Chapter 12. The laws of thermo-dynamics

12.1. Work and heat in a thermodymanic process

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12.1. Work and heat in a thermodymanic process

- Energy can be transferred to a system by **heat** and by **work** done on the system.
- State of a system:

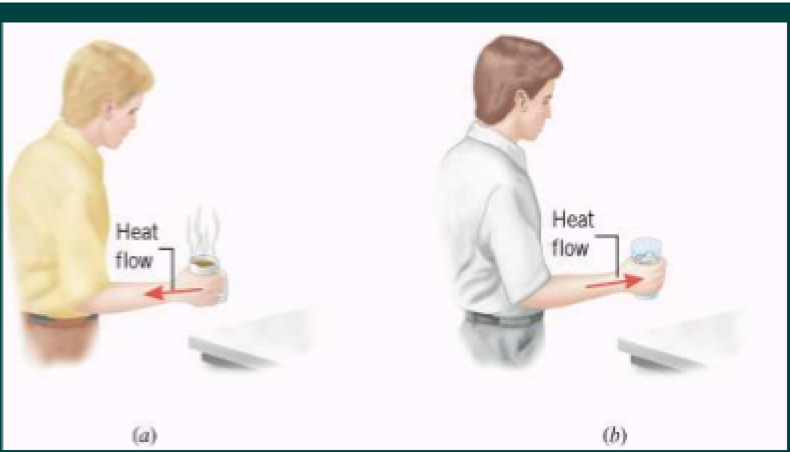
+ Description of the system in terms of state variables

Pressure, P.	Unit: Pa
Volume, V	Unit: m^3
Temperature, T	Unit: K
Internal Energy, U	Unit: J

+ A macroscopic state of an isolated system can be specified only if the system is in internal thermal equilibrium

12.1.1. Heat, Q

Heat is energy that flows from a higher-temperature object to a lower-temperature object because of the difference in temperatures.



Units for Heat

- SI unit for heat is the joule, J.
- Calorie is another unit for heat. It comes with a lower case and an upper case.
- Nutritionists use the word "Calorie," with a capital C, to specify the energy content of foods.
- The cgs unit of heat is the calorie, with a lower case. One calorie (1 cal) is defined as the amount of heat needed to raise the temperature of one gram of water by one Celsius degree.

1 food Calorie = 1000 calories = 1 kcal

1 cal

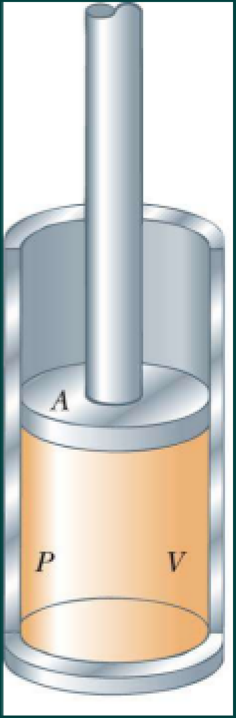
12.1.2. Work, W

- **Work** is an important energy transfer mechanism in thermodynamic systems

(Heat is another energy transfer mechanism)

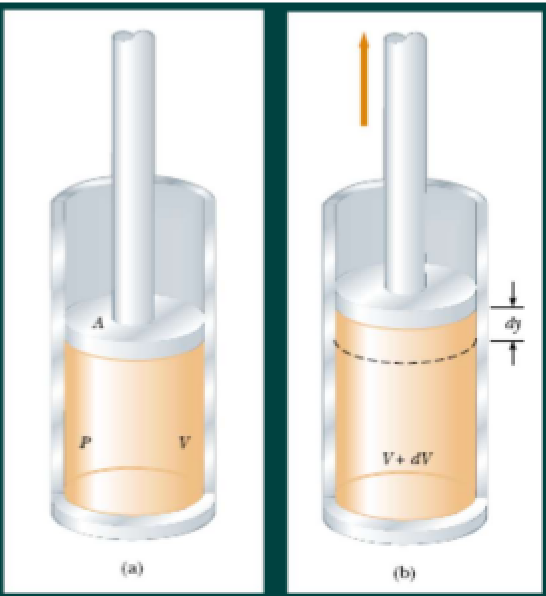
Example: gas cylinder with piston

- The gas is contained in a cylinder with a moveable piston.
- The gas occupies a volume V and *exerts pressure* *P* on the walls of the cylinder and on the piston.
- Work done if the piston move.



Work done by a gas

- Consider a gas contained in a cylinder fitted with a movable piston.
- At equilibrium, the gas occupies a volume *V* and exerts a uniform pressure *P* on the cylinder's walls and on the piston. If the piston has a cross-sectional area *A*, force exerted by the gas on the piston is : $F=PA$



- When the gas expands quasi-statically (slowly enough to allow the system to remain essentially in thermal equilibrium at all times)

As the piston moves up a distance *dy*, the work done by the gas on the piston:

$$dW' = Fdy \quad = PAdy \qquad = PdV$$

Work done by a gas (cont.)

- The work done by the gas on the piston

$$dW' = PdV$$

- If the gas expands : $dV > 0$

  → the work done *by* the gas : $dW' > 0$

- If the gas were compressed : $dV < 0$

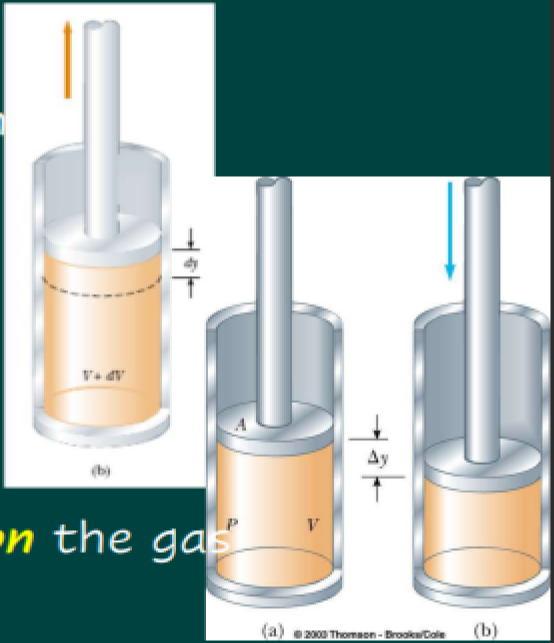
  → the work done by the gas $dW' < 0$

(which can be interpreted as work done **on** the gas **$dW > 0$**)

- When the volume remains constant:

  → No work is done on the gas

- Suppose : **P = const : *isobaric* process** $P(V_f - V_i)$



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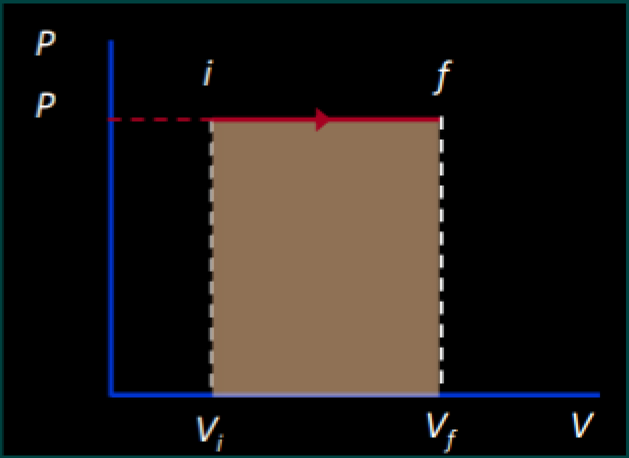
- The work done by the gas equals the area under the *PV* curve.

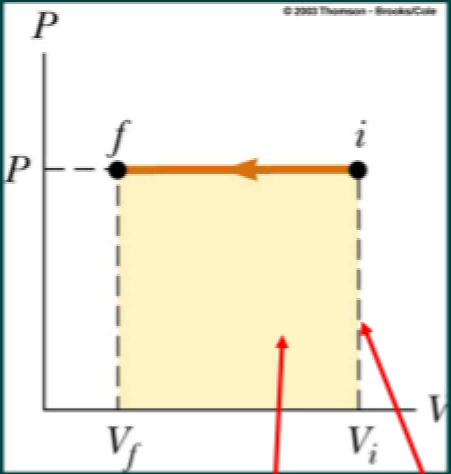


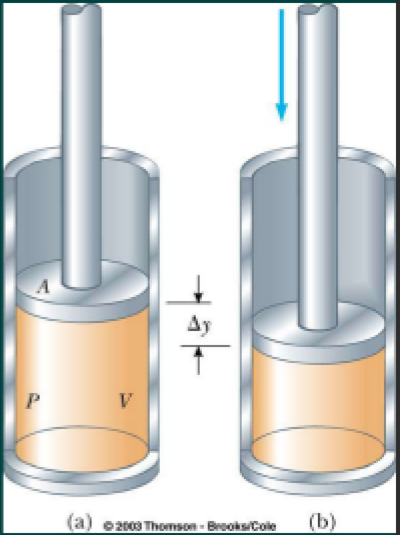
Work done by a gas (cont.)

If the gas were compressed : $dV < 0$

→ the work done **by** the gas: $dW' < 0$

(which can be interpreted as work done ***on*** the gas $dW > 0$)





$W = - P\,\Delta V > 0$ (and $W' < 0$)

Work = Area under the curve

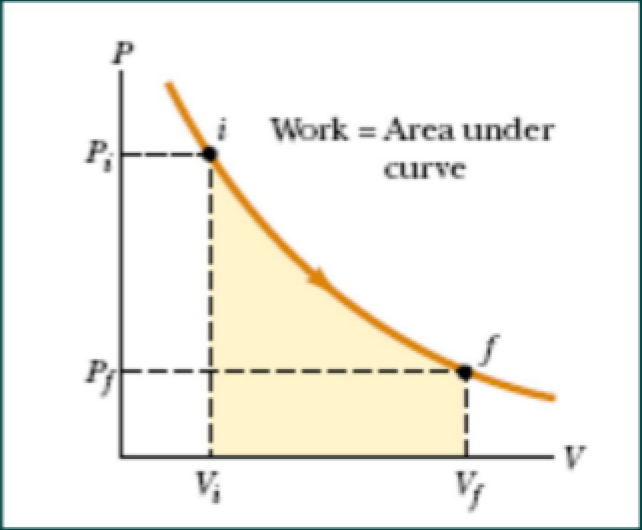
Work done on the gas

Work done by a gas (cont.)

- The total work done by the gas as its volume changes from V_i to V_f is given by the integral:

$$\boxed{W' = \int_{V_i}^{V_f} P\,dV}$$

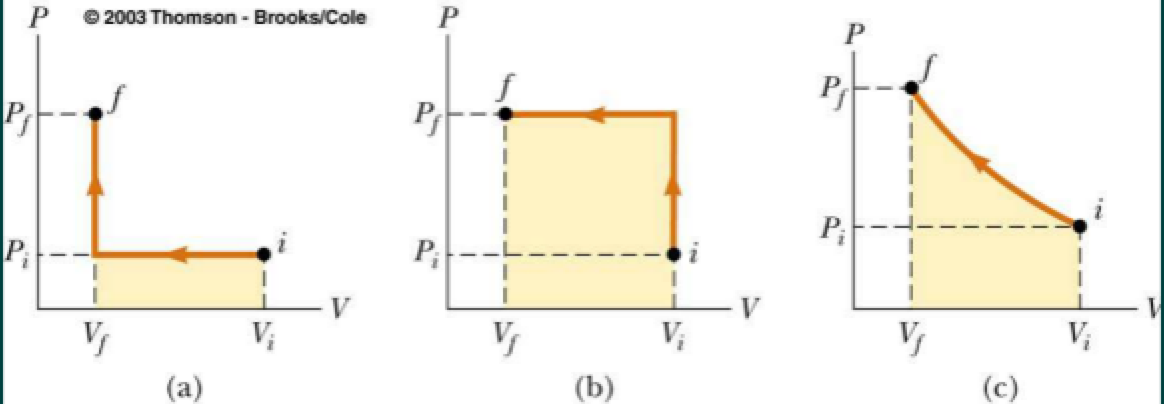
- The work done by a gas in the expansion from an initial state to a final state is the area under the curve connecting the states in a *PV* diagram



Work done by a gas (cont.)

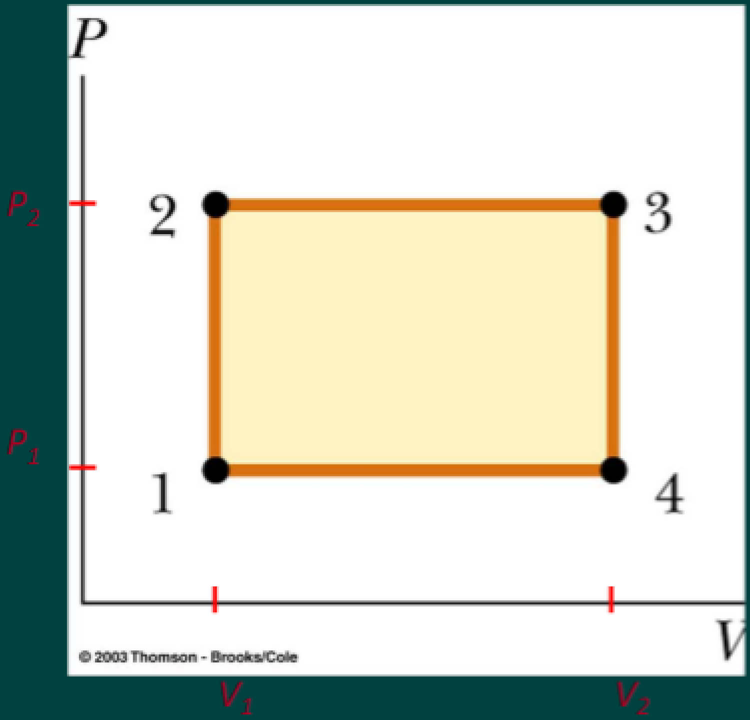
PV Diagrams

- The curve on the diagram is called the ***path*** taken between the initial and final states
- **The work done depends on the particular path**
  - Same initial and final states, but different amounts of work are done



Question

Find work done by the gas in this cycle.



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Work is equal to the enclose area :

$$W' = (p_2 - p_1)(V_2 - V_1)$$

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12.2. The First Law of Thermodynamics

- The law was stated by Rudolf Clausius in 1850. The change in internal energy of a system is equal to the **heat added to** the system plus the **work done on** the system.

$$\boxed{\Delta U = Q + W} \qquad \text{or} \qquad dU = \delta Q + \delta W$$

- The change, $\Delta U = U_{final} - U_{initial}$, is the same as the increase in internal energy.
- W′ is the work done **by** the system

$$Q = \Delta U - W = \Delta U + W'$$

Note that:

- The First Law is a general equation of Conservation of Energy
- There is **no** practical, macroscopic, distinction between the results of energy transfer by heat and by work
- Q and W are related to the properties of state for a system

Note that:

- The work W' (W) done **by (or on)** the system depends not only on the initial and final states, but also on the intermediate states, that is, ***on the path***
- Like work, heat Q depends not only on the initial and final states but also ***on the path***
- While Q and W depend on the path, $\Delta U = Q + W$ is ***independent of path***. The change in internal energy of a system during any thermodynamic process depends only on the initial and final states, not on the path leading from one to the other.

Note that:

- When a system undergoes an *infinitesimal* change in state in which a small amount of *energy dQ* is transferred by heat and a small amount of *work dW* is done **on** the gas, the *internal energy* changes by a small amount :

$$\boxed{dU = dQ + dW}$$

(first law of thermodynamics for infinitesimal processes)

- Because *dQ* and *dW* are *inexact differentials*

$$\longrightarrow \boxed{dU = \delta Q + \delta W}$$

$$dU = \delta Q - pdV$$

Chapter 12. The laws of thermo-dynamics

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12.3. Work and heat in equilibrium processes

♣ Equilibrium states

- For an ideal gas, the variables N, p, V , and T are related by the EOS. If N is fixed, only two of them are independent.
- In case p and V are chosen as independent variables, each state is represented by a point in the PV diagram. However, we can only represent equilibrium states..

Each variable has a single value in an equilibrium state, and its change between any two equilibrium states is single-valued.

12.3. Work and heat in equilibrium processes (cont.)

♣ Equilibrium processes

An equilibrium process is a series of equilibrium states.

- Each equilibrium process is represented by a curve segment in the PV diagram.
- In practice, a quasi-static process (a sufficiently slow process) can be considered as an equilibrium process.

♣ **Work done** in an equilibrium process (quasi-static work):

$$dW = -pdV \rightarrow W = -\int_1^2 pdV \quad \text{(path dependent)}$$

- This work is equal to the area under the pV curve.

♣ Heat

$$dQ = dU - dW = dU + dW' = dU + pdV$$

12.3. Work and heat in equilibrium processes

12.3.1. Isothermic process: T=const => dU = 0

An isothermic process is a constant-temperature process: $T = \text{const}$

- Equation: $PV = \boldsymbol{const}$

- Work done by the system:

$$W' = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \boldsymbol{nRT} \frac{dV}{V} = \boldsymbol{nRT} \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\boxed{W' = nRT \ln \frac{V_2}{V_1}}$$

$$\boxed{W' = nRT \ln \frac{P_1}{P_2}}$$

Because:

$$\boldsymbol{P_1 V_1 = P_2 V_2}$$

- When a system expands : work W' is positive.
- When a system is compressed, its volume decreases and it does negative work on its surroundings

- **Heat**:

$$\boxed{\delta Q = -dW}$$

$$\boxed{Q = -W = W' = n.RT.ln\frac{V_2}{V_1}}$$

12.3.2. Isochoric Process: V=const

An isochoric process is a constant-volume process:

$$V = \text{const}$$

- Equation: $\frac{P}{T} = const$
- Work: $W = 0$ (and $W' = 0$)
- **Heat**:

$$\boxed{Q = \Delta U = U_2 - U_1 = \frac{M}{\mu}\frac{i}{2}R.\Delta T}$$

$$\boxed{\delta Q = dU = \frac{M}{\mu}\frac{i}{2}R.dT}$$

In an isochoric process, all the energy added as heat remains in the system as an increase in internal energy.

Example: Heating a gas in a closed constant-volume container

12.3.2. Isochoric Process: V=const

- **Definition**: **Molar heat capacity** at constant volume

$$\boxed{C_V = \frac{\mu}{M}\left(\frac{\delta Q}{dT}\right)_V = \frac{i}{2}R}$$

Recall: Molar heat capacity is heat need to supply to rise temperature of 1 mole of the gas by 1°C (1 degree)

12.3.3. Isobaric Process: P=const

An isobaric process is a constant-pressure process:

P = const

- **Equation:** $\frac{V}{T} = const$
- **Work:** $W = -P\Delta V$ (and $W' = P\Delta V = \frac{M}{\mu} R.\Delta T$)
- **Heat:** $$\boxed{Q = \Delta U - W = \frac{M}{\mu}\frac{i}{2} R.\Delta T + P\Delta V = \frac{M}{\mu}(\frac{i}{2} + 1) R.\Delta T}$$

$$\boxed{\delta Q = dU + pdV = \frac{M}{\mu}\left(\frac{i}{2} + 1\right) R.dT =}$$

- **Definition**: Molar heat capacity at constant pressure

$$\boxed{C_P = \frac{\mu}{M}\left(\frac{\delta Q}{dT}\right)_P = \left(\frac{i}{2} + 1\right) R}$$

Heat capacity ratio:

- **Heat capacity ratio** (adiabatic index)

$$\boxed{\gamma = \frac{C_P}{C_V}}$$

- **For ideal gas:**

$$\boxed{C_V = \frac{i}{2}R}$$

$$\boxed{\gamma = \frac{i+2}{i}}$$

$$\boxed{C_P = \left(\frac{i}{2} + 1\right)R}$$

12.3. Work and heat in equilibrium processes (continues)

12.3.4. Adiabatic Process

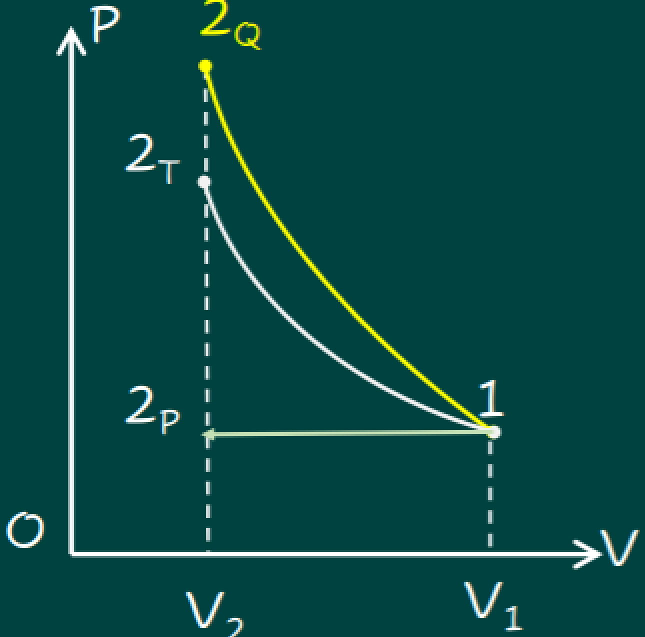
An adiabatic process is defined as one with **no heat transfer** into or out of a system : $Q = 0$

(We can prevent heat flow either by surrounding the system with thermally insulating material or by carrying out the process so quickly that there is not enough time for appreciable heat flow)

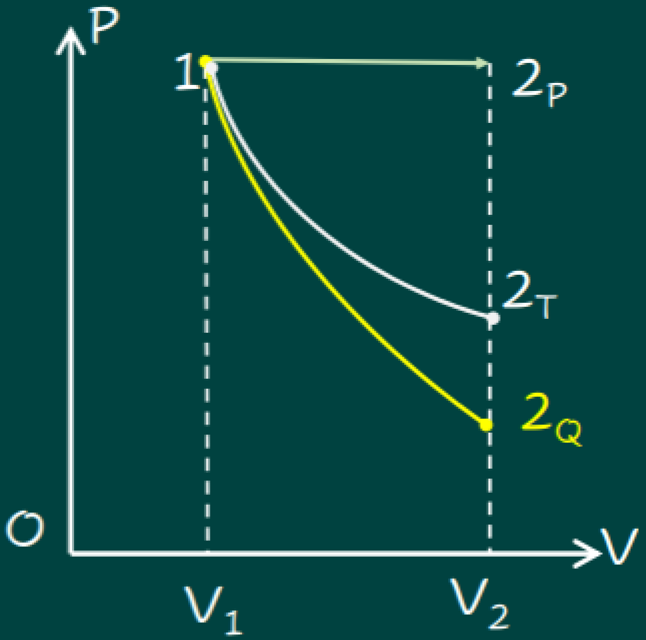
$$\boxed{\Delta U = U_2 - U_1 = W}$$

- When a system expands adiabatically :
  $W < 0$ (the system does work on its surroundings $W' > 0$)
  $\Delta U < 0$ (the internal energy decreases)
- When a system is compressed adiabatically :
  $W > 0$ (work is done on the system)
  (work is done on the system by its surroundings)
  $\Delta U > 0$ (the internal energy increases)

Camparing PV curve of isobaric and adiabatic process



Compression



Expansion

12_Q: temperature increases
12_p : temperature decreases

12_Q: temperature decreases
12_p : temperature increases

12.3. Work and heat in equilibrium processes (continues)

12.3.4. Adiabatic Process (cont.)

- **Equation:** $PV^{\gamma} = const$

  or: $TV^{\gamma-1} = const$

- **We have relation:** $dU = \delta A + \delta Q = \delta A$ và $\delta Q = 0$

  where , $U = \frac{M}{\mu}\frac{iR}{2}T = \frac{M}{\mu}C_V T$, and $\delta A = -pdV$

$=> \frac{M}{\mu}\frac{iR}{2}dT = -pdV = -\frac{M}{\mu}\frac{RT}{V}dV$ hay : $\frac{i}{2}dT = -T\frac{dV}{V}$

$\frac{dT}{T} + \frac{2}{i}\frac{dV}{V} = 0 \Leftrightarrow \ln T + \frac{2}{i}\ln V = const \Rightarrow \ln(T.V^{\frac{2}{i}}) = const$

Knowing that, $\frac{2}{i} = \frac{R}{C_V} = \frac{C_p - C_V}{C_V} = \gamma - 1$

☞ **Equation**

$$\boxed{T.V^{\gamma-1} = const}$$

$$\begin{cases} T.V^{\gamma-1} = T_1.V_1^{\gamma-1} = T_2.V_2^{\gamma-1} & (1) \\ p.V^{\gamma} = p_1.V_1^{\gamma} = p_2.V_2^{\gamma} & (2) \\ Tp^{\frac{1-\gamma}{\gamma}} = T_1 p_1^{\frac{1-\gamma}{\gamma}} = T_2 p_2^{\frac{1-\gamma}{\gamma}} & (3) \end{cases}$$

12.3. Work and heat in equilibrium processes (continues)

12.3.4. Adiabatic Process (cont.)

☞ Work done ON the system::

Because: $Q = 0$ => $W = \Delta U - Q = \Delta U = \frac{M}{\mu}\frac{iR}{2}\Delta T$

$$W = \frac{p_1 V_1^{\gamma}\left(V_2^{1-\gamma} - V_1^{1-\gamma}\right)}{\gamma - 1}$$

$$A = \frac{p_2 V_2^{\gamma} V_2^{1-\gamma} - p_1 V_1^{\gamma} V_1^{1-\gamma}}{\gamma - 1} = \frac{p_2 V_2 - p_1 V_1}{\gamma - 1} = \frac{P_1 V_1 (T_2 - T_1)}{(\gamma - 1) T_1}$$

An example

12.3.4. Cyclical Process: chu trình (kín)

A process that eventually returns a system to its initial state is called a cyclic(al) process. For such a process, the final state is the same as the initial state

The total internal energy change must be zero :

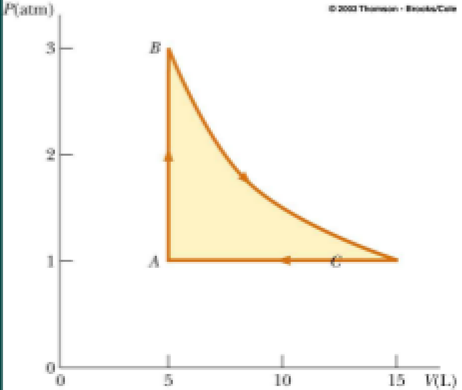
$$\Delta U = U_2 - U_1 = 0 \; ; \; U_2 = U_1$$

From the first law : $\Delta U = Q + W$ $\longrightarrow$ $Q = -W = W'$

If a net quantity of work *W'* is done **BY** the system during this process, an equal amount of energy must have flowed **into** the system as heat *Q*.

An example:

- ► This is an ideal monatomic gas confined in a cylinder by a moveable piston
- ► A to B : isovolumetric process which increases the pressure
- ► B to C : isothermal expansion and lowers the pressure
- ► C to A : isobaric compression
- ► The gas returns to its original state at point A



12.3.4. Cyclical Process (Cont.)

A cyclic process: clockwise
=> in a HEAT ENGINE

Net work done by the gas in the system:
W' = the area enclosed.

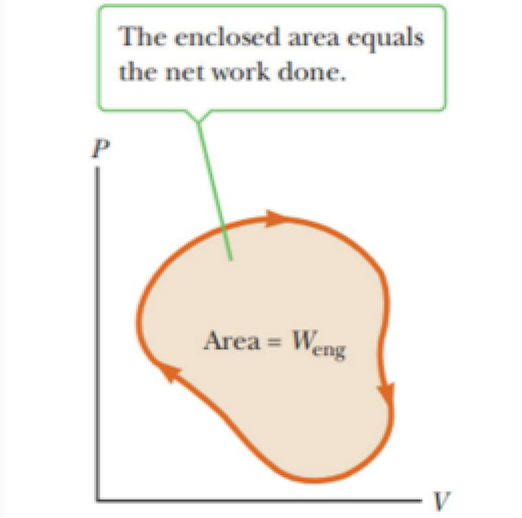

The enclosed area equals the net work done.

Figure 12.12 The *PV* diagram for an arbitrary cyclic process.

Review of 12.3. Work and heat in equilibrium processes

12.3.1. Isothermic process: T=const; dU = 0, PV=const

$$Q = -W = W' = n.RT.ln\frac{V_2}{V_1}$$

12.3.2. Isochoric Process: V=const $\Rightarrow$ P/T=const

W=0, $Q = \Delta U = U_2 - U_1 = \frac{M}{\mu}\frac{i}{2}R.\Delta T$; $C_V = \frac{i}{2}R$

12.3.3. Isobaric Process: P=const $\Rightarrow$ V/T=const

$$W = -P\Delta V = -\frac{M}{\mu}R.\Delta T\ ,\ Q = \frac{M}{\mu}\left(\frac{i}{2}+1\right)R.\Delta T$$

$$C_P = \left(\frac{i}{2}+1\right)R$$

12.3.4. Adiabatic Process: $Q = 0$, $p.V^{\gamma}$=const

$$W = \Delta U = \frac{M}{\mu}\frac{iR}{2\Delta\backslash\Delta}\Delta T = \frac{M}{\mu}C_V\Delta T = \frac{p_2V_2 - p_1V_1}{\gamma - 1}$$

$$\boxed{\gamma = \frac{C_P}{C_V} = \frac{i+2}{i}}$$

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12.4. The Second Law of Thermodynamics

Starting points:

- All natural processes **obey the first law**. However, there are processes that obey the first law but **cannot occur naturally**.
- The **second law** deals with these limitations using a new state function, the **entropy S**. It asserts that a natural process runs only in one direction, and is **irreversible**.
- For example, heat always flows spontaneously from a hotter body to a colder body. (In order to transfer heat from a colder body to a hotter body, work must be done, or there must be some change in the surrounding environment.)
- For an **idealized reversible process**, the entropy change obeys an equality and can be calculated. That is why it is important even though it is a hypothetical process.

12.4. The Second Law of Thermodynamics

12.4.1. Postulates of the second law

- Postulate of Clausius

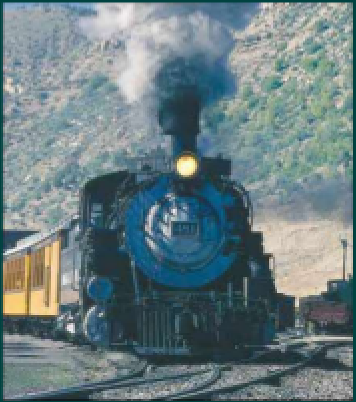
A transformation whose only final result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible.

- Postulate of Kelvin

It is impossible to convert the heat from a single source into work without any other effect.

12.4. Heat Engines and the Second Law of Thermodynamics

12.4.2. Heat engine



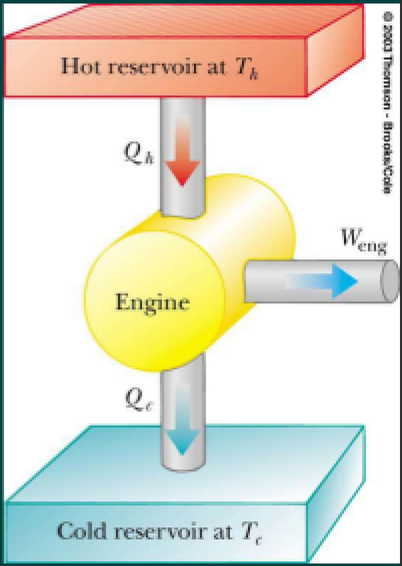
…. is a device that converts internal energy (heat) to other useful forms, such as electrical or mechanical energy

A heat engine carries some working substance through a cyclical process

In **internal-combustion engines**, such as those used in automobiles, the working substance is a mixture of air and fuel; In a steam turbine it is **water**.

Working principle of a heat engine

- Energy is transferred from a **source** at a high temperature (Q_h)
- Work is done by the engine (W_{eng} , W')
- Energy is expelled to a **sink** at a lower temperature (Q'_c)



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Schematic representation of a heat engine

Working principle of a heat engine

- Since it is a cyclical process, $\Delta U = 0$
  - Its initial and final internal energies are the same
- The work done by the engine W_{eng} $(=W') = -W$
- Therefore, from the first law of thermodynamics :

$$\Delta U = Q_{net} + W = 0$$

$$\Delta U = Q_{net} - W_{eng} = 0$$

$$\rightarrow Q_{net} = W_{eng}\ ;\ Q_h - Q'_c = W'$$

- The work done by the engine equals the net (heat) energy absorbed by the engine

- The work is equal to the area enclosed by the curve of the PV diagram

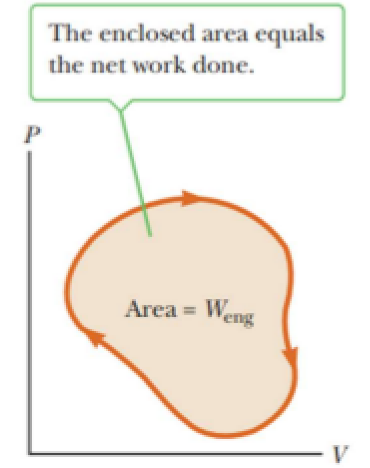
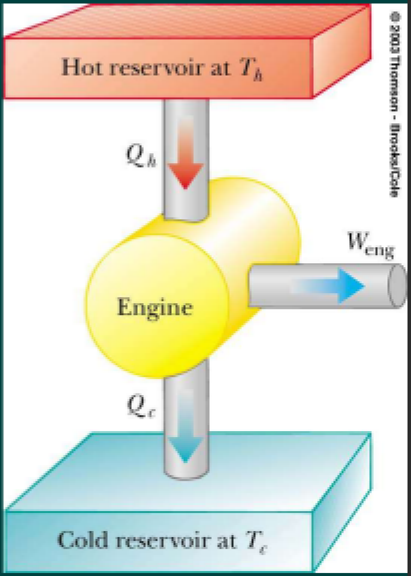


Figure 12.12 The *PV* diagram for an arbitrary cyclic process.

12.4.3. Thermal Efficiency of a Heat Engine



- Thermal efficiency is defined as the ratio of the work done by the engine to the energy absorbed at the higher temperature

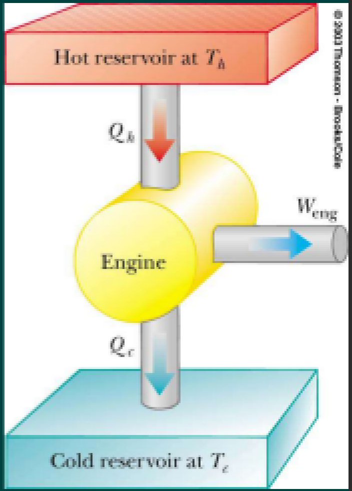
$$e = \frac{W_{eng}}{Q_h} = \frac{Q_h - Q'_c}{Q_h} = 1 - \frac{Q'_c}{Q_h}$$

- $e = 1$ (100% efficiency) only if $Q'_c = 0$ **(that not real)**

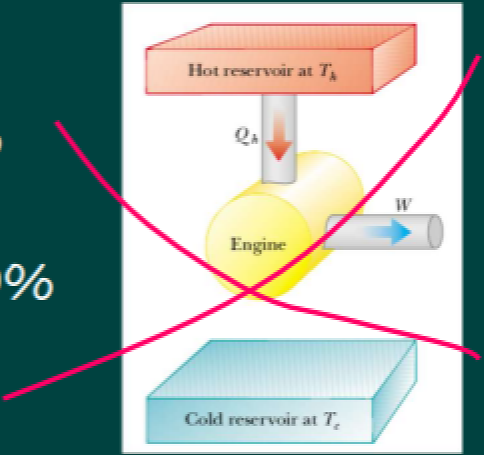
No energy expelled to cold reservoir.

- Reality: $0 < e < 1$

12.4.4 Second Law of Thermodynamics



- **Thompson:** “It is **impossible** to construct a heat engine that, operating in a cycle, produces no other effect than the absorption of energy from a reservoir and the performance of an equal amount of work”
  - Means that Q'_c cannot equal 0
    - Some Q'_c must be expelled to the environment
  - Means that ***e*** cannot equal 100%



The impossible engine

PROBLEM 1

Find the efficiency of a heat engine that absorbs 2000 J of energy from a hot reservoir and exhausts 1500 J to a cold reservoir.

SOLUTION

Heat absorbed from hot reservoir: $Q_1 = Q_h = 2000$ J

Heat **exhausted** to a cold reservoir: $Q_2' = Q_c = 1500$ J

$$e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{1\,500\ \text{J}}{2\,000\ \text{J}} = 0.25, \text{ or } \boxed{25\%}$$

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12.1. Work and heat in a thermodymanic process

12.2. The First Law of Thermodynamics

12.3. Thermo processes

12.4. The Second Law of Thermodynamics

12.5. Reversible and Irreversible Processes

12.6. The Carnot Engine

12.7. Entropy

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12.5. Reversible and Irreversible Processes

Thermodynamic processes that occur in nature are all **irreversible processes**.
These are processes that proceed spontaneously **in one direction** but not the other

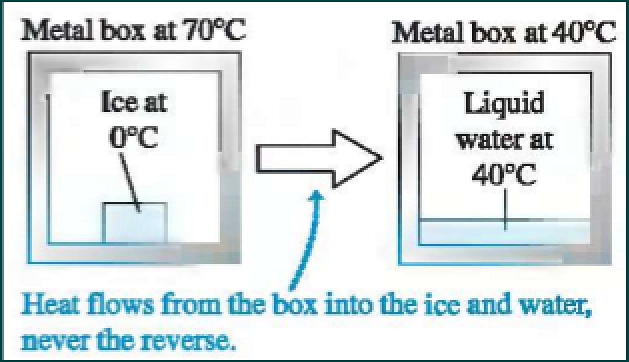
EXAMPLE :

- The flow of heat from a hot body to a cooler body

- Sliding a book across a table converts mechanical energy into heat by friction

(a book initially at rest on the table would spontaneously start moving and the table and book would cool down ?).

- A block of ice melts irreversibly when we place it in a hot (70°C) metal box.



Heat flows from the box into the ice and water, never the reverse.

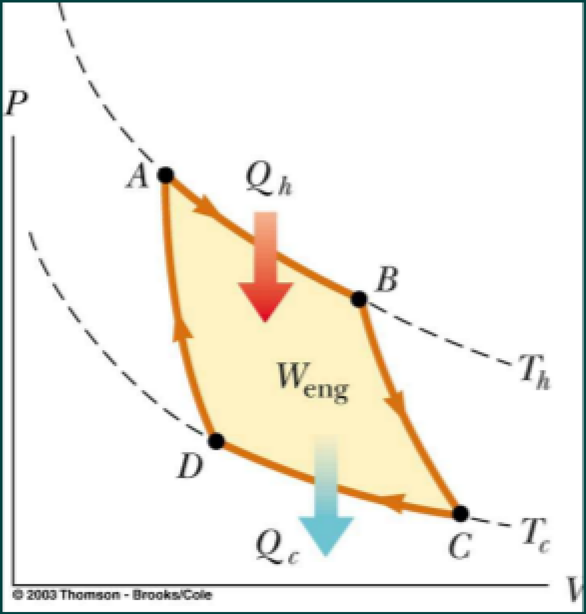
12.5. Reversible and Irreversible Processes (cont.)

Definition:

- A ***reversible*** process is one in which every state along some path is an equilibrium state
  - And one for which the system can be returned to its initial state along the same path.
- An ***irreversible*** process does not meet these requirements
  - Most natural processes are irreversible
  - Reversible process is an idealization, but some real processes are good approximations

Reversible processes are thus equilibrium processes, with the system always **in thermodynamic equilibrium.**

12.6. THE CARNOT ENGINE



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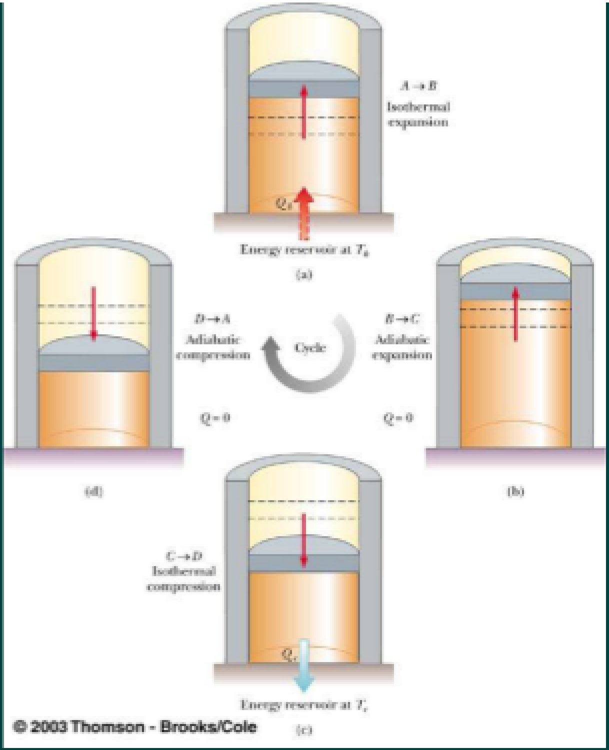

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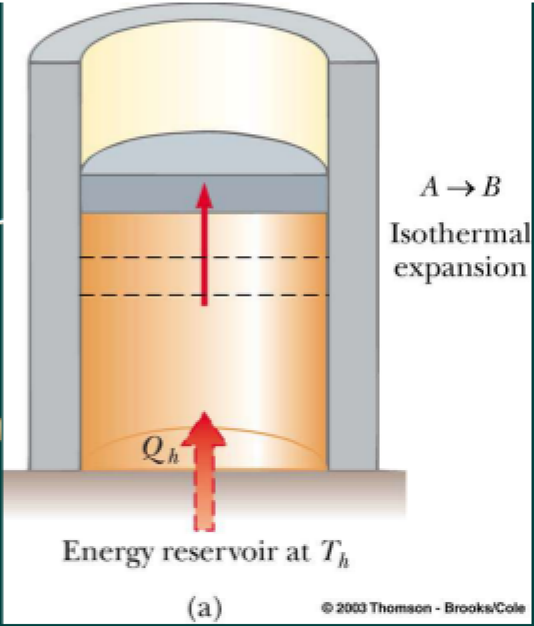
- A theoretical engine developed by Sadi Carnot
- A heat engine operating in an **ideal, reversible cycle** (now called a *Carnot Cycle*) between two reservoirs is the most efficient engine possible
- *Carnot's Theorem*: **No real engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs**

Carnot Cycle: A to B process

- A to B is an **isothermal** expansion
- The gas is placed in contact with th high temperature reservoir
- The gas absorbs heat Q_h
- The gas does work W_{AB} in raising th piston



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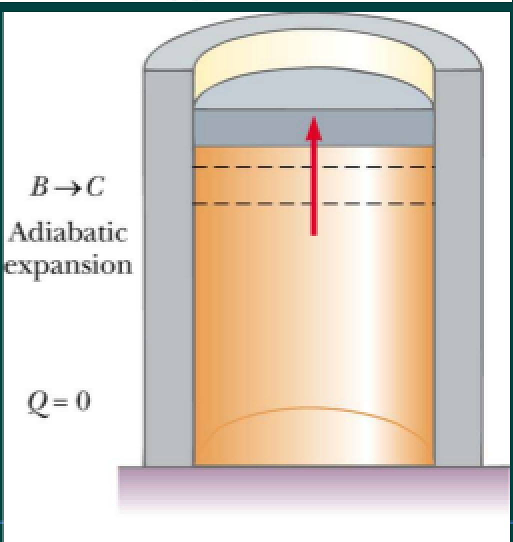
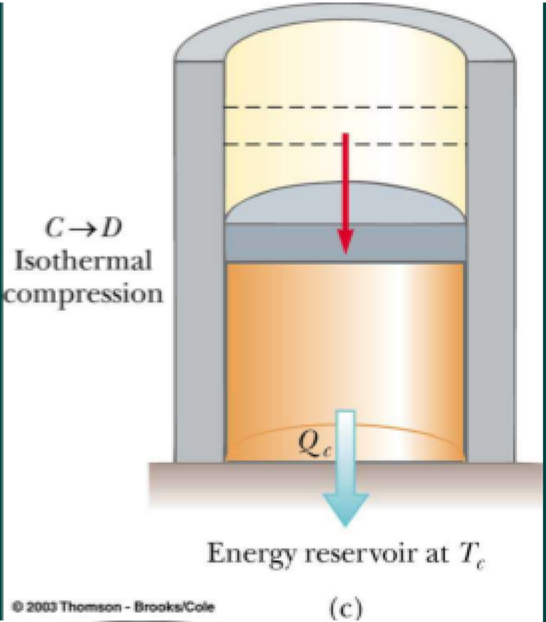
Carnot Cycle: B to C process

- B to C is an **adiabatic** expansion
- The base of the cylinder is replaced by a thermally nonconducting wall
- No heat enters or leaves the system
- The temperature falls from T_h to T_c
- The gas does work W_{BC}



Carnot Cycle: C to D process

- The gas is placed in contact with the cold temperature reservoir
- C to D is an **isothermal** compression
- The gas expels energy Q_C
- Work W_{CD} is done on the gas



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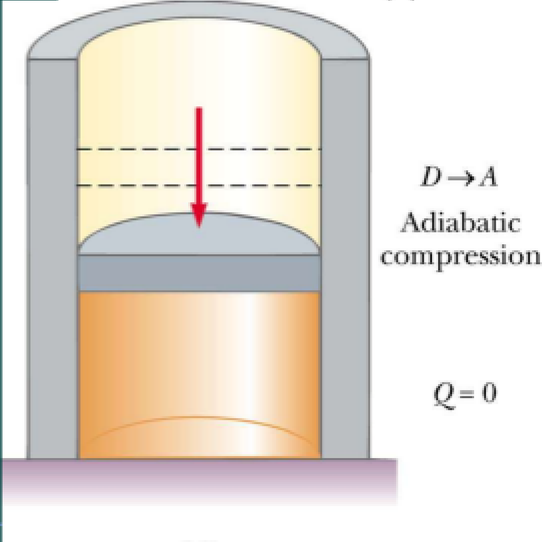
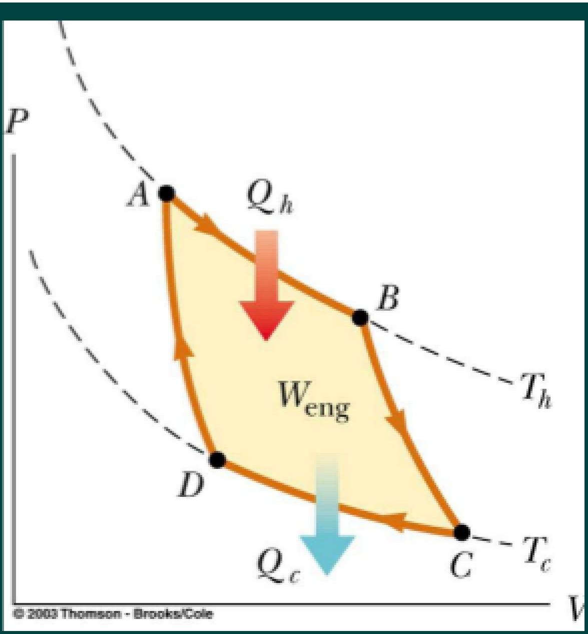
Carnot Cycle: D to A process

- D to A is an **adiabatic** compression
- The gas is again placed against a thermally nonconducting wall
  - So no heat is exchanged with the surroundings
- The temperature of the gas increases from T_C to T_h
- The work done on the gas is W_{CD}



Carnot Cycle: PV diagram



- The work done by the engine is shown by the area enclosed by the curve
- The net work is equal to $Q_h - Q'_c$
  - The thermal efficiency of the engine :

$$e = \frac{W_{eng}}{Q_h} = \frac{Q_h - |Q_c{}'|}{Q_h} = 1 - \frac{Q'_C}{Q_h}$$

  - We can demonstrate : $\frac{Q'_C}{Q_h} = \frac{T_c}{T_h}$

→ The thermal efficiency of a Carnot engine : $\boxed{e_C = 1 - \frac{T_c}{T_h}}$

(The efficiency of a Carnot engine depends only on the temperatures of the two heat reservoirs)

The efficiency of a Carnot engine

☞ Efficiency of a heat engine :

$$e = 1 - \frac{Q_c}{Q_h}$$

♦ Heat aborbed from **Hot Reservoir**

$$Q_h = Q_{AB} = \frac{m}{\mu} R T_h \ln \frac{V_B}{V_A}$$

♦ Heat exhausted to **Cold Reservoir**

$$Q_c = Q'_{CD} = -Q_{CD} = W_{CD}$$
$$= -\frac{m}{\mu} R T_c \ln \frac{V_4}{V_3}$$

=> $$e = 1 - \frac{T_c \ln \frac{V_C}{V_D}}{T_h \ln \frac{V_B}{V_A}}$$

♦ BC and DA are adiabatic processes:

$$\begin{cases} T_h V_B^{\gamma-1} = T_{cold} V_C^{\gamma-1} \\ T_h V_A^{\gamma-1} = T_{cold} V_D^{\gamma-1} \end{cases} \Rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

☞ $$\boxed{e = 1 - \frac{T_c}{T_h}}$$

♦ **The efficiency of a Carnot engine depends only on the temperatures of the two heat reservoirs**

Notes About Carnot Efficiency

$$e = 1 - \frac{T_c}{T_h}$$

- Efficiency is 0 if $T_h = T_c$
- Efficiency is 100% only if $T_c = 0$ K
    - Such reservoirs are not available
- The efficiency increases at T_c is lowered and as T_h is raised
- In most practical cases, T_c is near room temperature, 300 K
    - So generally **T_h is raised to increase efficiency**

- All real engines are less efficient than the Carnot engine
    - Real engines are irreversible because of friction
    - Real engines are irreversible because they complete cycles in short amounts of time

- Carnot's Theorem:

No real engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs

$$e_{real} = 1 - \frac{Q_C'}{Q_h} \leq e_{carnot} = 1 - \frac{T_C}{T_h}$$

12.7. Entropy and statement of the second law

Definition: The entropy S of a system is defined by

$$dS = \frac{\delta Q}{T}$$ in a **reversible** process

- For an irreversible process: $\frac{\delta Q}{T} < dS$
- Some properties of Entropy:

- Unit: J/K

- Entropy is a state function: $\Delta S = S_2 - S_1 = \int_{(1)}^{(2)} \frac{\delta Q}{T}$
  where 1-2 is a reversible process.

- Entropy of a system is equal to the sum of entropies of all of its subsystems

Entropy and disorder

♣ Entropy: is the measure of how energy spreads to disorder in a system. When disorder increases, entropy increases.

- Whenever energy freely transforms from one form to another, the direction of transformation is toward a state of greater disorder and, therefore toward one of greater **entropy**.

- The greater the disorder

  => the higher the **entropy.**

- 2nd Law of thermodynamics: (restatement)

  In natural processes, high-quality energy tends to transform into lower-quality energy—order tends to disorder.

- Energy tends to degrade and disperse with time. The total amount of entropy in any system tends to increase with time.

MCQ

Qx. Your garage gets messier each week. In this case, the entropy of your garage is

(A). Increasing.

(B). decreasing.

(C). Hanging steady

(D). nonexistent

12.7. Entropy and statement of the second law

- According to the Carnot's theorem:

$$1-\frac{Q_2{}'}{Q_1}\le 1-\frac{T_2}{T_1} \qquad \Rightarrow \frac{Q_2{}'}{Q_1}\ge\frac{T_2}{T_1}$$

$$-\frac{Q_2}{Q_1}\ge\frac{T_2}{T_1}\Leftrightarrow-\frac{Q_2}{T_2}\ge\frac{Q_1}{T_1} \qquad \text{or} \qquad \frac{Q_1}{T_1}+\frac{Q_2}{T_2}\le 0$$

- For a cycle of n isothermal processes in alternate between n adiabatic processes:

$$\sum_i\frac{Q_i}{T_i}\le 0$$

- An arbitrary cycle corresponds to the case n → ∞

$$\oint\frac{\delta Q}{T}\le 0$$

'equal' for reversible cycles

'less than' for irreversible cycles

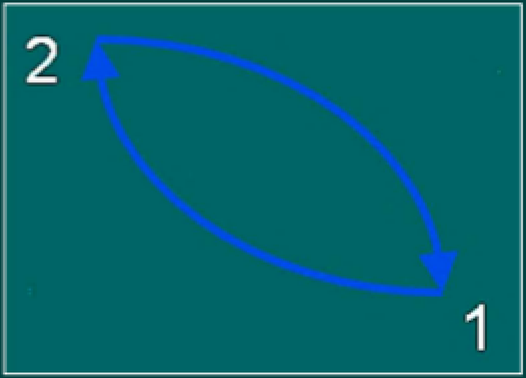
12.7. Entropy and statement of the second law

Consider a reversible cycle 1a2b1:

$$\int_{1a2b1}\frac{\delta Q}{T}=0 \quad => \quad \int_{1a2}\frac{\delta Q}{T}+\int_{2b1}\frac{\delta Q}{T}=0$$

Or: $$\int_{1a2}\frac{\delta Q}{T}+\int_{1b2}-\frac{\delta Q}{T}=0$$

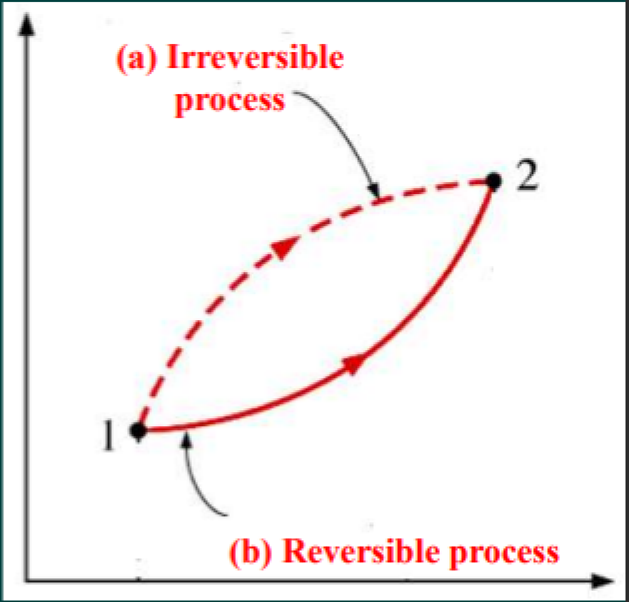
=> $\int_{1a2}\frac{\delta Q}{T}=\int_{1b2}\frac{\delta Q}{T}$ => (Clausius integral path independent/state function)



12.7. Entropy and statement of the second law

Consider a irreversible cycle 1a2b1:

- **(1a2): Irreversible process**
- **And (2b1) Reversible process**
- $0 > \int_{1a2b1} \frac{\delta Q}{T} = \int_{1a2} \frac{\delta Q}{T} + \int_{2b1} \frac{\delta Q}{T} = \int_{1a2} \frac{\delta Q}{T} + \int_{1b2} - \frac{\delta Q}{T}$
-
- $\int_{1a2} \frac{\delta Q}{T} < \int_{1b2} \frac{\delta Q}{T} = \Delta S$



Finally:

- $\int_{1a2} \frac{\delta Q}{T} \leq \int_{1b2} \frac{\delta Q}{T} = \Delta S$ or: $\frac{\delta Q}{T} \leq dS$

= when reversible

< when irrevesible

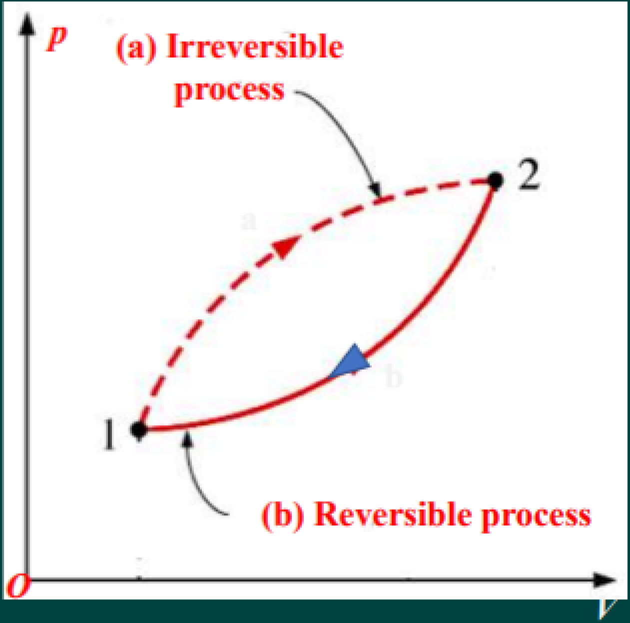
Principle of increase of entropy

☞ For closed/isolated system it is usually in the irreversible process:

$$\Delta S \geq \int_{irr.} \frac{dQ}{T} \text{ however } \int_{irr.} \frac{dQ}{T} < 0 \Rightarrow \Delta S \geq 0$$

♦ For reversible process: entropy is constant, that is $\Delta S = 0$.

♦ For irreversible process: entropy increases that is $\Delta S > 0$.



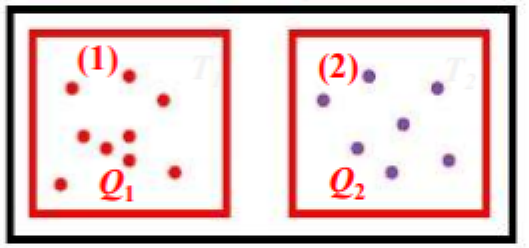
☞ **Statement**

No matter what process takes place within an isolated system, its entropy must increase or remain the same in the limit of a reversible process. These processes cannot occur in the direction of decreasing entropy.

♦ Once entropy gets maximum value, it does not increase anymore then processes is no longer to exist and the system reaches the thermodynamic equilibrium.

Increase of entropy and the 2nd law

☞ Consider an isolated system consisting object (1) at temperature T_1 and (2) at T_2 have energy transition in the form of heat that is (2) receives heat dQ_1 from (1), and (1) receives heat dQ_2 from (2).


Isolated system

- From the second consequence of 1st law: $dQ_1 = - dQ_2$
- Change in entropy of system:

$$dS = dS_1 + dS_2 = \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = -\frac{dQ_2}{T_1} + \frac{dQ_2}{T_2} = dQ_2\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- if $dS > 0$, in RHS, since $dQ_2 > 0$

$$\Rightarrow \frac{1}{T_2} - \frac{1}{T_1} > 0 \text{ or } T_1 > T_2$$

- if $dS = 0$

$$\Rightarrow \frac{1}{T_2} - \frac{1}{T_1} = 0 \text{ or } T_1 = T_2$$

☞ Increase of entropy

- *demonstrates the direction of varied process as statement of 2nd law;*
- *steadily and eventually reach a maximum value at which the system will be in a state of uniform temperature.*

Calculation the change of Entrooy of an ideal gas in an reversible process

- $\Delta S = S_2 - S_1 = \int_{(1)}^{(2)} \frac{\delta Q}{T}$
- In an adiabatic process: $Q = 0$, $\delta Q = 0$ then $\Delta S = 0$ or S=const.
- In an isothermal process: $T = const$, then

$$\Delta S = \frac{Q}{T} = \frac{W'}{T} = \frac{M}{\mu} R \ ln\frac{V_2}{V_1} = \frac{M}{\mu} R \ ln\frac{P_1}{P_2}$$

- For an arbitrary process:

$$\delta Q = dU - \delta A = dU + PdV = \frac{M}{\mu}\frac{i}{2}RdT + \frac{M}{\mu}\frac{RT}{V}dV$$

$$\Delta S = \int_{(1)}^{(2)} \frac{\delta Q}{T} = \int_{(1)}^{(2)} \frac{M}{\mu}\frac{i}{2}R\,\frac{dT}{T} + \int_{(1)}^{(2)} \frac{M}{\mu}R\,\frac{dV}{V}$$

$$= \frac{M}{\mu}\left(C_V\, ln\frac{T_2}{T_1} + R\, ln\frac{V_2}{V_1}\right)$$

- For an arbitrary process: (cont.)

$$\Delta S = \frac{M}{\mu}\left(C_V \, ln\frac{T_2}{T_1} + R \, ln\frac{V_2}{V_1}\right)$$

Where: $ln\frac{T_2}{T_1} = ln\frac{P_2}{P_1} + ln\frac{V_2}{V_1}$

- $\Delta S = \frac{M}{\mu}\left\{C_V \, ln\frac{P_2}{P_1} + (C_V + R) \, ln\frac{V_2}{V_1}\right\} = \frac{M}{\mu}\left\{C_V \, ln\frac{P_2}{P_1} + C_P . ln\frac{V_2}{V_1}\right\}$