Thermal Properties of Matter

Want to begin looking at the macroscopic properties of matter with a focus on ideal gases, whose structure is relatively easy to understand. We will then explore how the macroscopic properties follow from the actual dynamics of the molecules in a gas

The ideal gas law

The temperature of an object is a measure of the energy stored in the object or the gas that we are now considering. The pressure p of a gas is the force per unit area

units: $p \sim \frac{N}{m^2} = P_a$ (Pascal)

$T \sim$ °K (Kelvin scale)

Given a certain mass of a dilute gas, and its volume, we want a relation between the pressure and temperature.

$\Rightarrow$ the relation between P, V, T, m is the equation of state

Rather than specify the mass of a gas, it is better to specify a number that is related to the number of molecules in the gas. If the mass of one molecule of the gas is m_m then the number of molecules in a mass of gas m is

$$N = \frac{m}{m_m} = \# \text{ of molecules}$$

There is a standard # of molecules

$$1 \text{ mole} = 6.022 \times 10^{23} \text{ molecules} \equiv N_A$$
$$= \text{Avagadro's } \#$$

N_A is by definition the # of atoms of C^{12} in 12 gm. The number of moles of a gas in then given by

$$n = \frac{N}{N_A} = \# \text{ of moles of the gas.}$$

The experimental observations for a dilute gas are that

$$PV = nRT$$

where

$$R = 8.314 \frac{J}{\text{mole } {}^\circ K} = \text{same for all gases}$$

units: $PV = \frac{N}{m^2} m^3 = N\text{-}m = J$

The ideal gas law is valid for dilute gases where the volume occupied by individual molecules is small compared with the volume between molecules.

example: what is the volume occupied by 1 mole of ideal gas at

$T = 0°c = 273°K$

$P = 1 \text{ atmosphere} = 1.013 \times 10^5 \, Pa$

$$V = \frac{nRT}{P} = \frac{8.314 \, J}{mole \, °K} \; \frac{1 \, mole \; 273°K \; m^2}{1.013 \times 10^5 \, N}$$

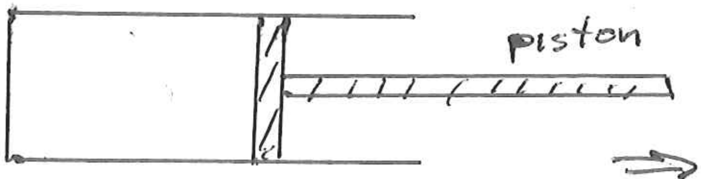
$$= 0.0224 \, m^3$$

$$= 22.4 \text{ liters } \left(1 \text{ liter} = 10^3 \, cm^3\right)$$

Experiments with ideal gases

Can carry out experiments in which the pressure, volume and temperature of a gas are changed.

⇒ gas chamber with a piston



⇒ use piston to change volume

experiment ①

Fix the volume and # of molecules

$\Rightarrow$ vary T by injecting heat

$$P = \left(\frac{nR}{V}\right) T \Rightarrow \frac{P}{T} = \text{const}$$

$\Rightarrow$ Charles' Law

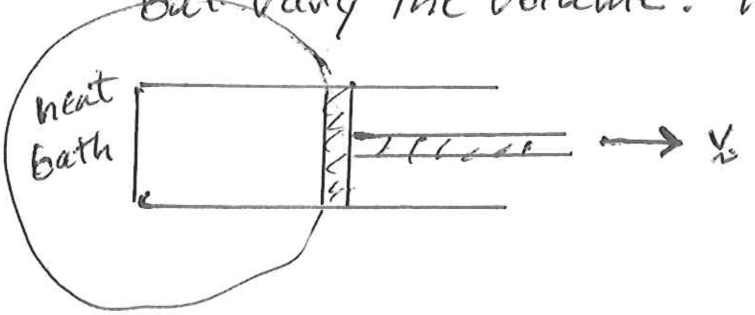
example A gas at 290°K has a pressure of 2 atm. The temperature is raised to 310°K. What is the pressure?

$$\frac{P}{T} = \text{const.} = \frac{2\text{ atm}}{290°K} = \frac{P_{final}}{310°K}$$

$$P_{final} = 2\text{ atm}\,\frac{310}{290} \simeq 2.14\text{ atm}$$

experiment 2

Maintain T (with a heat bath) and # of molecules but vary the volume. How does p change?



$PV = nRT = \text{const.}$

$\Rightarrow$ Boyle's law

$P_i V_i = P_f V_f$

$\Rightarrow$ double volume

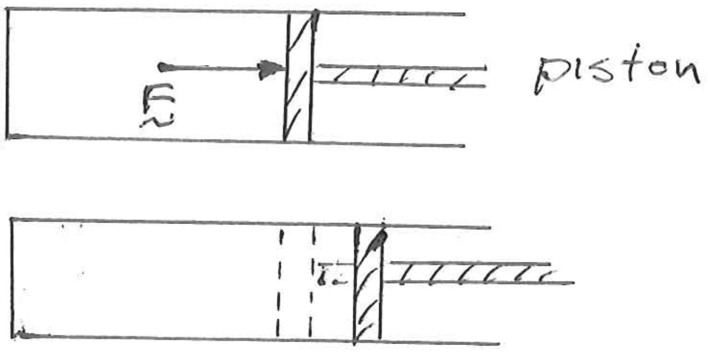
$\Rightarrow$ pressure is $\frac{1}{2}$

Work done by an ideal gas during volume chanes

How can a gas exchange energy with its environment?

① Heat can flow in or out of the gas.

② A gas can also directly do work on the external environment.



Work is the force times the distance

$$dW = F\,dx$$

$$= P\underbrace{A\,dx}_{\text{volume change}}$$

⇒ work done by gas

$$\Rightarrow dW = P\,dV$$

$$W = \int_{V_1}^{V_2} P\,dV$$ ⇒ note that P may change as V changes

① Constant pressure (must increase temp. or supply more gas)

$$W = P(V_2 - V_1)$$

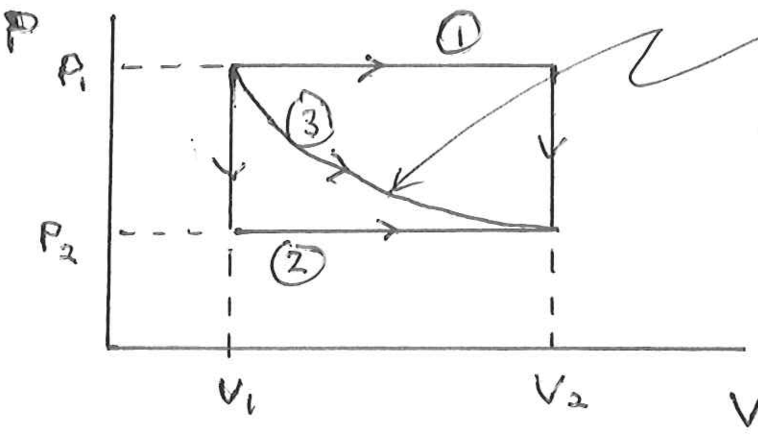
② Constant temperature

$$PV = nRT = \text{const} = P_1 V_1$$

$$\Rightarrow P = \frac{P_1 V_1}{V}$$

$$W = \int_{V_1}^{V_2} P\,dV = \int_{V_1}^{V_2} P_1 V_1 \frac{dV}{V} = P_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$$

For a specified change in the pressure and volume of a gas, how does the work depend on how the changes in P and V take place?



T = const.

$$P = \frac{P_1 V_1}{V}$$

Consider three paths:

① Change ~~velocity~~ volume with initial pressure P_1 and then drop to P_2 leaving V at V_2

$$W = P_1 (V_2 - V_1) = \text{area under curve}$$

② First drop pressure from P_1 to P_2 at fixed V_1. Then increase volume to V_2

$$W = P_2 (V_2 - V_1) = \text{area under curve}$$
$$= \text{less work}$$

③ Constant Temperature

$$P = \frac{P_1 V_1}{V}$$

$$W = P_1 V_1 \ln\left(\frac{V_2}{V_1}\right) = \text{area under curve}$$

⇒ work between that of ① and ②.

⇒ the work depends on how the expansion takes place.

Energy conservation and the first law of thermodynamics

The thermodynamics of a system describes how it (gas, liquid or solid) interacts with it's environment.

⇒ this interaction can take place through work or by exchanging heat.

The energy conservation law for a system is given by

$$\boxed{\Delta U = U_2 - U_1 = Q - W}$$

First law of thermodynamics

ΔU is the change in internal energy of a system. Q is the heat added to the system and W is the work done by the system.

⇒ The law basically says that the energy flow into the system is stored in the form of thermal motion and the molecular structure of the material.

Thermodynamic processes

Thermodynamic systems can exchange energy with the external world by exchanging heat or doing work during volume changes.

The types of interactions can be defined by what is held constant during the interaction.

① No heat flow (adiabatic) $Q = 0$

$$\Delta U = -W$$

This includes any thermally isolated system or any system where things happen so fast that there is no time for heat to flow

⇒ e.g. quickly compress a gas with a piston.

② Constant volume (isochoric)
No work is done so

$$\Delta U = Q$$

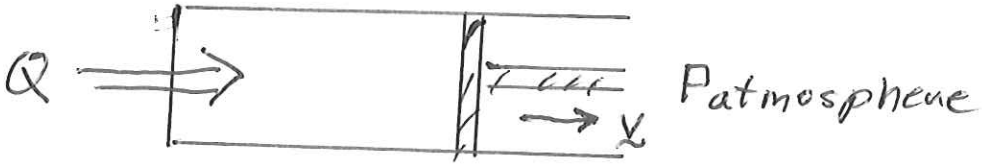
$\Rightarrow$ e.g. heating a gas in a closed container

③ Constant pressure (isobaric)

$$\Delta U = Q - W$$

$\Rightarrow$ Generally ΔU, W, Q are all non zero.

$\Rightarrow$ Heating a gas ~~with~~ that has a moveable piston balanced by atmospheric pressure



④ Constant temperature
$\Rightarrow$ contact with a heat bath
$\Rightarrow$ slow process so thermal equilibrium is maintained.

$$\Delta U = -W + Q$$

If the internal energy U only depends on T, then $\Delta U = 0$ $\Rightarrow$ e.g. ideal gas and

$$W = Q$$

Heat capacity and internal energy of an ideal gas

The heat capacity of a solid liquid or gas governs how the temperate of the material changes as heat is added. The heat capacity of a gas depends on whether the volume of the gas is held fixed as heat is added. This volume change is typically not important in solids where volume changes are typically small. The heat capacity of a gas when the volume is a constant is called C_V while at constant pressure it is C_p.

For an ideal gas the internal energy of the gas depends only on T so the heat capacity at ~~constant~~ constant temperature is zero. For a gas the heat capacity is specified per mole

$$C_V, C_p \sim \frac{J}{\text{mole}\,{}^\circ K}$$

We will show that for ideal gases

$$C_V = \frac{3}{2} R \text{ (monatomic molecules)}$$
$$= \frac{5}{2} R \text{ (diatomic molecules)}$$

For a process in which V is a constant

$$C_V = \frac{1}{n} \frac{\Delta Q}{\Delta T}$$

with n the number of moles, ΔQ the heat added or extracted ΔT the temperature change. Thus,

$$\Delta Q = n C_V \Delta T .$$

Since no work is done when V is constant, the heat must go into the internal energy of the gas,

$$\Delta U = -W + \Delta Q = \Delta Q$$

or

$$\Delta U = n C_V \Delta T$$

For an ideal gas C_V is independent of T, V, P so can integrate the equ.

$$U = n C_V T$$

or

$$U = \frac{3}{2} n R T$$

for a monatomic gas. Given n and T can calculate the total stored energy.

If heat is added to a gas with P constant, some of the heat goes into the internal energy and some is expended as the gas volume increases to maintain constant pressure. Since

$$p = \frac{nRT}{V},$$

As heat is added both T and V must increase together so P remains constant. ~~Some of the~~

Because the added heat goes into both the internal energy and the work, ~~the~~ Cp is greater than Cv. The definition of Cp is

$$c_p = \frac{\Delta Q}{n \Delta T}$$

or $\Delta Q = n c_p \Delta T$ but

$$\Delta W = P\, dV$$

From the first law

$$\Delta U = -\Delta W + \Delta Q$$

$$= -P\Delta V + n c_p \Delta T$$

We want to eliminate ΔV ~~so we can integrate this equation~~

$\Rightarrow$ use ideal gas law with P constant

$$V = \frac{nRT}{p}$$

$$\Rightarrow \Delta V = \frac{nR\Delta T}{p} \quad (p\,\text{constant})$$

Thus, $$\Delta U = -p\left(\frac{nR}{p}\right)\Delta T + n c_p \Delta T$$

$$\Delta U = n\left(c_p - R\right)\Delta T$$

$$\equiv n c_V \Delta T$$

so

$$c_p = c_V + R$$

$$= \frac{5}{2} \text{ monatomic}$$

$$= \frac{7}{2} \text{ polyatomic}$$

An important parameter is the ratio of specific heats

$$\gamma \equiv \frac{c_p}{c_V} = \frac{c_V + R}{c_V} = 1 + \frac{R}{c_V}$$

$$\gamma = \frac{5}{3} \text{ monatomic}$$

$$= \frac{7}{5} \text{ diatomic}$$

Adiabatic processes for an ideal gas

For an isothermal process

$$PV = nRT = \text{const}$$

For a constant volume process

$$\frac{P}{T} = \frac{nR}{V} = \text{const.}$$

In an adiabatic process $\Delta Q = 0$. That is, no heat enters or leaves the gas. Can do experiments in an insulated container with a moveable piston

$\Rightarrow$ change volume with

$$\Delta Q = 0$$

The work done is $\Delta W = p\,dV$ so from the first law

$$du = -p\,dV.$$

The internal energy is $U = nC_V T$ so

$du = nC_V\,dT$

$$\Rightarrow nC_V\,dT = -p\,dV$$

Want to integrate this equation to find how T changes as V changes but P ~~d~~depends on V and T,

$$P = \frac{nRT}{V}$$

so

$$n C_V \, dT = -\left(\frac{nRT}{V}\right) dV$$

Rewrite the equation as

$$C_V \frac{dT}{T} = -R \frac{dV}{V}$$

Recall that $R = C_p - C_V$ so

$$\frac{dT}{T} = -\left(\frac{C_p - C_V}{C_V}\right) \frac{dV}{V}$$

$$\frac{dT}{T} = -(\gamma - 1) \frac{dV}{V}$$

Integrate over T and V,

$$\ln(T)\Big|_{T_0}^{T} = -(\gamma-1) \ln V \Big|_{V_0}^{V}$$

where V_0, T_0 are the initial values.

$$\ln\left(\frac{T}{T_0}\right) + (\gamma - 1)\ln\left(\frac{V}{V_0}\right) = 0$$

$$\ln\left(\frac{T}{T_0}\right) + \ln\left[\left(\frac{V}{V_0}\right)^{\gamma-1}\right] = 0$$

$$\ln\left[\frac{T}{T_0}\left(\frac{V}{V_0}\right)^{\gamma-1}\right] = 0$$

$$\frac{T}{T_0}\left(\frac{V}{V_0}\right)^{\gamma-1} = 1$$

$$T V^{\gamma-1} = T_0 V_0^{\gamma-1} = \text{const.}$$

This gives the relation between T and V during an adiabatic process

$\Rightarrow$ as V goes up, T goes down

$\Rightarrow$ T goes down because the gas does work as V increases and it loses internal energy

example Consider a 1 liter volume of O_2 at 300°K. For O_2 $\gamma = 1.4$ since it is diatomic. The gas expands to 2 liters by pushing against a piston. What is the final temperature?

$$T V^{\gamma-1} = \text{const}$$

$$T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$$

$$T_f = T_i \left(\frac{V_i}{V_f}\right)^{\gamma-1}$$

$$= 300°K \frac{1}{2^{0.4}} = 227°K$$

Can also obtain a relation between P and V during adiabatic processes by using the ideal gas law to eliminate T

$$\Rightarrow T = \frac{PV}{nR}$$

$$\Rightarrow \frac{PV}{nR} V^{\gamma-1} = \text{const.}$$

$$\Rightarrow PV^{\gamma} = \text{const.}$$

How much work ~~is done~~ does a gas do as it expands adiabatically?

$$\Rightarrow W = \int_{V_i}^{V_f} P\,dV$$

Can plug in $P = \text{const.}\ V^{-\gamma}$ and integrate but it is easier to calculate the work from the first law

$$\Delta U = -W + \Delta Q = -W$$

since $\Delta Q = 0$

$$\Rightarrow W = -\Delta U = -n c_v (T_f - T_i)$$

$$W = -n c_v (T_2 - T_1)$$

<u>example</u> How much work was done in the Q_2 expansion? Take $n = \frac{1}{20}$ mole

$c_v = \frac{5}{2}R$

$$W = -n c_v (T_f - T_i) = -\tfrac{1}{20}\text{ mole}\ \frac{8.314\text{ J}}{{}^{\circ}\text{K mole}}\ \frac{5}{2}\,(300 - 227)\,{}^{\circ}\text{K}$$

$$= 75.9\text{ J}$$

Molecular structure of an ideal gas

An ideal gas consists of molecules in motion that collide with themselves and the walls of a container that may enclose the gas. We want to develop an understanding of an ideal gas from the molecular level.

First we need to review what we mean by an ideal gas

① There must be a large # of molecules moving with random velocities

② The average distance between molecules is much greater than their characteristic size

$\Rightarrow$ they spend most of their time traveling in free space

$\Rightarrow$ occaisonal collisions

At STP, $N \sim 6 \times 10^{23}$ molecules
$V \sim 20 \times 10^{3}\ \text{cm}^3$

Take d to be the average spacing between molecules. Then

$$N d^3 \sim V$$

$$d^3 \sim \frac{V}{N} \sim \frac{20 \times 10^3\ \text{cm}^3}{6 \times 10^{23}} \sim 3 \times 10^{-20}\ \text{cm}^3$$

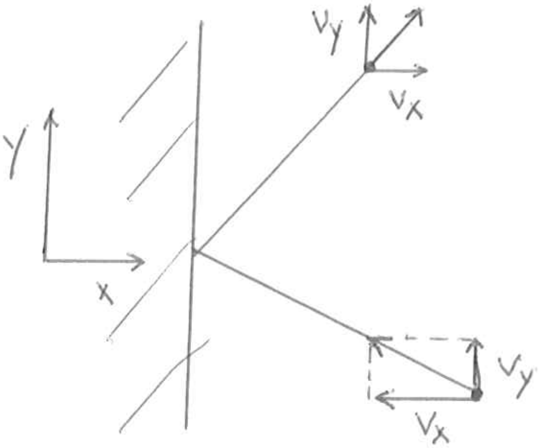
$$d \sim 3 \times 10^{-7}\ \text{cm}$$

The scale length of an O_2 molecule is around

$$\sim 0.1 \times 10^{-9}\,\mathrm{m} \sim 10^{-8}\,\mathrm{cm}$$

$$\ll d$$

Consider a volume V containing N molecules of mass m. The collisions of the molecules with the wall produces a pressure on the wall

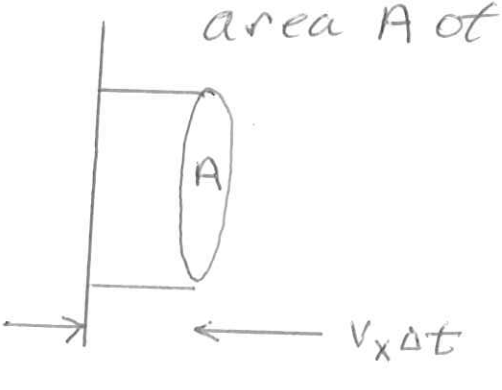


During the collision, V_y remains constant but V_x changes sign

$$V_x \longrightarrow -V_x$$

$\Rightarrow$ momentum change $= 2mV_x$

Assume that all the molecules have velocity V_x (we will eventually average over V_x). During a time Δt, how many molecules will collide with an area A of the wall?



The volume of molecules hitting the wall is

$$\Delta V = A V_x \Delta t$$

Half of the molecules in the volume will hit the wall since half move left and half move right. Calculate the momentum change

$$\Delta P_x = \underbrace{\left(\frac{N}{V}\frac{A v_x \Delta t}{2}\right)}_{\substack{\#\text{ of molecules} \\ \text{hitting wall} \\ \text{in } \Delta t}} \underbrace{2 m v_x}_{\substack{\text{momentum} \\ \text{change}}}$$

$$F_x = \frac{\Delta P_x}{\Delta t} = \frac{N}{V} A\, m v_x^2$$

$= $ average force

$$P = \text{pressure} = \frac{\text{force}}{\text{area}} = \frac{N}{V} m v_x^2$$

$\Rightarrow$ must average over v_x^2

Let v = total velocity

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$\langle v^2\rangle_{av} = \underbrace{\langle v_x^2\rangle_{av} + \langle v_y^2\rangle_{av} + \langle v_z^2\rangle_{av}}$$

all these are the same

$\Rightarrow$ direction doesn't matter

$$\langle v_x^2\rangle_{av} = \frac{1}{3}\langle v^2\rangle_{av}$$

$$PV = N\frac{m}{3}\langle v^2\rangle_{av}$$

$\frac{1}{2}m\langle v^2\rangle_{av}$ = average KE of molecule

$$U = N\,\frac{1}{2}m\langle v^2\rangle_{av}$$

$$\Rightarrow P\bar{V} = \frac{2}{3}U$$

Since $U = \frac{3}{2}nRT$, we have derived the ideal gas law. We also know that

$$\frac{3}{2}nRT = N\,\frac{1}{2}m\langle v^2\rangle_{av}$$

$$\frac{3}{2}\,\frac{N}{N_A}RT = N\,\frac{1}{2}m\langle v^2\rangle_{av}$$

$$\frac{3}{2}\,\frac{R}{N_A}T = \frac{1}{2}m\langle v^2\rangle_{av}$$

$$k = \frac{R}{N_A} = \text{Boltzmann's constant}$$

$$= 1.38\times10^{-23}\,\frac{J}{{}^{o}K}$$

$$\frac{1}{2}m\langle v^2\rangle_{av} = \frac{3}{2}kT$$

$\Rightarrow$ The average kinetic energy depends only on T.

V_t = mean thermal speed

$$\frac{1}{2}mV_t^2 = \frac{3}{2}kT$$

$$V_t = \left(\frac{3kT}{m}\right)^{\frac{1}{2}}$$

In terms of Boltzmann's constant, the ideal gas law is

$$PV = NkT$$

$\Rightarrow$ note again the the ideal gas law does not depend on the type of molecule that the gas is made of

$\Longrightarrow$ just the number N and temperature

Equipartition of energy

We have shown that

$$\frac{1}{2} m \langle v^2 \rangle_{av} = \frac{3}{2} kT$$

$$\frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} m \langle v_y^2 \rangle = \frac{1}{2} m \langle v_z^2 \rangle = \frac{1}{2} kT$$

Each direction a molecule can move is called a degree of freedom. The motion of an atom or molecule in 3-D space has three degrees of freedom. Each degree of freedom of an atom or molecule has an average energy of

$$\frac{1}{2} kT$$

$\Rightarrow$ all degrees of freedom share energy equally

$\Rightarrow$ equipartition of energy

monatomic

If have N monatomic molecules the total kinetic energy associated with their motion is

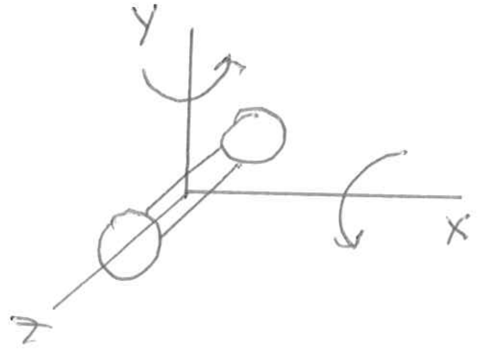
$$U = N\underbrace{(3)}_{\substack{\#\text{ of degrees}\\ \text{of freedom}}}\frac{1}{2}kT = \frac{3}{2}NkT$$

$$= \frac{3}{2}nRT$$

$$\Rightarrow C_V = \frac{3}{2}R$$

diatomic (rigid)

Consider a diatomic molecule that is like a dumbell



The dumbell has 3 degrees of freedom in translational motion and two degrees of freedom in rotational motion

$\Rightarrow$ rotation around z axis is small

$\Rightarrow$ 5 degrees of freedom

$$U = N(5)\tfrac{1}{2}kT$$
$$= \tfrac{5}{2}NkT = \tfrac{5}{2}nRT$$
$$C_V = \tfrac{5}{2}R$$

diatomic (non-rigid)

Some molecules can oscillate along the bond direction

$$\text{energy} = \tfrac{1}{2}mv_s^2 + \tfrac{1}{2}k_s x_s^2$$

k_s = spring constant

v_s = velocity along the bond direction

⇒ kinetic energy v_s is a degree of freedom

⇒ potential energy $\frac{1}{2}k_s x_s^2$ is another

⇒ total of 7 degrees of freedom

$$U = N(7)\tfrac{1}{2}kT = \tfrac{7}{2}NkT$$
$$C_V = \tfrac{7}{2}R$$

In some molecules the # of degrees of freedom changes with temperature

⇒ e.g. the vibration of the molecule starts at high temperature