Chapter 5
The Second Law Of Thermodynamics

- Thermodynamics main concern is in the **transformation of energy**.

- **1-st law states naturally conservation of energy in ordinary process**. However, does not say any thing about the "**spontaneity**". (The spontaneous direction of the process).

- Experience indicates that the **direction of process is not arbitrary but restricted**. (Ex. Hot and cold object).

- In addition, the **difference between heat and work** provide some insight into the 2-nd law.

  Work: Easily transferred into other forms of energy. Such conversation can be made to approach **100% efficiency** by elimination of friction. (reversible).

  Heat: Can't be as efficiently converted to work or into mechanical or electrical energy. Such conversation efficiency does not exceed **40%**.

5.1 Statements Of The Second Law

1) It is impossible by a cyclic process to convert the heat absorbed by a system completely into work.

2) No process is possible which consists solely in the transfer of heat from one temperature level to a higher one.

5.2 Heat Engines

- **It is a device or machine that produce work from heat in a cyclic process.**

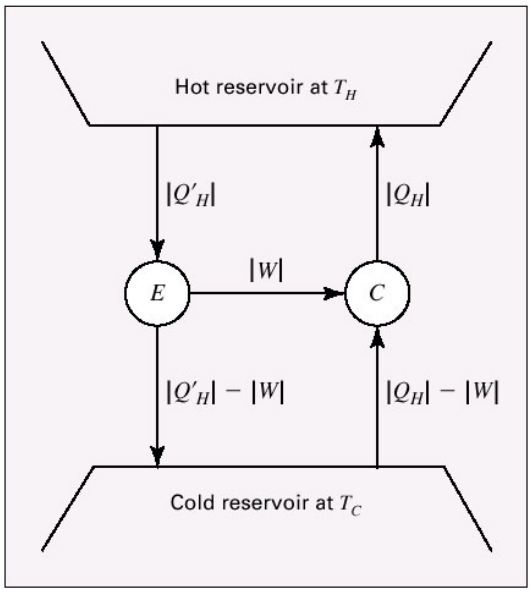

Figure 5.1: Engine E operating a Carnot refrigerator C.

Thus from first law,

$$|W| = |Q_H| - |Q_C| \qquad (5.1)$$

- **The efficiency of the heat engine** is defined as: The ratio between the work output and the heat input.

$$\eta = |W| / |Q_H| = |Q_H| - |Q_C| / |Q_H|$$

Or

$$\eta = 1 - |Q_C| / |Q_H| \qquad (5.2)$$

For η to be 100%, $|Q_C|$ must be zero.
However, no engine can be built for which this is true. **{*Impossible*}**

- **Maximum thermal efficiency is achieved if the heat engine operates completely in a reversible manner. Such ideal engine is special and is called the *Carnot engine.***
  (Reversible engine ≡ The difference in the temperatures of each cycle is very small). Thus, any reversible engine operation between two heat reservoirs is a carnot engine.

- **Carnot Observation: For a reversible heat engine, the efficiency depends only on the temperature levels, T_H and T_C.**

- **Carnot Cycle: Is a heat engine but the working fluid is assumed to be IDEAL.**

5.3 Thermodynamic Temperature Scale

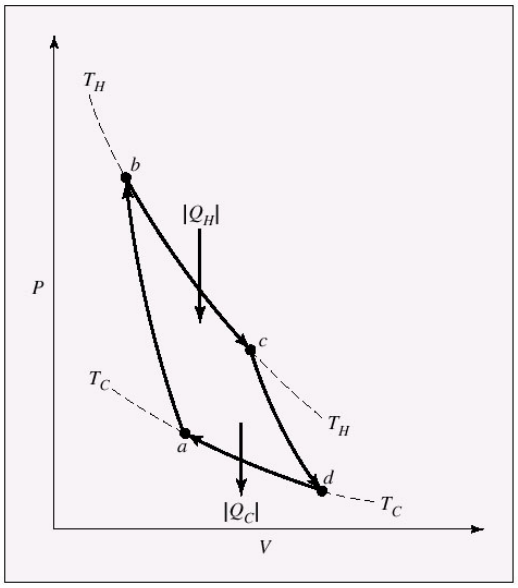

Figure 5.3: *P V* diagram showing Carnot cycle for an ideal gas.

- Four reversible steps:
  - **1)** a→ b Adiabatic compression, until the temperature rises from T_C to T_H.
  - **2)** b→ c Isothermal expansion to point c during which it absorbs a quantity of heat $|Q_H|$.
  - **3)** c→ d Adiabatic expansion until the temperature decrease to T_C.
  - **4)** d→ a Isothermal compression to the initial state with rejection of heat $|Q_C|$.

- For any reversible process, using an ideal gas as the system in a closed system, the first law:

$$dU = dQ + dW$$
$$C_V\, dT = dQ + PdV$$

Solving for Q and W of the above four steps gives:

$$|Q_H| / |Q_C| = T_H / T_C \qquad (5.7)$$

And since, $\eta = 1 - |Q_C| / |Q_H|$

Then, $\eta = 1 - T_C / T_H \qquad (5.8)$

5.7 & 5.8 Carnot's Equations

For $\eta = 1$ T_C has to be zero OR T_H to be infinite. Which can't be realized on earth.

Cold reservoirs naturally available on earth: atmosphere, sea water & rivers $T_C \cong 300K$.
Hot reservoirs: furnaces fueled by fossil fuel or nuclear reactors $T_H \cong 600K$.
Then, $\eta = 1 - 300/600 = 0.5$, approximate limit for thermal efficiency of Carnot engines.
Actual heat engines are irreversible and η rarely exceeds 0.35.

5.4 Entropy

- Write equation 5.7 as,

$$| Q_H | / T_H = | Q_C | / T_C$$

Consider the signs for heat,

$$Q_H / T_H = - Q_C / T_C$$

Then,

$$Q_H / T_H + Q_C / T_C = 0 \qquad (5.9)$$

So, their exist a property of the system (Q/ T) for which the sum of its change is zero for any complete reversible cycle.

$$\oint dQ_{rev} / T = 0 \qquad (5.10)$$

Clausius (1850) had introduced this property and called it ***entropy*** (***S***).

$$dS^t = dQ_{rev} / T \qquad (5.11)$$

Where S^t is the total entropy of the system. Alternatively,

$$\boxed{dQ_{rev} = T\, dS^t} \qquad (5.12)$$

- The change in entropy of any system undergoing a finite ***reversible*** process:

$$\Delta S^t = \int dQ_{rev} / T \qquad (5.13)$$

- When a system undergoes an ***irreversible*** process from an equilibrium state to another, ΔS^t is still evaluated by application of equation 5.13 to an arbitrarily chosen reversible process that accomplishes the same change of state.

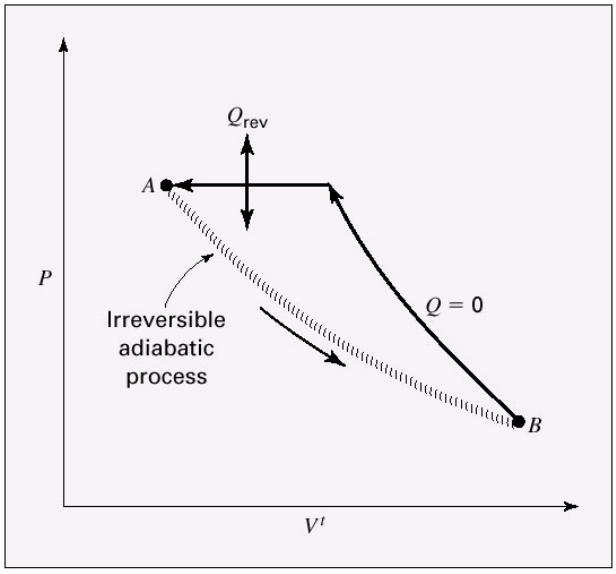

Figure 5.6: Cycle containing an irreversible adiabatic process A to B.

- Entropy is useful because it is a state function. It is based on the 2-nd law.

5.5 Entropy Changes Of An Ideal Gas

1-st law for one mole or unit mass of fluid,

$$dU = dQ + dW$$

For a reversible process,

$$dU = dQ_{rev} - PdV$$

Differentiation of enthalpy equation, $H = U + PV$, yields:

$$dH = dU + PdV + VdP$$

Substitute for dU,

$$dH = dQ_{rev} - PdV + PdV + VdP$$

Or

$$dQ_{rev} = dH - VdP$$

Now for ideal gas, $dH = C_P^{ig} dT$ & $V = RT / P$

Substitute back, $dQ_{rev} = C_P^{ig} dT - RT / P \, dP$ Or

$$dQ_{rev} / T = C_P^{ig} dT / T - R / P \, dP$$

From 5.11,

$$dS = C_P^{ig} dT / T - R \, dP/P$$

Integrate from initial state (P1,T1) to final state (P2,T2)

$$\boxed{\Delta S = \int_{T1}^{T2} C_P^{ig} dT / T - R \ln P_2/P_1} \quad (5.14)$$

Based on equation 4.4, $C_P^{ig} / R = A + BT + C T^2 + DT^{-2}$

Integrate 5.14, and define the **mean heat capacity ($C_P^{ig}{}_s$)**,

$$C_P^{ig}{}_s = \int_{T1}^{T2} (C_P^{ig} dT / T) / \ln (T_2/T_1) \quad (5.16)$$

Substitute into 4.4,

$$C_P^{ig}{}_s / R = A + B \, T_{lm} + T_H \, T_{lm} [C + D/(T_1T_2)^2] \quad (5.17)$$

Where,

T_H (arithmetic mean temp.) $= T_1 + T_2 / 2$

T_{lm} (logarithmic mean temp.) $= T_2 - T_1 / \ln (T_2 / T_1)$

Solving for integral in 5.16,

$$\int_{T1}^{T2} (C_P^{ig} dT / T) = C_P^{ig}{}_s \ln T_2 / T_1$$

Equation 5.14 becomes,

$$\boxed{\Delta S = C_P^{ig}{}_s \ln T_2 / T_1 - R \ln P_2/P_1} \quad (5.18)$$

Example 5.3

5.6 Mathematical Statement Of The Second Law

Consider two heat reservoirs one at T_H and another at lower temperature T_C.

$$\Delta S_H = - Q / T_H$$

And

$$\Delta S_C = Q / T_C$$

Then,

$$\Delta S_{tot} = \Delta S_H + \Delta S_C = Q / Tc - Q / T_H = Q (1/ T_C - 1/ T_H)$$
$$= Q (T_H – T_C / T_C T_H)$$

Since $T_H > T_C \Rightarrow \Delta S_{tot} = +$ ve For this ***irreversible process***.

To make the ***process reversible***, reduce T_H as close as possible to T_C.

$$\Rightarrow \Delta S_{tot} = 0$$

Conclusion:

For irreversible heat transfer process $\Delta S_{tot}>0$ and as the process becomes reversible ΔS_{tot} approach zero.

$$\boxed{\Delta S_{tot} \geq 0} \quad (5.19)$$

Every process proceeds in such direction that the total entropy change associated with it is positive, the limiting value of zero being reached only by a reversible process.

Example 5.4.

HW#1

Just as thermo professor was hurrying into the classroom building, a big 20 kg bag of sand smashed to the ground behind him, just missing him. He looked up and saw that it fell (or dropped) 50 m from the roof deck of the building. His first thoughts were:

a) What was ΔS of the bag of sand for this event?
b) What was ΔS of the surroundings?
c) What was ΔS_{total} for this process?

Please answer the above questions.

Additional information: Although frictional heat may have been generated when the bag hit the ground, this heat is lost to the surroundings as the bag returned to the original temperature of 7^{o}C.