

Thermodynamical Processes

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1 Quantities

1.1 Work, Quasi-static, and Polytropic Processes

Definition 1.1 (Work). *From mechanics, work is defined as*

$$W = F \cdot \Delta x,$$

where F is the force applied and Δx is the displacement of the point of application. Additionally, recall

$$P = \frac{F}{A},$$

where P is pressure and A is area. The volume change is area A times displacement,

$$\Delta V = A \Delta x.$$

Therefore, substituting force for pressure times area, the work can be expressed in terms of pressure and volume change as

$$W = PA \Delta x = P \Delta V.$$

We can therefore define the boundary work, or energy transferred when there is a change in the boundary of a system from an external pressure, as

$$W = \int P dV.$$

Definition 1.2 (Quasi-static Process). *A quasi-static process is one where the thermodynamic state variables are always well-defined at any given time, meaning the distribution of each variable is uniform at a macroscopic level. This can only occur if the transition between states is sufficiently slow, allowing the system time to adjust.*

Definition 1.3 (Polytropic Process). *A polytropic process is a quasi-static process that follows the relationship*

$$PV^n = C,$$

where C is a constant. This is because pressure and volume are well-defined by definition.

2 Work of Polytropic Processes

2.1 Isobaric Process ($n = 0$)

Definition 2.1. *An isobaric process is defined as a process in which the pressure change is negligible, such that we may assume it is constant.*

When $n = 0$, we obtain

$$P = C.$$

Treating pressure as constant, the work becomes

$$W = P \int_{V_1}^{V_2} dV = P(V_2 - V_1) = P \Delta V.$$

2.2 Isothermal Process ($n = 1$)

Definition 2.2. An isothermal process is defined as a process in which the temperature change is negligible, such that we may assume it is constant.

When $n = 1$, we have

$$PV = C,$$

which implies temperature is constant since

$$C = nRT.$$

From the ideal gas law,

$$P = \frac{nRT}{V}.$$

Substituting into the work formula,

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV.$$

As temperature is constant,

$$W = nRT \int_{V_1}^{V_2} \frac{1}{V} dV = nRT (\ln V_2 - \ln V_1) = nRT \ln \frac{V_2}{V_1}.$$

2.3 Isochoric Process ($V = \text{constant}$)

Definition 2.3. An isochoric process is defined as a process in which the volume remains constant. To compare with the limit $n \rightarrow \infty$, take the differential form of the polytropic relationship,

$$d(PV^n) = d(C) = 0.$$

Using the product rule,

$$nPV^{n-1}dV + V^n dP = 0.$$

Dividing by PV^n ,

$$\frac{dP}{P} + n \frac{dV}{V} = 0.$$

Thus,

$$\frac{dV}{V} = -\frac{1}{n} \frac{dP}{P}.$$

Therefore, when $n \rightarrow \infty$,

$$\frac{dV}{V} = 0 \Rightarrow V = C.$$

2.4 General Polytropic Process

Definition 2.4. A polytropic process holds for all of these specific cases, except when $n = 1$. We derive the work by isolating pressure from the polytropic relation,

$$P = \frac{C}{V^n} = CV^{-n}.$$

Substituting into the work formula,

$$W = \int_{V_1}^{V_2} CV^{-n} dV.$$

Evaluating,

$$W = C \int_{V_1}^{V_2} V^{-n} dV = \frac{C}{1-n} (V_2^{1-n} - V_1^{1-n}).$$

Since

$$C = P_1 V_1^n = P_2 V_2^n,$$

we obtain

$$W = \frac{P_2 V_2^{n+1-n} - P_1 V_1^{n+1-n}}{1-n} = \frac{P_2 V_2 - P_1 V_1}{1-n}.$$

2.5 Adiabatic Process ($Q = 0$)

Definition 2.5. A process is adiabatic if there is no heat transfer.

From the first law of thermodynamics,

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

In differential form, using the internal energy relation,

$$dU = -dW \Rightarrow nC_v dT = -PdV.$$

The differential form of the ideal gas law gives

$$PdV + VdP = nRdT = nR \frac{-PdV}{nC_v} = -\frac{RPdV}{C_v}.$$

Solving for VdP and using Mayer's relation,

$$VdP = -PdV \left(\frac{R}{C_v} + 1 \right) = -PdV \left(\frac{R + C_v}{C_v} \right) = -PdV \left(\frac{C_p}{C_v} \right) = -\gamma PdV.$$

Integrating,

$$\int \frac{dP}{P} = -\gamma \int \frac{dV}{V} \Rightarrow \ln P = -\gamma \ln V + C.$$

Thus,

$$\ln P + \gamma \ln V = \ln(PV^\gamma) \Rightarrow PV^\gamma = C.$$

Therefore, an adiabatic process satisfies $n = \gamma$. The work is

$$W = \frac{P_2 V_2 - P_1 V_1}{1 - \gamma}.$$