Thermodynamics Lecture Notes:
Chapter 7

Michaela Hirschmann

Contents

7 The First Law of Thermodynamics and Thermal Processes

7.1 The First Law of Thermodynamics

Thermodynamical State
A thermodynamic state is described by a set of state variables. Examples of state variables are, P, V, T, number of moles, E_{int} etc. They are uniquely defined, independent of how the system arrived at that particular state. As seen later, heat or work are not state variables since they depend on *how* the system reached a particular state. Once a sufficient number of variables have been specified, all other variables can be uniquely determined. The number of variables needed to specify the system depends on the system.

Example: System of an ideal gas
The gas law for ideal gas $PV = NkT$ shows that a set of three variables out of four, i.e. P, V, T, and N determines the thermodynamic system.

The First Law of Thermodynamics
Extending the concept of energy conservation to a thermodynamical system, in a closed system, we have

$$\Delta E_{int} = Q - W \tag{1}$$

ΔE_{int}: Change of the internal energy, Q: heat into the system, W: work done by the system.

In an isolated system, no energy transfer can occur, i.e. Q = 0 and W = 0, hence $\Delta E_{int} = 0$.

Example: 2500 J of heat is added to a closed system and 1800 J of work is done ON the system. What is the change of internal energy?

$$\rightarrow \text{First Law}: \ \Delta E_{int} = 2500J - (-1800J) = 4300J \tag{2}$$

Be careful with the signs here, both head and work are added to the system.
What would be the result, if 1800 J of work were done BY the system?

$$\Delta E_{int} = 2500J - 1800J = 700J \tag{3}$$

7.2 Thermal Processes

In Thermodynamics, we have the following four thermal processes for gas to change its state:

- Isothermal ($\Delta T = 0$): while the state changes, the temperature is kept constant.
- Adiabatic (Q = 0): process with no heat exchange, i.e. thermally isolated system or a very fast process.
- Isobaric ($\Delta P = 0$): while the state changes, the pressure is kept constant.
- Isovolumetric/Isochoric ($\Delta V = 0$): while the state changes, the volume is kept constant.

Below we go through these different processes assuming a closed system and assuming for simplicity, ideal gas.

7.2.1 Isochoric processes ($\Delta V = 0 \rightarrow W = 0$) and Isobaric processes ($\Delta P = 0$)

Change of internal energy for ideal gas
For isovolumetric process, we have $\Delta V = 0$, thus

$$\Delta E_{int} = Q_V = nC_V \Delta T \tag{4}$$

and for isobaric process

$$\Delta E_{int} = nC_P \Delta T - P\Delta V \tag{5}$$

For ideal gas, we have $C_P - C_V = R$ and $\Delta V = nR\Delta T/P$, thus

$$\Delta E_{int} = n(C_V + R)\Delta T - nR\Delta T = nC_V \Delta T \tag{6}$$

i.e. the change of internal energy for a temperature change of ΔT is given by

$$\Delta E_{int} = nC_V \Delta T \tag{7}$$

for both isovolumetric and isobaric processes.

For ideal gas, any change from one to another thermal state can be seen as combinations of isovolumetric and isobaric processes; this implies that the change of internal energy for a temperature change of ΔT **for any processes is given by**

$$\Delta E_{int} = nC_V \Delta T \tag{8}$$

7.2.2 Isothermal processes ($\Delta T = 0 \rightarrow \Delta E_{int} = 0$)

Let us consider two states A: (V_a, P_a, T_0) to B: (V_b, P_b, T_0) of the same gas, where $V_a < V_b$. Since the temperatures are the same, the internal energy at A and B are the same, i.e.

$$\Delta E_{int} = E_{int,b} - E_{int,a} = 0 \tag{9}$$

From the first law of thermodynamic

$$\Delta E_{int} = Q - W \tag{10}$$

it follows that

$$Q = W_{a\rightarrow b} \tag{11}$$

i.e. if work is done, there must be heat.

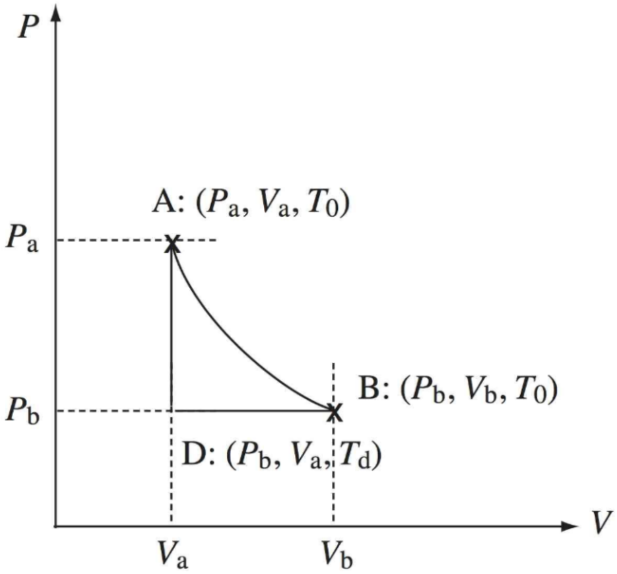
We now determine the work for two different paths: 1) $A \rightarrow B$ and 2) $A \rightarrow D \rightarrow B$:

1) Work done for the isothermal expansion of an ideal gas from A to B at the temperature. From the ideal gas law,

$$P = \frac{nRT_0}{V} \tag{12}$$

the work is given by

$$W_{1:a\rightarrow b} = \int_{V_a}^{V_b} PdV = \int_{V_a}^{V_b} \frac{nRT_0}{V} dV = nRT_0 \int_{V_a}^{V_b} = nRT_0 \ln V \Big|_{V_a}^{V_b} = nRT_0 \ln \frac{V_b}{V_a} > 0 \tag{13}$$



Note that from the ideal gas law, $P_a > P_b$ and W corresponds to the area under the $P(V)$ line in the figure above.

2) Work done for the isovolumetric process from $P = P_a$ to $P = P_b$, with constant volume to the state D:(V_a, P_b), followed by the isobaric process with a constant $P = P_b$ from $V = V_a$ to $V = V_b$. For the isovolumetric part, we have

$$W_{a\to d} = \int_{V_a}^{V_b} P dV = 0 \tag{14}$$

i.e. no work is done.

Note that at D:(V_a, P_b), the temperature has to change. This can be seen by comparing the equation of the state at a, and d,

$$T_0 = \frac{P_a V_a}{nR}, \quad T_d = \frac{P_b V_a}{nR} \tag{15}$$

and

$$T_d - T_0 = \frac{V_a}{nR}(P_b - P_a) < 0 \tag{16}$$

i.e. the temperature drops. In the second process, $P = P_b$ and the work is given by

$$W_{d\to b} = \int_{V_a}^{V_b} P_b dV = P_b \int_{V_a}^{V_b} dV = P_b V\Big|_{V_a}^{V_b} = P_b(V_b - V_a) > 0 \tag{17}$$

In this process, the temperature has to increases from T_d to T_0. The total work done is

$$W_{2:a\to b} = W_{a\to d} + W_{d\to b} = P_b(V_b - V_a) \tag{18}$$

With the ideal gas law,

$$P_b = \frac{nRT_0}{V_b} \tag{19}$$

it follows that

$$W_{2:a\to b} = P_b(V_b - V_a) = nRT_0(1 - \frac{V_a}{V_b}) \tag{20}$$

Note that

$$W_{1:a\to b} \neq W_{2:a\to b} \tag{21}$$

i.e. the **work done depends on the path of the process**. In both cases, the work is positive hence there must be the heat into the gas. Since $Q = W$, the heat Q also depends on the process.

7.2.3 Adiabatic processes (Q = 0, no heat exchange with environment)

As mentioned, for a defined gas, among three state variables, T, V and P, there are only two independent variables. Let us use T and V, leading to

$$\Delta E_{int} = \left(\frac{\partial E_{int}}{\partial V}\right)_T \Delta V + \left(\frac{\partial E_{int}}{\partial T}\right)_V \Delta T \tag{22}$$

for a very small change of the state, i.e. $|\frac{\Delta V}{V}| \ll 1$ and $|\frac{\Delta P}{P}| \ll 1$, and also

$$W = \int_{V_i}^{V_i+\Delta V} P(V)dV \approx P(V_i)\int_{V_i}^{V_i+\Delta V} dV = P(V_i)\Delta V \tag{23}$$

The first law of thermodynamics gives

$$\Delta E_{int} = Q - W = Q - P\Delta V \tag{24}$$

By combining the two equations, we obtain

$$Q = P\Delta V + \left(\frac{\partial E_{int}}{\partial V}\right)_T \Delta V + \left(\frac{\partial E_{int}}{\partial T}\right)_V \Delta T \tag{25}$$

For ideal gas, recalling that the internal energy depends only on temperature, i.e. $\left(\frac{\partial E_{int}}{\partial V}\right)_T = 0$ and the definition of C_V, it follows that

$$Q = P\Delta V + nC_V\Delta T \tag{26}$$

In an adiabatic process, no heat exchange is allowed. This can happen when the system is thermally well isolated or the process happens very fast. Let us consider a very slow (quasistatic) process where the state of ideal gas is adiabatically changed from A:(V_a, P_a, T_0) to C:(V_b, P_c, T_0), i.e. C has the same volume as B. Since there is no heat involved in the process, $Q = 0$, we have:

$$P\Delta V + nC_V\Delta T = 0 \tag{27}$$

Using $PV = nRT$ for the ideal gas, we obtain

$$\frac{\Delta V}{V} + \frac{C_V}{R}\frac{\Delta T}{T} = 0 \tag{28}$$

and furthermore,

$$\Delta T = \frac{P\Delta V + V\Delta P}{nR} \quad \text{and } T = \frac{PV}{nR} \tag{29}$$

lead to

$$\frac{\Delta V}{V} + \frac{C_V}{R}\left(\frac{\Delta V}{V} + \frac{\Delta P}{P}\right) = 0. \tag{30}$$

It follows that

$$(R + C_V)\frac{\Delta V}{V} + C_V\frac{\Delta P}{P} = C_P\frac{\Delta V}{V} + C_V\frac{\Delta P}{P} = 0 \tag{31}$$

i.e.

$$\gamma\frac{\Delta V}{V} + \frac{\Delta P}{P} = 0 \tag{32}$$

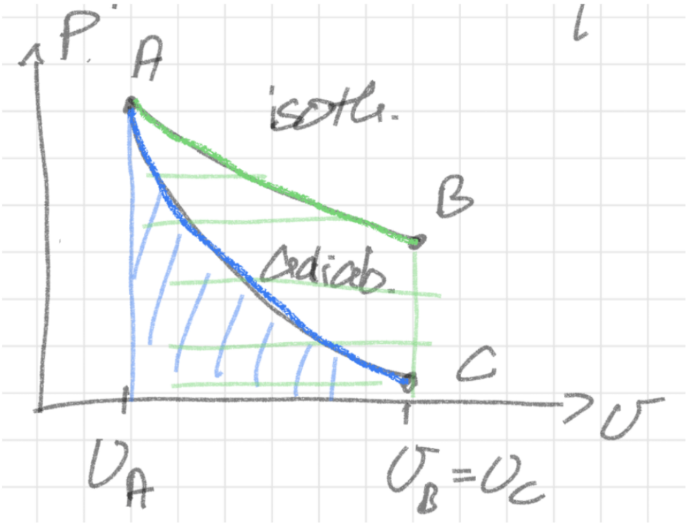
where, $\gamma = C_P/C_V$. By replacing ΔV and ΔP by dV and dP, respectively, integration gives

$$\gamma \ln V + \ln P = \ln V^\gamma + \ln P = \ln(V^\gamma P) = \text{constant} \tag{33}$$

leading to

$$V^\gamma P = \text{constant} \tag{34}$$

Conceptual example: Imagine, we have a system of gas expanding at an initial volume V_A with the same Pressure P_A to a final volume V_B. Is more work done via isothermal (T=const) or adiabatic expansion (Q=0)?



- Isothermes: $P \sim 1/V$, Adiabates: $P \sim 1/V^\gamma$
- Average pressure is higher for isothermal process than for adiabatic process → PV work higher
- Area under each curve represents the work $W = \int_{V_A}^{V_B} PdV$: area for isothermal curve is larger than for adiabatic process

Example for adiabatic processes: Air expands adiabatically from $P_1 = 2\text{atm}$ and $V_1 = 2\text{l}$ at 20 °C to $V_2 = 4\text{l}$. What is the final pressure, the final temperature and the work done by the gas? Note: $\gamma_{air} = 1.4$

For the solution, see the slides...