

Part II: Thermodynamics

II.4 Applications: ideal gas

Class schedule: Feb 17, 19

Readings: S10, S12A-C, R5.1-5.4, R5.7, F4-6

II.4.1 The ideal gas assumption

By definition, an ideal gas is a gas with interactions (other than collisions) between constituent gas particles ignored. In general, particle interactions, such as the gravitational force or electric force, are related to the mean distance between gas particles. Therefore, it can be stated that the internal energy of an ideal gas does not depend on space coordinates or external parameters like the size (volume) of the gas (see Reif Equations 5.1.3 – 5.1.10 for a rigorous mathematical proof).

Note: the independence of E on (x, y, z) is our starting point when we tried to obtain the number of micro-states of an monatomic ideal gas by calculating how many cells of size h are in the phase space, where $p = \sqrt{2mE}$ – internal energy is the total kinetic energy of gas particles.

For example, the gravitational force and Coulomb force, and gravitational and electrical potential, all decrease rapidly with the distance. Therefore, an idea gas is a rarefied gas. One can see that as an ideal gas is compressed, interaction will grow, the ideal gas assumption will no longer hold, and the gas is approaching the real gas.

Example 1: estimate the electric potential between dipoles in comparison with the mean internal energy per gas particle, given that 1 mole gas occupies 22.4 liter volume at room temperature.

II.4.2 Equations of State

From *microscopic* calculations, (i.e. $\Omega \sim E^{\nu/2N} V^N$ for an ideal gas), we derive the relations between macroscopic properties of an ideal gas:

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T} \implies E = \frac{\nu}{2} NkT = \frac{\nu}{2} nRT$$
$$\left(\frac{\partial S}{\partial V}\right)_E = \frac{P}{T} \implies PV = NkT = nRT$$

Remark 1: $n = N/N_a$, $k = R/N_a$, k and N_a are bridges between micro- and macro- worlds.

Remark 2: in the history of thermodynamics, these properties of an ideal gas were first empirically established by *macroscopic* experimental measurements.

II.4.3 Heat capacity and specific heats

Definition of heat capacities: $C_y = dQ/dT)_y$ is the heat capacity of a system with the condition that y is kept constant. Heat capacities measure the ability of a system to change its temperature given an amount of heat transfer. Depending on the conditions (i.e., what y is kept constant), the

heat capacity of a system varies. The macroscopic measurements of specific heats or heat capacities, therefore, provide important information to find out the entropy change of the system.

Specifically, we often use two kinds of heat capacities: the heat capacity at constant volume: $C_V = \partial Q/\partial T)_V = \partial E/\partial T)_V$, and the heat capacity at constant pressure: $C_P = \partial Q/\partial T)_P$. In general gas systems, $C_P > C_V$, if the gas kept at constant pressure expands with increasing temperature. For an ideal gas, $C_P = C_V + nR$.

The specific heats are heat capacities per mole or per unit mass: $c_y = C_y/n$, or $c_y = C_y/m$. Specifically, $c_V = C_V/n$ or $c_V = C_V/m$, and $c_P = C_P/n$ or $c_P = C_P/m$.

Example 2: heat capacities and specific heats of a monatomic ideal gas: $C_V = 3/2nR$, $c_V = 3/2R$, and $C_P = 5/2nR = 5/3C_V$, $c_P = 5/2R = 5/3c_V$.

Example 3: specific heats of different materials: water has fairly large specific heats, making it a good heat reservoir.

II.4.4 Expansions and compressions

For obviously practical reasons, we often need to study the expansion and compression of a system, such as a gas. Expansion and compression of an ideal gas are studied using the first law and the equation of state (ideal gas law).

Example 4: find the changes in internal energy and entropy in isobaric, isothermal, and adiabatic expansions or compressions.

In general, the volume of a system may change with both the temperature and pressure variations. To examine such, we define the “isothermal compressibility” κ and “coefficient of volume expansion” β :

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T, \quad \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

.

Example 5: find κ and α for an ideal gas.

*Example 6: relationship between P , V , and T for an ideal gas in the adiabatic evolution, i.e., $dQ = 0$.

Example 7: adiabatic convection in the Earth’s atmosphere (Reif Prob. 5.7)

Summary of II.4: properties of an ideal gas:

Definition: no particle interaction, $E \equiv E(T)$

Equation of state: $PV = nRT = NkT = \frac{\rho}{\mu}RT = \frac{\rho}{m}kT$

Internal Energy: $E = \frac{f}{2}kT$, for monatomic gas, $f = 3N$, for diatomic gas, $f = 5N$.

Specific heats:

$$C_V \equiv \left. \frac{dQ}{dT} \right)_V = \left. \frac{\partial E}{\partial T} \right)_V \equiv \frac{dE}{dT}, C_P \equiv \left. \frac{dQ}{dT} \right)_P = C_V + nR$$
$$c_P = c_V + R, \gamma = \frac{c_P}{c_V} = 1 + \frac{R}{c_V}$$

For monatomic gas, $c_V = 3/2R, c_P = 5/2R, \gamma = 1.67$

For diatomic gas, $c_V = 5/2R, c_P = 7/2R, \gamma = 1.4$

Entropy:

$$dS = \frac{C_V}{T} dT + \frac{P}{T} dV$$
$$\Delta S = C_V \ln(T_f/T_i) + nR \ln(V_f/V_i) \quad (C_V = \text{const.})$$

Microscopically $\Omega = BE^{f/2} V^N, S = k \ln \Omega$

Coefficient of volume expansion:

$$\beta = - \left. \frac{1}{V} \frac{\partial V}{\partial T} \right)_P = \frac{1}{T}$$

Isothermal compressibility:

$$\kappa = - \left. \frac{1}{V} \frac{\partial V}{\partial P} \right)_T = \frac{1}{P}$$

Adiabatic compressibility:

$$\kappa_S = - \left. \frac{1}{V} \frac{\partial V}{\partial P} \right)_S$$

Adiabatic relations:

$$\gamma \frac{dV}{V} + \frac{dP}{P} = 0, PV^\gamma = \text{const.}, P\rho^{-\gamma} = \text{const.}$$
$$\gamma - 1 \frac{dV}{V} + \frac{dT}{T} = 0, TV^{\gamma-1} = \text{const.}, T\rho^{1-\gamma} = \text{const.}$$
$$\frac{\gamma}{1-\gamma} \frac{dT}{T} + \frac{dP}{P} = 0, PT^{\frac{\gamma}{1-\gamma}} = \text{const.}$$