

# Thermodynamics Notes

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# 1 Introduction

The word thermodynamics is a combination of the Greek *therme*, meaning heat, and *dynamis*, meaning force, and thermodynamics is often defined as the science that studies the relationship between heat and work

- **Energy** - The ability to do work.
- **Work** - The transfer of energy from one system to another.
- **Heat Engine** - Any continuously operating device to which we input heat, and from which we extract work.

The energy of the universe is constant. The first law of thermodynamics states that energy can neither be created nor destroyed. In a continuously operating engine, the energy added to the engine as heat  $Q_H$  leaves the engine as work  $W$  and waste heat  $Q_C$ .

$$Q_H = W + Q_C \quad (1)$$

The thermal efficiency of an engine is defined as

$$\eta = \frac{W}{Q_H} \quad (2)$$

$$= 1 - \frac{Q_C}{Q_H} \quad (3)$$

The entropy of the universe is always increasing. The second law of thermodynamics states that over a cycle, the net change in entropy  $\Delta S$  of the engine must be zero.

$$\Delta S = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0 \quad (4)$$

Rearranging the above equation and substituting into Equation 3, we get

$$\boxed{\eta = 1 - \frac{T_C}{T_H}} \quad (5)$$

## 2 Concepts and Definitions

### 2.1 Thermodynamic Systems

A **thermodynamic system** can be any piece of matter or region of space that we identify for purposes of analysis. The **surroundings** are everything outside the system. The **boundary** is the surface that separates the system from the surroundings.

In a **closed system** (control mass), the amount of mass is fixed, and no mass can cross the boundary. However, energy in the form of either heat or work can enter or leave the system, and the volume of the system can change.

Both energy and mass can cross the boundaries in an **open system** (control volume), but the volume is constant.

If no mass or energy crosses the boundaries of a system, it is an **isolated system**.

A system whose properties do not change with time, even though it is exchanging energy or mass with its surroundings, is said to be at **steady state**.

## 2.2 Thermodynamic Properties

A **property** of a system is any attribute that can be measured without knowing the history of the system. Examples of thermodynamic properties include mass, volume, and energy.

**Intensive Properties** are independent of the mass of the system and can be specified at a point within the system. Examples of intensive properties include temperature and pressure.

**Extensive Properties** depend on the size of the system. Examples of extensive properties include mass, energy, and volume.

Dividing any extensive property by the mass of the system gives a new intensive property. For example  $v = V/m$  is the specific volume of the system, and  $e = E/m$  is the specific energy of the system.

**Path functions** depend on the path taken to get from the initial state to the final state. Examples of path functions include work and heat. To mathematically denote path functions such as work, we write  $W_{12}$  to represent the work done on the system as it goes from state 1 to state 2.

## 2.3 Equilibrium

All physical systems that are left isolated eventually reach a state of equilibrium (different from steady state since steady state systems interact with its surroundings).

- **Mechanical Equilibrium** - A cylinder is separated into two sections by sliding a piston. When the pressure on both sides of the piston is equal, the system is in mechanical equilibrium.
- **Thermal Equilibrium** - Two masses in contact with each other are in thermal equilibrium if they are at the same temperature.
- **Phase Equilibrium** - Liquid water evaporates to fill in empty space above the liquid. When the rate of evaporation equals the rate of condensation, the system is in phase equilibrium.

## 2.4 State and Process

A complete list of properties defines the **state** of a system. The change of a system from one state to another is called a **process**.

- **Isothermal Process** - Temperature remains constant.
- **Isobaric Process** - Pressure remains constant.
- **Isochoric Process** - Volume remains constant.
- **Adiabatic Process** - No heat is added or removed from the system during the process.
- **Quasi-equilibrium Process** - The time rate of change of the process is slow relative to the time it takes for the system to reach thermodynamic equilibrium.

## 2.5 Cycles

Any process or series of processes that result in the system being restored to its initial state is known as a **cycle**.

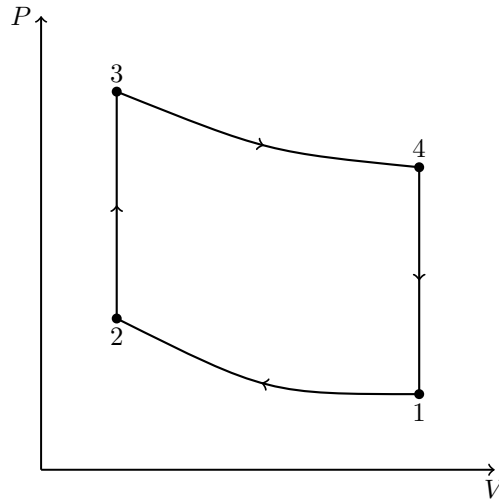


Figure 1: A fixed mass of gas in a cylinder is taken through processes 1,2,3 and 4 that make up a complete cycle.

The symbol  $\oint$  means integration over a cycle. Integrating any property over a cycle gives 0 since the value of the property depends only on the state of the system. However, integrating a path function over a cycle gives a non-zero value.

$$W = \oint F dx \neq 0 \quad (6)$$

### 3 Thermodynamics System Properties

Before we can begin to analyze the behavior of a thermodynamic system, we must first define the properties of the system.

#### 3.1 States of Pure Substances

A **pure substance** is one that has the same, distinct chemical composition throughout (element or compound).

A **homogeneous substance** has the same composition and properties throughout, but may be a mixture of several pure substances. Otherwise, it is a **heterogeneous substance**.

A **phase** is a quantity of matter with uniform chemical composition and physical properties: solid, liquid, gas.

#### 3.2 Pressure and Temperature

**Pressure** is the force per unit area exerted by a fluid on the walls of its container.

$$P = \frac{F}{A} \quad (7)$$

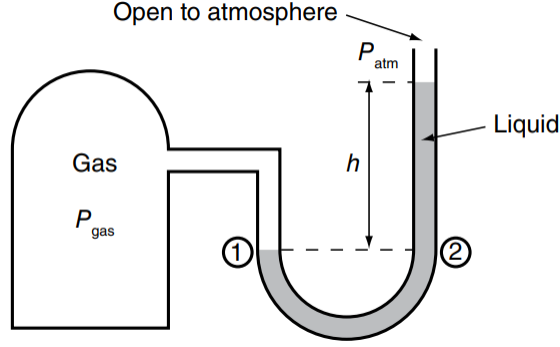


Figure 2: A manometer can be used to measure pressure.

$$P_{\text{gas}} = P_{\text{atm}} + \rho gh \quad (8)$$

The gas pressure is known as **absolute pressure**.

**Temperature** can be measured using a thermometer, and the unit of temperature is the kelvin (K) or degree Celsius ( $^{\circ}\text{C}$ ). The relationship between the two units is  $T(\text{K}) = T(^{\circ}\text{C}) + 273.15$ .

### 3.3 Ideal Gas Law

$$\boxed{PV = nR_u T} \quad (9)$$

where  $R_u = 8.314 \text{ J/mol K}$  is the universal gas constant. Defining  $R = R_u/M$  where  $M$  is the molar mass of the gas, we can write the ideal gas law as

$$\boxed{PV = mRT.} \quad (10)$$

To understand why low-density gases behave like ideal gases, we can consider the following assumptions based on the kinetic theory of gases:

1. A gas is made of a very large number of very small particles in constant random motion with the same mass  $m_e$ .
2. The total number of molecules ( $n$ ) is very large.
3. Molecules collide perfectly elastically with each other and the walls of the container.
4. There is no force acting on the molecules except during collisions.
5. The volume of the molecules is negligible.

The change of momentum of a molecule colliding with the wall is

$$\Delta p = 2m_e v_x. \quad (11)$$

The time it takes for a molecule to cross a wall of length  $L$  is  $\Delta t = L/v_x$ , but it takes  $2\Delta t$  for the molecule to return to the wall. Thus, the force exerted by the molecule on the wall is equal to

$$F = \frac{\Delta p}{2\Delta t} = \frac{m_e v_x^2}{L}. \quad (12)$$

Summing the forces of all the molecules divided by the area of the wall gives the pressure exerted by the gas on the wall.

$$P = \left( \sum_{i=1}^n \frac{m_e v_{x,i}^2}{L} \right) \left( \frac{1}{L^2} \right) \quad (13)$$

$$= \left( \frac{nm_e}{L^3} \right) \left( \frac{\sum_{i=1}^n v_{x,i}^2}{n} \right) \quad (14)$$

$$= \frac{m}{V} c_{x,\text{rms}}^2 \quad (15)$$

Since the magnitude of the total velocity of a molecule is obtained by summing the components in all three directions, we can write  $v_{\text{rms}} = 3v_{x,\text{rms}}$ .  $m$  is the total mass which can be written as  $m = NM$  where  $N$  is the moles of gas and  $M$  is the molar mass of the gas. Thus, we can write

$$PV = \frac{1}{3} m v_{\text{rms}}^2 = \frac{1}{3} NM v_{\text{rms}}^2 \quad (16)$$

### 3.4 Internal Energy

Combining Equation 16 with the ideal gas law, we get

$$\frac{1}{2} M v_{\text{rms}}^2 = \frac{3}{2} R_u T \quad (17)$$

$$\frac{1}{2} m_e v_{\text{rms}}^2 = \frac{3}{2} k T. \quad (18)$$

$k = R_u/N_A$  is known as the Boltzmann constant and has a value of  $1.38 \times 10^{-23}$  J/K. Equation 18 shows that the kinetic energy of a single molecule is proportional to its temperature. Multiplying Equation 18 by the number of molecules  $n$  gives the extensive property, internal energy.

$$U = \frac{3}{2} N R_u T \quad (19)$$

Furthermore, if we take the differences of the internal energy at two different states, and divide by the mass of the gas  $m$ , we get

$$u_2 - u_1 = \frac{3}{2} R (T_2 - T_1) = c (T_2 - T_1) \quad (20)$$

$c$  is a gas property known as the specific heat which will be discussed in the next section.

## 4 Energy and the First Law of Thermodynamics

Energy exists in many forms: kinetic, potential, internal.

### 4.1 Energy Transfer

Energy can be transferred in two ways: heat and work. **Heat transfer** is an exchange of energy that occurs due to a temperature difference between a system and its surroundings. All other forms of energy transfer are classified as **work**.

**Sign Convention:** Energy transfer into the system is positive, and energy transfer out of the system is negative.

The rate of doing work is known as **power** and is given by  $\dot{W} = \frac{dW}{dt}$ . The rate of heat transfer is given by  $\dot{Q} = \frac{dQ}{dt}$ .

## 4.2 Work

### Boundary Work

When a force acts on the boundaries of a system and deforms them, it is known as boundary work.

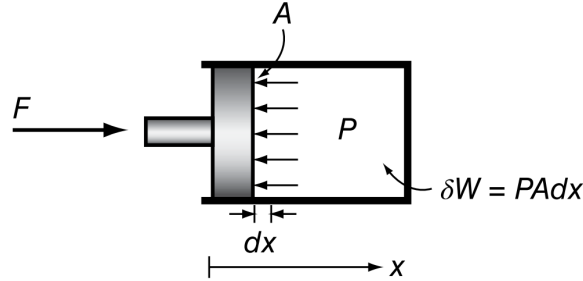


Figure 3: Boundary work done during compression of gas.

The boundary work done is

$$\partial W = -P dV. \quad (21)$$

The work done in compression or expanding a gas from state 1 to state 2 is given by

$$W_{12} = - \int_{V_1}^{V_2} P dV. \quad (22)$$

The negative sign is there since if work done by the surroundings is greater than 0, the change in volume is less than 0.

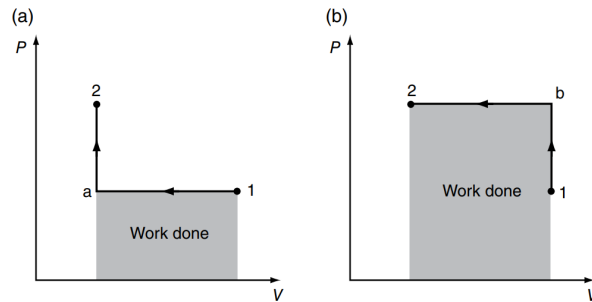


Figure 4: Two processes that begin and finish with the same pressure and volume but require very different amounts of work.

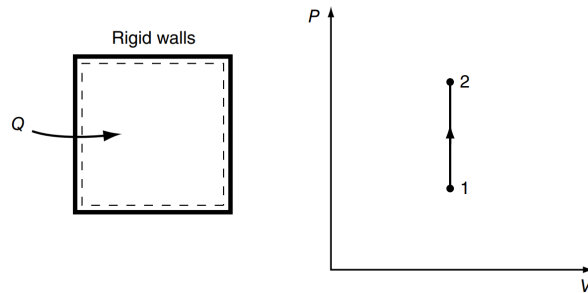


Figure 5: An example of a **constant volume process** is one in which heat is added to a system confined within rigid walls. Work done is 0.



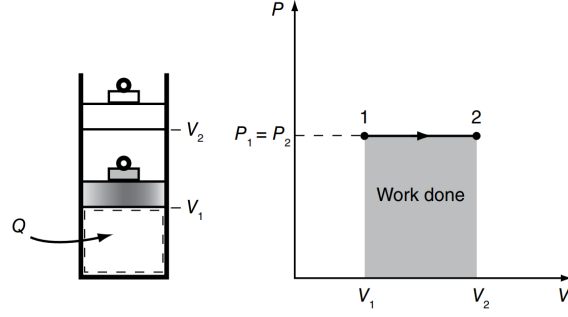


Figure 6: An example of a **constant pressure process** is a system with a piston that is free to move at a constant pressure.  $W_{12} = P_1 V_1 - P_2 V_2$ .

For an isothermal process,

$$W_{12} = - \int_{V_1}^{V_2} \frac{nR_u T}{V} dV = nR_u T \ln \frac{V_1}{V_2}. \quad (23)$$

Furthermore, a variety of common thermodynamic processes can be modeled by a curve of the form  $PV^n = C$  known as **polytropic processes**. For example, setting  $n = 0$  gives a constant pressure process, setting  $n = 1$  gives an isothermal process, and setting  $n = \infty$  gives a constant volume process. The formula for when  $n \neq 1$  is

$$W_{12} = \frac{P_2 V_2 - P_1 V_1}{1 - n}. \quad (24)$$

## Flow Work

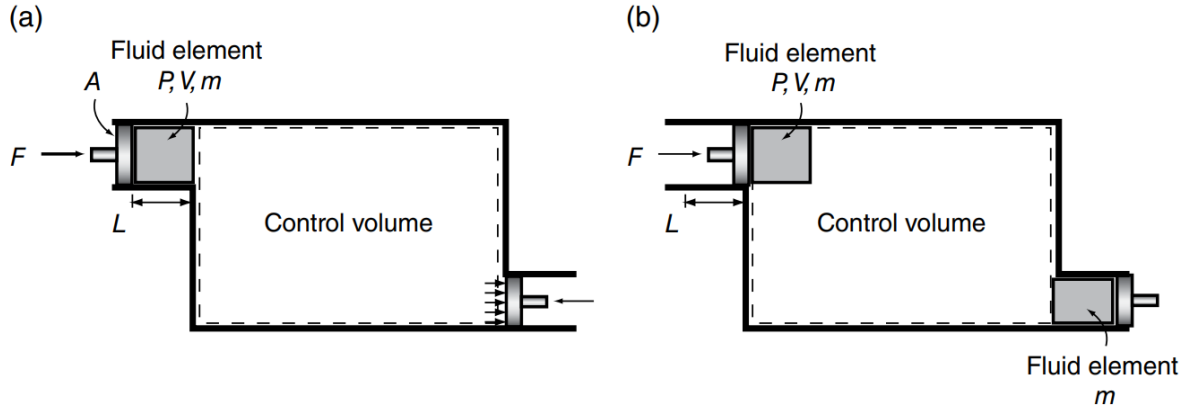


Figure 7: Flow work is the work done to push fluid into a system.

$$W_{\text{flow}} = FL = PAL = PV \quad (25)$$

## Shaft Work

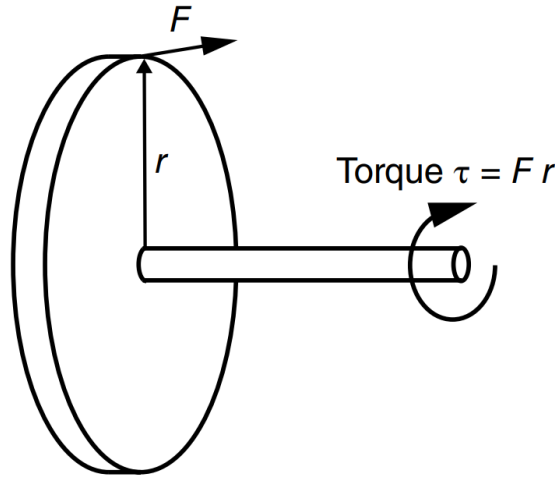


Figure 8: The transfer of energy from fluid to a rotating shaft is known as **shaft work**.

If the shaft revolves  $N_r$  times, the work done by the shaft is

$$W_{\text{shaft}} = 2\pi N_r \tau \quad (26)$$

## Spring Work

Compressing a spring requires work given by

$$W_{\text{spring}} = \frac{1}{2} k (x_2^2 - x_1^2) \quad (27)$$

## Electrical Work

Energy enters the control mass through electricity is not heat transfer since it is not the result of a temperature difference. The work done by the electrical energy is

$$W_{\text{electrical}} = VI = \frac{V^2}{R}. \quad (28)$$

## 4.3 The First Law and Enthalpy

The first of thermodynamics states that

$$Q_{12} + W_{12} = \Delta E = \Delta U \quad (29)$$

where  $Q$  is the heat transfer,  $W$  is the work done, and  $\Delta E$  is the change in energy of the system.  $\Delta E$  can be approximated by the internal energy  $\Delta U$  because the change in kinetic and potential energy is usually negligible.

Enthalpy is an extensive property which measures the capacity of a fluid to do work. It is defined as

$$H = U + PV \quad (30)$$

Note that the  $PV$  defined in enthalpy is different from that defined in internal energy. The  $PV$  in the enthalpy equation is the amount of energy required to hold the fluid in its current state.

## 4.4 Specific Heats of Ideal Gases

Specific heat is defined the amount of energy required to raise the temperature of a unit mass of a substance by one degree  $Q = mc\Delta T$ .

There are two specific heats: **specific heat at constant volume**  $c_v$  and **specific heat at constant pressure**  $c_p$ . Since internal energy is only a function of its temperature  $c_v(T) = \frac{du}{dT}$ . For an ideal gas,

specific enthalpy is also a function of only temperature  $h = u + RT$ , so  $c_p(T) = \frac{dh}{dT}$ .

The two specific heats are related.

$$c_p = c_v + R \quad (31)$$

For, molar properties,

$$\bar{c}_p = \bar{c}_v + R_u. \quad (32)$$

It was shown previously, that the specific internal energy of a monoatomic ideal gas is given by

$$u = \frac{3}{2}RT. \quad (33)$$

Combining this with the specific heat equation gives

$$h = u + RT = \frac{5}{2}RT. \quad (34)$$

Thus, differentiating the two, we get

$$c_p = \frac{5}{2}R, \quad c_v = \frac{3}{2}R. \quad (35)$$

The ratio  $\frac{c_p}{c_v} = \gamma \approx 1.667$  is known as the **specific heat ratio**.

We do not require that the volume or pressure remain constant during a process to use  $c_v$  and  $c_p$  to calculate changes in  $u$  and  $h$ .

For non-monoatomic gases, the specific heat increases with temperature, and it is possible to fit a polynomial curve of the form

$$\bar{c}_p = Mc_p = a + bT + cT^2 + dT^3. \quad (36)$$

For incompressible substances,  $c_p$  and  $c_v$  are equal.

## 4.5 Steady Flow Devices

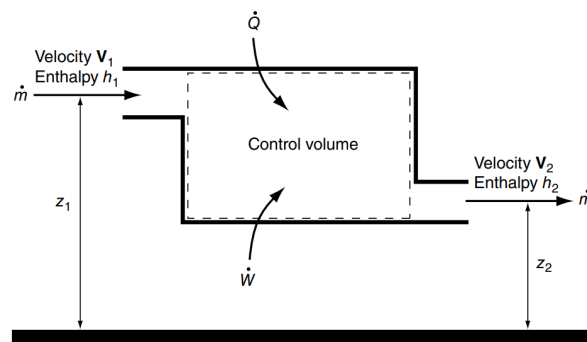


Figure 9: Energy transfers with fluid flowing through a control volume.

The rate of energy input must be equal to the rate of energy output.

The energy entering the control volume per unit mass of fluid is  $e = h + ke + pe = h + \frac{V^2}{2} + gz$ . Thus,

$$\boxed{\dot{Q} + \dot{W} = \dot{m} \left( (h_2 - h_1) + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1) \right)} \quad (37)$$

$$e = q + w = (h_2 - h_1) + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1). \quad (38)$$

The transient flow through a control volume is

$$\frac{dE}{dt} = \dot{Q} + \dot{W} + \sum_i \dot{m}_i \left( h_i + \frac{V_i^2}{2} + gz_i \right) - \sum_e \dot{m}_e \left( h_e + \frac{V_e^2}{2} + gz_e \right). \quad (39)$$

### Turbines and Compressors

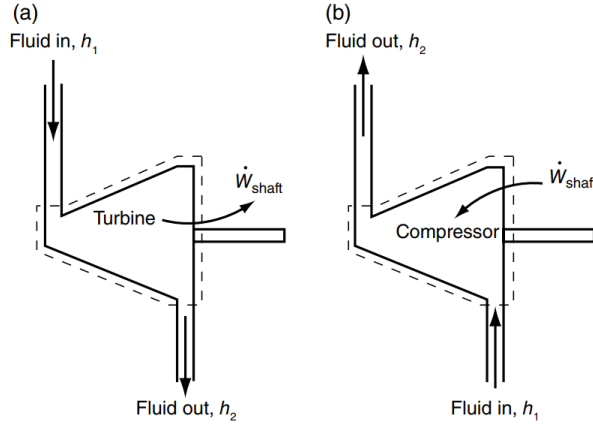


Figure 10: A turbine is a device that uses the flow of a fluid to turn a shaft. A compressor is simply a turbine in reverse.

If we assume that heat loss is negligible  $\dot{Q} = 0$ , and changes in kinetic  $V_2 = V_1$  and potential energy  $z_2 = z_1$  are negligible, then the energy balance reduces to

$$\dot{W}_{\text{shaft}} = \dot{m}(h_1 - h_2). \quad (40)$$

## Pumps

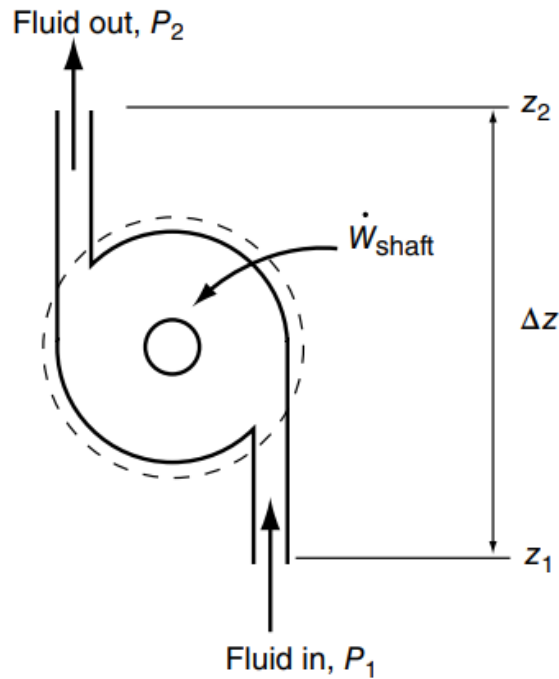


Figure 11: Pumps are used to raise liquids from a lower to a higher elevation, or to raise their pressure.

If the liquid is assumed to be incompressible,

$$h_2 - h_1 = c(T_2 - T_1) + v(P_2 - P_1) \quad (41)$$

$$\dot{W}_{\text{shaft}} = \dot{m}(h_2 - h_1) = \dot{m} [c(T_2 - T_1) + v(P_2 - P_1)] . \quad (42)$$

## Nozzles and Diffusers

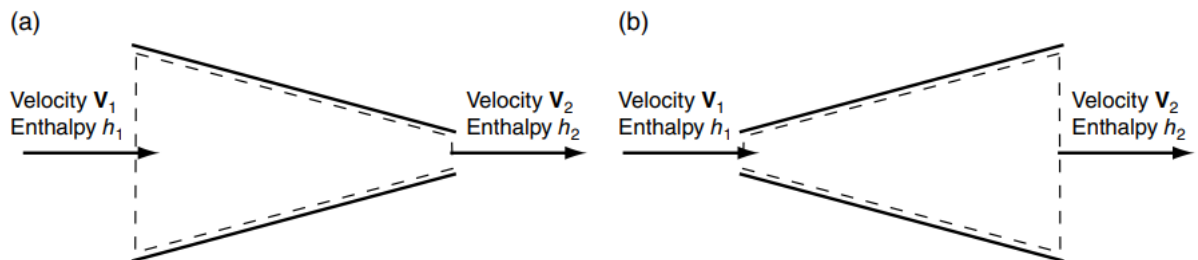


Figure 12: Flow through (a) a nozzle and (b) a diffuser.

If we assume that changes in potential energy are negligible  $z_2 = z_1$ , there is no work done on the fluid  $\dot{W} = 0$ , the heat transfer is negligible  $\dot{Q} = 0$ , and the exit velocity in a nozzle is much greater than the inlet velocity, the velocity of the fluid exiting the nozzle is given by

$$V_2 = \sqrt{2(h_1 - h_2)} . \quad (43)$$

For a diffuser this is

$$V_1 = \sqrt{2(h_2 - h_1)} . \quad (44)$$

## 5 Entropy

The change in entropy is defined as the amount of heat transfer divided by temperature.

$$dS = \frac{\partial Q}{T} \quad (45)$$

$$\Delta S = \int_1^2 \frac{\partial Q}{T} \quad (46)$$

$$\dot{S} = \frac{\dot{Q}}{T} \quad (47)$$

- Entropy is an extensive property.
- Energy is conserved, but entropy can be generated.
- Entropy is created when heat is transferred through a finite temperature difference.
- Entropy cannot be destroyed.

### 5.1 The Second Law of Thermodynamics and Reversible Processes

The entropy of an isolated system will increase until the system reaches a state of equilibrium.

The entropy of an isolated system remains constant.

Quasi-equilibrium processes, without any dissipation of energy in the form of heat, are **reversible**. Processes that are both reversible and adiabatic are called isentropic processes.

- $\Delta S = 0$  for a reversible process.
- $\Delta S > 0$  for an irreversible process.

### 5.2 Equilibrium in a Gas

By the state postulate, we can describe entropy in terms of mass volume and internal energy.

$$S = S(U, V, m) \quad (48)$$

A gas is in a state of equilibrium if it follows the Maxwell-Boltzmann distribution. For a total of  $n$  molecules in the gas, the fraction  $\Delta n_\varepsilon/n$  with energies lying between  $\varepsilon$  and  $\varepsilon + \Delta\varepsilon$  is given by

$$\frac{\Delta n_\varepsilon}{n} = \frac{2}{\sqrt{\pi}} (kT)^{-3/2} \varepsilon^{1/2} e^{-\varepsilon/(kT)} \Delta\varepsilon. \quad (49)$$

At equilibrium, the number of microstates  $\Omega$  is at its maximum.  $\Omega$  represents the number of permutations of molecules for a given energy distribution. Then, entropy can be defined as

$$S = k \ln \Omega \quad (50)$$

The natural log is applied, so we can add entropies in a way that mathematically makes sense. Additionally, Boltzmann modified the equation with his constant  $k = 1.38 \times 10^{-23} J/K$  to adjust the units of entropy to match those proposed by Clausius.

Using Schrödinger's equation, it can also be shown that

$$\Omega(U, V, n) = f(n) V^n U^{3n/2} \quad (51)$$

where  $f$  is a function of  $n$  only. Substituting this into our definition of entropy gives us

$$\Delta S = mR \left[ \ln \frac{V_2}{V_1} + \frac{3}{2} \ln \frac{T_2}{T_1} \right]. \quad (52)$$

### 5.3 Third Law of Thermodynamics, The Production of Entropy

The third law of thermodynamics states that entropy of a pure substance in thermodynamic equilibrium is zero at a temperature of absolute zero.

Entropy increases when the volume increases from  $V_1$  to  $V_2$ , and  $\Omega \propto V^n$ .

$$\frac{\Omega_2}{\Omega_1} = \left( \frac{V_2}{V_1} \right)^n \quad (53)$$

$$\Delta S = k \ln \frac{\Omega_2}{\Omega_1} = N R_u \ln \frac{V_2}{V_1}. \quad (54)$$

Entropy can also be increased by applying work since internal energy is equal to

$$U = \sum_i \varepsilon_i n_i. \quad (55)$$

## 6 Applying The Second Law of Thermodynamics

### 6.1 Relating Thermal Equilibrium and Temperature

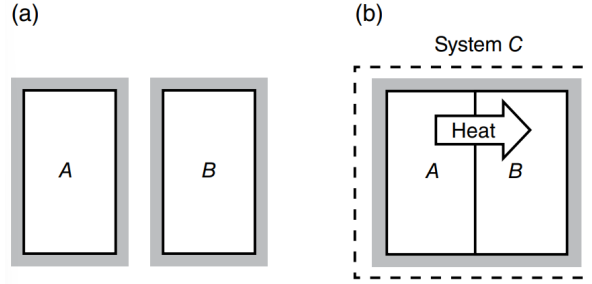


Figure 13: Thermal Equilibrium Example Diagram.

When two systems are brought close to each other as shown in the diagram above, we can add the entropies of two systems to determine the final entropy. At equilibrium, the system's entropy does not change. Differentiating with respect to internal energy gives:

$$\frac{\partial S_A}{\partial U_A} dU_A + \frac{\partial S_B}{\partial U_B} dU_B = dS_C = 0. \quad (56)$$

Since there is no change in internal energy  $dU_A + dU_B = 0$ , this gives

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}. \quad (57)$$

Intuitively, from this equation, since there is no exchange in temperature, we can reason that

$$T \equiv \frac{\partial U}{\partial S}. \quad (58)$$

## 6.2 Relating Entropy with Pressure

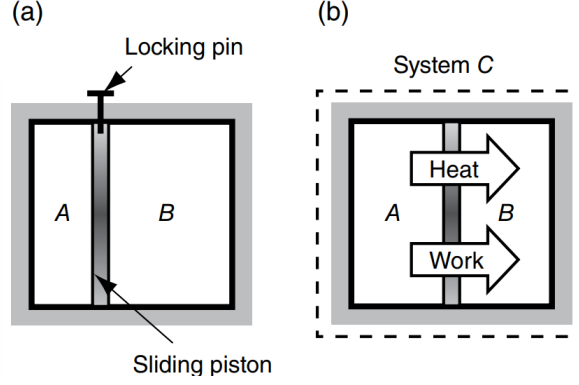


Figure 14: Sliding Piston Example Diagram.

Similar to the previous example with temperature, we can add the entropies of two systems to determine the total entropy. Differentiating with respect to volume and substituting the definition of temperature gives

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}. \quad (59)$$

Since  $\partial S$  has units of J/K, we can reason that

$$\frac{P}{T} \equiv \frac{\partial S}{\partial V}. \quad (60)$$

## 6.3 Gibbs Equation

Combining the previous relationships of entropy with temperature and pressure, we can write the Gibbs equation as

$$ds = \frac{\partial S}{\partial U} du + \frac{\partial S}{\partial V} dv = \frac{1}{T} du + \frac{P}{T} dv. \quad (61)$$

The Gibbs equation gives us a relationship between changes in entropy and easily measurable properties of a system: temperature, pressure, volume, and internal energy.

## 6.4 Entropy Change in Solids and Liquids

Because solids and liquids are incompressible  $dV = 0$ , the Gibbs equation reduces to

$$ds = \frac{c(T)}{T} dT \quad (62)$$

$$\Delta s = c_{\text{avg}} \int_{T_1}^{T_2} \frac{1}{T} dT = c_{\text{avg}} \ln \frac{T_2}{T_1}. \quad (63)$$

## 6.5 Entropy Change in Ideal Gases

Making the substitutions  $du = c_v(T) dT$  and  $P/T = R/v$ , we can write the Gibbs equation as

$$ds = c_v(T) \frac{dT}{T} + R \frac{dv}{v}. \quad (64)$$

$$\Delta s = \int_{T_1}^{T_2} \frac{c_v(T)}{T} dT + \int_{v_1}^{v_2} \frac{R}{v} dv. \quad (65)$$



For constant specific heats, the entropy change is

$$\Delta s = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}. \quad (66)$$

Alternate forms of the equation can be derived by using the ideal gas law  $Pv = RT$  and  $R = c_p - c_v$ .

$$\Delta s = c_v \ln \frac{P_2}{P_1} + c_p \ln \frac{v_2}{v_1} \quad (67)$$

$$\Delta s = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}. \quad (68)$$

When temperature intervals are too large that specific heats are no longer constant, values of  $s^0 = \int_{T_{\text{ref}}}^T \frac{c_p(T)}{T} dT$  from ideal gas tables can be used to calculate entropy changes.

$$\Delta s = s^0(T_2) - s^0(T_1) - R \ln \frac{P_2}{P_1} \quad (69)$$

## 6.6 Isentropic Processes

When setting  $\Delta s = 0$ , we can derive the relationship between pressure and volume for an isentropic process.

$$\frac{T_2}{T_1} = \left( \frac{v_1}{v_2} \right)^{\gamma-1} \quad (70)$$

$$\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} \quad (71)$$

$$Pv^\gamma = \text{constant} \quad (72)$$

$$(73)$$

where  $\gamma = c_p/c_v$  is the specific heat ratio.

## 6.7 Reversible Heat Transfer

For an internally reversible process, the change in entropy is given by

$$\Delta S = \int_1^2 \frac{\partial Q}{T}. \quad (74)$$

Note that when entropy is transferred to the system, the entropy of the surroundings must decrease for the total entropy to remain constant.

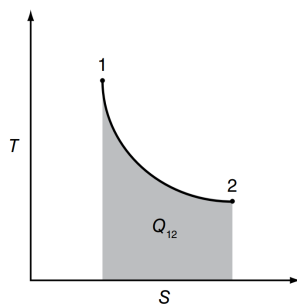


Figure 15: A T-S Diagram can be used to visualize the relationship between temperature and entropy.

## 6.8 Entropy Balance

The entropy balance equation for a control mass is given by

$$S_{\text{in}} - S_{\text{out}} + S_{\text{gen}} = 0 \quad (75)$$

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}}. \quad (76)$$

For a control volume, the entropy balance equation is given by

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{m}_{\text{in}}s_{\text{in}} - \dot{m}_{\text{out}}s_{\text{out}} + \dot{S}_{\text{gen}}. \quad (77)$$

## 6.9 Isentropic Efficiency

### Turbine

Isentropic turbine efficiency is defined as the ratio of the actual work done by the turbine to the work done by an isentropic turbine.

$$\eta_{\text{turbine}} = \frac{h_2 - h_1}{h_{2s} - h_1}. \quad (78)$$

$h_{2s}$  is the enthalpy of the fluid at state 2 if the turbine were isentropic.

### Nozzle

Isentropic nozzle efficiency can be calculated in the same ways as

$$\eta_{\text{nozzle}} = \frac{\mathbf{V}_2^2}{\mathbf{V}_{2s}^2}. \quad (79)$$

### Compressor and Pump

Isentropic compressor efficiency is defined as

$$\eta_{\text{compressor}} = \frac{h_{2s} - h_1}{h_2 - h_1}. \quad (80)$$

## 6.10 Exergy

Exergy is the maximum amount of useful work a system can do before it reaches equilibrium with its surroundings

### Exergy of a Control Mass

The exergy of the system is defined as

$$\Phi = (U - U_o) + P_o(V - V_o) - T_o(S - S_o) + \frac{m\mathbf{V}^2}{2} + mgz \quad (81)$$

where the subscript  $o$  indicates a property of the surroundings.

The useful work done by a system going from state 1 to state 2 is given by

$$W_{\text{useful}} = \Phi_2 - \Phi_1 + T_o S_{\text{gen}}. \quad (82)$$

## Exergy of a Control Volume

The exergy of a control volume is given by

$$\psi = (h - h_o) - T_o(s - s_o) + \frac{\mathbf{V}^2}{2} + gz. \quad (83)$$

The work output of the control volume is

$$\dot{W} = \dot{m}(\psi_2 - \psi_1) + T_o\dot{S}_{\text{gen}}. \quad (84)$$

## 6.11 Bernoulli's Equation

Bernoulli's equation for incompressible fluids is a more specific form of the energy balance equation of a control volume.

$$\frac{P}{\rho} + \frac{V^2}{2} + gz = \text{constant}. \quad (85)$$

# 7 Phase Equilibrium

## 7.1 Phase Change

- **Phase Equilibrium** - The rate of molecules leaving a phase is equal to the rate of molecules entering the phase.
- **Saturated Liquid** - A liquid that is in equilibrium with its vapor.
- **Saturated Vapor** - A vapor that is in equilibrium with its liquid.
- **Saturation Temperature and Pressure** - The temperature and pressure at equilibrium.
- **Latent Heat of Vaporization** - The energy carried away by a unit mass of evaporating liquid.

## 7.2 Phase Change on P-v and T-v Diagrams

Suppose we keep pressure constant, and we slowly increase the temperature of a **subcooled** liquid. Once the liquid begins to evaporate, its temperature remains constant. When all the liquid has evaporated, further heating produces **superheated vapor**.

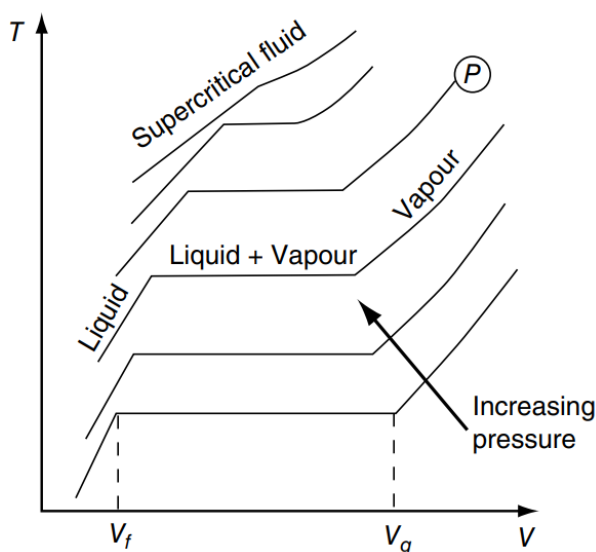


Figure 16: Lines of constant pressure (isobars) on  $T - V$  axis.

If we plot multiple lines of constant pressure on a  $T - V$  diagram as shown in Figure 16, we can see that transition points phases form a vapor dome.

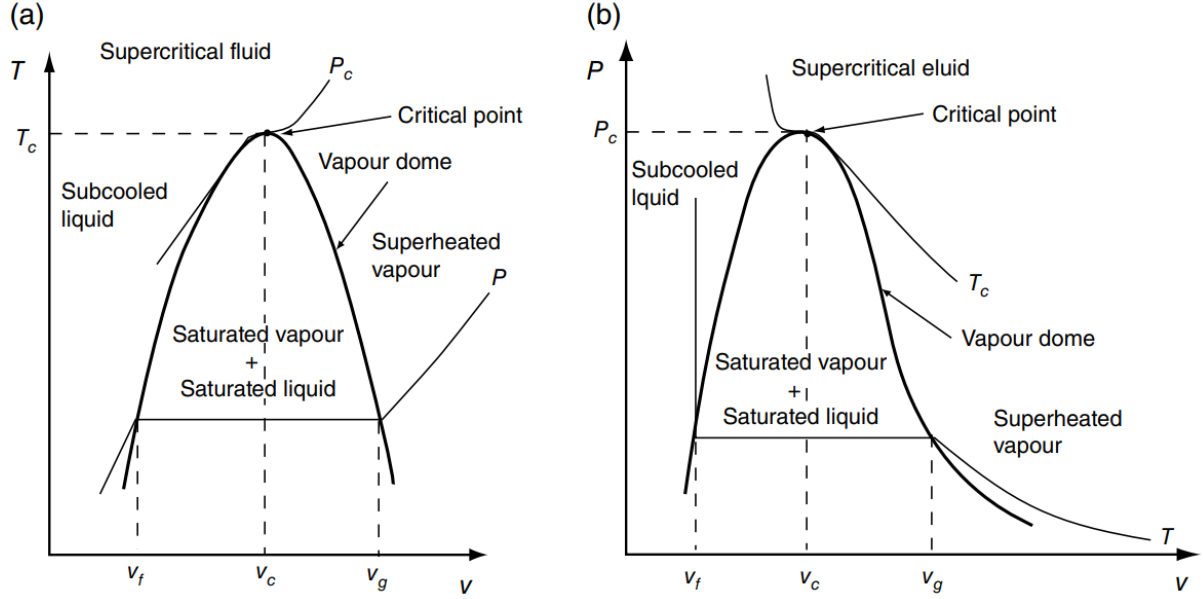


Figure 17: Liquid-vapour phase change shown on (a)  $T - v$  and (b)  $P - v$  diagrams. The peak of the dome is known as the **critical point**. The specific volume corresponding to it is known as the **critical volume**.

### 7.3 Quality

The quality of a mixture is defined by

$$x = \frac{\text{mass of vapor}}{\text{mass of mixture}} = \frac{m_g}{m}. \quad (86)$$

It can be used to determine the intensive properties of the mixture. Since  $1 - x = \frac{m_f}{m}$ , we can write

$$v = \frac{m_g}{m} v_g + \frac{m_f}{m} v_f = x v_g + (1 - x) v_f. \quad (87)$$

Similarly,

$$u = x u_g + (1 - x) u_f \quad (88)$$

$$h = x h_g + (1 - x) h_f \quad (89)$$

$$s = x s_g + (1 - x) s_f. \quad (90)$$

## 8 Heat Engines and Refrigerators

### 8.1 Heat Engines

A heat engine is any device that operates in a cycle and does work  $W_{\text{net}}$  on the surroundings as long as heat  $Q_{\text{in}}$  is supplied to it. The thermal efficiency of a heat engine is defined as

$$\eta = \frac{W_{\text{net}}}{Q_{\text{in}}} = \frac{\dot{W}_{\text{net}}}{\dot{Q}_{\text{in}}}. \quad (91)$$

## 8.2 Perpetual Motion Machine

Any device that violates the laws of thermodynamics is known as a perpetual motion machine.

A perpetual motion machine of the first kind is a device that does work but does not interact with the surroundings in any way.

A perpetual machine of the second kind is an engine that violates the second law of thermodynamics.

## 8.3 Carnot Engine

The Carnot engine is the most efficient heat engine possible. Over a cycle, the change in entropy of the engine must equal zero,

$$\Delta S_{\text{cycle}} = \oint \frac{\partial Q}{T} = 0. \quad (92)$$

This can only occur when

$$\Delta S_{\text{cycle}} = \Delta S_{\text{heat added}} - \Delta S_{\text{heat rejected}} = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0. \quad (93)$$

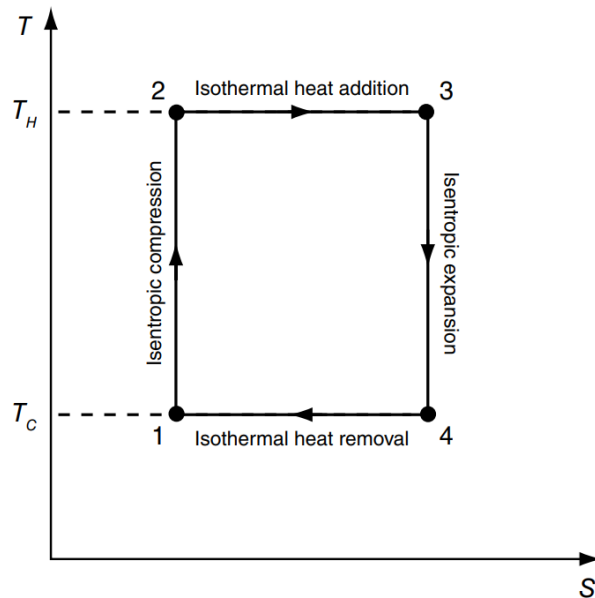


Figure 18: A Carnot cycle shown on a  $T$ - $S$  diagram.

Thus, since  $W_{\text{net}} = Q_H - Q_C$ , the efficiency of a Carnot engine is given by

$$\eta = 1 - \frac{T_C}{T_H}. \quad (94)$$

### Two-Phase Carnot Engine

A two-phase Carnot Engine takes advantage of the fact that the temperature remains constant in a two-phase region when heated or cooled.

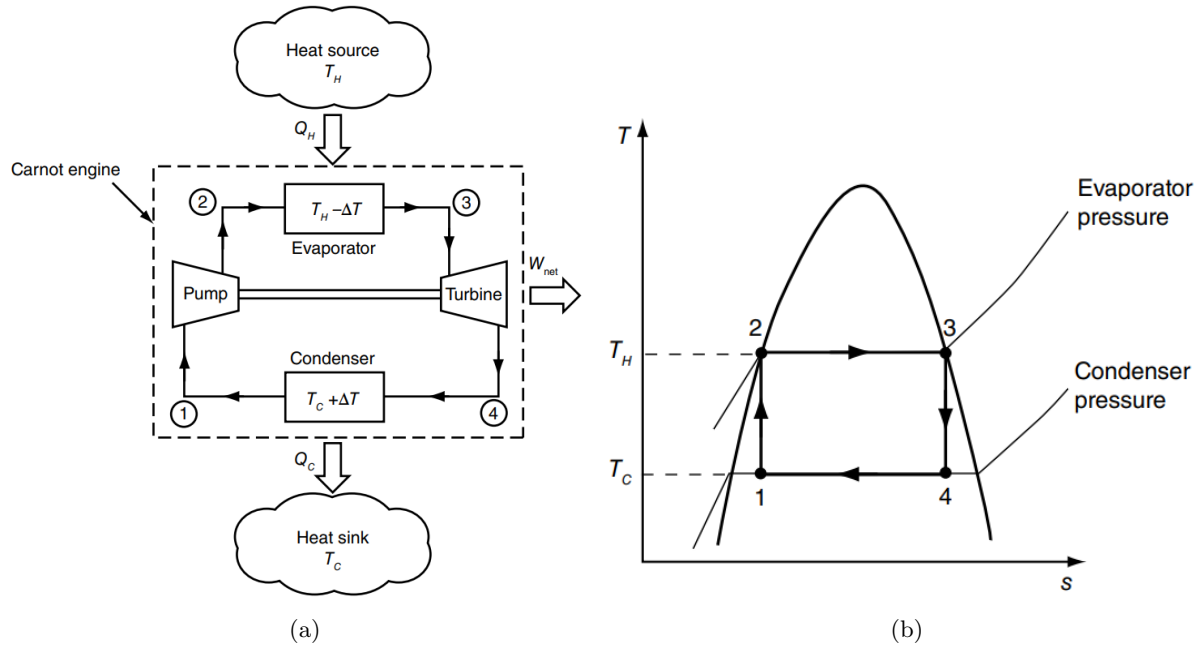


Figure 19: (a) A two-phase Carnot engine. (b) The cycle shown on a  $T-s$  diagram.

### Single Phase Carnot Engine

A single phase Carnot engine uses an ideal gas which undergoes isothermal expansion and compression.

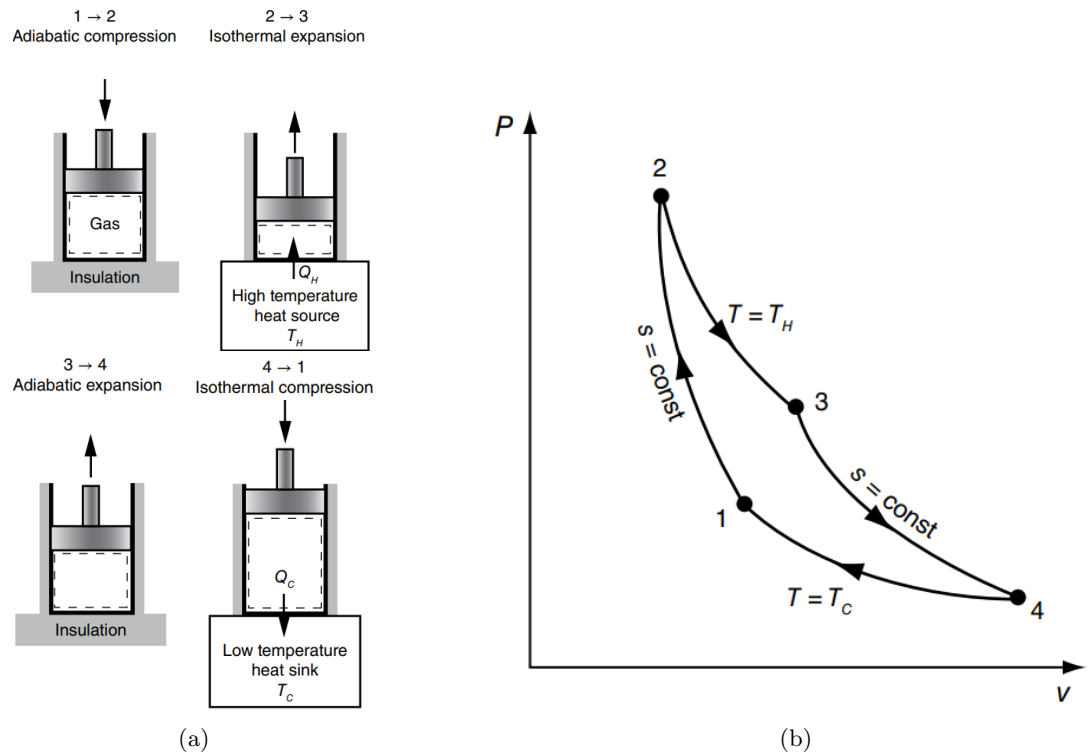


Figure 20: (a) A single phase Carnot engine. (b) The cycle shown on a  $P-v$  diagram.

## 8.4 Refrigerators and Heat Pumps

### Refrigerator

An engine operating in reverse becomes a refrigerator, defined as a device that takes heat from a low temperature region and transfers it to a high temperature region while being supplied with work.

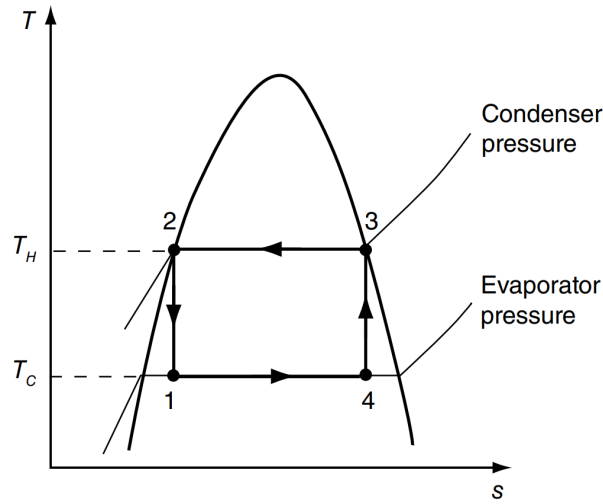


Figure 21: A two-phase reverse Carnot cycle shown on a  $T$ - $s$  diagram.

The coefficient of performance of a refrigerator is defined as

$$COP_R = \frac{Q_{\text{out}}}{W_{\text{net}}} = \frac{1}{Q_H/Q_C - 1} \quad (95)$$

If entropy does not change over a cycle,

$$COP_R = \frac{1}{T_H/T_C - 1}. \quad (96)$$

The  $COP_R$  for a typical refrigerator lies between 2 and 3 while that of a freezer lies between 1 and 1.5.

### Heat Pump

A heat pump takes heat from a low temperature region and transfers it to a high temperature region. The coefficient of performance of a heat pump is

$$COP_{HP} = \frac{1}{1 - Q_C/Q_H} = \frac{1}{1 - T_C/T_H}. \quad (97)$$

The  $COP_{HP}$  for a typical heat pump lies between 2 and 3 meaning that they would provide two to three times the heat that would be obtained by simply dissipating the electricity in a resistance heater.

## 8.5 Carnot Principles

1. The efficiency of a reversible heat engine is always greater than that of an irreversible heat engine operating between the same two temperatures.
2. The efficiencies of all reversible heat engines operating between the same two temperatures are the same.