Chapter 4. Nature of Thermodynamics

1. What is Thermodynamics?

A. Thermodynamics deals with macroscopic systems that made up of a large number of subsystems (particles) such that (1) the details of each subsystem are not measured, or not measurable, (2) the system is in thermodynamic equilibrium, or at a given temperature. (The concept of temperature will be defined later).

B. A thermodynamic state is characterized by a set of measurable parameters, such as $T$, $V$ (volume), $P$ (pressure), $S$ (entropy), ....

The thermodynamic parameters are classified into intensive parameters $P$, $T$, ...

extensive parameters $V$, $S$, ...

C. Thermodynamics studies properties of thermodynamic systems and their transformation from one state to another.

D. Thermodynamics can be derived by a set of thermodynamic laws.

E. Statistical Mechanics at the end of this course will serve as microscopic basis of thermodynamic laws.
Galileo and 1715 measured T of fluid expansion

Celsius defined °C at melting point of ice and 100°C at boiling point

Count Rumford (Benjamin Thompson) began the quantitative study of the conversion of work into heat by means of his famous cannon-boring experiments.

Sir Humphry Davy studied the conversion of work into heat by means of his ice-rubbing experiments.

Sadi Carnot published his famous thesis "Reflections on the Motive Power of Fire," which includes the new concept of cycle and the principle that the reversible cyclic engine operating between two heat reservoirs depends only on the temperatures of the reservoirs and not on the working substance.

Mayer postulated the principle of conservation of energy.

Helmholtz formulated the principle of conservation of energy, independent of Mayer.

James Prescott Joule laid the experimental foundation of the first law of thermodynamics by performing experiments to establish the equivalence of work and heat. We now honor this great scientist by using J to denote the mechanical equivalent of heat.

Lord Kelvin (William Thomson) defined an absolute temperature scale based on the Carnot cycle.

Rudolf J. Clausius was probably the first to see that there were two basic principles: the first and second laws of thermodynamics. He also introduced the concept of U, which we now call the internal energy.

James Clerk Maxwell derived from the mechanics of individual molecular collisions the expected distribution of molecular speeds in a gas.

Clausius stated the first and second laws of thermodynamics in two lines:
1. The energy of the universe is constant.
2. The entropy of the universe tends toward a maximum, or it is impossible to convert heat completely to work.

Kelvin: It is impossible to transfer heat from a cold source to a hot reservoir without work being done.

Ludwig Boltzmann proved the so-called H Theorem

Josiah Willard Gibbs published his monumental work "On the Equilibrium of Heterogeneous Substances," which extends thermodynamics in a general form to heterogeneous systems and chemical reactions. This work includes the important concept of chemical potential.

Max Planck stated the second law of thermodynamics in the following form: "It is impossible to construct an engine which, working in a complete cycle, will produce no effect other than the raising of a weight and the cooling of a heat reservoir."

Caratheodory published his structure of thermodynamics on a new axiomatic basis, which is entirely mathematical in form.
Definitions:

1. An equilibrium state is a state that does not change with time. (uniform)
2. Open system: can exchange mass + energy with its surroundings
   Closed system: can not exchange mass, but can exchange energy with its surroundings
   Isolated system: can not exchange mass or energy with its surroundings.
3. Intensive parameters: \( P, T \)
   Extensive parameters: \( V, S \)
   Specific quantities: \( \frac{\text{value of extensive parameters}}{\text{mass of the system}} \)
4. 1 mole = \( \frac{N_A}{4} \times 6.02 \times 10^{23} \) molecules
   1 atm = \( 1.013 \times 10^5 \) Pa = 760 torr
   1 Pa = \( 1 \times 10^{-5} \) mbar
   \( T \) (K) = \( T \) (°C) + 273.15
   \( T \) (°K) = \( \frac{5}{2} \) \( T \) (°C) + 273
5. A macroscopic system can be in solid phase, liquid phase, gas phase, ... Change of phases can occur called phase transformation
6. An equation of state takes the form
   \[ f(P, V, T) = 0 \]
   The function of specific state of system. A state is represented by a point in 3-D P-V-T space. The equation of state defines a surface in this space.
A process is a change of state expressed in terms of a path along the equation of state surface.

- Isothermal: constant temperature
- Adiabatic: isolated, no heat transfer
- Quasi-static process - each step is equilibrium
- Reversible: quasi-static without dissipative forces
- Irreversible
- Isochoric: constant volume
- Isohelic: constant pressure

1.7 The Zeroth Law of Thermodynamics - Temperature

If two systems are separately in thermal equilibrium with a third system, they are in equilibrium with each other.

\[
\begin{bmatrix}
A \\
B \\
C
\end{bmatrix} \Rightarrow \begin{bmatrix}
A \\
B
\end{bmatrix}
\]

\[
F_1(P_A, V_A, P_c, V_c) = 0 \quad F_2(P_B, V_B, P_c, V_c) = 0 \quad F_3(P_B, P_c, V_c) = 0
\]

\[P_c = f_1(P_A, V_A, V_c) \quad P_c = f_2(P_B, V_B, V_c)\]

\[
\Rightarrow \frac{f_1(P_A, V_A, V_c)}{f_2(P_B, V_B, V_c)} = \frac{P_A}{P_B} = \frac{f_3(V_A, P_c, V_c)}{f_3(V_B, P_c, V_c)}
\]

\[
\frac{f_1}{v_1} = \phi_1(P_A, V_A) s(V_c) + \eta(V_c) \quad \frac{f_2}{v_2} = \phi_2(P_B, V_B) s(V_c) + \eta(V_c)
\]

\[
\Rightarrow \frac{\phi_1(P_A, V_A)}{\phi_2(P_B, V_B)} = \frac{\phi_3(P_c, V_c)}{\phi_3(P_c, V_c)} \equiv \gamma_f
\]
Temperature Scales - Gas Thermometer

Observations:
1. P-T is very nearly linear over a wide range of temperatures, particularly as P ascends.
2. A linear extrapolation of the plot gives $P = 0$ at $T = -273.15^\circ C$. This turns out to be true for all gases.

In 1954, International Convention defined $T_{T_p} = 273.16 \text{ K}$ exactly.

\[
\therefore T(K) = 273.16 \frac{P}{P_{T_p}} \bigg|_{P_{T_p} \to 0}
\]

$P_{T_p}$ = pressure of the gas thermometer at thermal contact with water at the triple point.
Chapter 2  Equations of State

1) Ideal Gas  (Boyle, Gay-Lussac, Charles, Avagadro)

\[ PV = nRT \quad \text{and} \quad pV = nRT \]

\[ \frac{pV}{nR} = nM = \text{mole} \]

\[ R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1} \]

\[ m = \text{# of moles} \]

1811; Avagadro postulated that at a given temperature and pressure, equal volumes of all gases contain equal numbers of molecules.

\[ f(p,V,T) = pV - nRT = 0 \]

2) Van der Waals equation of state

among gases condense and become liquid state

\[ (p + \frac{a}{v^2})(v - b) = RT \]

Van der Waals derived his equation of state from considerations based on kinetic theory. The parameters \(a, b\) are constant for a gas, with \(a/v^2\) arising from intermolecular force, and \(b\) from the finite volume occupied by each molecule.

Property of Van der Waals equation of state:

A) At high temperature \( T \), \( \Rightarrow pV = RT \)

\[ PV^3 - (pV + RT) v^2 + a(v - b) = 0 \]

\[ p(v - v_c)^3 = 0 \]

At \( T = T_c \) (Critical temperature), the curve has a divergence point, i.e., \( (\frac{\partial^2 p}{\partial v^2})_{v = v_c} = 0 \)

\[ P_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2} \]

\[ \frac{\partial P}{\partial v} = 0 = -\frac{RT_c}{v_c - b} + \frac{2a}{v_c^2} \]

\[ \frac{\partial^2 P}{\partial v^2} = 0 = \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} \]

\[ v_c = 3b \quad T_c = \frac{8a}{27RT_b} \quad P_c = \frac{a}{2RT_b} \quad \frac{P_c v_c^3}{RT_c} = \frac{3}{8} T_c \]
(1) Express \( P, V, T \) in units of \( P_c, V_c, T_c \)

\[
\begin{align*}
\bar{P} &= \frac{P}{P_c} \quad \bar{V} = \frac{V}{V_c} \quad \bar{T} = \frac{T}{T_c} \\
\left[ a = 3P_cV_c^2, \quad b = \frac{1}{3}V_c \right] \\
(P + \frac{9bP_c}{V^2})(v - \frac{1}{3}V_c) &= RT \\
\left( \bar{P} + \frac{9}{V^2} \right)(\bar{V} - \frac{1}{3}) &= \frac{R T_c}{P_c V_c} \quad \bar{T} = \frac{P_c}{3} \frac{\bar{T}}{T_c}
\end{align*}
\]

(universal equation for all gases)

(2) \( P + \frac{9b}{V^2} = \frac{RT}{V} \left( 1 - \frac{3b}{V} \right) \)

\[Z = \frac{PV}{RT} = 1 + \frac{B_2(V)}{V^2} + \frac{B_4(V)}{V^4} + \frac{B_6(V)}{V^6} + \ldots \]

compressibility

\[= (1 + B_2(V)P + B_2(V)P^2 + B_4(V)P^4 + \ldots) \]

\(\text{Virial coefficients}\)
$T_R = \frac{T}{T_C}$

$P_R = \frac{P}{P_C}$
Mathematical Derivation: (Appendix A)

(1) Consider \( f(x, y, z) = 0 \), \( \Rightarrow x = x(y, z) \)
\[ \frac{dx}{dy} = \frac{-\frac{\partial f}{\partial x}}{\frac{\partial f}{\partial y}} \]

\[ \frac{dx}{dy} = \frac{-\frac{\partial f}{\partial x}}{\frac{\partial f}{\partial y}} \]
\[ \frac{dy}{dz} = \frac{-\frac{\partial f}{\partial y}}{\frac{\partial f}{\partial z}} \]

\[ \frac{dz}{dx} = \frac{-\frac{\partial f}{\partial z}}{\frac{\partial f}{\partial x}} \]

Example:
\[ f = xy - z = 0 \]
\[ x = \frac{z}{y} \]
\[ y = \frac{z}{x} \]

\[ \frac{dx}{dy} = -\frac{z}{y^2} \]
\[ \frac{dy}{dz} = \frac{x}{y^2} \]
\[ \frac{dz}{dx} = -\frac{x}{y^2} \]

A function \( u(x, y, z) \) can be expressed as a function of only two variables \( u = u(x, y) \)

\[ \frac{dx}{dy} = \frac{\partial x}{\partial y} \frac{dy}{dz} + \frac{\partial x}{\partial z} \frac{dz}{dy} \]

\[ \frac{\partial x}{\partial y} + \frac{\partial x}{\partial z} \frac{\partial z}{\partial y} = 0 \]
Expansion coefficient \( \alpha_p \) —
\[
\beta \equiv \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \rightarrow \beta = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T
\]

Isothermal compressibility \( K \) —
\[
K \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \rightarrow K = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T
\]

Applications:
\[
f(p,v,T) = 0 \quad \text{Equation of state} \quad \Rightarrow \quad v = v(p,T)
\]
\[
dV = \left( \frac{\partial V}{\partial T} \right)_P \, dT + \left( \frac{\partial V}{\partial P} \right)_T \, dP = \beta V \, dT + \kappa V \, dP
\]
(a) Ideal gas
\[
u = \frac{V}{T} \, dT - \frac{V}{P} \, dP
\]
(b) Liquid or solid
\[
u = \frac{V}{P} \, dP - \kappa V \, dP
\]
\[
\Delta V = \int_{V_0}^{V} \left[ \beta V_0 \left( \frac{dT}{P} \right)_T - \kappa V_0 \, dP \right]_0^P
\]
\[
u = V_0 \left[ 1 + \beta \left( T - T_0 \right) - \kappa \left( P - P_0 \right) \right]
\]

Example: What is pressure required to keep a block of copper at a constant volume?
\[
\Delta v = 0 = \beta V \, dT - \kappa V \, dP
\]
\[
\Delta P = \frac{\beta}{\kappa} \Delta T = \left( \frac{8.6 \times 10^{-12} \text{ Pa}^{-1}}{8.6 \times 10^{-12} \text{ Pa}^{-1}} \right) \Delta T
\]
\[
= 6.84 \times 10^4 \Delta T \text{ Pa}
\]
\[
\left( \frac{dP}{dT} \right)_V = \frac{\beta}{\kappa}
\]
Mathematical Digression — Exact and Inexact differentials.

Let: \( \text{d}z = M(x,y) \, \text{d}x + N(x,y) \, \text{d}y \).

\( M(x,y) \) and \( N(x,y) \) are functions of variables \( x \) and \( y \).

We consider an arbitrary closed path in \( x, y \) plane.

\[
\oint \text{d}z = \oint (M \, \text{d}x + N \, \text{d}y)
\]

\[
= \int \left[ \frac{\partial N}{\partial y} - \frac{\partial M}{\partial x} \right] \, \text{d}x \, \text{d}y
\]

If \( z \) is a total differential

\[
\oint \text{d}z = z_f - z_i = 0
\]

Then

\[
\frac{\partial N}{\partial y} = \frac{\partial M}{\partial x}
\]

\[
M = \frac{\partial z}{\partial x} \quad N = \frac{\partial z}{\partial y}
\]

Example

\[
\text{d}z = \frac{x+y}{x+y} \, \text{d}x + \left( \frac{x+y}{x+y} \right) \, \text{d}y
\]

\[
z = \frac{x}{y} + \frac{y}{x} + \frac{1}{2} \left( \frac{x}{y} \right)^2 + C
\]

\[
\frac{\partial z}{\partial x} = \frac{y}{x} + \frac{1}{2} \frac{2x}{y} \quad \frac{\partial z}{\partial y} = \frac{x}{y} + \frac{1}{2} \frac{2y}{x}
\]

\[z = \frac{x}{y} + C\]
Chapter 3-5

1. Work: \[ dW = F \cdot dx = \int F \, dx = p \, dV \]

Table 3.1 (Textbook)

<table>
<thead>
<tr>
<th>System</th>
<th>Intensive Variable</th>
<th>Extensive Variable</th>
<th>( dW )</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas, liquid, solid</td>
<td>( p )</td>
<td>( v ) (volume)</td>
<td>( p , dv )</td>
</tr>
<tr>
<td>f.l.m.</td>
<td>( n ) (mole)</td>
<td>( A ) (area)</td>
<td>( n , dA )</td>
</tr>
<tr>
<td>electrolyte</td>
<td>( E ) (Elctric)</td>
<td>( q ) (charge)</td>
<td>( E , dq )</td>
</tr>
<tr>
<td>magnetic material</td>
<td>( B ) (magnetic)</td>
<td>( M ) (magnetization)</td>
<td>( B , dM )</td>
</tr>
<tr>
<td>dielectric material</td>
<td>( E ) (electric)</td>
<td>( P ) (polarization)</td>
<td>( E , dp )</td>
</tr>
</tbody>
</table>

- Examples
  - Isochoric process: \( dv = 0 \) \( \implies dW = 0 \)
  - Isobaric process
  - Isothermal (ideal gas)

- \( W \) is not a state variable

\[ \int p \, dv = \text{area inside the path} \]

\( \implies \) work depends on the path

\( \circ \) \( dW \) is not exact differential

\( \circ \) \( df \neq 0 \)

- Irreversible process

\[ dW = -I \, dq \]

\[ dW = -I \, E \, dt \]
2. Heat and First Law of Thermodynamics

Heat is a form of energy. The first law of thermodynamics states that

The heat supplied is equal to the increase in internal energy of the system plus work done by the system.

\[ \delta Q = \delta u + \delta w \quad \text{or} \quad \delta u = \delta Q - \delta w \]

1 calorie (cal) = the heat required to raise the temperature of 1 kg of water from 14.5°C to 15.5°C

1 cal = 10⁻³ kcal = 4.184 J

3. Heat Capacity

[Storage of Heat]

Heat capacity

\[ C_v = \text{constant volume} \]

\[ C_p = \text{constant pressure} \]

\[ C_v = \frac{\partial Q}{\partial T} = \frac{\delta Q}{\delta T} \quad \left[ \frac{J}{K} \right] \]

\[ C_p = \frac{1}{n} \frac{\partial Q}{\partial T} = \frac{\delta Q}{\delta T} \quad \left[ \frac{J}{molK} \right] \]

<table>
<thead>
<tr>
<th>Substance</th>
<th>( C_v ) [J/K pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>2.01</td>
</tr>
<tr>
<td>Water solid</td>
<td>4.18</td>
</tr>
<tr>
<td>Water liquid</td>
<td>2.01</td>
</tr>
<tr>
<td>Copper</td>
<td>0.38</td>
</tr>
<tr>
<td>Granite</td>
<td>0.20</td>
</tr>
<tr>
<td>Glass</td>
<td>0.28</td>
</tr>
<tr>
<td>Know body</td>
<td>0.47</td>
</tr>
<tr>
<td>Protein</td>
<td>1.70</td>
</tr>
</tbody>
</table>
Mayer's Equation: \[ C_p = C_v + R \]

We consider a reversible process,

\[ dU = dq - p\,dv \]

\[ dU = \left( \frac{\partial U}{\partial v} \right)_T \, dv + \left( \frac{\partial U}{\partial T} \right)_v \, dT \]

\[ dq = \left( \frac{\partial q}{\partial T} \right)_v \, dT + \left[ \left( \frac{\partial U}{\partial T} \right)_v + p \right] \, dv \]

\[ C_v = \left( \frac{\partial q}{\partial T} \right)_v = \left( \frac{\partial U}{\partial T} \right)_v \]

For ideal gas, we will find \( \left( \frac{\partial U}{\partial T} \right)_v = 0 \)

\[ dq = C_v \, dT + p \, dv = C_v \, dT + d(pv) - p \, dv \]

\[ p\,v = RT \]

\[ \frac{dp}{dT} = \frac{C_v + R}{p} \]

At room temperature:

Monatomic gas:

\[ C_p = \frac{5}{2} \, R \quad C_v = \frac{3}{2} \, R \quad \gamma = 1.67 \]

Diatomic gas:

\[ C_p = \frac{7}{2} \, R \quad C_v = \frac{5}{2} \, R \quad \gamma = 1.40 \]
\[ dh = d\rho + \varepsilon d\rho \]
\[ \rhodh = d\rho h + \varepsilon \rho d\rho = \left( \frac{\partial h}{\partial T} \right)_\rho dT + \left( \frac{\partial h}{\partial P} \right)_T dP - \varepsilon d\rho \]
\[ \varepsilon = \left( \frac{\partial h}{\partial P} \right)_T \]

\[ \text{Joule-Thomson coefficient} \]

For a gas through porous plug at a constant pressure \( P_t \) to a lower pressure \( P_2 \):

\[ \omega_1 = \int P_1 d\nu = -P_1 v_1 \]
\[ \omega_2 = \int P_2 d\nu = P_2 v_2 \]
\[ \omega = \omega_1 + \omega_2 = P_2 v_2 - P_1 v_1 \]

Since the process is adiabatic \( d\mu = 0 = d\nu + dw \)

\[ u_2 - u_1 + w = 0 \quad u_2 + P_2 v_2 = u_1 + P_1 v_1 \]

\[ h_2 = h_1 \quad \text{Joule-Thomson process} \]

Measure \( (T_1, P_1) \), \( (T_2, P_2) \), ... for all isenthalpic processes.

Define \( \frac{\partial T}{\partial P} \equiv \mu \)

\[ \text{Joule-Thomson coefficient} \]

If \( \mu > 0 \), \( \Delta T \approx \mu \Delta P \), \( \mu \) is negative when throttling.

If \( \mu < 0 \) \( \Rightarrow \) heating for \( T \)-process.
\[
\frac{\partial \mu}{\partial V_T} = -T \frac{\partial \mu}{\partial T_P} = -T \frac{\partial \mu}{\partial T_P} - P
\]

**Ideal gaseous**

\[\text{d}T = \text{d}u + \text{d}v \Rightarrow \mu_T = \text{C}_V(T) + \frac{\text{P}}{\text{V}}\]

\[\frac{\partial \mu}{\partial V_T} = -T \frac{\partial \mu}{\partial T_P} - P
\]

\[\text{d}h = \text{d}u + \text{P} \text{d}v + v \text{dP} = \text{d}u + \text{P} \text{d}v + v \text{dP} = \text{d}u + \text{R} \text{d}T
\]

\[\Rightarrow \frac{\partial \mu}{\partial T} = -T \frac{\partial \mu}{\partial T_P}
\]

\[\Rightarrow \mu_T = 0 \Rightarrow \mu = \left( \frac{\partial \mu}{\partial P} \right)_T = 0
\]

\[\mu_T = 0, \quad \frac{\partial \mu}{\partial T} = 0
\]
The Gay-Lussac-Joule Expansion

In general, \( u = u(v, T) \)

\[
\left( \frac{\partial u}{\partial T} \right)_v \cdot \left( \frac{\partial T}{\partial v} \right)_u = -1
\]

\[
\left( \frac{\partial u}{\partial v} \right)_T = -c \left( \frac{\partial T}{\partial v} \right)_u
\]

1. Measure temperature change while \( u \) is held constant

\[
\Rightarrow \left( \frac{\partial T}{\partial v} \right)_u \Rightarrow \left( \frac{\partial u}{\partial v} \right)_T
\]

Consider a sample of gas is enclosed in a portion of an isolated vessel.

Measure the temperature change in free expansion into volume \( V_1 \)

\[
T = T_0 + \int_{V_0}^{V_1} \left( \frac{\partial T}{\partial v} \right)_u dv
\]

Joule's result \( \Rightarrow |\eta| \leq 0 \) \( \Rightarrow \left( \frac{\partial u}{\partial v} \right)_T = 0 \) (ideal gas)

\[
\eta = \frac{\partial T}{\partial v} = \text{Joule effect}
\]

\[
\left( \frac{\partial u}{\partial v} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P
\]
Work \ [ \text{Ideal gas}] \\

- Isothermal process \\
\[ dW = P \, dv \]
\[ W = \int_{v_i}^{v_f} \frac{RT}{v} \, dv = RT \ln \frac{v_f}{v_i} \]

- Adiabatic process \\
\[ d\gamma = C_v \, dT + P \, dv = C_p \, dT - \gamma dP = 0 \]
\[ \frac{\gamma P}{\rho} \left( \frac{\rho}{\rho_0} \right)^{\gamma - 1} = \frac{P}{P_0} \]
\[ W = \int P \, dv = \int \frac{K}{\rho_0} \left( \frac{\rho}{\rho_0} \right)^{\gamma - 1} \, dv = K \left( \frac{v_f}{v_i} \right)^{\gamma - 1} \]

Example: 
- Monatomic gas \( P_1 = 8 \text{ atm} \), \( v_i = 4 \text{ m}^3 \), \( T_i = 400 \text{ K} \), \( Y = \frac{5}{3} \) \( \Delta U =? \)
- \( P_2 = 1 \text{ atm} \), \( v_f =? \), \( T_f =? \), \( W =? \)

- Ideal gas law \\
\[ P_1 V_1 = nRT_1 \quad \Rightarrow \quad P_2 V_2 = nRT_2 \]
\[ T_2 = \frac{P_2 V_2}{P_1 V_1} T_1 = \frac{8}{\frac{5}{3}} \cdot \frac{13.9 \text{ atm} \cdot \text{m}^3}{4 \text{ atm} \cdot \text{m}^3} = 174 \text{ K} \]

- Work \\
\[ W = \frac{1}{1-\gamma} \left( P_2 V_2 - P_1 V_1 \right) = \frac{1}{1-\left(\frac{5}{3}\right)} \left[ 13.9 \cdot 8 \cdot 4 \right] \cdot \left[ 1.013 \times 10^5 \text{ Pa} \right] \]
\[ = 2.74 \times 10^6 \text{ J} \]

- \( \Delta U = C_v \, \Delta T = n \frac{\Delta P}{\gamma} \left( T_f - T_i \right) = -2.74 \times 10^6 \text{ J} \)
Heat Engine & the Carnot Cycle.

\[ W = Q_2 \]

\[ T_2 > T_1 \]

\[ \eta = \frac{W}{Q_2} = \frac{\text{output}}{} \]

\[ \Delta U = Q_1 + Q_2 - W \]

\[ = Q_1 - W \]

\[ W = Q_1 + Q_2 \]

\[ \eta = \frac{Q_1 + Q_2}{Q_2} = 1 - \frac{1}{\frac{T_1}{T_2}} \]

Example: Carnot Cycle:

\[ dU = dQ - dW \]

--- Isothermal \[ dU = 0 \]

\[ Q_2 = W_2 = nRT_2 \ln \frac{V_b}{V_a} > 0 \]

\[ Q_1 = W_1 = nRT_1 \ln \frac{V_a}{V_c} < 0 \]

--- Adiabatic

\[ \frac{T_2 V_b^{y-1}}{T_1 V_a^{y-1}} = \frac{T_1 V_c^{y-1}}{T_2 V_d^{y-1}} \Rightarrow \frac{V_b}{V_a} = \frac{V_c}{V_d} \]

\[ \eta_1 = 1 - \frac{T_1}{T_2} \]

\[ \eta_2 = 1 - \frac{T_2}{T_1} \]