LECTURE 6

Properties of Ideal Gases

Ideal gases are a very simple system of noninteracting particles. The only energy involved is the kinetic energy of the gas particles. There is no potential energy. Let's study this system as a way to illustrate some of the concepts that we have been discussing such as internal energy, specific heat, etc.

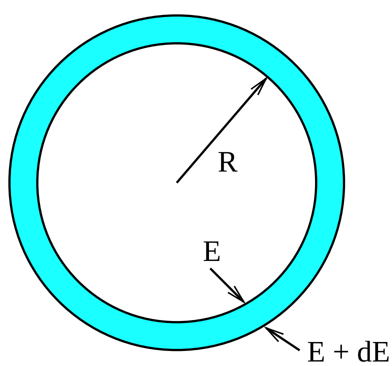
First of all, the internal energy of an ideal gas is solely a function of its temperature and is independent of its volume.

$$E = E(T) \quad \text{independent of } V \tag{1}$$

Perhaps this is not surprising since the energy is solely kinetic and hence just depends on the temperature. The energy does not depend on interactions between the particles, so it doesn't matter how close together the particles are, i.e., the density and volume don't matter.

One can prove that the energy is solely a function of the temperature in 2 different ways. One way is microscopic and uses phase space (Reif section 2.5); the other way is macroscopic and just uses the equation of state $pV = \nu RT$ (Reif section 5.1). Let's go over the microscopic proof. Let $\mathbf{r}_i$ denote the position of the ith particle and let $\mathbf{p}_i$ be it's momentum. The number of states $\Omega(E)$ lying between the energies E and $E + dE$ is proportional to the volume of phase space contained between the surface in phase space with energy E and the surface with energy $E + dE$:

$$\Omega(E) \propto \int_E^{E+dE} d^3r_1 \,...\, d^3r_N \; d^3p_1 \,...\, d^3p_N \tag{2}$$



Since there is no interaction between the particles ($U = 0$), the integrals over position are trivial:

$$\int d^3r_i = V \tag{3}$$

So

$$\Omega(E) \propto V^N \chi(E) \tag{4}$$

where

$$\chi(E) \propto \int_E^{E+dE} d^3p_1 \,...\, d^3p_N \tag{5}$$

is independent of V since the particles' momenta does not depend on their position, so that the integral does not depend on the volume. The total energy of the ideal gas is simply the kinetic energy of the particles:

$$2mE = \sum_{i=1}^{N} \sum_{\alpha=1}^{3} p_{i\alpha}^2 \tag{6}$$

where the sum over α is the sum over the x, y, and z components of the momenta. The sum contains $3N = f$ terms. For $E=$ constant, eq. (6) describes a sphere in the $f-$dimensional space of momentum components. The radius of the sphere is

$$R(E) = (2mE)^{1/2} \tag{7}$$

(This is just like a spherical surface in 3D which is described by the equation $x^2+y^2+z^2 =$ constant $= R^2$.) The volume of the sphere in $f-$dimensional space is proportional to

$$R^f = (2mE)^{f/2} \tag{8}$$

The number of states $\Omega(E)$ lying in the spherical shell between energies E and $E + \delta E$ is then given by

$$\Omega \propto R^{f-1} \propto E^{(f/2)-1} \propto E^{(3N/2)-1} \tag{9}$$

Combining this with our factor of V^N, we obtain

$$\Omega(E) \propto BV^N E^{3N/2} \tag{10}$$

where B is some constant independent of E and V.

It's easy to calculate the inverse temperature β.

$$\ln \Omega = \ln B + N \ln V + \frac{3N}{2} \ln E \tag{11}$$

So

$$\beta = \frac{\partial \ln \Omega}{\partial E} = \frac{3N}{2}\frac{1}{E} \tag{12}$$

Solving for E yields

$$E = \frac{3N}{2\beta} = \frac{3N}{2} k_B T \tag{13}$$

Notice that the energy is just a function of the temperature, and not of the volume as advertised. If N_a is Avogadro's number, then $N = N_a \nu$ where ν is the number of moles. Then

$$E = \frac{3}{2}\nu (N_a k_B) T = \frac{3}{2}\nu RT \tag{14}$$

where $R = N_a k_B$ is the gas constant.

Specific Heat of an Ideal Gas

We can now go on and calculate the specific heat at constant volume. It's important to specify what macroscopic parameters are being kept constant. As we mentioned earlier, the specific heat we measure at constant volume is different from the specific heat we measure at constant pressure. In either case we start with

$$dQ = dE + pdV \tag{15}$$

At constant volume, $dV = 0$ and

$$dQ = dE \tag{16}$$

So the molar specific heat at constant volume is

$$c_V \equiv \frac{1}{\nu}\left(\frac{dQ}{dT}\right)_V = \frac{1}{\nu}\left(\frac{dE}{dT}\right)_V \tag{17}$$

Using our result $E = 3\nu RT/2$, we see that

$$c_V = \frac{3}{2}R \tag{18}$$

Now let us compare the specific heat at constant pressure c_p to that at constant volume c_V for an ideal gas. In general, for any system, not just an ideal gas, the energy is a function of both temperature and volume:

$$E = E(T, V) \tag{19}$$

So

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \tag{20}$$

For an ideal gas where the energy is just a function of T, this reduces to

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT \tag{21}$$

or

$$dE = \nu c_V \, dT \tag{22}$$

for an ideal gas.

Now let us obtain an expression for the specific heat at constant pressure. We start with

$$\begin{aligned} dQ &= dE + pdV \\ &= \nu c_V dT + pdV \end{aligned} \tag{23}$$

At constant pressure the equation of state tells us

$$pdV = \nu RdT \tag{24}$$

Substituting this into (23) yields the heat absorbed at constant pressure

$$dQ = \nu c_V dT + \nu R dT \tag{25}$$

By definition

$$c_p = \frac{1}{\nu}\left(\frac{dQ}{dT}\right)_p \tag{26}$$

By (25) this becomes

$$c_p = c_V + R \tag{27}$$

Note that $c_p > c_V$ in agreement with earlier statements. The ratio γ of the specific heats is then given by

$$\gamma \equiv \frac{c_p}{c_V} = 1 + \frac{R}{c_V} \tag{28}$$

Using eq. (18) which states that $c_V = 3R/2$ for a monatomic ideal gas, we have

$$c_p = \frac{3}{2}R + R = \frac{5}{2}R \tag{29}$$

and

$$\gamma \equiv \frac{c_p}{c_V} = \frac{5}{3} \tag{30}$$

Adiabatic expansion or compression for an ideal gas

For an ideal gas, we can make certain statements concerning p, V and T when the gas expands under certain conditions. If the gas expands quasi-statically under isothermal conditions (constant temperature), the equation of state tells us that

$$pV = \text{ constant} \tag{31}$$

Suppose, however, that the gas is thermally isolated so that no heat is absorbed during the expansion, i.e., $dQ = 0$. This is called an adiabatic expansion. Adiabatic conditions correspond to thermal isolation. When the gas expands, it will do work and lose internal energy. As a result, its temperature will decrease.

How will the pressure be related to the volume of the gas under adiabatic conditions? We start with

$$dQ = dE + pdV \tag{32}$$

Adiabatic means $dQ = 0$. We also have $dE = \nu c_V dT$ for an ideal gas. So

$$0 = \nu c_V dT + pdV \tag{33}$$

Now let's eliminate T in favor of p and V. From the equation of state

$$d(pV) = \nu R dT \tag{34}$$

or

$$dp\,V + V\ dp = \nu R dT \tag{35}$$

Use this to substitute into eq. (33) for dT.

$$0 = \frac{c_V}{R}(pdV + V dp) + pdV = \left(\frac{c_V}{R} + 1\right) pdV + \frac{c_V}{R} V dp \tag{36}$$

or

$$(c_V + R)pdV + c_V V dp = 0 \tag{37}$$

Dividing both sides by $c_V pV$ and using $c_p = c_V + R$ yields

$$\gamma \frac{dV}{V} + \frac{dp}{p} = 0 \tag{38}$$

where

$$\gamma = \frac{c_p}{c_V} \tag{39}$$

For most gases it is a pretty good approximation to assume that γ is independent of temperature over a limited temperature range. Then we can integrate eq. (38) to obtain

$$\gamma \ln V + \ln p = \text{ constant} \tag{40}$$

or

$$pV^\gamma = \text{ constant} \tag{41}$$

Since $\gamma > 1$ ($c_P > c_V$), p will vary more rapidly with increasing V than in the isothermal case where $pV =$ constant.

We can use the equation of state to eliminate p in favor of V and T. Using $p = \nu RT/V$, we get

$$V^{\gamma-1}T = \text{ constant} \tag{42}$$