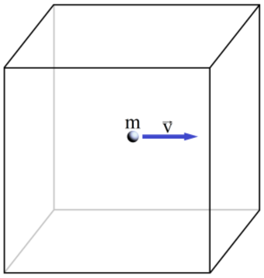
Lecture 20: Kinetic Theory of Gas & Thermodynamics

Physics for Engineers & Scientists (Giancoli): Chapters 18 & 19
University Physics V2 (Openstax): Chapters 2 & 3

The Kinetic Theory of Gas

Our goal is to find a relationship between the microscopic properties of the particles that make up a gas and the macroscopic properties of the gas.

Let's begin with a cube with sides of length L and the simplest possible gas inside it, a single particle moving with velocity v.



The pressure is the force per area: $\mathrm{P} = \frac{F}{A}$

The force is the momentum per time: $F = \frac{\Delta P}{\Delta t}$

The time interval is the time it takes the particle to return:

$$v\Delta t = 2L \qquad \Delta t = \frac{2L}{v}$$

The change in momentum of the wall is equal and opposite to the change in momentum of the particle.

$$\Delta P_{wall} = -(\Delta P_{particle}) = -(P_{final} - P_{initial}) = -[m(-v) - mv] = 2mv$$

$$F = \frac{\Delta P}{\Delta t} = \frac{2mv}{\frac{2L}{v}} = \frac{mv^2}{L} \qquad \mathrm{P} = \frac{\frac{mv^2}{L}}{L^2} = \frac{mv^2}{L^3}$$

This is the pressure created by a single particle. Now let's fill the container with N particles, but we must account for the "equipartition theorem".

Equipartition of Energy: Each degree of freedom (dimension) must have the same amount of energy carried through it.

To account for this, we will have all of our particles moving in one-dimension with a third moving in each direction. Then we will calculate the force and then the pressure on one face.

This may seem rather contrived, but if left for a short time collisions will return this system to a completely random state. Consequently, these states are equivalent (at least for our purposes here).

Instead of v^2, which varies from particles to particle, we must use the average value of v^2. To do this we will use "rms" values (which stands for "root mean square", the square root of the mean of squares).

$$v_{rms} = \sqrt{\overline{v^2}} \qquad \overline{v^2} = v_{rms}^2$$

$$F_{Tot} = (\#\,of\,particles)(F_{avg}) = \left(\frac{N}{3}\right)\left(\frac{m\overline{v^2}}{L}\right) = \frac{Nmv_{rms}^2}{3L}$$

$$P = \frac{F_{Tot}}{A} = \frac{\frac{Nmv_{rms}^2}{3L}}{L^2} = \frac{Nmv_{rms}^2}{3L^3} = \frac{Nmv_{rms}^2}{3V} \qquad PV = \frac{1}{3}Nmv_{rms}^2 = NkT$$

$$mv_{rms}^2 = 3kT \qquad KE_{avg} = \frac{1}{2}mv_{rms}^2 = \frac{3}{2}kT$$

Internal Energy of a Monoatomic Ideal Gas: $U = N\left(\frac{3}{2}kT\right) = \frac{3}{2}NkT = \frac{3}{2}nRT$

Example: Determine the change in internal energy of helium gas in a 56.0 m^3 tank as it is heated to 35.0°C starting in standard temperature and pressure.

$$V = 56.0\ m^3 \qquad T_{Final} = 35°\text{C} + 273.15 = 308.15\ K \qquad T_{init} = 273.15\ K \qquad P_{init} = 101.3\ kPa$$

$$\Delta U = U_{final} - U_{init} = \frac{3}{2}nRT_{final} - \frac{3}{2}nRT_{init} = \frac{3}{2}nR(T_{final} - T_{init})$$

$$PV = nRT \qquad nR = \frac{PV}{T} = \frac{P_{init}V_{init}}{T_{init}}$$

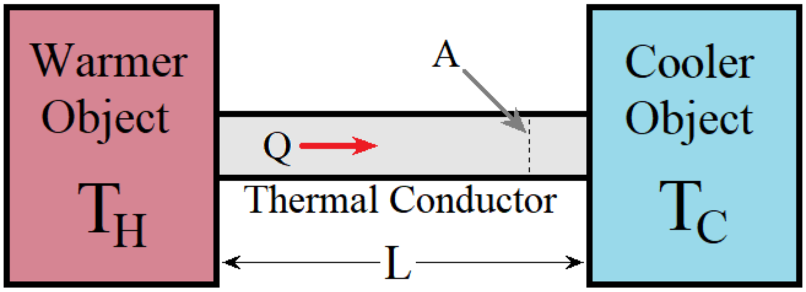
$$\Delta U = \frac{3}{2}\left(\frac{P_{init}V_{init}}{T_{init}}\right)(T_{final} - T_{init}) = \frac{3}{2}\left(\frac{(1.013 \times 10^5\ Pa)(56.0\ m^3)}{273.15\ K}\right)(308.15\ K - 273.15\ K) = 1.09\ MJ$$

Thermodynamics

- **Thermodynamics** is the relationship between heat and work.
- The **System** is a collection of objects of interest.
- The **Surroundings** are everything else.
- Typically the system is surrounded by walls.
    - **Diathermal** walls permit heat flow between the system and surroundings.
    - **Adiabatic** walls do not permit heat flow.
- The **State of the System** refers to the physical condition of the system (pressure, temperature, etc.)
- Two systems are in **Thermal Equilibrium** if there is no heat flow when the two systems are in thermal contact (i.e. heat could flow).

The 0th Law of Thermodynamics: Two systems that are individually in thermal equilibrium with a third system are in thermal equilibrium with each other.

Consider the equation for heat flow via conduction. In thermal equilibrium there is no heat flow (Q = 0). What condition makes this so?



$$Q = \left(\frac{kA\Delta T}{L}\right)t$$

L, k, and A are constants, and Q must be zero for all values of t.
Two objects are in thermal equilibrium if they are at the same temperature.

Two systems that are individually at the same temperature as a third system are at the same temperature as each other.

The 1^{st} Law of Thermodynamics

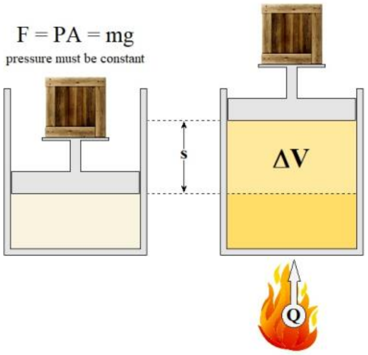
The 1st law of thermodynamics is applying conservation of energy with heat.

$$\Delta U = U_{final} - U_{init} = Q - W$$

The change in the internal energy of a system (ΔU) is equal the heat ADDED TO the system (Q) minus any work done BY the system (W).

The internal energy of a system depends only upon the state of a system and not on the method by which the system arrives at that state. In other words, the internal energy of a system is solely a function of the state of that system.

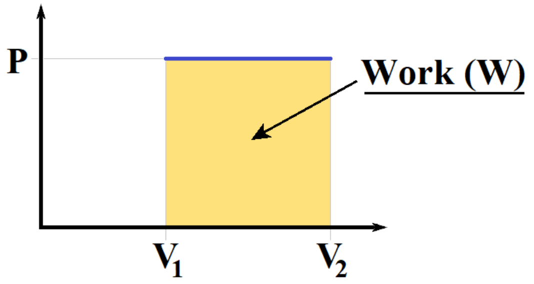
Isobaric Process (Constant Pressure)



The force from the gas pressure at the bottom of the piston must support the weight of the mass and the piston. As that weight is fixed (constant), the pressure must also be fixed (constant). If we account for outside air pressure (also fixed) it doesn't change that the pressure is constant.

When heat (energy) is added the temperature rises. The ideal gas law(PV = nRT) tells us that the temperature can't rise without a change in volume and/or pressure. As the pressure is fixed, the gas expands

$$W \text{ (work done } \textbf{BY} \text{ the gas)} = Fs = (PA)s = P(As) = P \cdot \Delta V = P \cdot (V_{final} - V_{init})$$



In a P-V Diagram, where the pressure (P) is plotted against volume (V), the work (W) is the area under the curve (W = P·ΔV).

Example: A gas is held at a constant pressure of 150 kPa as it expands, doing 750 J of work in the process. The initial volume of the gas is 2.00×10^{-3} m^3. Determine (A) the final volume of the gas, and (B) the change in internal energy of the gas.

$$W = P \cdot \Delta V = P \cdot (V_{final} - V_{init}) \qquad V_{final} - V_{init} = \frac{W}{P}$$

$$V_{final} = \frac{W}{P} + V_{init} = \frac{750\,J}{1.50 \times 10^5\,Pa} + 2.00 \times 10^{-3}\,m^3 = 7.00 \times 10^{-3}\,m^3$$

$$\Delta U = U_{final} - U_{init} = \frac{3}{2}nRT_{final} - \frac{3}{2}nRT_{init} = \frac{3}{2}PV_{final} - \frac{3}{2}PV_{init} = \frac{3}{2}P(V_{final} - V_{init}) = \frac{3}{2}P \cdot \Delta V = \frac{3}{2}W$$

$$\Delta U = \frac{3}{2}W = \frac{3}{2}(750\,J) = 1125\,J$$

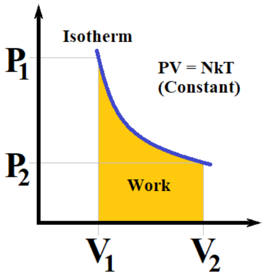
Isochoric Process (Constant Volume)

- If the volume is constant no work is done: $W = F\cdot d = F\cdot 0 = 0$
- Any heat added changes the internal energy of the gas: $\Delta U = Q - W = Q$

Adding heat increases the internal energy, which also increases the temperature of the gas. Increasing the temperature of the gas must increase the pressure (as the volume is constant).

$$Q = \Delta U = \frac{3}{2}Nk\Delta T \qquad P = \frac{NkT}{V} = \frac{Nk}{V}(T_0 + \Delta T)$$

Isothermal Process (Constant Temperature)



$$dW = PdV$$

$$W = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \frac{NkT}{V}dV = NkT\int_{V_1}^{V_2}\frac{dV}{V}$$

$$W = NkT[\ln(V)]_{V_1}^{V_2} = NkT[\ln(V_2) - \ln(V_1)]$$

$$W = NkT\ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta T = 0 \qquad \Delta U = \frac{3}{2}Nk\Delta T = 0 \qquad \Delta U = Q - W = 0 \qquad Q = W = NkT\ln\left(\frac{V_2}{V_1}\right)$$

Heat entering the system is immediately converted to work via expansion.

Example: 5.00 moles of a monoatomic gas is held at a constant temperature as it is compressed from 5.00 liters to 2.50 liters. 8.95 kJ of work is done on the gas to compress it. Determine (A) the change in energy of the gas, (B) the heat added to the gas, and (C) the temperature of the gas.

A) $\Delta U = Q - W = 0$

B) $Q = W = -8.95\ kJ$

It must be negative. Work was done "to the gas", not "by the gas".

C) $W = nRT\ln\left(\frac{V_2}{V_1}\right)$ $\qquad T = \frac{W}{nR\ln\left(\frac{V_2}{V_1}\right)} = \frac{-8950\ J}{(5\ mol)\left(8.314\frac{J}{mol\cdot K}\right)ln\left(\frac{2.50\ l}{5.00\ l}\right)} = 311\ K$

Adiabatic Process (Q = 0) *No heat is added or removed*

$$\Delta U = Q - W = -W \qquad W = -\Delta U = -\frac{3}{2}Nk\Delta T = -\frac{3}{2}Nk(T_{final} - T_{init}) = \frac{3}{2}Nk(T_{init} - T_{final})$$

Example: 10.0 moles of a monoatomic gas expands adiabatically. Its temperature falls from 425 K to 300 K. Determine (A) the work done by the gas, and (B) the change in the internal energy.

$$W = \frac{3}{2}nR(T_{init} - T_{final}) = \frac{3}{2}(10.0\ mol)\left(8.314\frac{J}{mol\cdot K}\right)[425\ K - 300\ K] = 15.6\ kJ$$

$$\Delta U = -W = -15.6\ kJ$$