

# 17. Examples of the First Law

## Introduction and Summary

The First Law of Thermodynamics is basically a statement of Conservation of Energy. The total energy of a thermodynamic system is called the Internal Energy  $U$ . A system can have its Internal Energy changed ( $\Delta U$ ) in two major ways:

(1) Heat  $Q > 0$  can flow into the system from the surroundings, in which case the change in internal energy of the system increases:  $\Delta U = Q$ .

(2) The system can do work  $W > 0$  on the surroundings, in which case the internal energy of the system

decreases:  $\Delta U = -W$ .

Generally, the system interacts with the surroundings by exchanging both heat  $Q$  and doing work  $W$ , and the internal energy changes

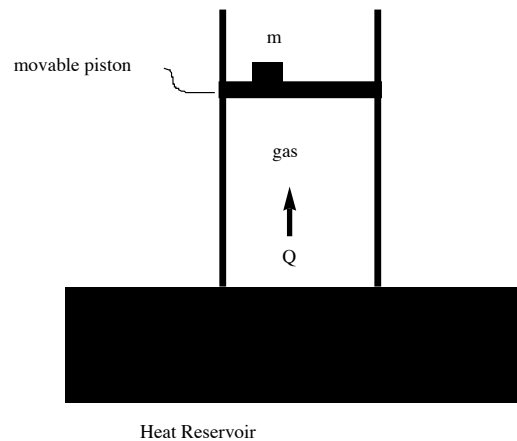
$$\Delta U = Q - W$$

This is the first law of thermodynamics and in it,  $W$  is the thermodynamic work done by the system on the surroundings. If the definition of mechanical work  $\mathcal{W}$  were used instead of  $W$ , then the 1st Law would appear  $\Delta U = Q + \mathcal{W}$  because doing work on the system by the surroundings would increase the internal energy of the system  $\Delta U = \mathcal{W}$ .

The 1st Law is simply the statement that the internal energy  $\Delta U$  of a system can change in two ways: through heat  $Q$  absorption where, for example, the temperature changes, or by the system doing work  $-W$ , where a macroscopic parameter like volume changes. Below are some examples of using the 1st Law.

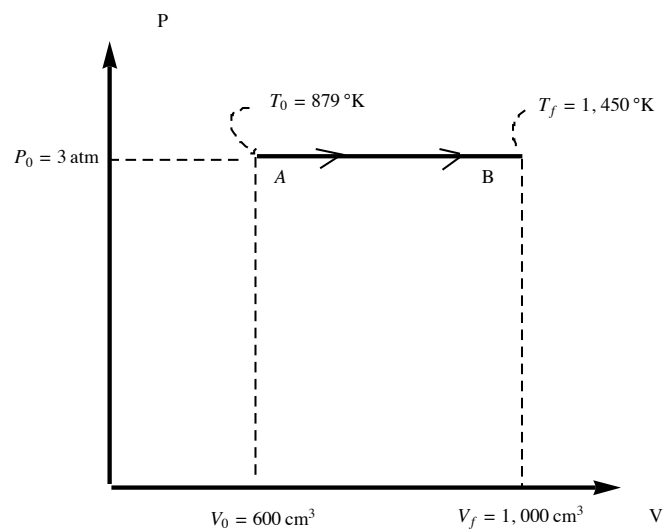
## The Work Done and the Heat Input During an Isobaric Expansion

Suppose a gas is inside a cylinder that has a movable piston. The gas is in contact with a heat reservoir that is at a higher temperature than the gas so heat  $Q$  flows into the gas from the reservoir. The pressure on the gas is constant at  $P_0$  because the atmospheric pressure plus the mass of the piston produce a constant downward force on the gas.



Gas temperature increases while the pressure  $P_0$  is constant. By the ideal gas law,  $P_0V=Nk_B T$ , so as the volume increases (the gas expands) from the initial volume  $V_0$  to the final volume  $V_f$ , the temperature of the gas increases from  $T_0$  to  $T_f$ . The work done by the gas is  $W=P_0(V_f-V_0)$  and this is positive since  $V_f>V_0$  because the gas expands. The internal energy of the gas decreases due to the work done by the gas--an amount  $\Delta U = -P_0(V_f-V_0)$ --but this is NOT the total change in internal energy since heat  $Q$  is also absorbed by the gas. The heat  $Q$  absorbed by the gas =  $m c_p (T_f - T_0)$

from the heat reservoir is given in terms of the specific heat  $c_p$  at a constant pressure.  $c_p$  is the specific heat of the gas at a constant pressure; for nitrogen, this is  $c_p = 0.248 \text{ kcal}/(\text{kg} \times ^\circ\text{K})$ . (The size of the specific heat of a gas  $c_p$  for a constant-pressure process is different from the heat capacity for a constant-volume process. There are theoretical reasons for this but you can take this as something that is determined by experiment.)  $Q$  is positive in this example, since  $T_f > T_0$ . That is, the final temperature after the gas expands is greater than the initial temperature of the gas.  $m$  is the mass of gas and  $m = m N$  where  $m$  is the mass of a gas molecule and  $N$  is the number of molecules inside the cylinder. The total change in the internal energy of the gas is, by the 1st Law,  $\Delta U = m c_p (T_f - T_0) - P_0(V_f - V_0)$  for an expansion at constant pressure. A phase diagram of this isobaric (constant pressure) expansion going from point A to point B is



## A Numerical Example

Consider  $N$  molecules of diatomic nitrogen  $N_2$  gas in a cylinder with a movable piston like above. Suppose the constant gas pressure is  $P_0 = 3 \text{ atm} = 3 \times 10^5 \text{ Nt} / \text{m}^2$ . The initial temperature of the gas is  $T_0 = 879^\circ\text{K}$  and the initial volume of the gas is  $V_0 = 600 \text{ cm}^3$ . Suppose the gas is allowed to expand to a final volume  $V_f = 1,000 \text{ cm}^3$  because heat  $Q$  is added from the reservoir.

**Questions:** How much heat  $Q$  is absorbed by the gas? How much work  $W$  is done by the gas?

What is the change in internal energy  $\Delta U$  of the gas? How many molecules of  $N_2$  gas are there?

**Answers:** Using the ideal gas law  $P_0 V_0 = N k_B T_0$ , you can calculate the number of molecules  $N$  in the cylinder ( $N$  is constant.).

$$N = \frac{P_0 V_0}{k_B T_0} = \frac{3 \times 10^5 \text{ Nt/m}^2 \times 600 \text{ cm}^3 \times (m/100 \text{ cm})^3}{1.38 \times 10^{-23} \text{ J/}^\circ\text{K} \times 879^\circ\text{K}} = 1.5 \times 10^{22} \text{ molecules.}$$

$$P_0 = 3 \times 10^5;$$

$$T_0 = 879.;$$

$$V_0 = 600 \times (1 / 100)^3;$$

$$k_B = 1.38 \times 10^{-23};$$

$$N_0 = (P_0 \times V_0) / (k_B \times T_0)$$

$$1.4839 \times 10^{22}$$

The mass of diatomic Nitrogen is  $m = 28 \frac{\text{amu}}{\text{molecule}} \times 1.67 \times 10^{-27} \frac{\text{kg}}{\text{amu}}$  since the diatomic Nitrogen molecule has 2 nitrogen atoms and each nitrogen atom has 7 protons and 7 neutrons; thus  $2 \times 14 = 28$  amu. An amu is the mass of a proton (or neutron) in kg. So the total mass  $m$  of nitrogen gas inside the cylinder is given by  $m = m N$

$$m = 28 \frac{\text{amu}}{\text{molecule}} \times 1.67 \times 10^{-27} \frac{\text{kg}}{\text{amu}} \times 1.5 \times 10^{22} \text{ molecules} = 7.0 \times 10^{-4} \text{ kg}$$

$$m = 28 \times 1.67 \times 10^{-27} \times 1.5 \times 10^{22}$$

$$0.0007014$$

The heat absorbed by the gas is  $Q = m c_p (T_f - T_0)$  where  $c_p = 0.248 \text{ kcal}/(\text{kg} \cdot ^\circ\text{K})$ , so we have everything needed except the final temperature  $T_f$  reached when the gas has expanded to a volume  $V_f = 1,000 \text{ cm}^3$ . The temperature  $T_f$  can be obtained using the ideal gas law in the form

$$T_f = \frac{P_f V_f}{k_B N} = \frac{3 \times 10^5 \text{ Nt}/\text{m}^2 \times 1000 \text{ cm}^3 \times (m/100 \text{ cm})^3}{1.38 \times 10^{-23} \text{ J}/^\circ\text{K} \times 1.5 \times 10^{22} \text{ molecules}} = 1,450 \text{ } ^\circ\text{K}$$

$$\begin{aligned} P_f &= 3 \times 10^5; \\ V_f &= 1000 \times (1 / 100)^3; \\ k_B &= 1.38 \times 10^{-23}; \\ N &= 1.5 \times 10^{22}; \\ T_f &= (P_f \times V_f) / (k_B \times N) \\ &= 1449.28 \end{aligned}$$

The heat absorbed by the gas  $Q$  in kiloJoules is

$$Q = m c_p (T_f - T_0) = 7.0 \times 10^{-4} \text{ kg} \times 0.248 \text{ kcal}/(\text{kg} \cdot ^\circ\text{K}) \times (1,450 \text{ } ^\circ\text{K} - 879 \text{ } ^\circ\text{K}) \times 4.2$$

$$\text{kJ/kcal} = 0.42 \text{ kJ}$$

$$\begin{aligned} c_p &= 0.248; \\ Q &= m \times c_p \times (T_f - T_0) \times 4.2 \\ &= 0.416631 \end{aligned}$$

The heat absorbed by the gas  $Q = 0.42 \text{ kJ}$  results in an increase in the internal energy  $\Delta U = 0.42 \text{ kJ}$ . This is not the total change in  $\Delta U$  since we must include the work done. The work done by the gas is  $W = P_0(V_f - V_0) > 0$  is positive since  $V_f > V_0$  so

$$W = 3 \times 10^5 \text{ Nt}/\text{m}^2 \times (1000 \times (1 / 100)^3 - 600 \times (1 / 100)^3) \text{ m}^3 \times (\text{KJ}/1000 \text{ J}) = 0.12$$

KJ

$$\begin{aligned} W &= P_0 \times (V_f - V_0) \times (1 / 1000.) \\ &= 0.12 \end{aligned}$$

The work done by the gas  $W=0.12$  KJ results in a decrease of the internal energy  $\Delta U = -0.12$  KJ of the gas. Combining  $Q=0.41$  KJ and  $W=0.12$  KJ in the 1st Law  $\Delta U=Q - W$  yields a net increase in internal energy of the gas  $\Delta U > 0$

$$\Delta U=Q - W = 0.41 \text{ KJ} - 0.12 \text{ KJ} = 0.30 \text{ KJ}$$

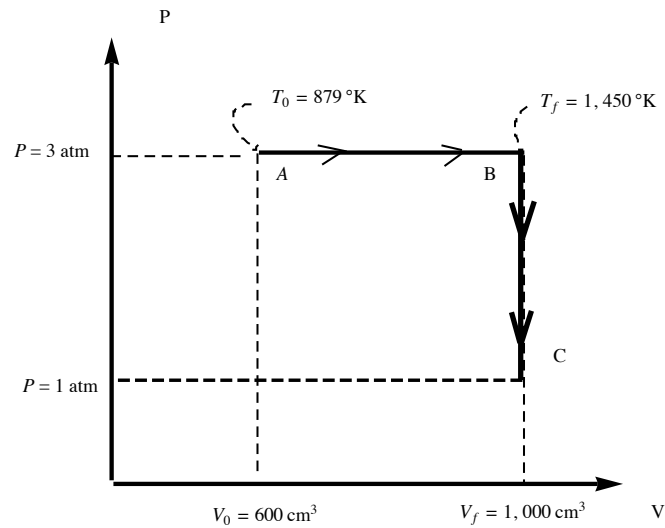
$$\Delta U = q - w$$

$$0.296631$$

The heat absorbed is greater than the work done  $Q > W$  by the gas, so  $\Delta U > 0$  and there is a net increase in the internal energy of the gas.

## A Constant Volume or Isochoric Process

Suppose after doing the isobaric (constant pressure) expansion described above, the  $N = 1.5 \times 10^{22}$  molecules of the gas are in a state of temperature  $T_0 = 1,450 \text{ }^\circ\text{K}$ , pressure  $P_0 = 3 \text{ atm} = 3 \times 10^5 \text{ Nt} / \text{m}^2$ , and volume  $V_0 = 1,000 \text{ cm}^3$ . Next, suppose the gas pressure is reduced to  $P_f = 1 \text{ atm} = 1 \times 10^5 \text{ Nt} / \text{m}^2$  by taking the small mass  $m$  off the top of the piston. Do this while the volume is held constant (the piston is not allowed to move):  $V_f = V_0$ . A phase diagram of this isochoric (constant volume) process going from B to C is below.



The ideal gas law gives the final temperature  $T_f=483^\circ\text{K}$  after the constant volume expansion.

$$\begin{aligned} P_f &= 1 \times 10^5; \\ V_f &= 1000 \times (1 / 100)^3; \\ k_B &= 1.38 \times 10^{-23}; \\ N_0 &= 1.5 \times 10^{22}; \\ T_f &= (P_f \times V_f) / (k_B \times N_0) \\ 483.092 \end{aligned}$$

There is no work done in this isochoric process since  $\Delta V=0$ , which means  $W=P\Delta V=0$ . The heat  $Q$  absorbed by the gas is given by the specific heat for a constant volume process  $c_V = 0.177$  kcal/(kg $\times$ °K), thus

$$Q = m c_V (T_f - T_0) = 7.0 \times 10^{-4} \text{ kg} \times 0.177 \text{ kcal / (kg} \cdot \text{°K)} \times (483 \text{ °K} - 1450 \text{ °K}) \times 4.2$$

$$\text{kJ/kcal} = - 0.50 \text{ kJ}$$

The heat absorbed by the gas is negative, which means heat is given off by the gas. A reservoir at a temperature lower than  $483^\circ\text{K}$  must be in contact with the gas in order for this to happen.

$$\begin{aligned} c_p &= 0.177; \\ m &= 28 \times 1.67 \times 10^{-27} \times 1.5 \times 10^{22}; \\ T_f &= 483.; \\ T_0 &= 1450.; \\ Q &= m \times c_p \times (T_f - T_0) \times 4.2 \\ -0.504214 \end{aligned}$$



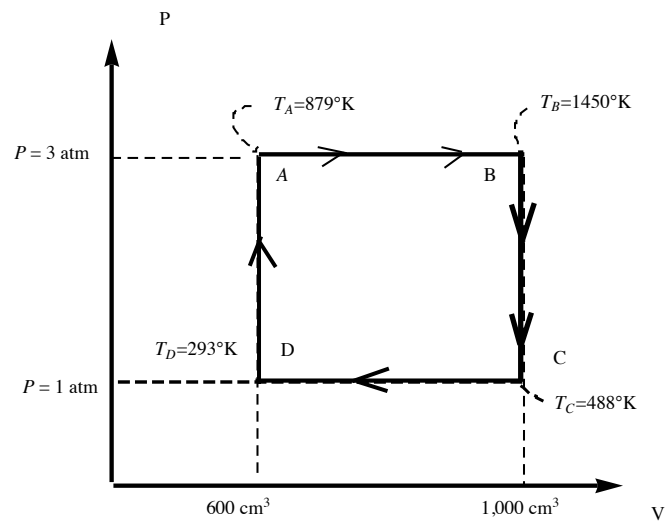
The 1st Law gives the change in internal energy of the gas as a result of this isochoric process:

$$\Delta U = Q - W = -0.50 \text{ kJ}$$

with  $Q = -0.50 \text{ kJ}$  and  $W = 0$ . The internal energy of the gas decreases.

### A Cyclic Process: Two Isobaric Processes and Two Isochoric Processes

Suppose the gas discussed above is next caused to decrease its volume at a constant pressure as indicated by going from C to D in the diagram below.  $T_D=293^\circ\text{K}$ .



### Total Work Done in Cyclic Process

Previously, the work done by the gas in the isobaric process A→B was calculated using  $W = P_0(V_f - V_0) > 0$

$$W_{AB} = 3 \times 10^5 \text{ Nt} / \text{m}^2 \times (1000 * (1 / 100)^3 - 600 * (1 / 100)^3) \text{m}^3 \times (\text{KJ}/1000 \text{ J}) =$$

0.12 KJ

$$\begin{aligned} P_0 &= 3. * 10^5; \\ V_B &= 1000 * (1 / 100)^3; \\ V_A &= 600 * (1 / 100)^3; \\ W_{AB} &= P_0 * (V_B - V_A) * (1 / 1000.); \\ W_{BC} &= 0.; \\ &0.12 \end{aligned}$$

The work done during the isochoric process B→C is zero since  $W=P\Delta V$  and the change in volume is zero  $\Delta V=0$ .

$$W_{BC} = 0$$

The work done by the system in the isobaric process C→D is calculated using  $W = P_0(V_f - V_0)$  which is **in the** same form as for the process A→B.

$$W_{CD} = 1 \times 10^5 \text{ Nt} / \text{m}^2 \times (600 * (1 / 100)^3 - 1000 * (1 / 100)^3) \text{m}^3 \times (\text{KJ}/1000 \text{ J}) = -$$

0.04 KJ

The work done by the gas is  $W = P_0(V_f - V_0) < 0$  is negative (so in fact work is done on the gas) since  $V_f < V_0$ .

$$W = 1 \times 10^5 \text{ Nt} / \text{m}^2 \times (600 * (1 / 100)^3 - 1000 * (1 / 100)^3) \text{m}^3 \times (\text{KJ}/1000 \text{ J}) = - 0.04$$

KJ

$$\begin{aligned} \text{Press} &= 1 * 10^5; \\ V_C &= 1000 * (1 / 100)^3; \\ V_D &= 600 * (1 / 100)^3; \\ W_{CD} &= \text{Press} * (V_D - V_C) * (1 / 1000.); \\ &- 0.04 \\ W_{DA} &= 0.; \end{aligned}$$

The work done for the process D→A is zero  $W_{DA} = 0$  since there is no change in volume  $\Delta V=0$ .

The total work done by the gas system is therefore

$$W_{\text{Total}} = W_{AB} + W_{BC} + W_{CD} + W_{DA} = 0.12 \text{ kJ} + 0 - 0.04 \text{ kJ} + 0 = 0.08 \text{ kJ}$$

Since the total work done by the gas system is positive, the gas system does a net amount of work on the environment over the complete cycle.

$$W_{\text{total}} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$$

$$0.08$$

### The Heat Absorbed During a Cyclic Process

The heat absorbed from the high-temperature heat reservoir during the isobaric process A→B was determined to be  $Q_{AB} = 0.42 \text{ kJ}$  using  $Q_{AB} = m c_V \Delta T$ . More specifically:

$$Q_{AB} = m c_V (T_B - T_A) = 7.0 \times 10^{-4} \text{ kg} \times 0.248 \text{ kcal} / (\text{kg} \times ^\circ\text{K}) \times (1,450 \text{ }^\circ\text{K} - 879 \text{ }^\circ\text{K}) \times 4.2$$

$$\text{kJ/kcal} = 0.42 \text{ kJ}$$

The plus sign means heat was absorbed by the system.

$$c_p = 0.248;$$

$$m = 28 \times 1.67 \times 10^{-27} \times 1.5 \times 10^{22};$$

$$T_A = 879;$$

$$T_B = 1450.;$$

$$Q_{AB} = m \times c_p \times (T_B - T_A) \times 4.2$$

$$0.41716$$

The process B→C is isochoric (constant volume) so the heat given off by the gas is

$Q_{BC} = -0.50$  kJ using  $Q_{BC}=m c_p \Delta T$ . More specifically:

$$Q_{BC} = m c_p (T_C - T_B) = 7.0 \times 10^{-4} \text{ kg} \times 0.177 \text{ kcal} / (\text{kg} \cdot ^\circ\text{K}) \times (488^\circ\text{K} - 1450^\circ\text{K}) \times 4.2$$

$$\text{kJ/kcal} = -0.50 \text{ kJ}$$

The minus sign means heat was given off by the system.

$$c_p = 0.177;$$

$$m = 28 * 1.67 * 10^{-27} * 1.5 * 10^{22};$$

$$T_A = 1450;$$

$$T_C = 488.;$$

$$Q_{BC} = m * c_p * (T_C - T_B) * 4.2$$

$$-0.501607$$

The process C→D is isobaric (constant pressure) so the heat absorbed by the gas is

$Q_{CD} = -0.14$  kJ using  $Q_{CD}=m c_V \Delta T$  and more specifically

$$Q_{CD} = m c_V (T_D - T_C) = 7.0 \times 10^{-4} \text{ kg} \times 0.248 \text{ kcal} / (\text{kg} \cdot ^\circ\text{K}) \times (293^\circ\text{K} - 488^\circ\text{K}) \times 4.2$$

$$\text{kJ/kcal} = -0.14 \text{ kJ}$$

The minus sign means heat was given off by the system.

$$c_p = 0.248;$$

$$m = 28 * 1.67 * 10^{-27} * 1.5 * 10^{22};$$

$$T_D = 293.;$$

$$T_C = 488.;$$

$$Q_{CD} = m * c_p * (T_D - T_C) * 4.2$$

$$-0.142463$$

The process D→A is isochoric (constant volume) so the heat given off by the gas is  $Q_{DA} = 0.31$  kJ using  $Q_{DA} = m c_p \Delta T$ . More specifically:

$$Q_{DA} = m c_p (T_A - T_D) = 7.0 \times 10^{-4} \text{ kg} \times 0.177 \text{ kcal} / (\text{kg} \cdot ^\circ\text{K}) \times (879^\circ\text{K} - 293^\circ\text{K}) \times 4.2$$

$$\text{kJ/kcal} = 0.31 \text{ kJ}$$

The plus sign means heat was absorbed by the system.

$$c_v = 0.177;$$

$$m = 28 * 1.67 * 10^{-27} * 1.5 * 10^{22};$$

$$T_A = 879;$$

$$T_D = 293.;$$

$$Q_{DA} = m * c_v * (T_A - T_D) * 4.2$$

$$0.305553$$

The total heat absorbed for the complete cycle is

$$Q_{\text{Total}} = Q_{AB} + Q_{BC} + Q_{CD} + Q_{DA} = 0.43 \text{ kJ} - 0.51 \text{ kJ} - 0.14 \text{ kJ} + 0.31 \text{ kJ} = 0.08 \text{ kJ}$$

Since the total heat absorbed by the gas system is positive, the gas system absorbs a net amount of heat from the environment over the complete cycle.

$$Q_{\text{total}} = Q_{AB} + Q_{BC} + Q_{CD} + Q_{DA}$$

$$0.0786432$$

## Efficiency of the Heat Engine Cycle

The total heat absorbed by the heat engine is  $Q_{\text{Total}} = 0.08 \text{ kJ}$  but actually a more detailed look is necessary to compute the efficiency. The percent efficiency is what you get divided by what you pay. What you get is work done by the heat engine and what you pay is the heat into the heat engine. We need to look at these costs and benefits in more detail.

When you look at the work done by the heat engine in four parts of the cycle,

$W_{\text{AB}} = 0.12 \text{ kJ}$  is positive but some of the useful work is used by the engine itself in running:

$W_{\text{CD}} = -0.04 \text{ kJ}$ . (The other two stages do not produce or cost any work;  $W_{\text{BC}} = W_{\text{DA}} = 0$ ). So the net amount of work produced is  $W_{\text{Output}} = 0.12 \text{ kJ} - 0.04 \text{ kJ} = 0.08 \text{ kJ}$ .

When you look at the heat absorbed by the heat engine in the four parts of the cycle,

$Q_{\text{AB}} = 0.43 \text{ kJ}$  and  $Q_{\text{DA}} = 0.31 \text{ kJ}$  are positive, and these cost money since you must have a

source of heat and this is usually done by burning fuel. The parts of the cycle  $Q_{\text{BC}} = -0.51 \text{ kJ}$  and

$W_{\text{CD}} = -0.14 \text{ kJ}$  where the heat absorbed is negative **means heat is actually given off** during

these parts of the cycle. This heat is given off by the engine and **usually** dumped into the

environment at **no economic cost**. There obviously is a cost to the environment but power plant

operators, investors, and the public do not pay anything directly. This is not quite true because, for

example, nuclear power plant operators quite often build cooling towers (the very symbol of the

Three Mile Island nuclear mishap) to dump heat into the environment, and this is a cost. In any

case, traditionally what you pay is considered the cost of burning fuel so the cost in heat is the

positive parts of the cycle  $Q_{\text{Cost}} = Q_{\text{AB}} + Q_{\text{DA}} = 0.43 \text{ kJ} + 0.31 \text{ kJ} = 0.74 \text{ kJ}$ .

The efficiency of the heat engine cycle above is therefore given by

$$\text{Eff} = \frac{W_{\text{output}}}{Q_{\text{Cost}}} = \frac{0.08 \text{ kJ}}{0.94 \text{ kJ}} \approx 9\%$$

0.08 / 0.94

0.0851064

which is much less than 100%. The French engineer Nicolas Carnot proved in the 1700s that the most efficient heat engine you could have would use a reversible cycle consisting of two isothermal processes and two adiabatic processes (what we now call the "Carnot Cycle"). Carnot cycle is something you can do in the laboratory but it is not very practical. Carnot proved that the ideal efficiency (the efficiency that cannot be exceeded by any other heat engine) is given by the Carnot cycle as

$$\text{Eff} = \frac{T_H - T_L}{T_H}$$

where  $T_H$  is the Kelvin temperature of the high temperature (say 373°K for boiling water) reservoir or source of heat and  $T_L$  is the Kelvin temperature of the low temperature reservoir (say 283°K for room temperature). So for example, the "ideal efficiency" is

$$\text{Eff} = \frac{373 - 282}{393}$$

0.231552

or 23% for this example. (It gets worse. The second law of thermodynamics says you cannot take an amount of heat and convert it entirely into work without dumping some heat into the environment. But more on this later.) One way to improve the efficiency of a heat engine would be to have a higher temperature heat source, since if  $T_H \rightarrow \infty$  then  $\text{Eff}=1$  or 100%. This is why some power plants use superheated steam, which is water boiled under high pressure so that the boiling point is increased. The value of Carnot's argument is that it tells people what to do to improve the efficiency of say for example, the steam engine. Before Carnot it was not clear how to proceed.

## Conceptual Warning Regarding the Internal Energy and the Equipartition Theorem

*(You can skip this section on a first reading.)*

You might associate the internal energy  $U$  of a gas of  $N$  molecules with the equipartition result

$$U = N \times \text{K.E.} = N \times \frac{1}{2} m \overline{v^2} = N \times \frac{3}{2} k_B T \quad ??$$

so the change in internal energy  $\Delta U$  would be

$$\Delta U = N \times \frac{3}{2} k_B \Delta T \quad ??$$

The question marks ?? are there because the above equation is something you might think is true.

That would be a mistake or, at the very least, you must proceed with caution. The equipartition result is valid only if the size of the gas **volume is fixed** (that is, a constant volume process).

Suppose the volume is fixed while the heat  $Q$  is added to the gas from the reservoir. For constant-volume processes (also called isochoric processes), the work done by the gas is zero  $W = P \Delta V = 0$



since  $\Delta V=0$ . The heat absorbed by the gas is given by  $Q = m c_V (T_f - T_0)$  where the specific heat  $c_V$  of Nitrogen for a constant volume process.  $c_V = 0.177$  kcal/(kg $\times$ °K) as measured experimentally. (Note this is different from  $c_p = 0.248$  kcal/(kg $\times$ °K) for nitrogen undergoing a constant-**pressure** process.) The 1st Law reduces to  $\Delta U = Q$  (since  $W=0$ ). Using the equipartition result for  $\Delta U$  together with  $Q = m c_V \Delta T$  yields

$$N \times \frac{3}{2} k_B \Delta T = m c_V \Delta T$$

and remember  $m = mN$  where  $m$  is the mass of a molecule in kg. So we get a theoretical expression for the specific heat  $c_V$

$$c_V = \frac{3}{2} \frac{k_B}{m}$$

Substituting numbers for the mass  $m$  the value for Nitrogen gas together with the Boltzmann constant  $k_B$

$$\begin{aligned} k_B &= 1.38 \times 10^{-23}; \\ m &= 28 \times 1.67 \times 10^{-27}; \\ c_V &= (3 \times k_B) / (2 \times m) \times (1 / 1000.) \times (1 / 4.2) \\ &0.105401 \end{aligned}$$

where we converted 1,000 J = 1 kJ and 4.2 kJ = 1 kcal to get the specific heat in kcal/(kg $\times$ °K). This result is a little disappointing, but it can be improved if you use a form of the equipartition theorem that includes the internal motion (so-called degrees of freedom) of the two nitrogen atoms in the  $N_2$  molecule. There are three internal degrees of freedom (2 rotational and 1 vibrational), and each of these contributes  $\frac{1}{2}k_B$  for a total of  $\frac{3}{2}k_B$  additional. So  $c_V = \frac{3}{2} \frac{k_B}{m} + \frac{3}{2} \frac{k_B}{m} = 3 \frac{k_B}{m}$  and now

$$\begin{aligned} k_B &= 1.38 \times 10^{-23}; \\ m &= 28 \times 1.67 \times 10^{-27}; \\ c_V &= (3 \times k_B / m) \times (1 / 1000.) \times (1 / 4.2) \\ &0.210803 \end{aligned}$$

which is sort of halfway between  $c_V = 0.177 \text{ kcal}/(\text{kg}\times^\circ\text{K})$  and  $c_p = 0.248 \text{ kcal}/(\text{kg}\times^\circ\text{K})$ . Then chemists argue that if the gas temperature is not large enough, the one vibrational degree of freedom is "frozen out" or not activated so effectively

$$c_V = \frac{3}{2} \frac{k_B}{m} + \frac{2}{2} \frac{k_B}{m} = \frac{5}{2} \frac{k_B}{m} \text{ and a numerical calculation gives}$$

$$\begin{aligned} k_B &= 1.38 * 10^{-23}; \\ m &= 28 * 1.67 * 10^{-27}; \\ c_V &= (5 * k_B / (2 * m)) * (1 / 1000.) * (1 / 4.2) \\ &0.175669 \end{aligned}$$

This is certainly in good agreement with  $c_V = 0.177 \text{ kcal}/(\text{kg}\times^\circ\text{K})$  so the argument is at least plausible.

**Question:** So should you think of the change in internal energy as given by  $\Delta U = N \times \frac{3}{2} k_B \Delta T$ ?

**Answer:** Recall the first example where a gas expands under constant pressure in which the 1st Law gives

$\Delta U = Q - W = 0.41 \text{ KJ} - 0.12 \text{ KJ} = 0.30 \text{ KJ}$ . If you calculate the change in internal energy using  $\Delta U =$

$N \times \frac{3}{2} k_B \Delta T$  you get (remembering the conversion 1,000 Joules= kJ)

$$\begin{aligned} k_B &= 1.38 * 10^{-23}; \\ N &= 1.5 * 10^{22}; \\ T_f &= 1450.; \\ T_0 &= 879.; \\ \Delta U &= (N * 3 * k_B * (T_f - T_0) / 2) * (1 / 1000.) \\ &0.177296 \end{aligned}$$

This is quite a bit different (roughly 50% off) from the actual  $\Delta U=0.30$  kJ result obtained from the 1st Law for the constant-pressure process.

**Conclusion:** It is not a good idea to think of the internal energy as given by  $U = N \times \frac{3}{2} k_B T$

because (1) this result is valid only for constant-volume situations and (2) even in constant-volume situations, you must include the internal motions of the molecules to get the correct energy of the system.

© Rodney L. Varley (2010).