

# Carnot Engines, Efficiency, and The Second Law

## Chemistry 213

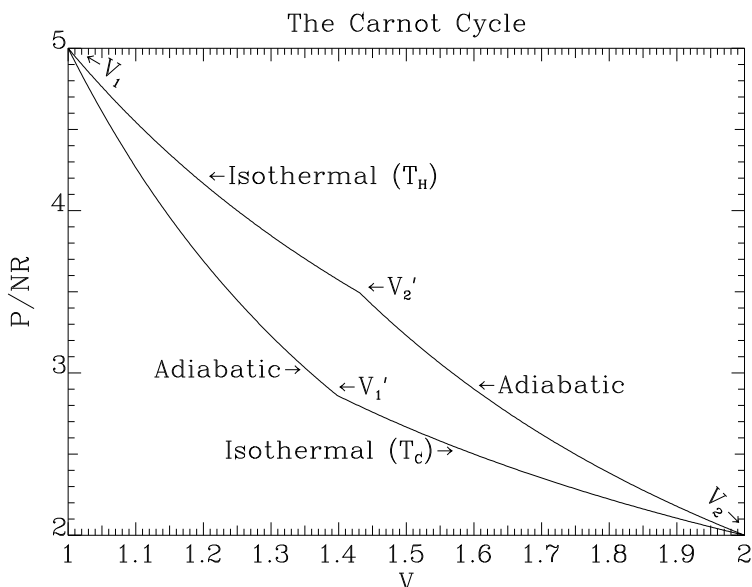


Fig. 1. The Carnot Cycle

The Carnot engine is a useful construction for relating the mathematical ( $\Delta S \geq 0$  for a spontaneous process in an isolated system) and the physical statements of the Second Law of Thermodynamics (heat spontaneously flows from hot to cold). This handout goes through the analysis of the amounts of work and heat produced in the isothermal and adiabatic parts of the Carnot cycle for an ideal gas.

### 1. Energy in an Ideal Gas: Joule's Experiment

In his study of the thermal properties of gases, Joule considered the isothermal expansion of dilute gases using the apparatus depicted below:

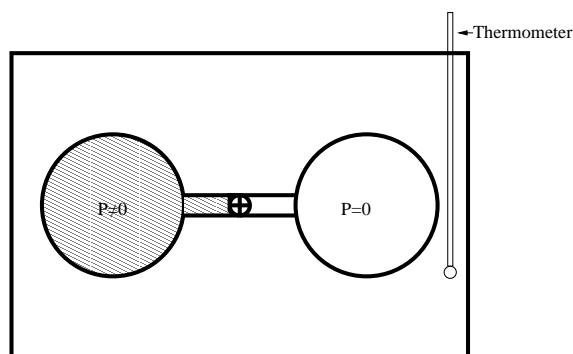


Fig. 2. Joule's Experiment

The bulb on the right was evacuated initially and heat was allowed to exchange with the heat bath, whose temperature was measured. For sufficiently dilute gases, Joule found that the temperature of the bath didn't change. This has some important consequences.

For this process,  $P_{op} = 0$ , and hence,  $W = 0$ . Moreover, since the temperature of the bath remained constant, no heat was absorbed by the system, and thus  $\Delta E = 0$ . What does this say about the functional form of the energy of an ideal gas?

We know that we can write the energy of a one-component system as

$$E(N, V, T) = N\bar{E}(T, N/V),$$

where density was chosen instead of pressure as an independent variable (as can always be done if the equation of state is known). In Joule's experiment  $T$  and  $N$  were held fixed but  $V$ , and hence  $N/V$ , changed. Nonetheless,  $E$  didn't change. Therefore, for an ideal gas,

$$E(N, V, T) = N\bar{E}(T);$$

i.e., the energy per mole of an ideal gas depends only on the temperature of the gas. Similarly, the heat capacity will only be a function of temperature (as it turns out, the heat capacity of an ideal gas is usually only weakly dependent on temperature).

## 2. Reversible, Adiabatic Expansion or Compression of an Ideal Gas

When an ideal gas is reversibly expanded (compressed) adiabatically, its temperature falls (rises). In order to relate the temperature and volume changes, we note that the energy of a ideal gas depends only on the temperature; hence,

$$dE = C_V dT = \delta Q - \delta W = \delta Q - NRT \frac{dV}{V}, \quad (1)$$

where  $C_V$  is the heat capacity at constant volume and where the last equality is obtained by using the ideal gas equation of state. For an adiabatic process,  $\delta Q = 0$ . After a little algebra, Eq. (1) can be rearranged to give:

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

If we assume that  $C_V$  is independent of temperature (this a good approximation for gases of simple molecules such as Ar,  $\text{CO}_2$  etc.), this equality can be summed (or integrated) over the entire adiabatic expansion; that is,

$$\frac{C_V}{NR} \int_{T_{initial}}^{T_{final}} \frac{dT}{T} = \frac{C_V}{NR} \ln \left[ \frac{T_{final}}{T_{initial}} \right] = - \int_{V_{initial}}^{V_{final}} \frac{dV}{V} = - \ln \left[ \frac{V_{final}}{V_{initial}} \right], \quad (2)$$

where the integrals have been evaluated and "ln" is the natural logarithm function. Finally, both sides of Eq. (2) are exponentiated, and we find that

$$\left[ \frac{V_{initial}}{V_{final}} \right] = \left[ \frac{T_{final}}{T_{initial}} \right]^{C_V/NR}. \quad (3)$$

This shows how volume and temperature changes are related along an adiabatic path. (No violation of Charles' law is implied; why?) Notice, if  $V_{initial} < V_{final}$ , then the gas is cooler after the expansion. This is to be expected since the expansion removes energy from the system, energy which is not replaced by the addition of heat from a heat reservoir.

Finally, for an adiabatic change in an ideal gas,

$$\Delta E = -W = +\Delta U_{mechanical} = \int_{T_{initial}}^{T_{final}} C_V(T) dT \approx C_V \Delta T$$

whether or not the path is reversible!

### 3. Reversible, Isothermal Expansion or Compression of an Ideal Gas

Since the energy of an ideal gas depends only on the temperature  $T$ , it remains constant during any isothermal process (i.e.,  $dE = 0$ ). From the first law, this implies that

$$\delta Q = dW = P dV = NRT \frac{dV}{V}. \quad (4)$$

If the  $dQ$ 's given by Eq. (4) are summed over the entire expansion (i.e., between the initial volume,  $V_{initial}$  and the final volume,  $V_{final}$ ) we find that

$$W = Q_{isothermal} = NRT \int_{V_{initial}}^{V_{final}} \frac{dV}{V} = NRT \ln \left[ \frac{V_{final}}{V_{initial}} \right], \quad (5)$$

### 4. Entropy Changes in the Carnot Cycle

Next we use Eq. (5) for the isothermal portions of the Carnot cycle (see Fig. 1, part 1 and 3); it is easy to show that

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = NR \ln \left[ \frac{V'_2 V'_1}{V_1 V_2} \right]. \quad (6)$$

However, if we use Eq. (3) on part 2 of the cycle, it follows that

$$\frac{V'_2}{V_2} = \left[ \frac{T_C}{T_H} \right]^{C_V/NR}.$$

Similarly, for the adiabatic compression,

$$\frac{V_1'}{V_1} = \left[ \frac{T_H}{T_C} \right]^{C_V/NR}.$$

Thus, if we use these two expressions in Eq. (6) the argument of the logarithm becomes equal to 1, and

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0. \quad (7)$$

This is an explicit demonstration of the Second Law of Thermodynamics (i.e., that the entropy is a state function).

Note that the efficiency, (denoted by the Greek letter eta,  $\eta$ ), of the Carnot cycle (i.e., how much work is produced per unit heat absorbed) is easily obtained using Eq. (7):

$$\eta \equiv \frac{W}{Q_H} = \frac{Q_H + Q_C}{Q_H} = 1 - \frac{T_C}{T_H},$$

where the second equality follows from the first law and where the last equality follows from Eq. (7). As is shown on the following pages of the handout, this efficiency formula must hold no matter what the working fluid in the Carnot engine, and hence, Eq. (7) must hold for materials other than ideal gases.

## 5. Entropy Changes in Arbitrary Cycles

What if we have a process which occurs in a cycle other than the Carnot cycle, e.g., the cycle depicted in Fig. 3.

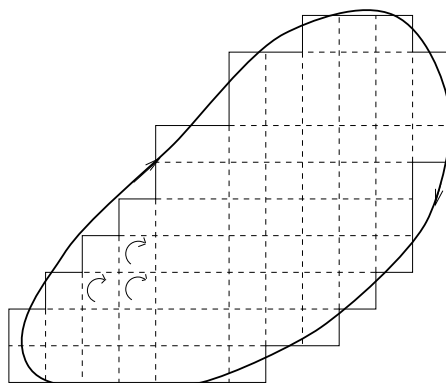


Figure 2

Fig. 3. An arbitrary cycle.

If entropy is a state function,

$$\int_{\text{cycle}} dS = 0$$

no matter what the nature of the cycle. In order to see that this is true, break up the cycle into

sub-cycles, each of which is a Carnot cycle, as shown in Fig. 3. If we apply Eq. (7) to each piece, and add the results, we get zero for the sum.

In summary, we have shown that the entropy

$$S \equiv \int \frac{dQ_{reversible}}{T}$$

is a state function. Moreover, since  $\delta Q \leq dQ_{reversible}$ ,

$$dS \geq \frac{\delta Q}{T};$$

the equality holds only for reversible processes.