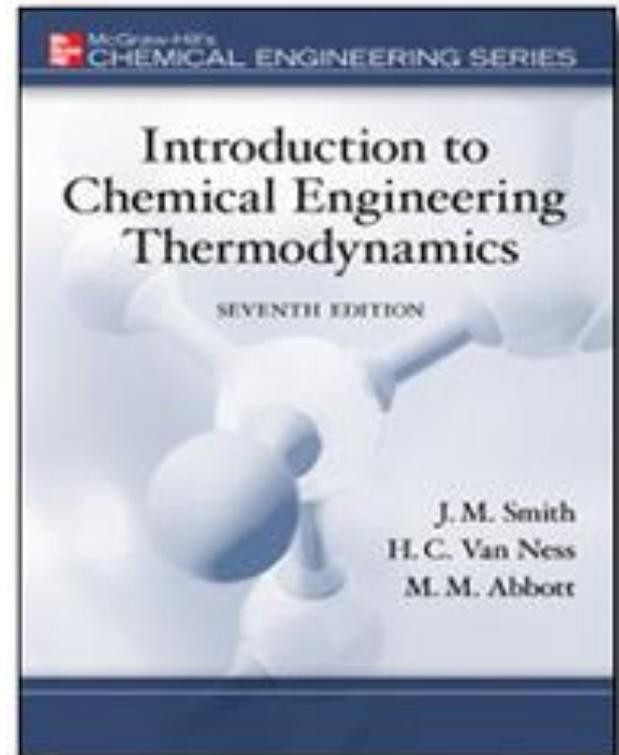


Chapter 5. The Second Law of Thermodynamics



Introduction

❑ Thermodynamics is concerned with transformation of energy

- The first law → conservation of energy
- There is no indication about the direction of energy transformation

❑ Heat and Work : Transit of energy

- Work : readily transformed into other forms of energy
- Heat : complete conversion into work / mechanical or electrical energy have failed (efficiency do not exceed 40 %)
- Heat is less valuable than mechanical work or electrical energy

5.1 Statement of the Second Law

- ❑ The second law is obtained from experience
- ❑ The second law suggest a general restriction on processes beyond that imposed by the first law.

Statement 1

No apparatus can operate in such a way that its **only effect** (in system and surroundings) is to convert heat absorbed by a system **completely** into work done by the system

- This statement does not mean that heat cannot be converted into work
- Production of work using heat require change in the system
- Continuous production of work from heat is impossible

5.1 Statement of the Second Law

Statement 1a

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

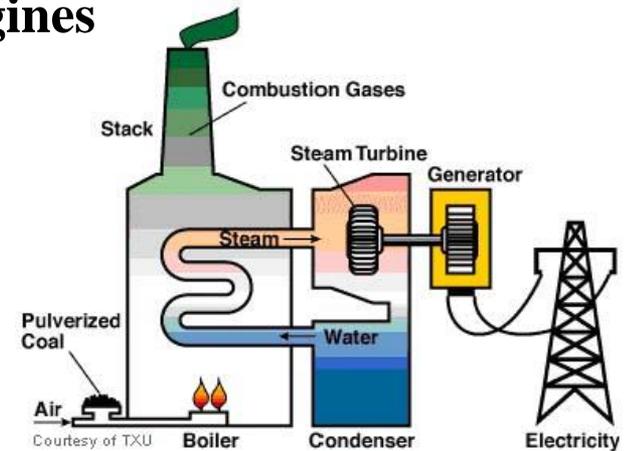
- **Cyclic process : system is periodically restored to its original state.**

Statement 2

No process is possible which consists *solely* in the transfer of heat from one temperature level to higher one

5.2 Heat Engines

- The second law arose from the study of heat engines
- An example - Steam Power Plant
 - Water is used as working fluid
 - Periodically return to its original state



- Liquid water from a condenser is pumped into a boiler at elevated pressure.
- Heat from a fuel is transferred in the boiler to the water, converting it to high-temperature steam at the boiler pressure.
- Energy is transferred as shaft work from the steam to the surroundings by a device such as turbine, in which the steam expands to reduced pressure and temperature.
- Exhaust steam from turbine is condensed by transfer of heat to surroundings, producing liquid water for return to the boiler, completing the cycle.

5.2 Heat Engines

□ Essentials of heat-engine cycle

- Absorption of heat into system at a high temperature
- Rejection of heat to surroundings at lower temperature

□ Heat engines normally operate at two temperature levels

- **Heat reservoir** : imaginary body capable of absorbing or rejecting unlimited quantities of heat without temperature change

5.2 Heat Engines

- Application of the first law to heat engines;

$$|W| = |Q_H| - |Q_C|$$

- Thermal efficiency :

$$\eta = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|} \quad \frac{\text{net work output}}{\text{heat absorbed}}$$

- For 100 % thermal efficiency : Q_c must be zero
- No engine has ever been built to approach 100 % efficiency → heat is always rejected to cold reservoir

If a thermal efficiency of 100 % is not possible,
what determines the upper limit ? → *Carnot Engine*

Carnot Engine

- An ideal engine first described by N.L.S Carnot in 1824.
- Carnot cycle

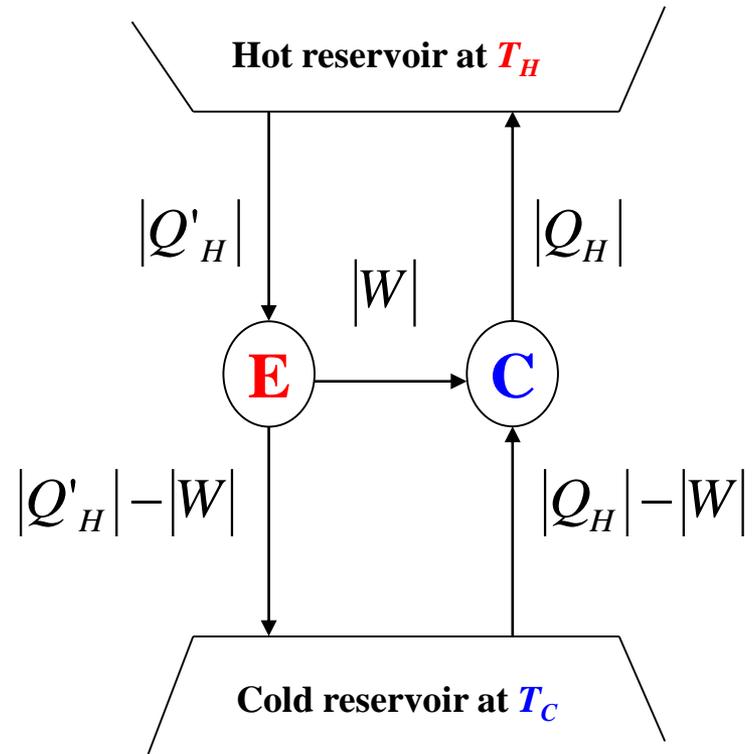
- **Step 1** : A system at an initial temperature of cold reservoir at T_C undergoes reversible adiabatic process that causes its temperature rise to that of hot reservoir at T_H .
- **Step 2** : The system maintains contact with hot reservoir at T_H , and undergoes a reversible isothermal process during which Q_H is absorbed from hot reservoir
- **Step 3**: The system undergoes a reversible adiabatic process in opposite direction of step 1 that brings its temperature back to that of the cold reservoir at T_C
- **Step 4**: The system maintains contact with the reservoir at T_C , and undergoes a reversible isothermal process in opposite direction of step 2 that returns it to its original state with rejection of heat Q_c to the cold reservoir.

Carnot's Theorem

For two given heat reservoirs no engine can have thermal efficiency higher than that of Carnot engine

□ Proof

- If an engine **E** exist with a thermal efficiency greater than that of Carnot engine
- **E** : engine with greater efficiency than Carnot engine
- **C** : Backward Carnot engine (refrigerator)
- With combination of **E+C** : Net result is heat transfer from T_C to T_H
- Violation of the second law



Carnot's Theorem

For two given heat reservoirs no engine can have thermal efficiency higher than that of Carnot engine

□ Proof

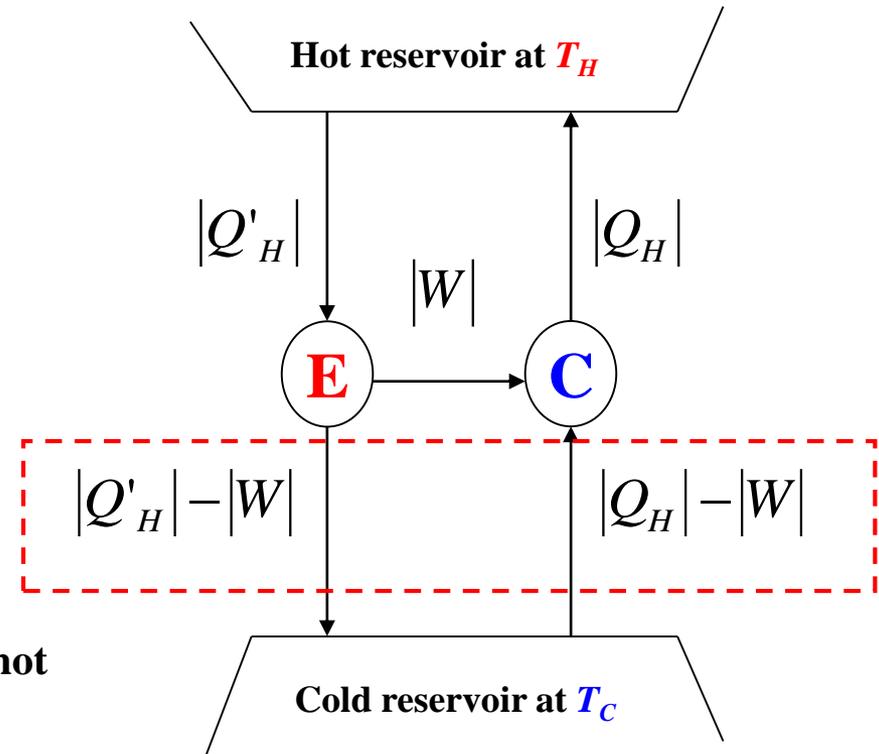
- Efficiency of **E** is greater than **C**

$$\frac{|W|}{|Q'_H|} > \frac{|W|}{|Q_H|} \quad |Q_H| > |Q'_H|$$

- Net effect of **E** + **C**

$$|Q_H| - |W| - (|Q'_H| - |W|) = |Q_H| - |Q'_H|$$

- Heat is delivered from cold reservoir to hot reservoir



Corollary to Carnot's Theorem

The thermal efficiency of Carnot engine depends **only on the temperature levels** and not upon the working substance of the engine.

5.3 Thermodynamic Temperature Scale

□ Kelvin Scale → Ideal Gas Thermometry

□ Thermodynamic Temperature Scale

- Carnot theorem

 - temperature levels independent of material properties

- θ : temperature levels (empirical scale)

- According to corollary to Carnot's Theorem;

 - Efficiency only depends on temperature levels (θ)

$$\eta = 1 - \frac{|Q_C|}{|Q_H|} = \phi(\theta_H, \theta_C) \quad \frac{|Q_H|}{|Q_C|} = \frac{1}{1 - \phi(\theta_H, \theta_C)} = f(\theta_H, \theta_C)$$

5.3 Thermodynamic Temperature Scale

□ Carnot engine 1 and 2 → combination constitute a third Carnot engine

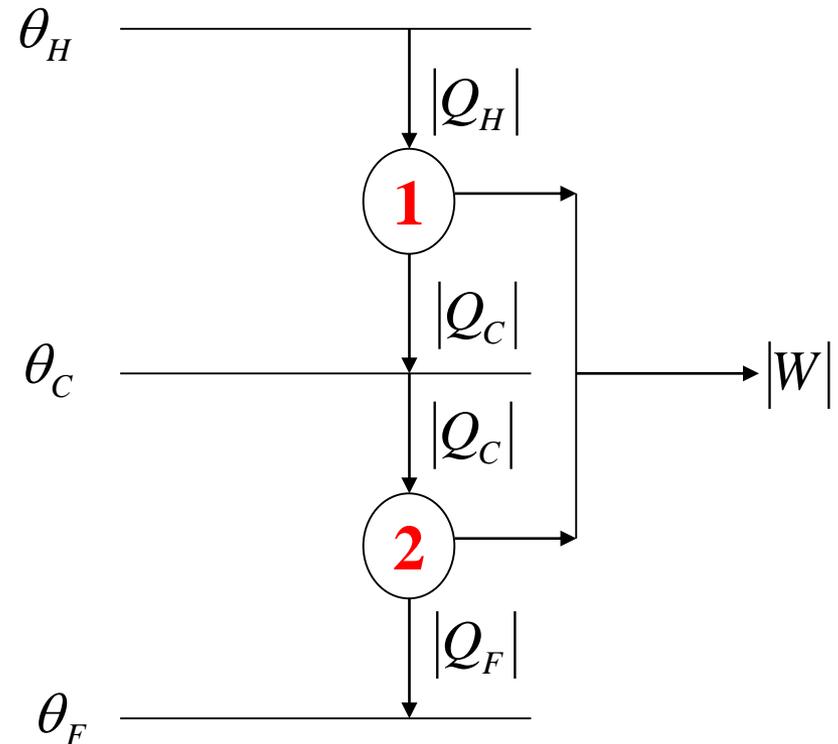
● Engine 1 $\frac{|Q_H|}{|Q_C|} = f(\theta_H, \theta_C)$

● Engine 2 $\frac{|Q_C|}{|Q_F|} = f(\theta_C, \theta_F)$

● Engine 1+2 $\frac{|Q_H|}{|Q_F|} = f(\theta_H, \theta_F)$

$$\frac{|Q_H|}{|Q_C|} = \frac{f(\theta_H, \theta_F)}{f(\theta_C, \theta_F)} = \frac{\psi(\theta_H)}{\psi(\theta_C)}$$

Must be cancelled out



Ideal-Gas Temperature Scale: Carnot's Equation

□ Relation between ideal gas temperature scale and thermodynamic temperature scale

□ Carnot engine : Ideal gas as working fluid

- $a \rightarrow b$: adiabatic compression (temperature rise)
- $b \rightarrow c$: isothermal expansion (absorption of heat)
- $c \rightarrow d$: adiabatic expansion (temperature decrease)
- $d \rightarrow a$: isothermal compression (rejection of heat)

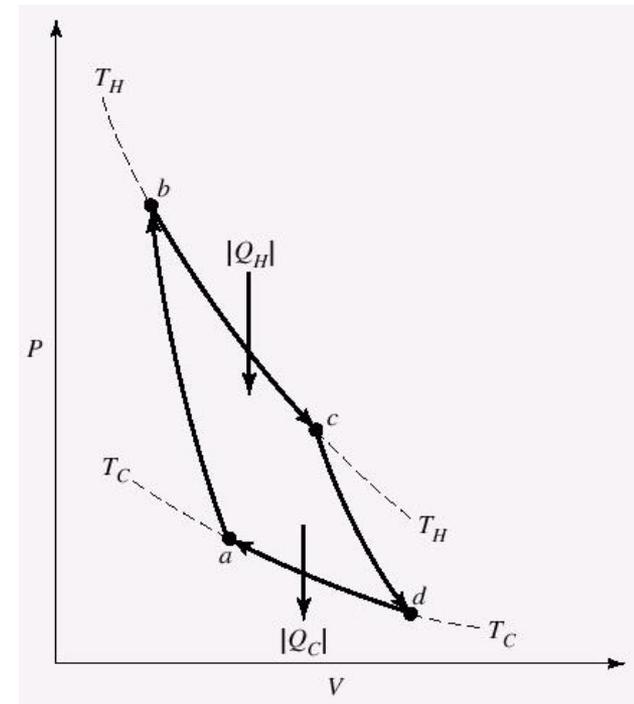
□ Derivations

- For isothermal steps : ($b \rightarrow c$, $d \rightarrow a$)

$$|Q_H| = RT_H \ln \frac{V_c}{V_b} \quad |Q_C| = RT_C \ln \frac{V_d}{V_a}$$

- For adiabatic steps : ($a \rightarrow b$, $c \rightarrow d$)

$$-\frac{C_V}{R} \frac{dT}{T} = \frac{dV}{V}$$



Ideal-Gas Temperature Scale: Carnot's Equation

□ Derivation

$$|Q_H| = RT_H \ln \frac{V_c}{V_b} \quad |Q_C| = RT_C \ln \frac{V_d}{V_a}$$

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H \ln(V_c/V_b)}{T_C \ln(V_d/V_a)}$$

$$-\frac{C_V}{R} \frac{dT}{T} = \frac{dV}{V}$$

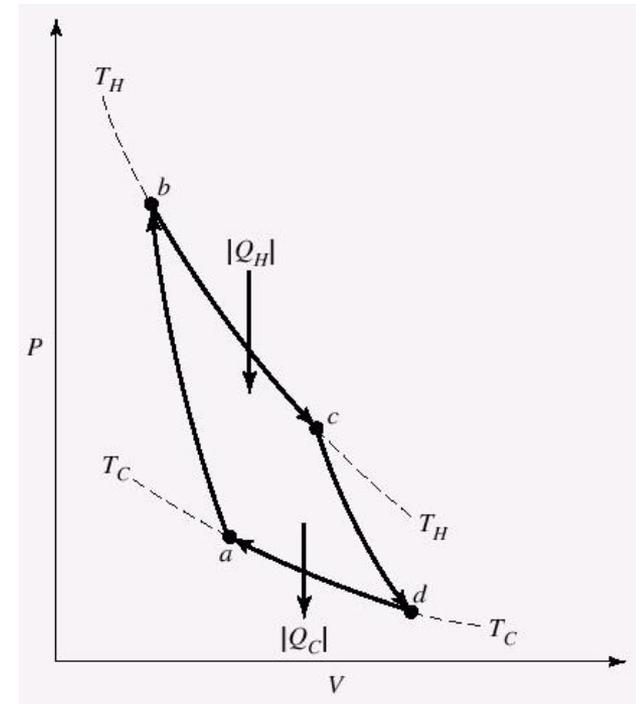
$$\int_{T_C}^{T_H} \frac{C_V}{R} \frac{dT}{T} = \ln \frac{V_a}{V_b}$$

$$\int_{T_C}^{T_H} \frac{C_V}{R} \frac{dT}{T} = \ln \frac{V_d}{V_c}$$

$$\ln \frac{V_a}{V_b} = \ln \frac{V_d}{V_c}$$



$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C}$$



Ideal-Gas Temperature Scale: Carnot's Equation

- Kelvin scale is identical to thermodynamic temperature scale

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C} \quad \psi(T) = T$$

$$\eta = 1 - \frac{|Q_C|}{|Q_H|} = 1 - \frac{T_C}{T_H}$$

Carnot's equation

- Efficiency of Carnot engine approaches 1 when $T \rightarrow -273.15 \text{ }^\circ\text{C}$
- Practical efficiency
 - Cold Reservoir : atmosphere, lake, rivers,... ($T \approx 300 \text{ K}$)
 - Hot Reservoir : combustion of fossil fuels, nuclear reactor ($T \approx 600 \text{ K}$)
 - Efficiency =
 - Actual heat engines are irreversible, the efficiency rarely exceed 0.35

Example 5.1

A central power plant, rated at 800,000 kW, generates steam at 585K and discards heat to a river at 295K. If the thermal efficiency of the plant is 70 % of the maximum possible value, how much heat is discarded to the river at rated power?

$$\eta_{max} = 1 - \frac{T_C}{T_H} = 1 - \frac{295}{585} = 0.4957 \qquad \eta = 0.7 \times 0.4957 = 0.3470$$

Since $|W| = 800,000$ kW and solving for $|Q_C|$,

$$|W| = |Q_H| - |Q_C| \qquad \eta = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|}$$

$$|Q_C| = \left(\frac{1 - \eta}{\eta} \right) |W| = \left(\frac{1 - 0.347}{0.347} \right) 800,000 = 1,505,500 \text{ kW}$$

5.4 Entropy

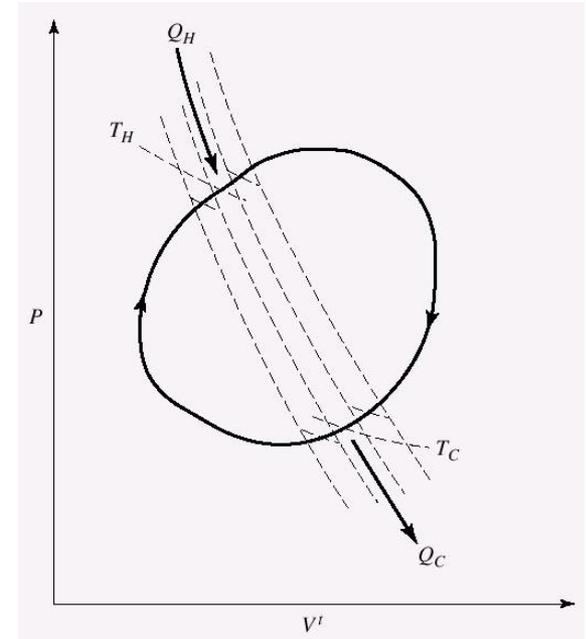
□ Q/T is related to absorption and rejection of heat by working fluid

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C} \quad \frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C} \quad \frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$$

□ Above relation also applies to other reversible cycle

- Divide the enclosed area by series of adiabatic curves
- Connect adjacent curves with short isotherms
- Each pair of adjacent adiabatic curves and their isothermal connecting curves represents a Carnot cycle

$$\frac{dQ_H}{T_H} + \frac{dQ_C}{T_C} = 0 \quad \longrightarrow \quad \oint \frac{dQ_{rev}}{T} = 0$$



5.4 Entropy

- dQ/T sum to zero for arbitrary reversible cycle → characteristics of property
 - Existence of property whose differential changes for arbitrary cycles are given by these quantities
 - Called “ENTROPY”

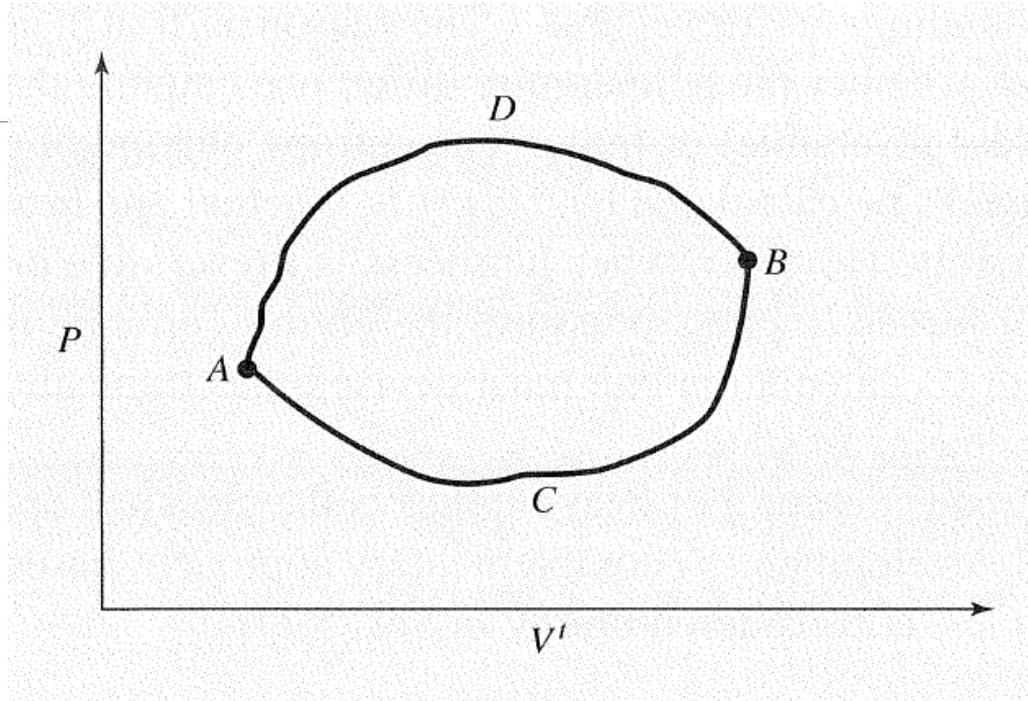
$$dS^t = \frac{dQ_{rev}}{T} \quad dQ_{rev} = TdS^t$$

- For reversible processes, integration of heat/temperature gives entropy changes

$$\Delta S^t = \int_A^B \frac{dQ_{rev}}{T} \quad \Delta S^t = S_t^B - S_t^A$$

- For irreversible processes, entropy changes are given by below equation but cannot be calculated by integral – integration should be performed along reversible path

$$\Delta S^t = S_t^B - S_t^A$$



- For reversible processes, integration of heat/temperature gives entropy changes

$$\Delta S^t = \int_A^B \frac{dQ_{rev}}{T} \quad \Delta S^t = S_t^B - S_t^A$$

- For irreversible processes, entropy changes are given by below equation but cannot be calculated by integral – integration should be performed along reversible path

$$\Delta S^t = S_t^B - S_t^A$$

Discussion of Entropy

□ Entropy owes its existence to the second law

- The first law → existence of internal energy (U)
- The second law → existence of entropy (S)

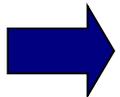
There exists a property called entropy (S), which is an intrinsic property of a system, functionally related to the measurable coordinates which characterizes the system. For reversible process, changes are given as; $dS^t = \frac{dQ_{rev}}{T}$

□ Entropy changes of reversible system;

□ Entropy changes of irreversible system;

- Alternative way ; arbitrary chosen reversible process which causes the same change

$$\Delta S^t = \int_A^B \frac{dQ_{rev}}{T}$$



Complimentary approach : molecular concept, statistical mechanics

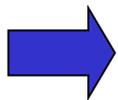
5.5 Entropy Changes of An Ideal Gas

- One mole of ideal gas undergoes mechanically **reversible** process

$$dU = dQ_{rev} - PdV$$
$$dH = dU + d(PV)$$
$$dQ_{rev} = dH - VdP = C_p^{id} dT - RT \frac{dP}{P}$$

$$\frac{dQ_{rev}}{T} = C_p^{id} \frac{dT}{T} - R \frac{dP}{P}$$
$$dS = C_p^{id} \frac{dT}{T} - R \frac{dP}{P}$$

$$\Delta S = \int_{T_0}^T C_p^{id} \frac{dT}{T} - R \ln \frac{P}{P_0}$$



Although derived for reversible process, this equation can be applied to irreversible processes causing the same change

Entropy is state function !

Example 5.3

Methane gas at 550K and 5 bar undergoes a reversible adiabatic expansion to 1 bar. Assuming methane to be an ideal gas at these conditions, find its final temperature.

For this process, $\Delta S = 0$ Then,
$$\frac{\Delta S}{R} = \int_{T_0}^T \frac{C_p^{id}}{R} \frac{dT}{T} - \ln \frac{P}{P_0} = 0$$

$$\frac{\Delta S}{R} = \int_{550}^T \frac{1.702 + 9.081 \times 10^{-3} T - 2.164 \times 10^{-6} T^2}{T} dT - \ln \frac{1}{5} = 0$$

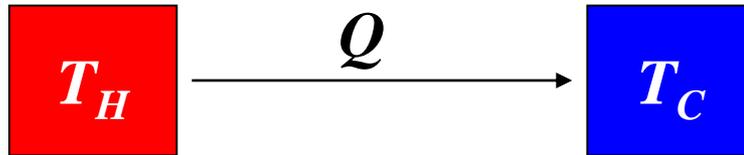
Solving for T using solver or iteration,

$$T = 411.34 \text{ K}$$

5.6 Mathematical Statement of the Second Law

□ Consider a process

- Heat is transferred from hot body to cold body



- Entropy changes of reservoirs

$$\Delta S_H^t = \frac{-|Q|}{T_H} \qquad \Delta S_C^t = \frac{|Q|}{T_C}$$

- Total entropy change

$$\Delta S_{total} = \Delta S_H^t + \Delta S_C^t = \frac{-|Q|}{T_H} + \frac{|Q|}{T_C} = |Q| \left(\frac{T_H - T_C}{T_H T_C} \right) > 0$$

- Total entropy change of irreversible process is positive.
- $T_H \rightarrow T_C$ then $\Delta S \rightarrow 0$

5.6 Mathematical Statement of the Second Law

□ Mathematical Statement of the Second Law

- Every process proceed in such a direction that the **total** entropy change associated with it is **positive**, the limiting value of zero being attained only by a reversible process.
- No process is possible for which the **total** entropy decreases.

$$\Delta S_{total} \geq 0$$

□ Work produced by engine

$$\Delta S_{total} = \frac{-|Q_H|}{T_H} + \frac{|Q_C|}{T_C} \longrightarrow |W| = -T_C \Delta S_{total} + |Q_H| \left(1 - \frac{T_C}{T_H} \right)$$
$$|W| = |Q_H| - |Q_C|$$

Example 5.4

A 40-kg steel casting ($C_p = 0.5 \text{ kJ/kg}\cdot\text{K}$) at a temperature of 450 °C is quenched in 150 kg of oil ($C_p = 2.5 \text{ kJ/kg}\cdot\text{K}$) at 25 °C. If there are no heat losses, what is the change in entropy of (a) the casting, (b) the oil, and (c) both considered together?

From the energy balance, $\Delta Q = 40 \times 0.5 \times (T - 450) + 150 \times 2.5 \times (T - 25) = 0$
 $\rightarrow T = 46.5 \text{ °C}$

(a) ΔS of the casting

$$\Delta S = m \int_{T_0}^T C_p \frac{dT}{T} = 40 \times 0.5 \times \ln \frac{273.15 + 46.52}{273.15 + 450} = -16.33 \text{ kJ} / \text{K}$$

(b) ΔS of the oil

$$\Delta S = m \int_{T_0}^T C_p \frac{dT}{T} = 150 \times 2.5 \times \ln \frac{273.15 + 46.52}{273.15 + 25} = 26.13 \text{ kJ} / \text{K}$$

(c) Total ΔS change

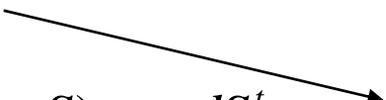
$$\Delta S = -16.33 + 26.13 = 9.80 \text{ kJ} / \text{K}$$

5.7 Entropy Balance for Open Systems

□ Entropy Balance Equation

● Important characteristics

- Entropy is **not** conserved
- Entropy generation term is required

$$\Delta(S\dot{m})_{fs} + \frac{d(mS)_{cv}}{dt} + \frac{dS_{surr}^t}{dt} = \dot{S}_G \geq 0$$


Page 176 for description

$$\frac{dS_{surr}^t}{dt} = -\sum_j \frac{\dot{Q}_j}{T_j}$$

$$\Delta(S\dot{m})_{fs} + \frac{d(mS)_{cv}}{dt} - \sum_j \frac{\dot{Q}_j}{T_j} = \dot{S}_G \geq 0$$

Just as an energy balance can be written for processes in which fluid enters, exits, or flows through a control volume (Sec. 2.12), so too can an entropy balance be written. There is, however, an important difference: *Entropy is not conserved*. The second law states that the *total* entropy change associated with any process must be positive, with a limiting value of zero for a reversible process. This requirement is taken into account by writing the entropy balance for both the system and its surroundings, considered together, and by including an *entropy-generation* term to account for the irreversibilities of the process. This term is the sum of three others: one for the difference in entropy between exit and entrance streams, one for entropy change within the control volume, and one for entropy change in the surroundings. If the process is reversible, these three terms sum to zero, making $\Delta S_{\text{total}} = 0$. If the process is irreversible, they sum to a positive quantity, the entropy-generation term.

The statement of balance, expressed as rates, is therefore:

$$\left\{ \begin{array}{l} \text{Net rate of} \\ \text{change in} \\ \text{entropy of} \\ \text{flowing streams} \end{array} \right\} + \left\{ \begin{array}{l} \text{Time rate of} \\ \text{change of} \\ \text{entropy} \\ \text{in control} \\ \text{volume} \end{array} \right\} + \left\{ \begin{array}{l} \text{Time rate of} \\ \text{change of} \\ \text{entropy in} \\ \text{surroundings} \end{array} \right\} = \left\{ \begin{array}{l} \text{Total rate} \\ \text{of entropy} \\ \text{generation} \end{array} \right\}$$

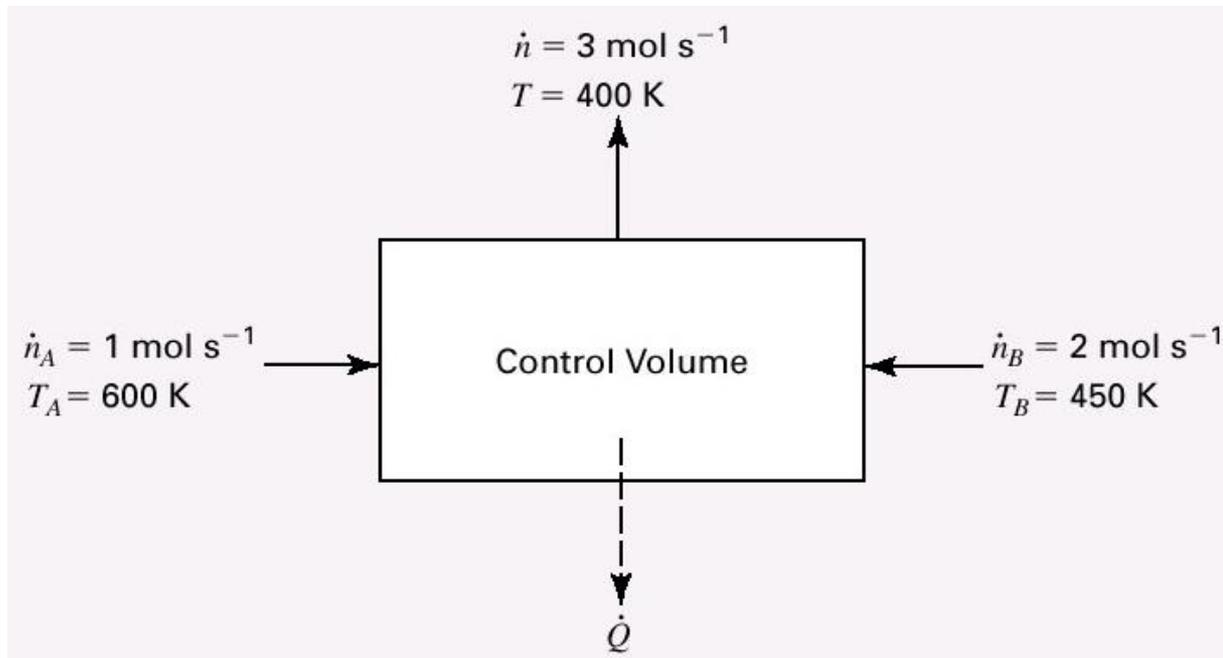
The equivalent *equation of entropy balance* is

$$\Delta(\dot{m}S)_{\text{fs}} + \frac{d(mS)_{\text{cv}}}{dt} + \frac{dS_{\text{surr}}^t}{dt} = \dot{S}_G \geq 0 \quad (5.20)$$

where \dot{S}_G is the rate of entropy generation. This equation is the general *rate* form of the entropy balance, applicable at any instant. Each term can vary with time. The first term is simply the net rate of gain in entropy of the flowing streams, i.e., the difference between the total entropy transported out by exit streams and the total entropy transported in by entrance streams. The second term is the time rate of change of the total entropy of the fluid contained within the control volume. The third term is the time rate of change of the entropy of the surroundings, resulting from heat transfer between system and surroundings.

Example 5.5

In a steady-state flow process, 1 mol/s of air at 600 K and 1 atm is continuously mixed with 2 mol/s of air at 450 K and 1 atm. The product stream is at 400 K and 1 atm. A schematic representation of the process is shown in Fig. 5.7. Determine the rate of heat transfer and the rate of entropy generation for the process. Assume that air is an ideal gas with $C_p = 7/2R$, that the surroundings are at 300 K and that kinetic- and potential-energy changes are negligible.



Example 5.5 - solution

From the energy balance on this process,

$$\Delta \left[\left(H + \frac{1}{2} u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}_s \quad \longrightarrow \quad \Delta(H\dot{m})_{fs} = \dot{Q}$$

$$\dot{Q} = \frac{7}{2} R [1 \times (400 - 600) + 2 \times (400 - 450)] = -8,729.7 \text{ J / s}$$

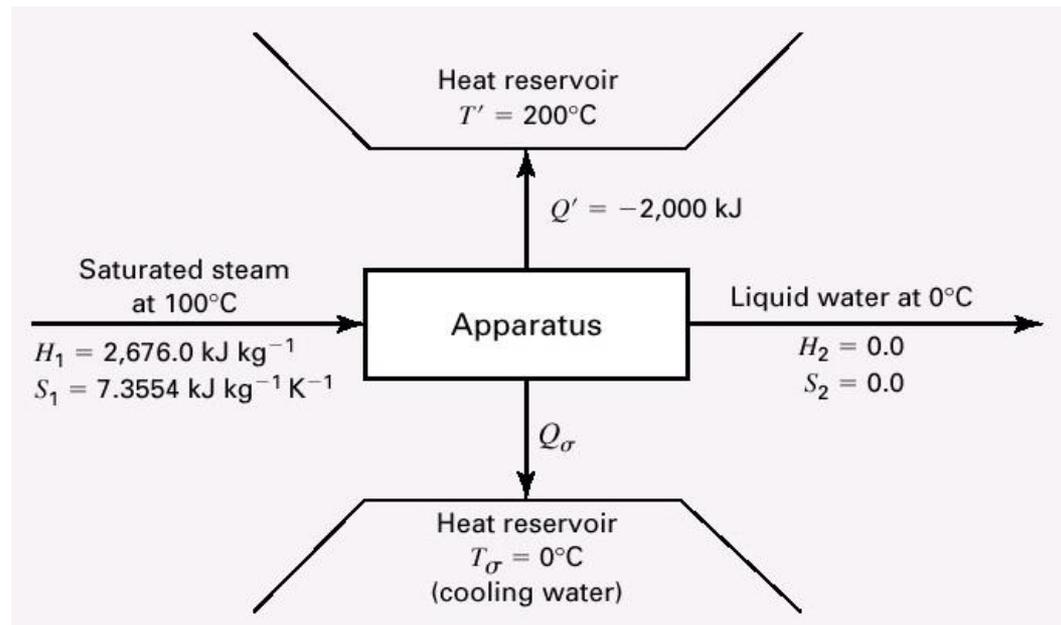
From the entropy balance,

$$\begin{aligned} \dot{S}_G &= \Delta(S\dot{m})_{fs} - \sum_j \frac{\dot{Q}}{T_\sigma} = \dot{n}_A(S - S_A) + \dot{n}_B(S - S_B) - \frac{\dot{Q}}{T_\sigma} \\ &= \dot{n}_A C_P \ln \frac{T}{T_A} + \dot{n}_B C_P \ln \frac{T}{T_B} - \frac{\dot{Q}}{T_\sigma} \\ &= (7/2)(8.314) \left[1 \ln \frac{400}{600} + 2 \ln \frac{400}{450} \right] + \frac{8729.7}{300} = 10.446 \text{ J / K} \cdot \text{s} \end{aligned}$$

Example 5.6

An inventor claims to have devised a process which takes in only saturated steam at 100 °C and which by a complicated series of steps makes heat continuously available at a temperature level of 200 °C, where 2,000 kJ of energy as heat is liberated for every kg of steam taken into the process. Show whether or not this process is possible. To give this process the most favorable conditions, assume cooling water available in unlimited quantity at a temperature of 0 °C.

Use the basis as 1 kg of steam.



Example 5.6 - solution

- The values of H and S for saturated steam at 100 °C and liquid water at 0 °C can be found in the steam table.

1. The energy balance

$$\Delta H = Q = Q' + Q_{\sigma} = -2,000 + Q_{\sigma}$$

$$\Delta H = H_2 - H_1 = 0.0 - 2,676.0$$

$$\therefore Q_{\sigma} = -676.0 \text{ kJ}$$

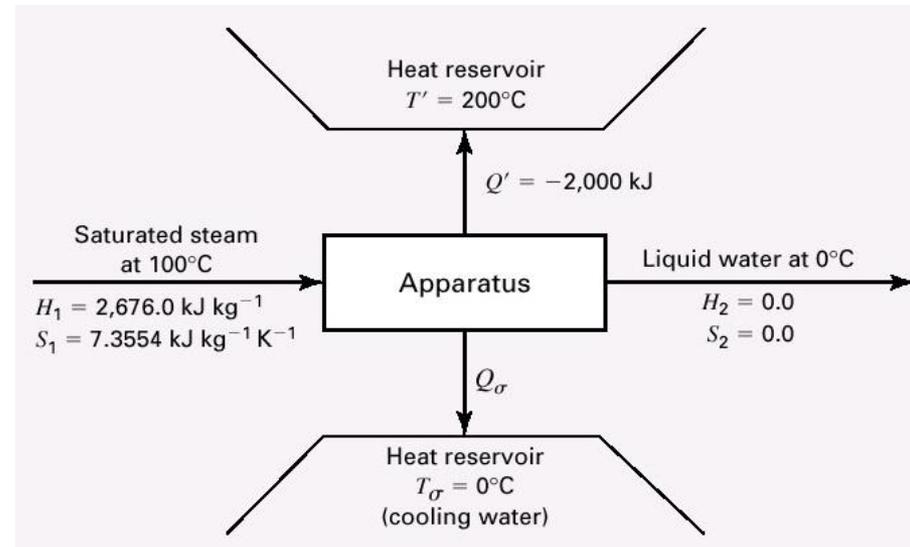
2. The entropy balance

$$\text{For steam, } \Delta S = 0.0 - 7.3554 = -7.3554 \text{ kJ/K}$$

$$\text{For the heat reservoir at } 200 \text{ }^{\circ}\text{C, } \Delta S = \frac{2,000}{200 + 273.15} = 4.2270 \text{ kJ / K}$$

$$\text{For the heat reservoir at } 0 \text{ }^{\circ}\text{C, } \Delta S = \frac{676}{0 + 273.15} = 2.4748 \text{ kJ / K}$$

$$\text{Therefore, } \Delta S_{\text{total}} = -7.3554 + 4.2270 + 2.4748 = -0.6536 \text{ kJ/K} < 0 \text{ (impossible!)}$$



Example 5.6 - solution

In this process, what is the maximum amount of heat that can be transferred to the heat reservoir at 200 °C?

1. The energy balance

$$\Delta H = Q = Q' + Q_{\sigma}$$

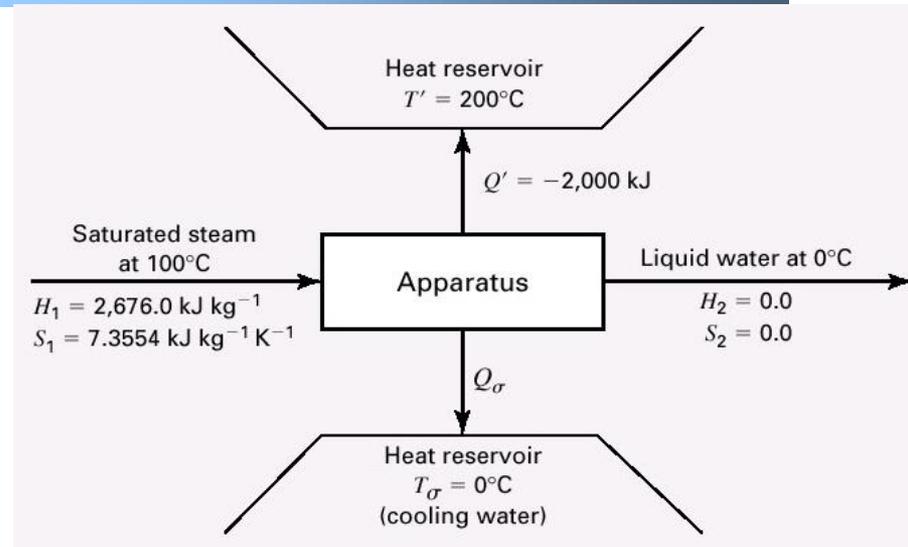
2. The entropy balance

$$\dot{S}_G = \Delta(S\dot{m})_{fs} - \sum_j \frac{\dot{Q}}{T_{\sigma}} \quad \text{assume } \dot{S}_G = 0 \quad (\text{reversible process})$$

$$\rightarrow \Delta S = \frac{Q'}{T'} + \frac{Q_{\sigma}}{T_{\sigma}}$$

Since $T' = 473.15$, $T_{\sigma} = 273.15$, $\Delta H = -2676.0$ kJ, and $\Delta S = 7.3554$ kJ

Solving for Q' gives $Q' = -1577.7$ kJ/kg



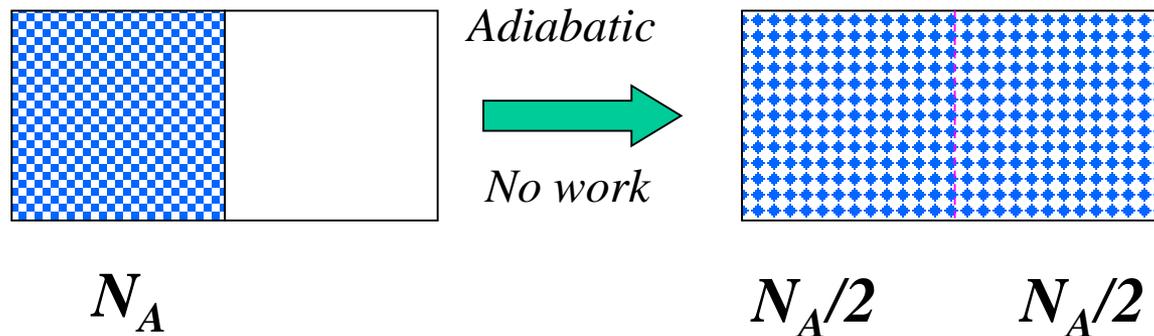
5.10 The Third Law of Thermodynamics

- ❑ Absolute value of entropy ?
- ❑ A postulate required to calculate values
 - The absolute entropy is zero for all perfect crystalline substances at zero temperature
 - At $T = 0$, $S=0$ for all substances
- ❑ Entropy calculation
 - Heat capacity and heat effect accompanying phase change are required
 - The absolute entropy of a gas at temperature T

$$S = \int_0^{T_f} \frac{(C_P)_s}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_v} \frac{(C_P)_l}{T} dT + \frac{\Delta H_v}{T_v} + \int_{T_v}^T \frac{(C_P)_g}{T} dT$$

5.11 Entropy from the Microscopic Viewpoint

- Microscopic interpretation of entropy is completely different from thermodynamic interpretation
- An Example) Adiabatic expansion of a gas



Thermodynamic Approach

$$\Delta U = C_v \Delta T = Q - W = 0$$

$$\Delta S = -R \ln \frac{P_2}{P_1} = R \ln 2$$

5.11 Entropy from the Microscopic Viewpoint

□ **Statistical Thermodynamics / Microscopic View Point**

□ **Developed by L. Boltzmann and J. W. Gibbs**

● **Number of Ways**

- Microscopic particles can be distributed among “states” accessible to them
- Based on quantum mechanical observations

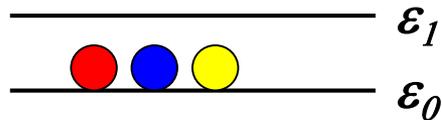
$$\Omega = \frac{N!}{(N_1!)(N_2!)(N_3!)...}$$

5.11 Entropy from the Microscopic Viewpoint

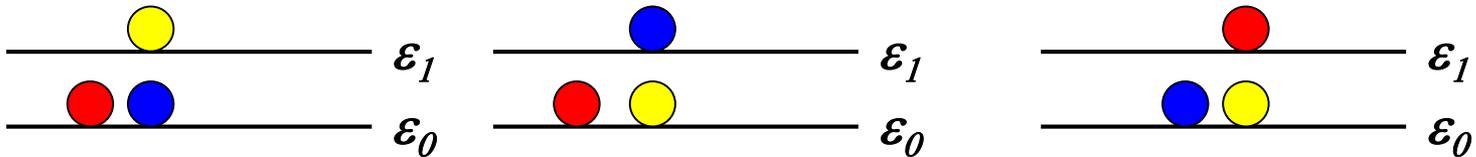
□ Weight

- Each configurations can be achieved in different ways

□ Example 1 : {3,0} configuration \rightarrow 1



□ Example 2 : {2,1} configuration \rightarrow 3



5.11 Entropy from the Microscopic Viewpoint

□ Calculation of Weight

- Weight (Ω) : number of ways that a configuration can be achieved in different ways
- General formula for the weight of $\{n_0, n_1, n_2, \dots\}$ configuration

$$\Omega = \frac{N!}{n_1!n_2!n_3!\dots} = \frac{N!}{\prod_i n_i!}$$

Example 1

$\{1,0,3,5,10,1\}$ of 20 objects

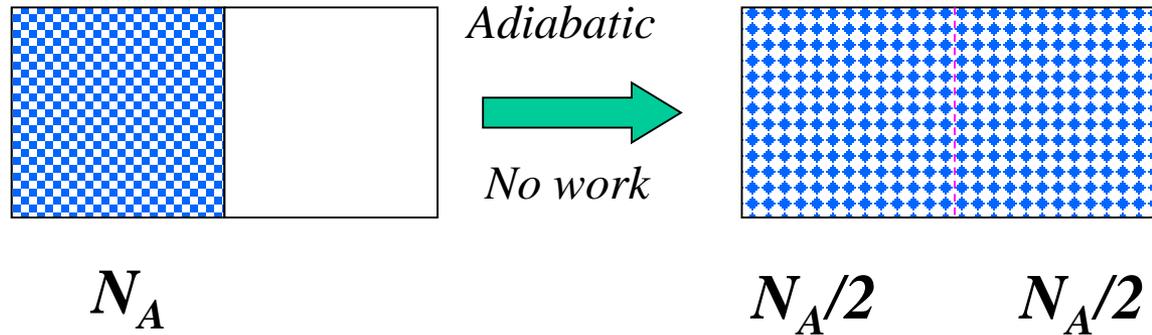
$\Omega = 9.31\text{E}8$

Example 2

$\{0,1,5,0,8,0,3,2,1\}$ of 20 objects

$\Omega = 4.19 \text{E}10$

5.11 Entropy from the Microscopic Viewpoint



$$\Omega_1 = \frac{N_A!}{(N_A!)(0!)}$$

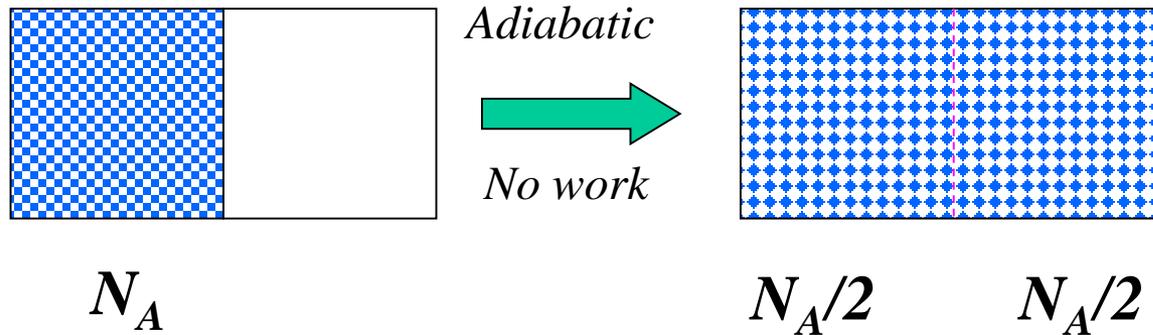
$$\Omega_2 = \frac{N_A!}{[(N_A/2)!][(N_A/2)!]}$$

□ Connection between entropy and weight

$$S = k \ln \Omega$$

$$k = R / N_A$$

5.11 Entropy from the Microscopic Viewpoint



$$S_2 - S_1 = k \ln \frac{\Omega_2}{\Omega_1} = k \ln \frac{N_A!}{[(N_A/2)!]^2} = k[\ln N_A! - 2 \ln (N_A/2)!]$$

□ **Stirling's Formula** $\ln X! = X \ln X - X$

—————> Useful formula when dealing with factorial of large numbers

$$S_2 - S_1 = k \left[N_A \ln N_A - N_A - 2 \left(\frac{N_A}{2} \ln \frac{N_A}{2} - \frac{N_A}{2} \right) \right] = k N_A \ln 2 = R \ln 2$$

Homework

Homework

- 5.4, 5.8, 5.12, 5.18(a)(c)(e), 5.22, 5.30
- Due:

Other Recommend Problems

- 5.3, 5.9, 5.10, 5.21, 5.26, 5.31