Chapter M

Ideal Gases and the First Law of Thermodynamics

Blinn College - Physics 2425 - Terry Honan

Ideal Gases

By an ideal gas we make the assumption that the gas is a collection of noninteracting point particles. By this we mean that the size of each molecule is small compared to the fraction of the total volume occupied each molecule (the total volume divided by the number of molecules). Also we assume that the forces between the molecules can be neglected.

Basic Definitions

P = Pressure   SI units = Pa = $\dfrac{\text{N}}{\text{m}^2}$

V = Volume   SI units = m^3

T = Temperature   SI units = K

N = # of molecules   Dimensionless

Pressure is the force per area. Temperature is the absolute temperature. Our emphasis will be different from that of a chemistry class. In chemistry it is important to keep track of the amount of material; this is related to the number of moles n. In physics our emphasis is relating macroscopic quantities to microscopic ones; the actual number of molecules N is then more important.

Ideal Gas Law

There are some basic proportionalities that are satisfied. Keeping N and T constant we get an inverse proportionality between pressure and volume $P \propto 1/V$. With N and V constant we get a proportionality between pressure and temperature $P \propto T$. For the same P and T we get $V \propto N$. The ideal gas law follows from this.

$$P\,V \propto N\,T$$

The constant of proportionality is a fundamental constant called Boltzmann's constant k_B

$$P\,V = N\,k_B\,T$$

where Boltzmann's constant has the value

$$k_B = 1.38\times 10^{-23}\ \frac{\text{J}}{\text{K}}.$$

Atomic and Molecular Masses

$$m_{\text{proton}} \simeq m_{\text{neutron}} \gg m_{\text{electron}}$$

Atoms consist of protons, neutrons and electrons. The masses of the proton and neutron are approximately equal and both are *much* larger than the mass of an electron.

$$m_{\text{proton}} = 1.6726\times 10^{-27}\text{ kg}$$
$$m_{\text{neutron}} = 1.6749\times 10^{-27}\text{ kg}$$
$$m_{\text{electron}} = 9.109\times 10^{-31}\text{ kg}$$

For atoms the *atomic number* Z is the number of protons in the nucleus, which is the same as the number of electrons in a neutral atom. A, the *atomic mass number*, is the number of nucleons, where protons and neutrons are nucleons.

$$\begin{aligned} Z &= \textit{atomic number} = \#\text{ of protons} = \#\text{ of electrons} \\ A &= \textit{atomic mass number} = \#\text{ of nucleons (protons and neutrons)} \\ A - Z &= \#\text{ of neutrons} \end{aligned}$$

One would expect, naively, that the mass of an atom should equal the sum of its constituent parts. This is not the case. It takes energy to break up an atom into its constituent parts. Using the mass-energy equivalence of relativity, $E = m c^2$, it follows that since the constituent parts have more energy, they have more mass.

$$m_{\text{atom}} = Z\, m_{\text{proton}} + (A - Z)\, m_{\text{neutron}} + Z\, m_{\text{electron}} - \begin{pmatrix}\text{Binding}\\ \text{Energy}\end{pmatrix} \Big/ c^2$$

In this expression, the Binding Energy is the amount of energy required to break up the atom into is constituent parts.

Because this naive approach doesn't work we introduce the atomic mass unit, u, which is defined to be the approximate contribution to the mass of an atom due to each proton and electron. Thus the approximate mass of an atom is A u.

$$m_{\text{atom}} \simeq A\text{ u}$$

We define u in terms of the carbon-12 isotope, ^{12}C. Carbon has $Z = 6$. The 12 refers to the mass number, $A = 12$. u is defined as $1/12^{\text{th}}$ the mass of ^{12}C.

$$\text{u} = \frac{1}{12}\text{mass}\left(^{12}C\right) \simeq m_{\text{proton}} \simeq m_{\text{neutron}}$$

Avogadro's number N_A is defined in terms of this constant. It is the conversion between u and grams.

$$N_A\text{ u} = 1\text{ g or } 1000\, N_A\text{ u} = 1\text{ kg}$$

It has the approximate value

$$N_A = 6.02\times 10^{23}.$$

One mole of something is defined as N_A of it. If n is the number of moles then the number of molecules N is

$$N = n\, N_A.$$

We can then write the ideal gas law in terms of the number of moles

$$\begin{aligned} P\, V &= N\, k_B\, T \\ &= n\, N_A\, k_B\, T. \end{aligned}$$

If we define the ideal gas constant R by

$$R = N_A\, k_B,$$

then the ideal gas law has the form

$$P\, V = n\, R\, T.$$

The mass of a mole of some molecule can be related to the molecular mass in atomic mass units, u; the value for the molecular mass in u is the same as the molar mass in grams. For example a molecule of CO_2 has molecular mass of 44u so its molar mass is 44g

$$m_{\text{mole}} = N_A \, m_{\text{molecule}} = N_A \, 44 \text{ u} = 44 \text{ g}, \text{ since } N_A \text{ u} = \text{g}.$$

The total mass of a gas can then be written as

$$m_{\text{tot}} = N \, m_{\text{molecule}} = n \, m_{\text{mole}}.$$

Work and the First Law

Thermodynamic Work

The work done in one dimension is $W = \int F \, dx$. Consider the expansion of gas in a piston. If the piston has a cross-sectional area of A and the piston expands by the infinitesimal dx then the infinitesimal work done by the gas is $F \, dx = P \, A \, dx = P \, dV$. Here we have used $F = P \, A$ and $dV = A \, dx$. This result is more general.

In general, the work done *by* a thermodynamic system is

$$W = \int P \, dV.$$

When a system expands it does work on the environment. This decreases the energy of the system. The work done *on* the system is $-W$.

For the simple case of expansion with a constant pressure we get

$$W = P \, \Delta V.$$

Generally, when the volume increases the work is positive; it is negative when volume decreases.

PV-Diagrams and Thermodynamic States

Suppose there is some thermodynamic system, for instance a fixed quantity of some substance. Knowledge of the pressure P and volume V uniquely specifies the thermodynamic state. For example, one could find the temperature uniquely from P and V. The equation that relates P, V and T is called the *equation of state*. For complex thermodynamic systems this is not a simple function that one can write down, but for an ideal gas it is just the ideal gas law.

A PV-diagram is a graph of P vs. V (P is the y-axis and V is the x-axis.) Work has a simple interpretation in terms of PV-diagrams; it is the area under the curve.

$$W = \int P \, dV = \pm \text{Area Under}$$

Since P is always positive the sign of $P \, dV$ is the same as on the sign of dV.

In thermodynamics we often deal with cycles. A cycle is a closed path in a PV-diagram. For a cycle there is a positive and a negative contribution. If the path is clockwise the positive contribution dominates and the result is positive and it just then enclosed area. When the path is counterclockwise the result is negative.

$$W = \int_{\text{cycle}} P \, dV = \pm \text{Area Enclosed}$$

Isothermal Expansion of an Ideal Gas

The word isothermal implies the temperature is constant. For an ideal gas we can use the ideal gas law, the equation of state, to write the pressure as a function of volume.

$$P(V) = \frac{n R T}{V} \quad (T \text{ is constant})$$

We can easily integrate this to get the work.

$$W = \int_{V_i}^{V_f} P(V)\, dV = n R T \int_{V_i}^{V_f} \frac{dV}{V}$$

This gives the result

$$W = n R T \ln \frac{V_f}{V_i}.$$

State Functions - Exact and Inexact Differentials

A *state function* is a function of pressure and volume. It has a unique value at each point in a *PV*-diagram. Temperature is a state function, since it follows from the equation of state.

$$f = f(V, P) \text{ is } a \text{ state function.}$$

For state functions we take *exact differentials*. An exact differential is the infinitesimal change in some variable between two nearby states. Integrating an exact differential of a state function f gives the change in f. This is path independent, meaning that it depends only on the endpoints

$$\int df = \Delta f = f\left(V_f, P_f\right) - f\left(V_i, P_i\right) \text{ (path independent)}$$

Since a cycle ends at the same position it begins, then it follows that for a cycle the integral of an exact differential is zero If df is an exact differential then

$$\int_{\text{cycle}} df = 0 \quad \text{(exact differential)}$$

We have seen that the work for a cycle is not zero. It follows that work is not a state function; one cannot assign a value to work at each state. Generally, for functions that are not state functions we use inexact differentials $\underline{d}$ to represent infinitesimal values. The infinitesimal amount of work is written as $\underline{d}W = P\, dV$. For a general inexact differential $\underline{d}g$ the integral depends on the path and thus the integral around a cycle is nonzero.

$$\int_{\text{cycle}} \underline{d}g \neq 0 \quad \text{(inexact differential)}$$

Internal Energy and the First Law

The energy of a thermodynamic system can be increased by adding thermal energy in the form of heat or by adding mechanical energy by doing work on the system. We will write the internal energy of a thermodynamic system as U. The first law of thermodynamics is

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

ΔU is the change in the internal energy of the system. Q is the heat *added* to the system. W is the work done *by* the system. It follows that $-W$ is the work done *on* the system. Internal energy is a state function. Since it is a state function then ΔU is independent of the path taken. Since the work is path dependent it follows from the first law that the heat is also path dependent, and not a state function.

If we write the first law in its infinitesimal form then we get

$$dU = \underline{d}Q - \underline{d}W.$$

Since work and heat are not state functions then we use inexact differentials for them. The internal energy being a state function means that we use exact differentials for it.