Slide 1

Second Law of Thermodynamics

- ***Implications of Second Law***
  - Limits the conversion of heat to work in a cyclic process
  - Sets the direction of spontaneous processes
  - Introduces the idealized limit of reversible processes
- ***Thermal Reservoir (Examples: Oceans, atmosphere)***
  - A large repository of heat that acts as a source or sink.
  - The reservoir temperature is virtually unaffected during heat transfer, since it has a large mass.
  - Also acts as a reversible heat source, since it contains no temperature gradients within itself.
  - Upon heat addition, only the thermal energy content of the reservoir changes, indicating that it is implicitly rigid. Therefore, by the First Law, $dU = \delta Q$.
- ***Mechanical Reservoir (Example: Large flywheel)***
  - A mechanical energy reservoir is a large body acting as a source or sink with which work can be exchanged without affecting its characteristics.

Slide 2

- ***Heat Engine***
  - A heat engine is a cyclic device in which the heat interactions with higher and lower temperature thermal energy reservoirs are converted into work interactions with mechanical energy reservoirs.
  - The efficiency η of a thermodynamic cycle is defined as the ratio of the work output to the thermal input, i.e.,

    η = Sought/Bought = W_{cycle}/Q_{in}.
- ***Refrigerator/ Heat Pump***
  - Systems in which work interactions with mechanical energy reservoirs result in heat transfer from lower– to higher–temperature thermal energy reservoirs are either heat pumps or refrigeration devices.
  - Coefficient of Performance of refrigerator/heat pump defined as $\{COP\}_{refrigeration}$ =Sought/ bought= Heat transferred from the lower temperature system/Work input.
  - $COP_{heat\ pump}$ = Sought/Bought= Heat transferred to the higher temperature system/Work input.

Slide 3

- ***Thermodynamic Cycle***
  - Final thermodynamic state after a (cyclic) process is the same as initial state ; e.g., steam power plant
- ***Mechanical Cycle***
  - Final mechanical position is same as initial position (e.g. position of piston at top of a cylinder returns back to same position after one revolution of a crank)
- ***Closed Cycle***
  - The working fluid undergoes a series of processes and returned to original state. i.e., fluid is retained in the system. e.g., Refrigeration Cycle ; Closed Cycle / Thermodynamic Cycle
- ***Open Cycle***
  - Working fluid is different from initial state at the conclusion or final state and is thrown out.

Slide 4

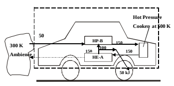
Statements of Second Law

- ***Informal Statements***
  1. The efficiency of a heat engine is less than unity
  2. An isolated system initially in a state of nonequilibrium will spontaneously achieve an equilibrium state.
- ***Kelvin-Planck Statement***
  - It is impossible to devise a machine (i.e., a heat engine) which, operating in a cycle, produces no effect other than the extraction of heat from a thermal energy reservoir and the performance of an equal amount of work.
- ***Clausius Statement***
  - It is impossible to construct a device that operates in a thermodynamic cycle and produces no effect other than the transfer of heat from a cooler to a hotter body.

Slide 5

Perpetual Motion Machines

– A machine that obeys the First Law but violates the Second Law of thermodynamics is known as a perpetual motion machine of the second kind (PMM2).



Example of PMM2

Slide 6

- ***Consequences of the Second Law***
  - ***Reversible and Irreversible Processes***
    - Presence of friction and internal gradients cause irreversibility
    - Certain processes (e.g., conversion of mechanical energy into heat energy) are irreversible as a consequence of Second Law
    - Spontaneous reversal of direction not possible for irreversible processes, as it violates Second Law, *though not First Law*.
  - ***For a reversible process,***
  - ***Corollaries of Second Law*** $\oint \frac{\delta Q}{T} = 0$
    1. The thermal efficiency of an irreversible power cycle is always less than the thermal efficiency of a reversible power cycle when each operates between the same two reservoirs.
    2. All reversible power cycles with any medium of fluid operating between the same two thermal reservoirs must have the same thermal efficiencies.

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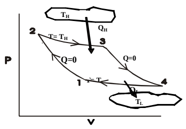

Schematic of Carnot Cycle

- ***Carnot Cycle***
  - Uses ideal gas as its working fluid
  - Consists of four quasi-equilibrium processes :
    - Adiabatic compression,
    - Isothermal heat addition Q_H from a higher–temperature reservoir at a temperature T_H ,
    - Adiabatic expansion, and
    - Heat rejection Q_L to a lower–temperature reservoir at T_L
  - Efficiency, $\eta = 1 - T_L/T_H$
  - $Q_L/Q_H = f(\Theta_L)/f(\Theta_H)$ where $T=f(\Theta)$

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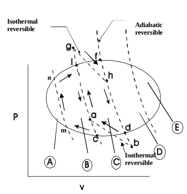

- ***Clausius Theorem***
  - Converts a reversible cycle into a series of Carnot cycles
  - For reversible processes, $\oint \frac{\delta Q}{T} = 0$
  - For irreversible processes, $\oint \frac{\delta Q}{T} < 0$

(Follows from Corollary 1)

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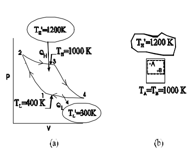

Internally reversible but externally irreversible systems

- Heat transfer across finite temperature difference implies *externally irreversible* system
- Absence of friction, internal gradients etc. ensure *internal reversibility*
- For internally reversible systems, $\oint \frac{\delta Q}{T} = 0$

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- ***Caratheodory's Axiom II***
  - Some states cannot be reached through an adiabatic process once the final volume is fixed.
- ***Entropy***
  - Mathematical definition: $\oint \frac{\delta Q_{rev}}{T} = 0 \Rightarrow \frac{\delta Q_{rev}}{T} \equiv dS$

    where S is an extensive property, ***entropy***
  - For reversible process, $\delta Q_{rev} = TdS$

    Area under a process curve on a T-S plane represents the heat transfer for a reversible process

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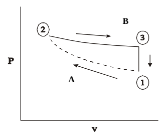

- Process 3-1 and 2-3: reversible; process 1-2: irreversible

$$\oint \frac{\delta Q_{irr}}{T} < 0 \Rightarrow \int_1^2 \frac{\delta Q}{T} + \int_2^3 \frac{\delta Q}{T} + \int_3^1 \frac{\delta Q}{T} < 0$$

- For reversible process 2-3-1

$$\int_2^3 \frac{\delta Q}{T} + \int_3^1 \frac{\delta Q}{T} = S_1 - S_2$$

- Hence for irreversible process 1-2,

$$S_2 - S_1 > \int_1^2 \frac{\delta Q}{T}$$

i.e. $$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + \delta\sigma$$

$\delta\sigma \geq 0$ is known as *entropy generation*

Slide 12

- ***Entropy Balance Equation for a Closed System***

  Infinitesimal form

  Uniform properties: $dS = \frac{\delta Q}{T} + \delta\sigma$

  Sub-systems with uniform properties: $dS = \sum_j \frac{\delta Q_j}{T_{b,j}} + \delta\sigma$

  For uniform boundary temperature: $dS = \frac{\delta Q}{T_b} + \delta\sigma$

  Integral form $S_2 - S_1 = \int \frac{\delta Q}{T_b} + \sigma_{12}$

  Rate form $\frac{dS}{dt} = \frac{\dot{Q}}{T_b} + \dot{\sigma}$

  Cyclic Process $\oint \frac{\delta Q}{T_b} \leq 0$

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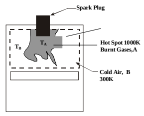


Example of Internal Irreversibility

- Choice of boundary location determines internal reversibility of system
  - For boundaries extended slightly beyond the system, $T_b = T_0$ and all irreversibilities are inside the system

Slide 14

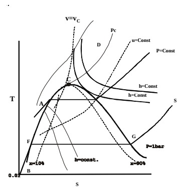
- ***Entropy of an Isolated System***
  - For an isolated system, $\frac{\delta Q}{T} = 0$
  - For irreversisble processes, dS = dσ > 0
- ***Entropy Change for Reversible Adiabatic Process***
  - For reversible process dσ =0
  - For adiabatic process $\frac{\delta Q}{T} = 0$
  - Hence, entropy change ds=0
- ***Irreversibility of a Process***
  - Heat transfer through a reversible heat engine produces work which is not obtained in an irreversible heat transfer process
  - This *loss of potential work* is known as *irreversibility* (I)
  - Irreversibility expressed as $I = T_0 \sigma$

Slide 15

- ***Evaluation of Entropy***
  - From 1st and 2nd Laws, for reversible process, δW=pdV and δQ=TdS imply **TdS = dU + pdV**
  - On a **unit mass basis**, ds = du/T + pdv/T
  - For **ideal gases**, $ds = C_v dT/T + Rdv/v$
  - Integrating, $$s_2 - s_1 = \int_{T_1}^{T_2} C_v dT + R \ln \frac{v_2}{v_1}$$
  - For **constant specific heat** $s_2 - s_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$
  - For **variable specific heat** $s(T_2, p_2) - s(T_1, p_1) = s^0(T_2) - s^0(T_1) + R \ln \frac{v_2}{v_1}$
    $$s^0(T) = \int_{T_{ref}}^{T} C_v dT$$
  - For **incompressible liquids and solids** ds **=** CdT/T

Refer to Example 1 of Example_3.pdf

Slide 16



- ***Entropy change during phase change***
  - Since temperature and pressure do not change generally during a phase change process for a pure substance, entropy change during a phase change from α to β is given by $s_\beta - s_\alpha = (h_\beta - h_\alpha)/T$

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- ***Entropy of a Mixture of Ideal Gases***
  - ***Gibbs-Dalton Law***
    - Ideal gases, partial pressure (p_k) of each component related to the total pressure (P) by $p_k = X_k P$, where X_k is the mole fraction of the species
    - Entropy of the mixture calculated as

$$S(T,P,N_k) = \sum S_k(T,p_k,N_k) = \sum N_k \bar{s}_k(T,p_k)$$

- ***Entropy Change for Incompressible Liquids***
  - $u = c\,(T - T_{ref})$, and $s = c \ln(T/T_{ref})$ lead to
    $s = c \ln\{(u/c + T_{ref})/T_{ref}\}$; $u = c\,T_{ref}\,(\exp(s/c) - 1)$ and
    $h = u + Pv_{ref} = c\,T_{ref}\,\{\exp(s/c) - 1\} + Pv_{ref}$

- ***Third Law of Thermodynamics***
  - The Third Law states that a crystalline solid substance at an absolute temperature of zero (i.e., 0 K) possesses zero entropy.

Slide 18

- ***Entropy Balance for an Open System***
  - For single inlet, single exit and single heat source

$$\frac{dS_{cv}}{dt} = \dot{m}_i s_i - \dot{m}_e s_e + \frac{\dot{Q}_{cv}}{T} + \dot{\sigma}$$

  - For multiple inlets, multiple exits and multiple heat sources

$$\frac{dS_{cv}}{dt} = \sum \dot{m}_i s_i - \sum \dot{m}_e s_e + \sum \frac{\dot{Q}_j}{T_j} + \dot{\sigma}$$

  - On a molar basis

$$\frac{dS_{cv}}{dt} = \sum \dot{N}_i \bar{s}_i - \sum \dot{N}_e \bar{s}_e + \sum \frac{\dot{Q}_j}{T_j} + \dot{\sigma}$$

  - For multicomponent systems,

$$\frac{dS_{cv}}{dt} = \sum \dot{N}_k \bar{s}_{k,i} - \sum \dot{N}_k \bar{s}_{k,e} + \sum \frac{\dot{Q}_j}{T_j} + \dot{\sigma}$$

$$\bar{s}_k(T,P) = \bar{s}_k^0(T) - \ln(PX_k)$$

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- For reversible systems $\frac{dS_{cv}}{dt} = \sum \dot{m}_i s_i - \sum \dot{m}_e s_e + \sum \frac{\dot{Q}_j}{T_j}$
- For steady state $\sum \dot{m}_i s_i - \sum \dot{m}_e s_e + \sum \frac{\dot{Q}_j}{T_j} + \dot{\sigma} = 0$
- For single inlet and exit at steady state on a unit mass basis

$$s_i - s_e + \sum \frac{\dot{Q}_j}{T_j} + \sigma_m = 0$$

Refer to Examples 2 and 3 of Example_3.pdf

Slide 20

- ***Evaluation of Entropy for a Single Component System for a Control Volume***
  - Illustration with a *reversible charging* process, i.e. *no mass outflow* and *no entropy generation*
  - Known initial (T_1, P_1 , N_1) and final (T_2, P_2 , N_2) states
  - Over a small time,

$$dU = dN_i \bar{h}_i + \delta Q - \delta W$$

$$dS = dN_i \bar{s}_i + \delta Q / T_b$$

  - Mass Conservation: $dN = dN_i$
  - Reversible Process: $\delta W = PdV$
  - Substituting $dN = dN_i$ and eliminating δQ,

$$dU = TdS - PdV + dN(\bar{h} - T\bar{s})$$

$$dU = TdS - PdV + \mu dN$$

  - $\mu = \bar{h} - T\bar{s}$ is the *chemical potential*

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- ***Multicomponent Systems***
  - For multicomponet systems

$$dU = TdS - PdV + \sum_k \mu_k dN_k$$

Alternative forms

$$dH = TdS + VdP + \sum_k \mu_k dN_k$$

$$dA = -SdT - PdV + \sum_k \mu_k dN_k$$

$$dG = -SdT + VdP + \sum_k \mu_k dN_k$$

In the above expressions,

A = U-TS is the *Helmholtz Function* and

G = H-TS is the *Gibbs Function*

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Energy Fundamental Equation

$$dU = TdS - PdV + \sum_k \mu_k dN_k$$

From energy fundamental equation, $U = U(S,V,N_1,N_2, \ldots ,N_k)$, i.e.,

$$dU = \left(\frac{\partial U}{\partial S}\right) dS + \left(\frac{\partial U}{\partial V}\right) dV + \sum_k \left(\frac{\partial U}{\partial N_k}\right) dN_k$$

Comparing the two equations and using Euler equation,

$$\left(\frac{\partial U}{\partial S}\right) S + \left(\frac{\partial U}{\partial V}\right) V + \sum_k \left(\frac{\partial U}{\partial N_k}\right) N_k = U$$

$U = ST - PV + \mu_1 N_1 + \mu_2 N_2 + \ldots,.$

Similarly,

$H = ST + \mu_1 N_1 + \mu_2 N_2 + \ldots,.$

$A = - PV + \mu_1 N_1 + \mu_2 N_2 + \ldots,.$

$G = \mu_1 N_1 + \mu_2 N_2 + \ldots,.$

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- ***Gibbs-Duhem Relation***

$$SdT - VdP + N_1 d\mu_1 + N_2 d\mu_2 + \ldots = 0$$

- ***Entropy Fundamental Equation***

$$dS = dU + \frac{P}{T} dV + \frac{1}{T} \sum_k \mu_k dN_k$$

- ***Reversible Work in a Steady Flow System***

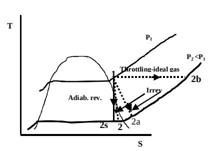
For reversible steady flows with negligible changes in KE and PE,

$$Tds - \delta w = dh$$

$Tds = dh - vdP$ implies $\delta w = -vdP$

Refer to Examples 5 through 9 of Example_3.pdf

Slide 24



- ***Isentropic Efficiency***

Adiabatic Processes

η_{ad} = actual work output ÷ isentropic work output = w/w_s (expansion)

η_{ad} = isentropic work input ÷ actual work input = w_s/w (compression).

$w = |h_1 - h_2|$, $w_s = |h_1 - h_{2s}|$.

Isothermal Efficiency

$\eta_{iso} = w/w_{iso}$ (expansion)

$\eta_{iso} = w_{iso}/w$ (compression)

Slide 25

- ***Entropy Balance in Integral Form***

$$\frac{d}{dt}\left(\int_{CV}\rho s dV\right) = \int \rho s \mathbf{V}.d\mathbf{A} + \int_{CV}\dot{\sigma} dV$$

- ***Entropy Balance in Differential Form***
  - Applying *Gauss Divergence Theorem*,

$$\frac{d}{dt}(\rho s) + \nabla.(\rho s \mathbf{V}) = -\nabla.\left(\frac{\mathbf{q}}{T}\right) + \sigma_{CV}$$

  - Using *mass conservation equation* it simplifies to

$$\rho\frac{ds}{dt} + \rho\mathbf{V}.\nabla s = -\nabla.\left(\frac{\mathbf{q}}{T}\right) + \sigma_{CV}$$

  - Applying *Fourier Law*,

$$\rho\frac{ds}{dt} + \rho\mathbf{V}.\nabla s = \nabla.\left(\frac{\lambda\nabla T}{T}\right) + \sigma_{CV}$$

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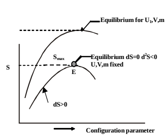
- ***Entropy Generation for Steady Flow of Ideal Gases***
  - Neglecting temperature and velocity gradients, $\dot{\sigma}_{CV} = \frac{R\rho v}{x}\ln\left(\frac{P_i}{P}\right)$
- ***Entropy Generation for Solids***

$$\dot{\sigma}_{CV} = -\frac{\mathbf{q}.\nabla T}{T^2} > 0$$

The above equation shows that flow of heat along the direction of decreasing temperature is a consequence of Second Law

Slide 27



- ***Entropy Maximum Principle***

  For an isolated system with fixed U, V and m during a process,

  $dS = d\,\sigma > 0$

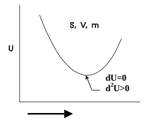
  At equilibrium (for fixed U,V,m)

  $dS = 0$

  Hence, $d^2S < 0$

  Spontaneous processes are irreversible

Slide 28



- ***Energy Minimum Principle***
  - For an isolated system with fixed S, V and m during a process with only PdV work,

    $dU = T_b dS - PdV - T_b\,\delta\sigma$

    $= -T_b d\sigma < 0$

  At equilibrium (for fixed S,V,m)

  $dU=0$

  Hence, $d^2U>0$

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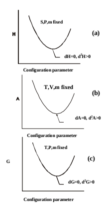


- ***Enthalpy Minimum Principle***

  At equilibrium (for fixed S,P,m)

  $dH=0$ and $d^2H>0$
- ***Helmholtz Function Minimum Principle***

  At equilibrium (for fixed T,V,m)

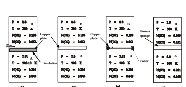
  $dA=0$ and $d^2A>0$
- ***Gibbs Function Minimum Principle***

  At equilibrium (for fixed T,P,m)

  $dG=0$ and $d^2G>0$

  Refer to Example 10 of Example_3.pdf

Slide 30



a. Initial state of a composite system;

b. Thermal equilibration with a copper plate in contact;

c. Mechanical equilibration with a movable partition;

d. Chemical equilibration with a porous partition.

$dU_A + dU_B = 0$; $dN_{1,A} + dN_{1,B} = 0$

$dV_A + dV_B = 0$; $dN_{2,A} + dN_{2,B} = 0$

$$dS_A = \frac{1}{T_A}dU_A + \frac{P_A}{T_A}dV_A + \frac{1}{T_A}\sum_k \mu_{k,A} dN_{k,A}$$

$$dS_B = \frac{1}{T_B}dU_A + \frac{P_B}{T_B}dV_B + \frac{1}{T_A}\sum_k \mu_{k,A} dN_{k,A}$$

For isolated system, $dS = dS_A + dS_B \geq 0$

Hence,

$$dS_A = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)dU_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)dV_A + \sum_k \left(\frac{\mu_{k,A}}{T_A} - \frac{\mu_{k,B}}{T_B}\right)dN_{k,A} \geq 0$$

At equilibrium, $dS = 0$. Hence

Thermal Equilibrium: $T_A=T_B$

Mechanical Equilibrium: $P_A=P_B$ (for same initial temperature)

Chemical Equilibrium: $\mu_A= \mu_B$ (for same initial pressure and temperature)