\partial T} \right)_V \implies d\bar{U} = \bar{C}_V dT \implies \Delta U = n\bar{C}_V \Delta T$
- $\bar{C}_P = \left(\frac{\partial \bar{H}}{\partial T} \right)_P = \left(\frac{\partial \bar{H}}{\partial T} \right)_P \implies d\bar{H} = \bar{C}_P dT \implies \Delta H = n\bar{C}_P \Delta T$
 - While these are written in terms of the heat capacities at constant volume and pressure, it works for any process because U is a state function
 - Here, heat capacities are treated independently of temperature, which is usually an acceptable approximation
- For an ideal gas, $\bar{C}_P - \bar{C}_V = R$
Derivation:
 $H = U + PV = U + nRT$
 $dH = dU + nRdT$
 $n\bar{C}_P dT = n\bar{C}_V dT + nRdT$

4.5: Gas Expansion

- Isothermal expansion when T constant
 - $dU = dH = 0, q = -w$
 - Reversible and irreversible work calculated in section 4.1
- Adiabatic expansion when no heat exchange
 - $q = 0, dU = w$
 -