Quasi-static Adiabatic Expansion of a Gas

A process in which no heat flows in or out of the system is called adiabatic. This is achieved through thermal insulation of the system.

Figure 19-15 of Tipler considers the quasi-static adiabatic expansion of an ideal gas ($T_1 \neq T_2$ now). We find the equation for the curve using the first law of thermodynamics and the equation of state. We have

$$0 = dQ = dU + dW = C_V \, dT + P \, dV \ .$$

Then, using $P = n\,R\,T/V$:

$$C_V \, dT + n\,R\,T \frac{dV}{V} = 0 \quad \text{or} \quad \frac{dT}{T} + \frac{n\,R}{C_V} \frac{dV}{V} = 0 \ .$$

This can be written as

$$\frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0$$

with $\gamma = C_P/C_V$, because

$$\gamma - 1 = \frac{C_P - C_V}{C_V} = \frac{n\,R}{C_V} \ .$$

Integration gives

$$\ln(T) + (\gamma - 1)\ \ln(V) = \text{constant}\ .$$

Using properties of the logarithm

$$\ln\left(T\,V^{\gamma-1}\right) = \text{constant} \quad \text{or} \quad T\,V^{\gamma-1} = \text{constant}'\ .$$

Using $n\,R\,T = P\,V$, the P versus V relationship follows:

$$P\,V^{\gamma} = \text{const}''\ .$$

The work done by a gas in an adiabatic expansion follows from $dQ = 0$:

$$dW_{\text{adiabatic}} = -dU = -C_V\,dT$$

and then

$$W_{\text{adiabatic}} = -C_V \int dT = -C_V\,\triangle T\ .$$

The Second Law of Thermodynamics (Chapter 20)

How do we "conserve energy" when energy is always conserved according to the first law of thermodynamics? The answer is that some energy forms are more useful than others for the purpose of performing mechanical work. Based on experimental observations, this has been summarized by Kelvin into the following statement:

It is impossible to remove thermal energy from a system at a single temperature and convert it into mechanical work without changing the system or its surroundings in some other way (Kelvin).

A common example of the conversion of mechanical energy into heat (thermal energy) is a block sliding on a table. The reverse process – a table converting some of its thermal energy spontaneously into kinetic energy of the block – never occurs! Some processes are irreversible. This lack of symmetry is expressed in Clausius version of the second law of thermodynamics:

There can be no process whose only final result is to transfer thermal energy from a cooler object to a warmer one (Clausius).

Heat Engines

A heat engine is a cyclic device whose purpose is to convert as much heat input into work as possible. Heat engines contain a working substance that absorbs a quantity of heat $Q_{\rm in}$, does work W, and gives off heat $|Q_{\rm out}|$ ($Q_{\rm out} < 0$ according to our sign convention) as it returns to the initial state.

Examples: Steam engines (figure 20-1), internal combustion gasoline engines (figures 20-2, 20-3).

Figure 20-4 shows a schematic representation of a basic heat engine. The engine removes heat energy $Q_{\rm in} = Q_{\rm h}$ from a hot reservoir at temperature T_h, does work W, and gives off heat $Q_{\rm c} = Q_{\rm out}$ to a cold reservoir at temperature T_c. According to the first law of thermodynamics the work done equals the net heat absorbed:

$$W = Q_{\rm in} - |Q_{\rm out}| \ .$$

The efficiency ϵ of a heat engine is the ratio of work done to the heat absorbed from the hot reservoir:

$$\epsilon = \frac{W}{Q_{\rm in}} = \frac{Q_{\rm in} - |Q_{\rm out}|}{Q_{\rm in}} = 1 - \frac{|Q_{\rm out}|}{Q_{\rm in}} \ .$$

The heat engine statement of the second law of thermodynamics is:

It is impossible to make a heat engine whose efficiency is 100%.

In other words, it is impossible for a heat engine working in a cycle to produce no other effect that that of extracting thermal energy from a reservoir and performing an equivalent amount of work.

This is equivalent Kelvin's statement.

The best steam engines operate near 40% efficiency, the best internal combustion engines near 50%.

Refrigerators

A refrigerator is essentially a heat engine running backward. Figure 20-5 gives a schematic representation. The refrigerator removes heat energy $Q_{\rm in} = Q_c$ from a cold reservoir and gives off heat $|Q_{\rm out}| = |Q_{\rm h}|$ to a hot reservoir using work W. (The sign convention of W is changed by a minus sign with respect to the heat engine.)

The refrigerator statement of the second law of thermodynamics is:

It is impossible for a refrigerator working in a cycle to produce no other effect than the transfer of thermal energy from a cold object to a warmer object.

This is equivalent to Clausius statement.

The coefficient of performance COP of a refrigerator is the ratio of the heat removed by the work used:

$$\mathrm{COP} = \frac{Q_c}{W} \ .$$

The greater COP, the better the refrigerator. Typical values are between 5 and 6. The second law of thermodynamics says that COP cannot be infinite.

The heat engine and refrigerator statements are equivalent:

A perfect refrigerator could be used to transfer heat from a cold to a hot reservoir. This would allow to run an engine, which transfers some of the heat of the hot reservoir into work and the rest back to the cold reservoir.

A perfect heat engine can be used to transfer heat from a hot reservoir into work, which can be used by a refrigerator to cool a cold reservoir and to transfer the remaining work back to the hot reservoir.

The Carnot Engine

What is the maximum possible efficiency of an engine? This questions was answered 1824 by the French engineer Carnot, before either the first or the second law of thermodynamics had been established. The results is known as the Carnot theorem:

No engine working between two given heat reservoirs can be more efficient than a reversible engine working between these two reservoirs.

What makes a process irreversible? The conversion of mechanical energy into heat is not reversible, nor is the conduction of heat from a hot object to a cold one. A third type of irreversibility occurs when the systems moves through non-equilibrium states, e.g., when there is a turbulence or a gas explodes. For a process to be reversible, we must be able to move it backward through the same equilibrium states in the reverse order. Therefore, for a process to be reversible:

1. No work must be dissipated into heat.

2. Heat conduction can only occur thermally.

3. The process must be quasi-static.

The Carnot cycle, depicted in figure 20-8, consists of four reversible steps:

1. A quasi-static isothermal absorption of heat from a hot reservoir.

2. A quasi-static adiabatic expansion to a lower temperature.

3. A quasi-static isothermal exhaustion of heat to a cold reservoir.

4. A quasi-static adiabatic compression back to the original state.

It can be shown that the efficiency

$$\epsilon = 1 - \frac{|Q_{\mathrm{out}}|}{Q_{\mathrm{in}}}$$

of a Carnot engine does not depend on the working substance. So, we use an ideal gas to calculate it. Since $\triangle U = 0$ during an isothermal expansion of an ideal gas, the heat absorbed during step 1 is

$$Q_{\mathrm{in}} = W = \int_1^2 P\, dV = \int_1^2 \frac{n\, R\, T_{\mathrm{h}}}{V}\, dV = n\, R\, T_{\mathrm{h}} \ln\left(\frac{V_2}{V_1}\right) .$$

Similarly, the heat given off to the cold reservoir in step 3 is

$$|Q_{\rm out}| = n\,R\,T_{\rm c}\,\ln\left(\frac{V_3}{V_4}\right)\ .$$

The ratio of these heat energies is

$$\frac{|Q_{\rm out}|}{Q_{\rm in}} = \frac{T_{\rm c}\,\ln(V_3/V_4)}{T_{\rm h}\,\ln(V_2/V_1)}$$

The volumes (V_2, V_3) and (V_1, V_4) are related by the equation for a quasi-static adiabatic expansion:

$$T_{\rm h}\,V_2^{\gamma-1} = T_{\rm c}\,V_3^{\gamma-1} \quad \text{and} \quad T_{\rm h}\,V_1^{\gamma-1} = T_{\rm c}\,V_4^{\gamma-1}\ .$$

Dividing these two equations, we obtain

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}\ .$$

Therefore, $\ln(V_2/V_1) = \ln(V_3/V_4)$ and we can cancel the logarithmic terms in the ratio of heat energies. The Carnot efficiency depends only on the temperatures of the two reservoirs

$$\epsilon_C = 1 - \frac{T_{\rm c}}{T_{\rm h}}\ .$$