

Chapter N

Ideal Gases and the First Law of Thermodynamics

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N.1 - Ideal Gases

Basic Definitions

The assumption behind an ideal gas is that it is a collection of non-interacting 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.

P = Pressure	SI units = Pa = N/m ²
V = Volume	SI units = m ³
T = Temperature	SI units = K
N = # of molecules	Dimensionless

Pressure is force per area measured in Pascals, Pa. Temperature is the absolute temperature in K. 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

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

Note that Boltzmann's constant could be viewed as a conversion between Joules and Kelvins, and temperatures could be measured in Kelvins. This approach is not standard at this level and will be avoided here.

Example N.1 - Number of Molecules

How many air molecules are in a room with dimensions, 8 m by 10 m by 3 m? Assume 1 atm of pressure and a temperature of 20 °C.

Solution

This is a straight-forward application of the ideal gas law.

$$V = 8 \text{ m} \times 10 \text{ m} \times 3 \text{ m} = 240 \text{ m}^3, \quad P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}, \quad T = 20 \text{ }^\circ\text{C} = 293 \text{ K}$$

$$P V = N k_B T \implies N = \frac{P V}{k_B T} = 6.01 \times 10^{27}$$

Atomic and Molecular Masses

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

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.

$$Z = \text{atomic number} = \# \text{ of protons} = \# \text{ of electrons}$$

$$A = \text{atomic mass number} = \# \text{ of nucleons (protons and neutrons)}$$

$$A - Z = \# \text{ of neutrons}$$

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, $E = mc^2$, it follows that since the constituent parts have more energy, they have more mass.

$$m_{\text{atom}} = Z m_{\text{proton}} + (A - Z) m_{\text{neutron}} + Z m_{\text{electron}} - \left(\frac{\text{Binding Energy}}{\text{Energy}} \right) / c^2$$

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

$$u \approx m_{\text{proton}} \approx m_{\text{neutron}}$$

Thus the approximate mass of an atom is Au .

$$m_{\text{atom}} \approx Au$$

We precisely 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 .

$$u = \frac{1}{12} \text{mass}(^{12}\text{C}) = 1.6605 \times 10^{-27} \text{ kg} = \frac{1}{6.0221 \times 10^{23}} \text{ g}$$

The mole, abbreviated mol, is an SI base unit related to this. A mole is defined as the number of atoms in 12-grams of carbon-12; this number, known as Avogadro's number, has the approximate value

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

The number of moles n and the number of molecules N are related by

$$N = n N_A.$$

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

$$\begin{aligned} PV &= N k_B T \\ &= n N_A k_B T \end{aligned}$$

If we define the ideal gas constant R by

$$R = N_A k_B,$$

then the ideal gas law has the form

$$PV = nRT.$$

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 44 u , so its molar mass is 44 g/mol.

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

The total mass of a gas can then be written as

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

Example N.2 - The Density of Air

(a) Estimate the density of (dry) air at 20 °C and 1 atm, assuming air is composed entirely of nitrogen N_2 .

Solution

$$P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}, \quad T = 20^\circ\text{C} = 293 \text{ K} \quad \text{and} \quad R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

First we need to find the molar mass.

$$m_{\text{molecule}} = m_{N_2} = 2 m_N = 2 \times 14 \text{ u} = 28 \text{ u} \implies m_{\text{mol}} = 28 \text{ g/mol} = 0.028 \text{ kg/mol}.$$

We can find an expression for the number of moles n using the ideal gas law and then get an expression for the mass

$$PV = nRT \implies n = \frac{PV}{RT} \quad \text{and} \quad m_{\text{tot}} = n m_{\text{mol}} = m_{\text{mol}} \frac{PV}{RT}$$

Density ρ is mass per volume. The volume V will cancel.

$$\rho = \frac{m_{\text{tot}}}{V} = m_{\text{mol}} \frac{P}{RT} = 1.16 \text{ kg/m}^3$$

(b) The accepted value for the density of dry air at 20°C is 1.204 kg/m^3 . Calculate a more accurate result for the density of dry air by taking air to be 78% N_2 , 21% O_2 and 1% Argon, where the atomic mass of argon is: $m_{\text{Ar}} = 40 \text{ u}$.

Solution

$$m_{O_2} = 2 m_O = 2 \times 16 \text{ u} = 32 \text{ u} \implies m_{\text{mol}, O_2} = 32 \text{ g/mol} = 0.032 \text{ kg/mol}$$

Also for Argon, which is monatomic, we have

$$m_{\text{Ar}} = 40 \text{ u} \implies m_{\text{mol}, \text{Ar}} = 40 \text{ g/mol} = 0.040 \text{ kg/mol}.$$

The molar mass of air can be found as a weighted average.

$$m_{\text{mol}} = 0.78 m_{\text{mol}, N_2} + 0.21 m_{\text{mol}, O_2} + 0.01 m_{\text{mol}, \text{Ar}} \implies \rho = \frac{m_{\text{tot}}}{V} = m_{\text{mol}} \frac{P}{RT} = 1.20 \text{ kg/m}^3$$

N.2 - 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 $F dx = PA dx = P dV$. Here we have used $F = PA$ 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.

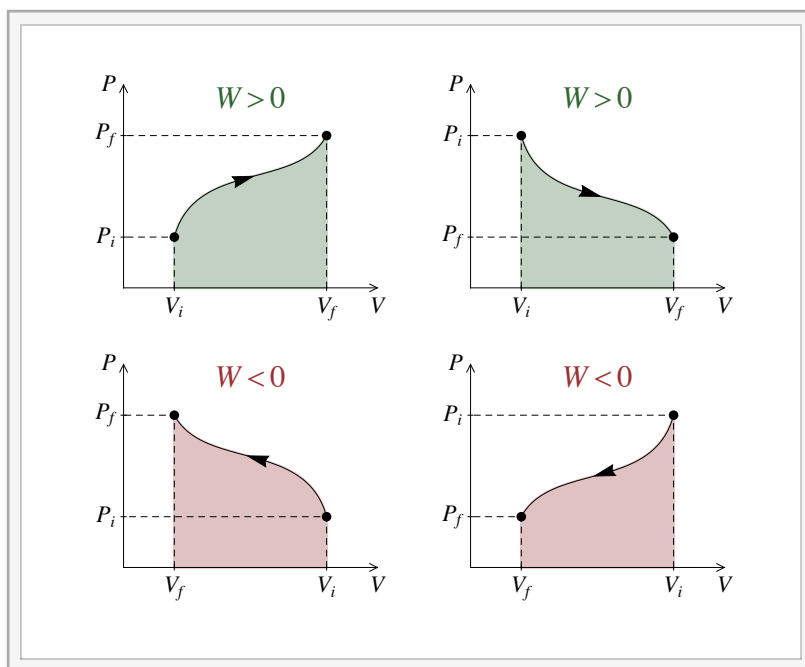
PV-Diagrams and Thermodynamic States

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.

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

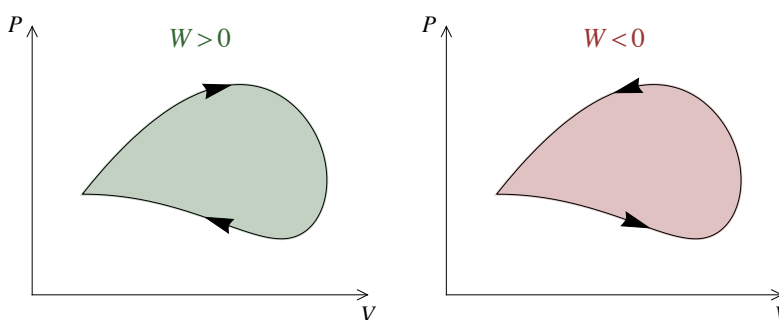
Since P is always positive the sign of $P dV$ is the same as on the sign of dV .



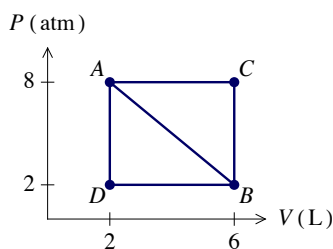
Interactive Figure

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.

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



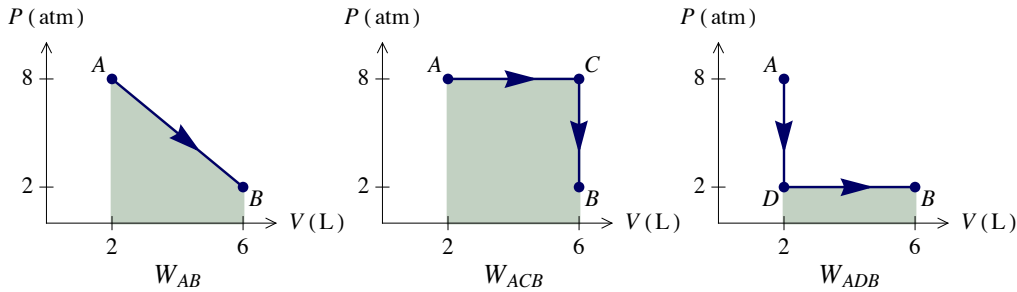
Example N.3 - The PV-Diagram



(a) What is the work for different processes taking a system from point A to point B ? Find W_{AB} (the direct path), W_{ACB} and W_{ADB} .

Solution

Since all three cases correspond to increasing volumes we have $W = +(\text{Area under})$.



The SI unit of work is Joule, where $J = \text{Pa m}^3$. Our axes have the units of atmospheres and liters. We need to convert the units of our areas from atmL to J.

$$1 \text{ atm} = 1.013 \times 10^5 \text{ Pa} \quad \text{and} \quad 1 \text{ L} = 10^{-3} \text{ m}^3 \quad \Rightarrow \quad 1 \text{ atmL} = 101.3 \text{ J}$$

For W_{AB} we have a trapezoid. The area of a trapezoid with a base width of b and sides with heights of h_1 and h_2 is $\text{Area} = \frac{1}{2} b (h_1 + h_2)$. It follows that

$$W_{AB} = +\frac{1}{2} 4 \text{ L} (2 \text{ atm} + 8 \text{ atm}) = +20 \text{ atmL} = +2026 \text{ J}$$

For W_{ACB} and W_{ADB} we have rectangles.

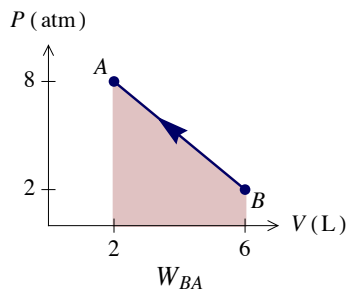
$$W_{ACB} = +4 \text{ L} \times 8 \text{ atm} = +32 \text{ atmL} = +3242 \text{ J} \quad \text{and} \quad W_{ADB} = +4 \text{ L} \times 2 \text{ atm} = +8 \text{ atmL} = +810 \text{ J}$$

This shows the path-dependent nature of work explicitly.

- (b) What is the work for a process that takes the system from point B to point A , W_{BA} ?

Solution

Here we have a process with decreasing volume, so $W = -(\text{Area under})$.



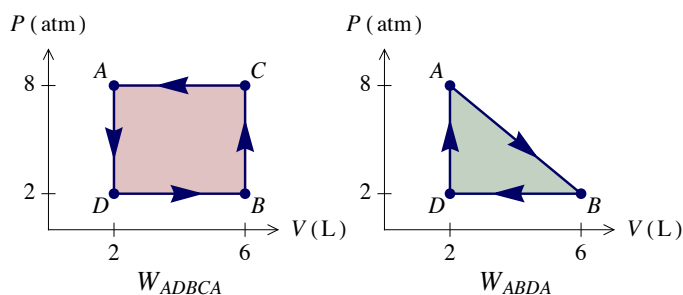
For W_{AB} we have a trapezoid. The area of a trapezoid with a base width of b and sides with heights of h_1 and h_2 is $\text{Area} = \frac{1}{2} b (h_1 + h_2)$. It follows that

$$W_{BA} = -W_{AB} = -2026 \text{ J}$$

- (c) What is the work for the cycles $ADBCA$ and $ABDA$?

Solution

For a cycle we have $W = \pm(\text{Area enclosed})$, where clockwise gives positive and counterclockwise gives negative.



For W_{ADBCA} there is a counterclockwise path around a rectangle.

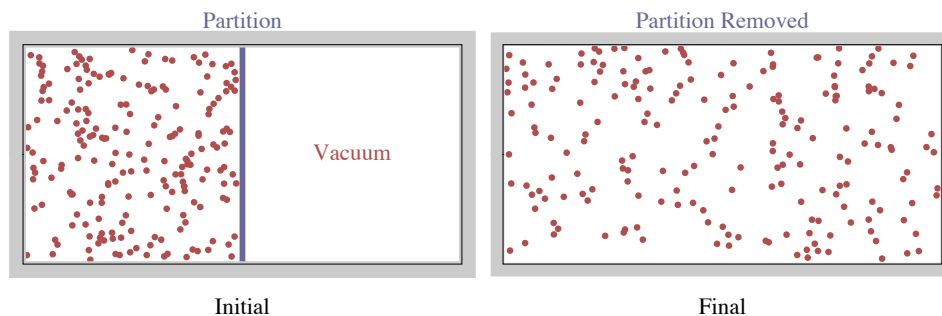
$$W_{ADBCA} = -4 \text{ L} \times 6 \text{ atm} = -24 \text{ atm L} = -2431 \text{ J}$$

There is a clockwise path around a triangle for W_{ABDA} .

$$W_{ABDA} = +\frac{1}{2} 4 \text{ L} \times 6 \text{ atm} = +12 \text{ atm L} = +1215 \text{ J}$$

Quasi-static Processes

This discussion of clear paths in a PV -diagram implies that we are undergoing a *quasi-static* process. A process is quasi-static if it is performed sufficiently slowly, so that at each intermediate state the system stays in thermal equilibrium. As an example of a process that is *not* quasi-static, consider the free expansion of a gas. Start with a container containing two regions separated by a partition. On one side of the partition is a pressurized gas and on the other side is a vacuum. When the partition is removed, the gas undergoes a free expansion. The initial and final states are in equilibrium but the intermediate states are not. When a system is not in equilibrium, pressure and temperature are not well-defined quantities.



The free expansion of a gas is not quasi-static.

It is possible, theoretically, to do this expansion with a quasi-static process by slowly dragging a piston from initial to final positions.

In this example with an expanding gas, approximating a quasi-static process need not be too slow. To be in thermal equilibrium the system must be at a uniform temperature; there can be no temperature gradients. Suppose heat is added to a solid block. To be in equilibrium every point in the block must stay at the same temperature. An approximately quasi-static process here would be very slow; each time after a small amount of heat is added, one must wait for the system to equilibrate.

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.

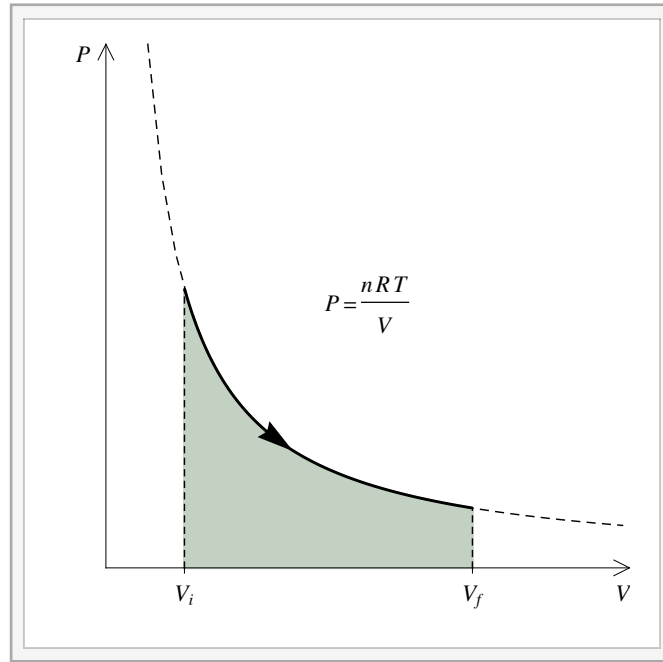
$$P(V) = \frac{nRT}{V} \quad (T \text{ is constant})$$

We can easily integrate this to get the work.

$$W = \int_{V_i}^{V_f} P(V) dV = nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

This gives the result

$$W = nRT \ln \frac{V_f}{V_i}$$



Interactive Figure

Note that the natural log function guarantees that result of the work formula has the correct sign, since the natural log of a ratio less than one is negative.

Example N.4 - Isothermal Expansion

What is the work done by 50-g of oxygen O_2 gas as it is compressed by tripling its pressure at a constant temperature of 20 °C?

Solution

$$m = 0.050 \text{ kg}, \quad T = 20 \text{ °C} = 293 \text{ K} \quad \text{and} \quad \frac{P_f}{P_i} = 3$$

The mass of O_2 will tell us the number of moles n . The mass of a molecule in u gives the molar mass

$$m_{O_2} = 2 m_O = 2 \times 16 \text{ u} = 32 \text{ u} \implies m_{\text{mol}} = 32 \text{ g/mol} = 0.032 \text{ kg/mol}$$

and this gives us the number of moles.

$$m = n m_{\text{mol}} \implies n = \frac{m}{m_{\text{mol}}} = 1.56 \text{ mol}$$

The ideal gas law with constant n and T relates the ratio of the volumes to the ratio of the pressures. This is known as Boyle's law.

$$PV = nRT \xrightarrow{n, T \text{ const.}} P_i V_i = P_f V_f \implies \frac{V_f}{V_i} = \frac{P_i}{P_f} = \frac{1}{3}$$

$$W = nRT \ln \frac{V_f}{V_i} \quad \text{and} \quad R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \implies W = -4180 \text{ J}$$

Note that increasing the pressure will decrease the volume and the work will then be negative.

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.

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

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

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

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

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

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 δ to represent infinitesimal values. The infinitesimal amount of work is written as $\delta W = P dV$. For a general inexact differential δg the integral depends on the path and thus the integral around a cycle is nonzero.

$$\int_{\text{cycle}} \delta g \neq 0 \text{ (inexact differential)}$$

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

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

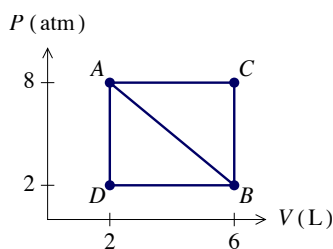
ΔU is the change in the internal energy of the system. Q is the heat *added* to the system. W is the work done *by* the system. It follows that $-W$ is the work done *on* the system. Internal energy is a state function. Since it is a state function then ΔU is independent of the path taken. Since the 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

$$dU = \delta Q - \delta W.$$

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.

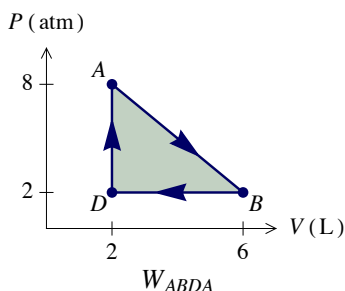
Example N.5 - The PV-Diagram (Continued)



(d) What is the heat added to the system over the $ABDA$ cycle?

Solution

First we need the work which we calculated in part (c).



There is a clockwise path around a triangle for W_{ABDA} .

$$W = W_{ABDA} = +12 \text{ atm L} = +1215 \text{ J}$$

Because it is a cycle, $\Delta U = 0$ and the first law implies that $Q = W$.

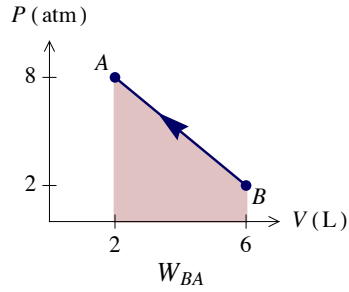
$$0 = \Delta U = Q - W \implies Q = W = +1215 \text{ J}$$

(e) If 0.30 kcal of heat flow out of the system as it goes from point B to point A, then what is the change in internal energy for this process?

Solution

We are given the heat that flows out so the heat that flow in is negative and we have to convert kcal to J.

$$Q = -0.30 \text{ kcal} \times \frac{4186 \text{ J}}{\text{kcal}} = -1256 \text{ J}$$



We calculated the work in part (b) as the negative of the area under the trapezoid.

$$W = W_{BA} = -2026 \text{ J}$$

The first law of thermodynamics gives us the change in internal energy.

$$\Delta U = Q - W = +770 \text{ J}$$