



**Chapter  
Four**

**Heat Engines, Entropy and the Second Law of  
Thermodynamics**



***Dr Basma Elbadry***

# THE SECOND LAW OF THERMODYNAMICS

مختصاً بقانون الثاني بحدوده العمليات وإمكانية حدوثها

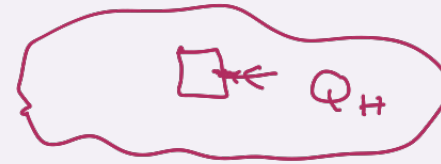
- Second Law of Thermodynamics establishes the processes which do and which do not occur
- This directionality is governed by the second law.  
بأنه كدبر اتجاه حدوث العمليات من خلال القانون الثاني
- These types of processes are irreversible.
  - An irreversible process is one that occurs naturally in one direction only.  
عملية غير عكسية العمليات التي تحدث بشكل طبيعي باتجاه
  - No irreversible process has been observed to run backwards.  
لا يمكن لعملية غير عكسية أن تعود لتتحل عكسي و حدوثها
- An important engineering implication is the limited efficiency of heat engines.

كفاءة

محركات حرارية



# DEFINITIONS



- The heat exchange between the system and the hot reservoir (High temperature) is  $|Q_H|$   
محزنه حراري
- The heat exchange between the system and the cold reservoir (Low temperature) is  $|Q_L|$
- The work exchange between the system and surroundings is  $|W|$

$Q_H$

$Q_L$

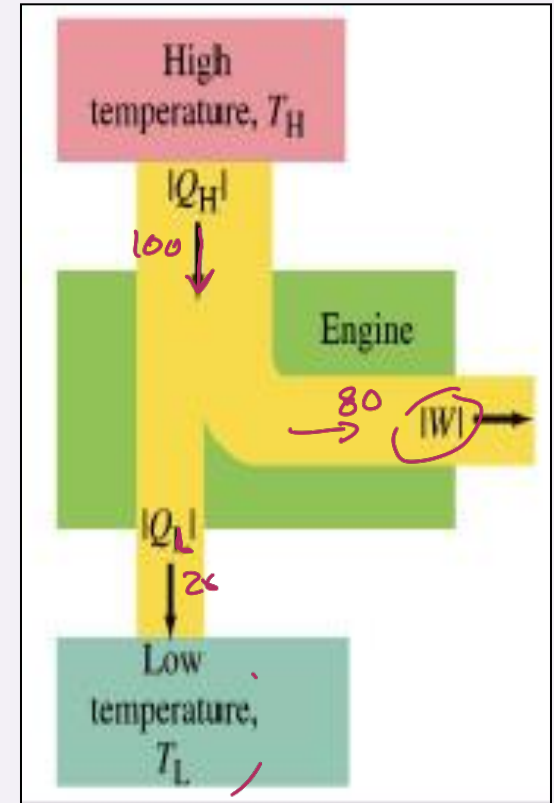
$W$



# HEAT ENGINE

حرک سازي

- If  $Q_H$  is larger than  $|Q_L|$  and If  $|W|$  done by the system, then the machine that cause the system to undergo the cycle called a heat engine.
- A heat engine is a device that takes in energy by heat and, operating in a cyclic process, expels a fraction of that energy by means of work.
- A heat engine carries some working substance through a cyclical process.



خلال العملية، الموریه نيم استهلاكه او استخدام بعض المواد

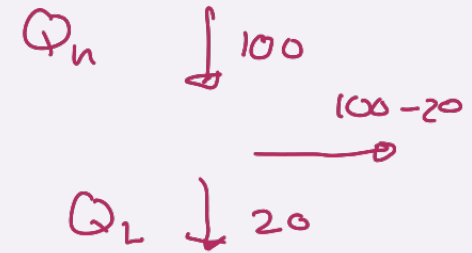


## HEAT ENGINE, CONT.

- Since it is a cyclical process,  $\Delta E_{\text{int}} = 0$ 
  - Its initial and final internal energies are the same.

○ Therefore,  $W_{\text{eng}} = Q_{\text{net}} = |Q_{\text{h}}| - |Q_{\text{c}}|$

- The net work done by a heat engine equals the net energy transferred to it.



العمل المحصل الناتج عن محرك سادس تحطه حجم  
الطاقة المتقوله اليه



كفاءة المحرك

# THERMAL EFFICIENCY OF A HEAT ENGINE

$e$

Thermal efficiency is defined as the ratio of the net work done by the engine during one cycle to the energy input at the higher temperature.

$$e \equiv \frac{W_{\text{eng}}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

$$e = \frac{\text{work}}{m}$$

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

دائماً الكفاءة ستكون أقل

من 1 (0.8) = 80%

We can think of the efficiency as the ratio of what you gain to what you give.

In practice, all heat engines expel only a fraction of the input energy by mechanical work.

Therefore, their efficiency is always less than 100%.

- To have  $e = 100\%$ ,  $Q_c$  must be 0

$$e = 100\%$$

كيف نحصل الكفاءة الحرارية

$$0 = Q_c$$



# حرارة حرارية مثالية

## PERFECT HEAT ENGINE

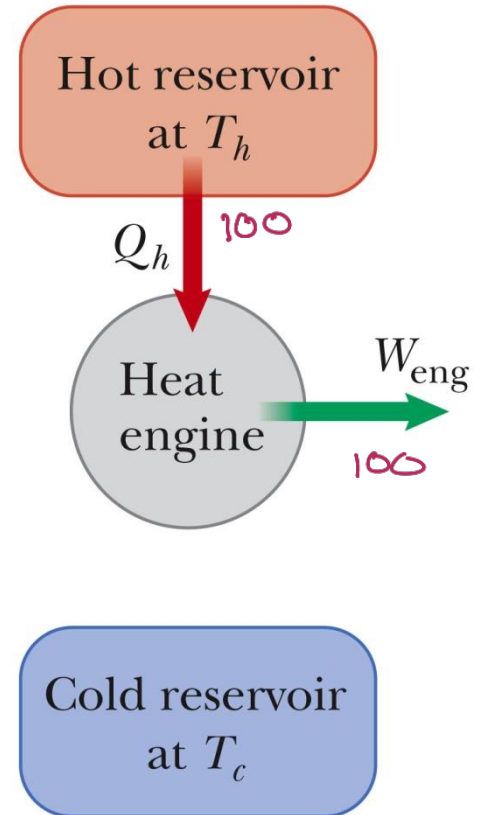
لم يتم تصدير أي طاقة للمخزن البارد

- No energy is expelled to the cold reservoir.
- It takes in some amount of energy and does an equal amount of work.
- $e = 100\%$
- It is impossible to construct such an engine.

أخذ طاقة وحوّلها جميعاً إلى شغل

فإنه لا يمكن إنشاء هذا المحرك

An impossible heat engine



مخزن الطاقة الثاني :- (كلفن بلانك)

## SECOND LAW: KELVIN-PLANCK FORM

It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the input of energy by heat from a reservoir and the performance of an equal amount of work.

- $W_{eng}$  can never be equal to  $|Q_h|$
- Means that  $Q_c$  cannot equal 0
  - Some energy  $|Q_c|$  must be expelled to the environment
- Means that  $\eta$  cannot equal 100%

$$[Q_h \neq W]$$

$$Q_c \neq 0$$

متحيل الكفاءة تكون صفر

من المتحيل ان وضع محرك حراري دوري لا ينتج طاقة  
للمخزن البارد ، جميع الطاقة التي تدخله يحولها الى شكل





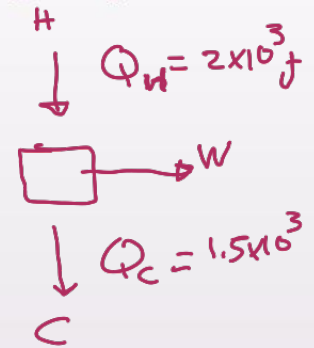
## EXAMPLE

$$e = \frac{W}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

An engine transfers  $2.00 \times 10^3$  J of energy from a hot reservoir during a cycle and transfers  $1.50 \times 10^3$  J as exhaust to a cold reservoir.

- (A) Find the efficiency of the engine.

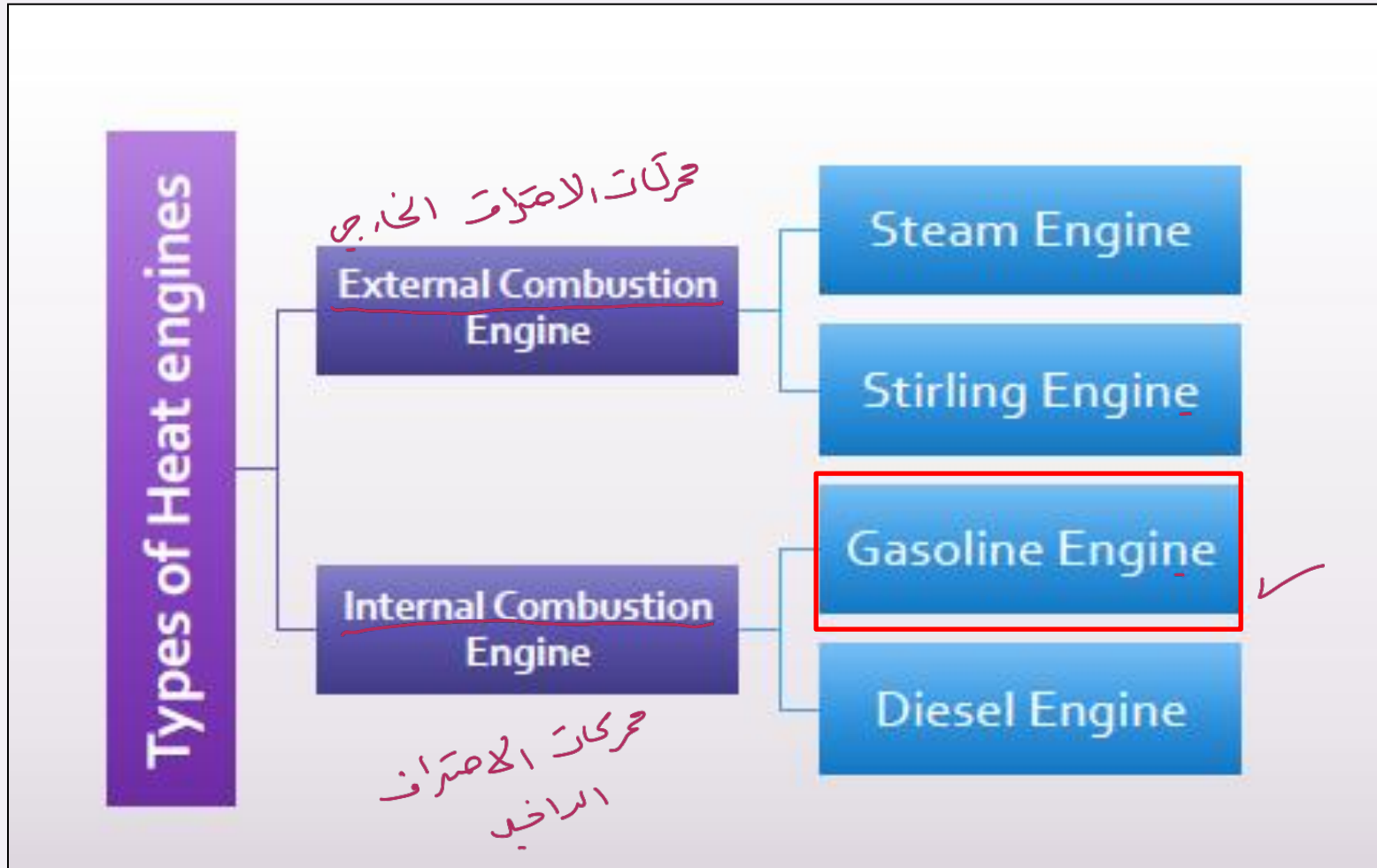
$$e = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{1.50 \times 10^3 \text{ J}}{2.00 \times 10^3 \text{ J}} = 0.250, \text{ or } 25.0\%$$



- (B) How much work does this engine do in one cycle?

$$|W| = |Q_H| - |Q_L| = 2.00 \times 10^3 \text{ J} - 1.50 \times 10^3 \text{ J} = 5.0 \times 10^2 \text{ J}$$

# TYPE OF HEAT ENGINE



حركات الغازولين

## GASOLINE ENGINE

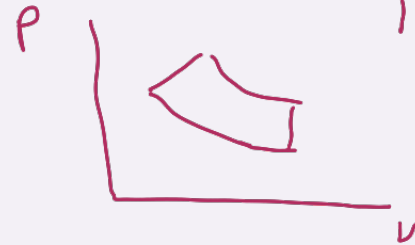
○ In a gasoline engine, six processes occur during each cycle.

في كل دورة يحدث هناك 6 عمليات

○ For a given cycle, the piston moves up and down twice.



○ This represents a four-stroke cycle.



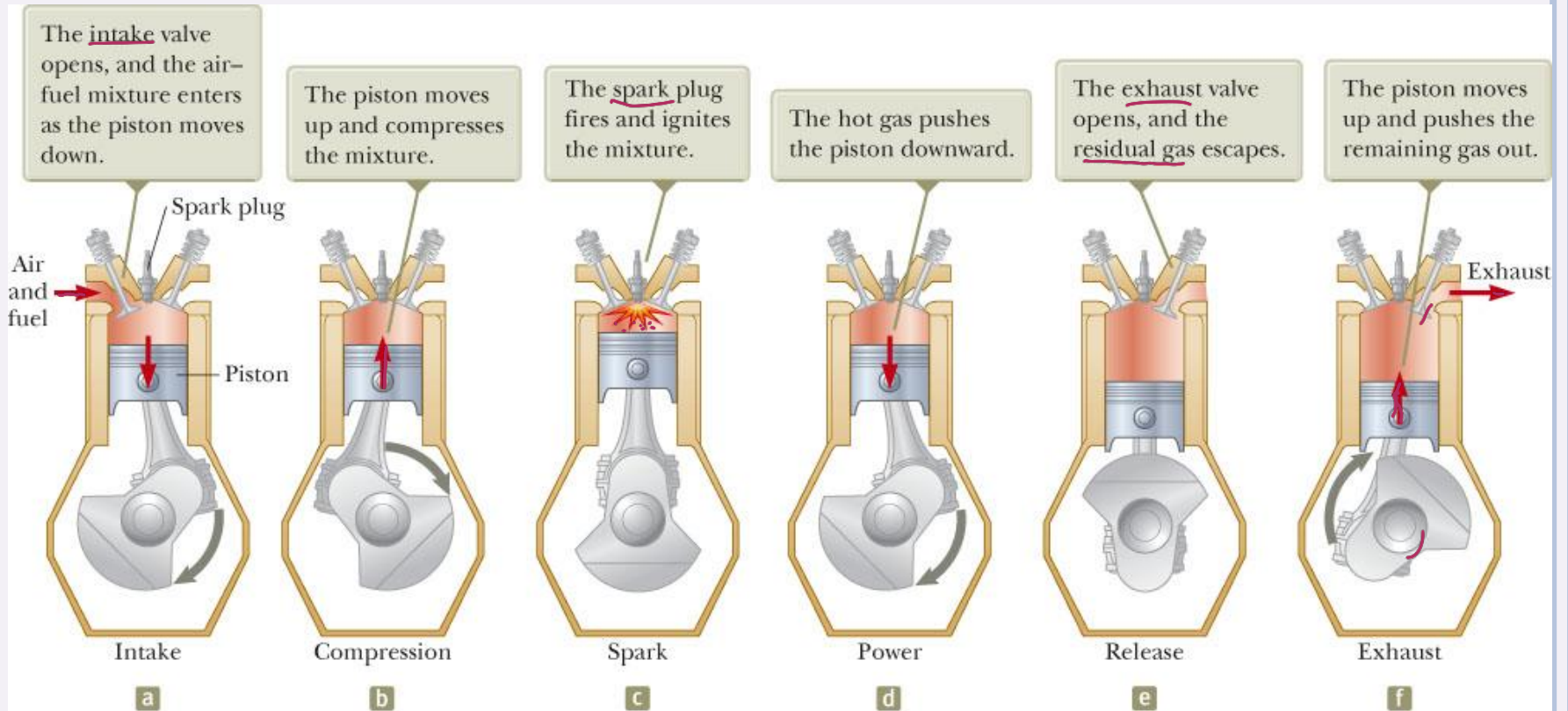
○ The processes in the cycle can be approximated by the Otto cycle.

تتم شرح محرك الغازولين بالاعتقاد في دورة Otto



حمله الفازولينى

# THE CONVENTIONAL GASOLINE ENGINE

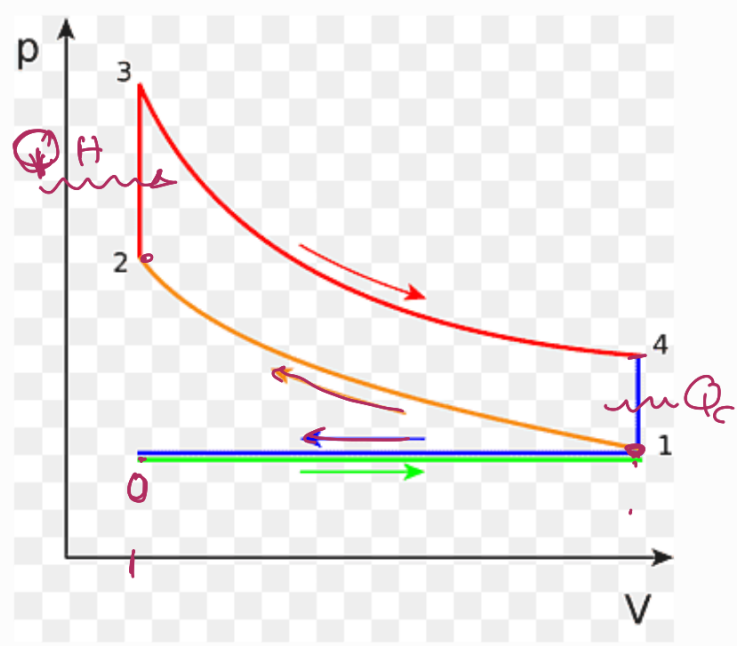


otto cycle



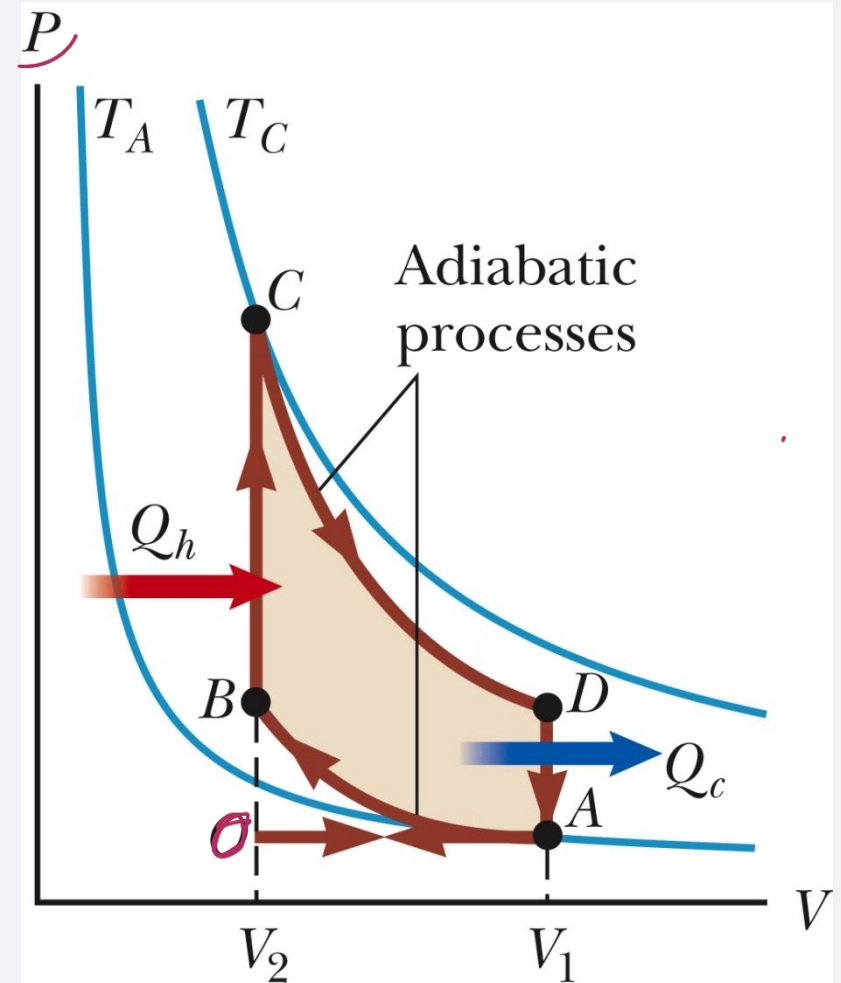
زیادا حجم  
 توتر ضغط  
 درجه حرارت  
 ضغط زار  
 حجم قبل  
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 و P و زياده  
 حجم  
 حجم ثابت  
 انضغاف  
 حجم قبل  
 الضغط ثابت

Process 0 to 1 Isobaric process
Process 1 to 2 <u>Adiabatic Compression</u>
Process 2 to 3 <u>Isochoric process</u>
Process 3 to 4 Adiabatic Expansion
Process 4 to 1 <u>Isochoric process</u>
Process 1 to 0 Isobaric process



# OTTO CYCLE

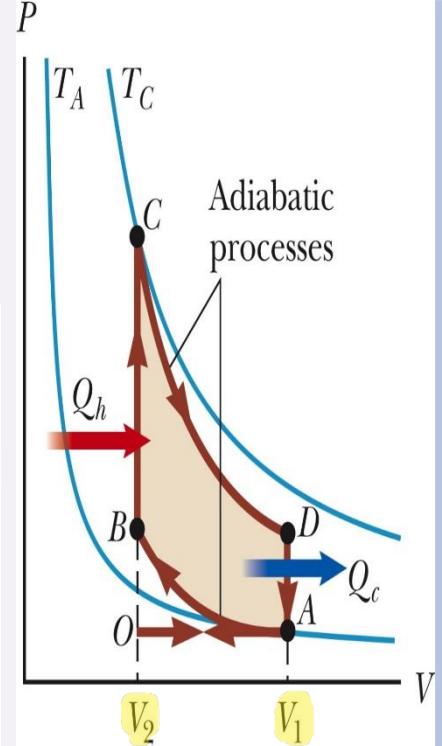
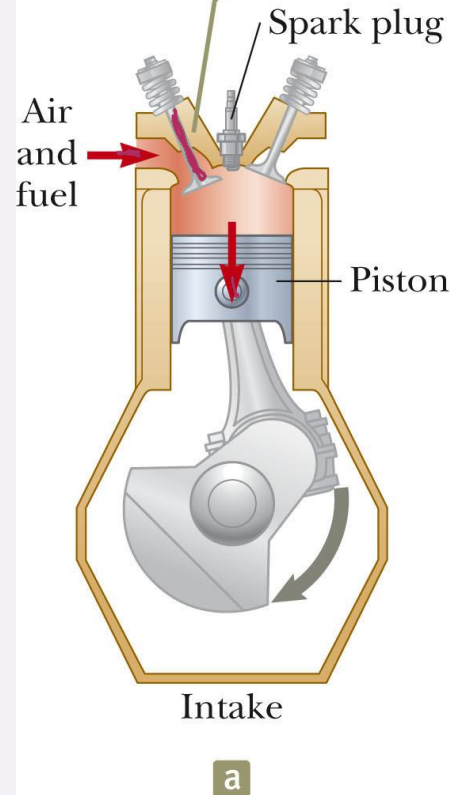
- The PV diagram of an Otto cycle is shown at right.
- The Otto cycle approximates the processes occurring in an internal combustion engine.



# GASOLINE ENGINE – INTAKE STROKE

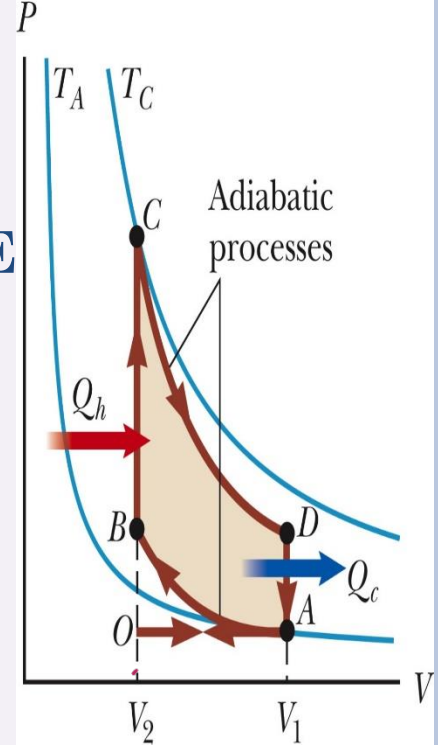
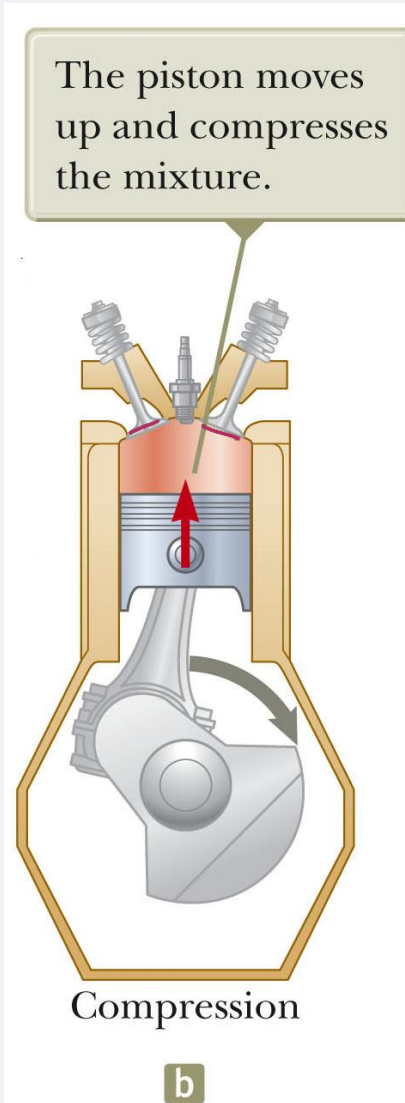
- During the intake stroke, the piston moves downward.
- A gaseous mixture of air and fuel is drawn into the cylinder.
- Energy enters the system by matter transfer as potential energy in the fuel.
- The volume increases from  $V_2$  to  $V_1$ .
- $O \rightarrow A$  in the Otto cycle PV diagram.

The intake valve opens, and the air-fuel mixture enters as the piston moves down.



# GASOLINE ENGINE – COMPRESSION STROKE

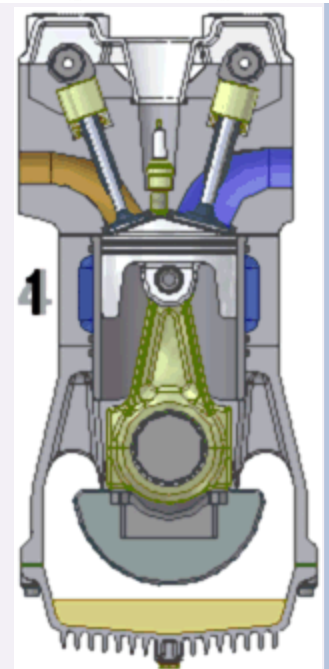
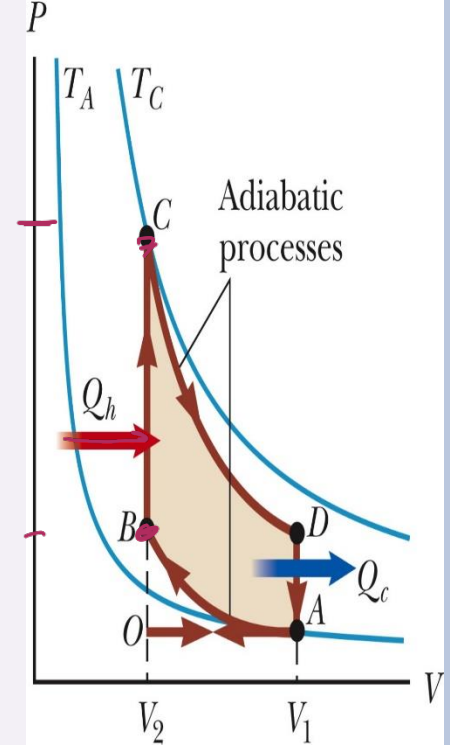
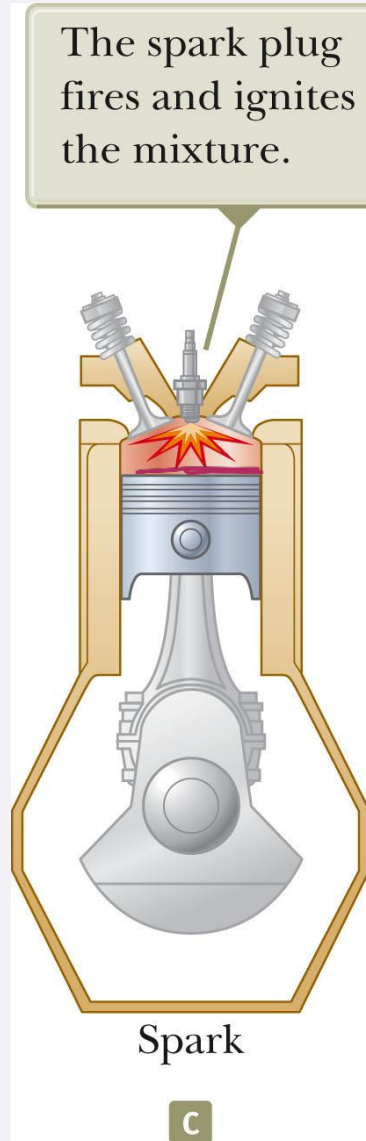
- The piston moves upward.
- The air-fuel mixture is compressed adiabatically.
- The volume changes from  $V_1$  to  $V_2$ .
- The temperature increases.
- The work done on the gas is positive and equal to the negative area under the curve.  $w = \int p dv$
- $A \rightarrow B$  in the Otto cycle PV diagram.





# GASOLINE ENGINE – SPARK

- Combustion occurs when the spark plug fires.
- It occurs very quickly while the piston is at its highest position.
- The combustion represents a rapid energy transformation from potential energy to internal energy.  $Q_H$  تحويل طاقة كيميائية إلى طاقة داخلية
- The temperature changes from  $T_B$  to  $T_C$  but the volume remains approximately the same.
- $B \rightarrow C$  in the Otto cycle PV diagram.

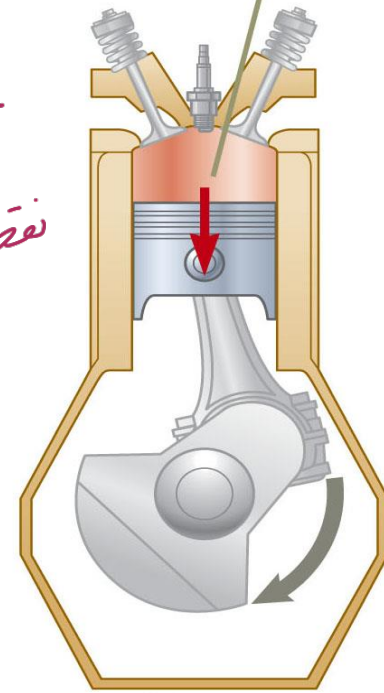


# GASOLINE ENGINE – POWER STROKE

- In the power stroke, the gas expands adiabatically.
- Volume changes from  $V_2$  to  $V_1$
- The temperature drops from  $T_c$  to  $T_D$ .
- Work is done by the gas
- $C \rightarrow D$  in the Otto cycle PV diagram

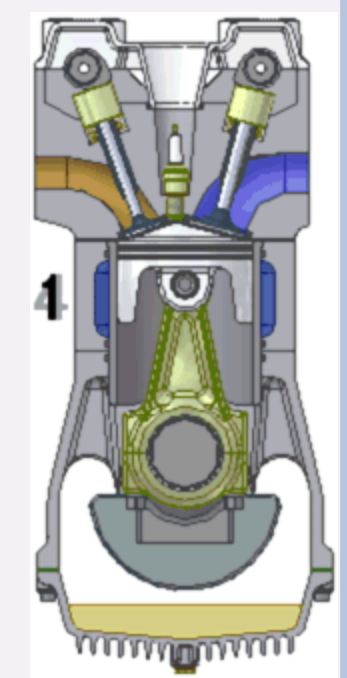
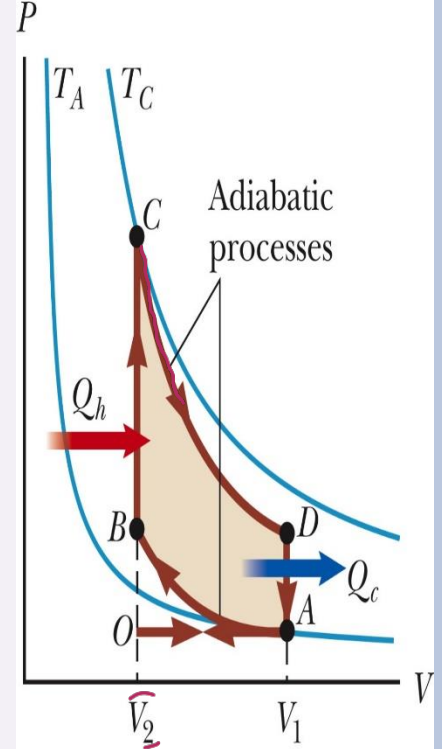
تحد و زیادہ منجانبہ  
 نقصان فی T

The hot gas pushes the piston downward.



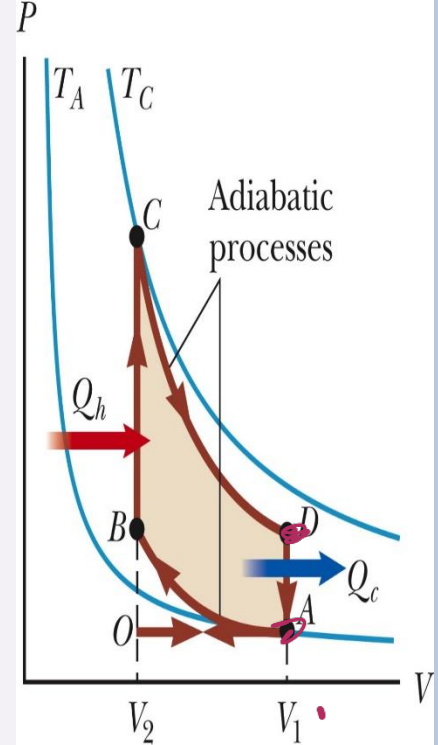
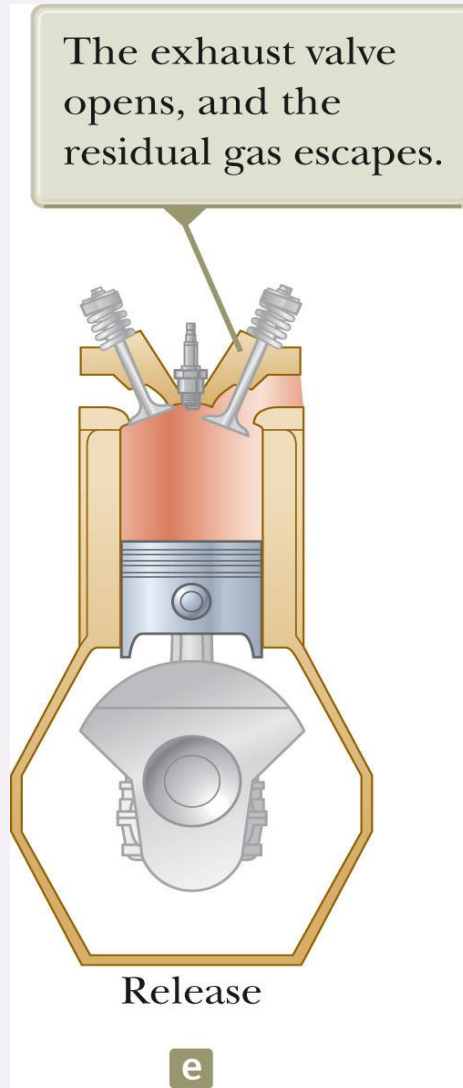
Power

d



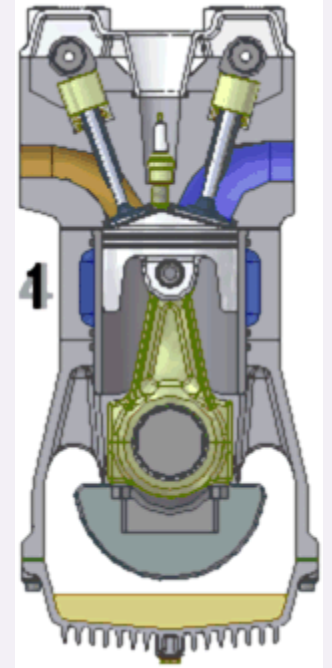
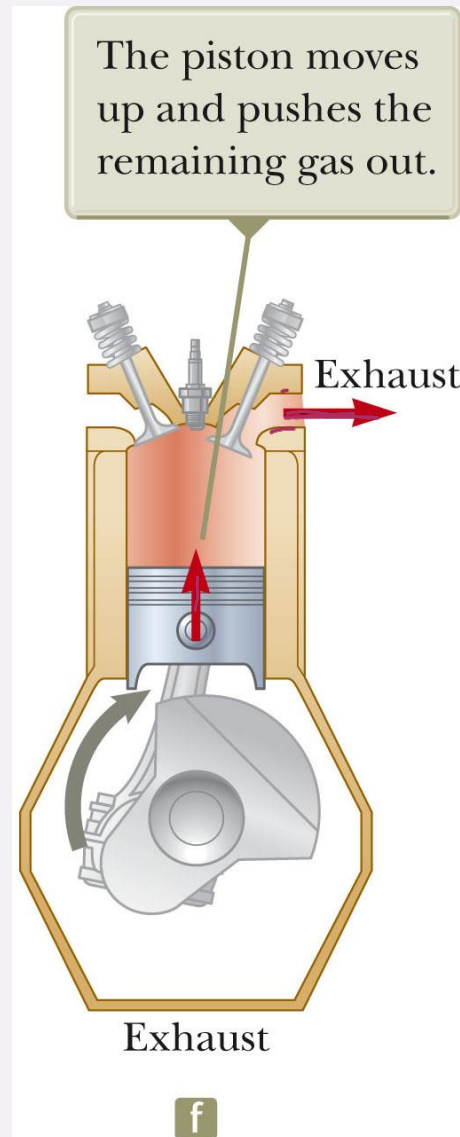
# GASOLINE ENGINE – VALVE OPENS

- This is process  $D \rightarrow A$  in the Otto cycle PV diagram
- An exhaust valve opens as the piston reaches its bottom position. *ضغط قل حجم ثابت*
- The pressure drops suddenly.
- The volume is approximately constant.  *$Q_c$* 
  - So no work is done
- Energy is expelled from the interior of the cylinder.
  - It continues to be expelled during the next process.



# GASOLINE ENGINE – EXHAUST STROKE

- In the exhaust stroke, the piston moves upward while the exhaust valve remains open.
- Residual gases are expelled to the atmosphere
- The volume decreases from  $V_1$  to  $V_2$ .
- $A \rightarrow \overline{O}$  in the Otto cycle PV diagram
- The cycle then repeats



كفاءة

## OTTO CYCLE EFFICIENCY, CONT

○ If the air-fuel mixture is assumed to be an ideal gas, then the efficiency of the Otto cycle is

$$e = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}}$$

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

- $\gamma$  is the ratio of the molar specific heats.
- $V_1 / V_2$  is called the compression ratio.

صاعلي الانضغاط

الحجم الكبير  
 $V_1$

$V_2$

الحجم الصغير

$$e = 1 - \frac{1}{(8)^{1.4-1}} = 1 - \frac{1}{8^{0.4}}$$

$$= 0.56 = 56\%$$



# OTTO CYCLE EFFICIENCY, CONT

## Typical values:

- Compression ratio of 8
- $\gamma = 1.4$
- $e = 56\%$

هذا القانون

## Efficiencies of real engines are 15% to 20%

- Mainly due to friction, energy transfer by conduction, incomplete combustion of the air-fuel mixture

الافتراض غير المتكامل

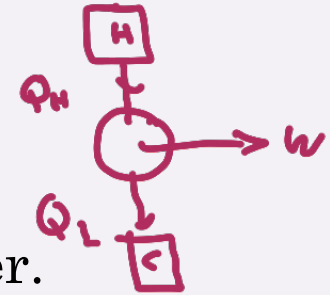
اصدمات

فقد الحرارة بسبب التوصيل



محركات التبريد والتكييف

## HEAT PUMPS AND REFRIGERATORS



- Heat engines can run in reverse.
  - This is not a natural direction of energy transfer.
  - Must put some energy into a device to do this
  - Devices that do this are called heat pumps or refrigerators
- Examples تلافة
  - A refrigerator is a common type of heat pump.
  - An air conditioner is another example of a heat pump. تكييف



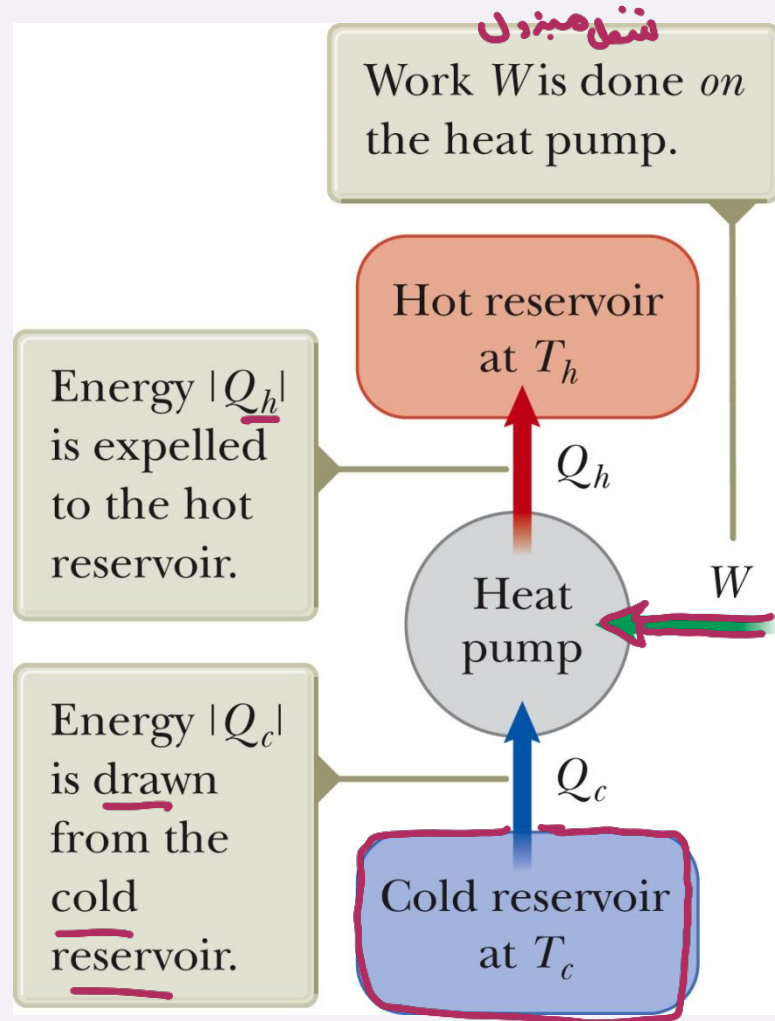
# HEAT PUMP PROCESS

تستخلص الطاقة من الخزان البارد

Energy is extracted from the cold reservoir,  $|Q_c|$

Energy is transferred to the hot reservoir  $|Q_h|$ , work must be done *on* the engine,  $W$

تقل الحرارة الى الخزان الحار  
بمساعدة النقل العكسي  
لتي تضخ الحرارة





ضخه حراريه مثاليه

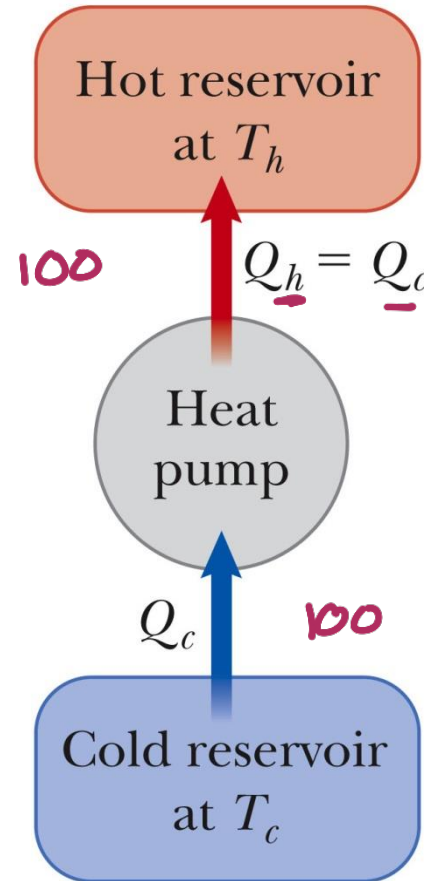
# PERFECT HEAT PUMP

- Takes energy from the cold reservoir
- Expels an equal amount of energy to the hot reservoir
- No work is done
- This is an impossible heat pump

$W = 0$   
 $Q_h = Q_c$

ضخه مثاليه  
Perfect

An impossible heat pump



صيفه اخرى لقانون الة نياميكيا الكرابيه الثاني

## SECOND LAW – CLAUSIUS FORM

○It is impossible to construct a cyclical machine whose sole effect is to transfer energy continuously by heat from one object to another object at a higher temperature without the input of energy by work.

من المستحيل انشاء الة نقل لل طاقة بشكل مستمر من حرارة منخفضة الى اخرى عالية بدون وجهد متصل

○Or – energy does not transfer spontaneously by heat from a cold object to a hot object.

مستحيل انتقال الطاقة بشكل تلقائي من جسم بارد الى جسم ساخن



معامل الاداء

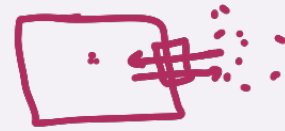
## COEFFICIENT OF PERFORMANCE

- The effectiveness of a heat pump is described by a number called the coefficient of performance (COP).
- Similar to thermal efficiency for a heat engine
  - It is the ratio of what you gain (energy transferred to or from a reservoir) to what you give (work input).

نسبة بين الطاقة و التبريد



مفرد التبريد



## COP, COOLING MODE

- In **cooling mode**, you “gain” energy removed from a cold temperature reservoir.

تحت، الحرارة من، مخزن البارد  
فيصبح أخذ برودة

$$\text{COP} = \frac{\text{energy transferred at low temp}}{\text{work done on the pump}} = \frac{|Q_c|}{W}$$

- A good refrigerator should have a high COP.
  - Typical values are 5 or 6

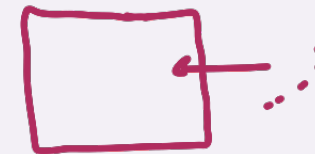


نقطه التسخين

## COP, HEATING MODE

○ In **heating mode**, the COP is the ratio of the heat transferred in to the work required.

$$\text{COP} = \frac{\text{energy transferred at high temp}}{\text{work done by heat pump}} = \frac{|Q_h|}{W}$$



- $Q_h$  is typically higher than  $W$ 
  - Values of COP are generally about 4
    - For outside temperature about 25° F
- The use of heat pumps that extract energy from the air is most satisfactory in moderate climates.

لوصول الى طينى عصيد



## EXAMPLE

$$COP = \frac{Q_L}{W} = 5$$

$$5 = \frac{Q_H - W}{W}$$

$$Q_H - Q_L = W$$

$$Q_L = Q_H - W$$

$$5W = Q_H - W$$

$$6W = Q_H$$

If the coefficient of performance of a refrigerator is 5 find the ratio of the heat rejected to the work done on the refrigerant.

$$COP = \frac{Q_L}{W} = 5$$

and

$$Q_L = Q_H - W$$

$$\frac{Q_H - W}{W} = 5$$

$$\frac{Q_H}{W} = 6$$



$$Q_H = 6W$$



عكسيه

غير عكسيه

## REVERSIBLE AND IRREVERSIBLE PROCESSES

○ A reversible process is one in which every point 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.

- All natural processes are known to be irreversible.
- Reversible processes are an idealization, but some real processes are good approximations.

العمليات العكسيه هي مثاليه لكن بعضها العمليات قصير تقريبا عكسيه



تتبع النظام ان يعود للحاله الاصلية بنفس المسار

كل العمليات الطبيعيه هي عمليات غير عكسيه



# REVERSIBLE AND IRREVERSIBLE

## PROCESSES, CONT

هذا العملية التي يمكن تقريبها والاعتبارها كالتامة هي العملية التي تحدث

○ A real process that is a good approximation of a reversible one will occur very slowly.

- The system is always very nearly in an equilibrium state.

ببطء شديد ويبقى النظام فيها صافيا على التوازن

○ A general characteristic of a reversible process is that there are no dissipative effects that convert mechanical energy to internal energy present.

- No friction or turbulence, for example

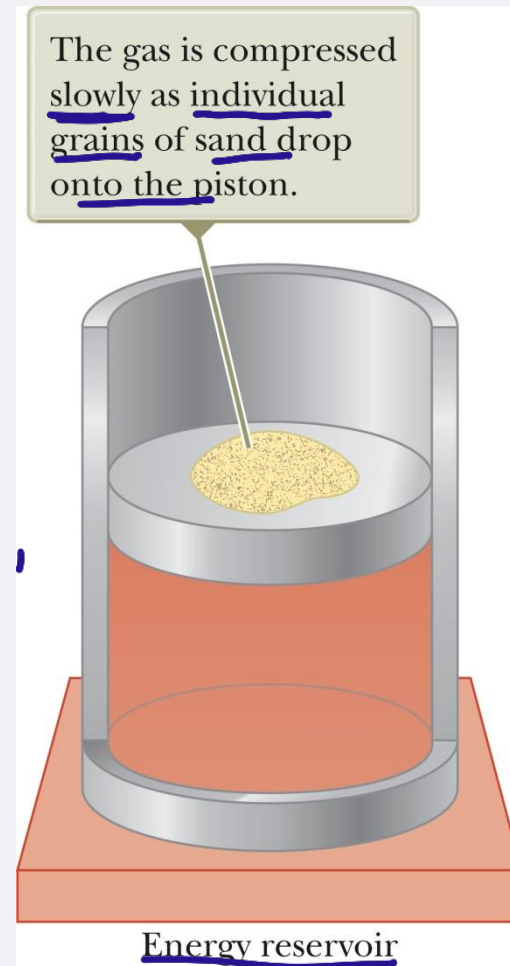
تعتبر العملية العكسية عملية لا يتغير فيها متغير للطاقة  
او تحويل الطاقة الميكانيكية الى طاقة داخلية





# REVERSIBLE AND IRREVERSIBLE PROCESSES, SUMMARY

- The reversible process is an idealization. العملية العكسية هي مثالية
- All real processes on Earth are irreversible. كل العمليات في الأرض غير عكسية
- Example of an approximate reversible process: مثال على عملية عكسية
  - The gas is compressed isothermally
  - The gas is in contact with an energy reservoir
  - Continually transfer just enough energy to keep the temperature constant



حرك كارنوت

## CARNOT ENGINE

- 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
  - This sets an upper limit on the efficiencies of all other engines.

اعلى كفاءة  
حرك كارنوت  
كيفية  
حسابه  
حرارة (Carnot)

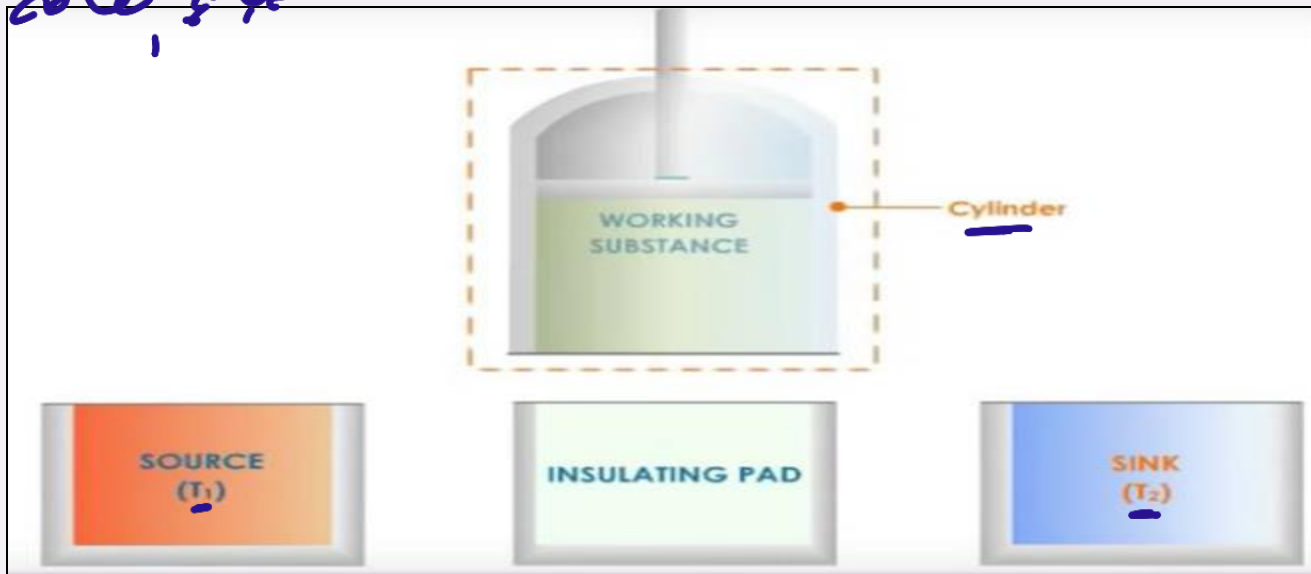


# CARNOT'S THEOREM

لا يوجد محرك حراري يعمل على حيزين حراريين احدهما عند درجة حرارة عالية والآخر عند درجة حرارة منخفضة

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

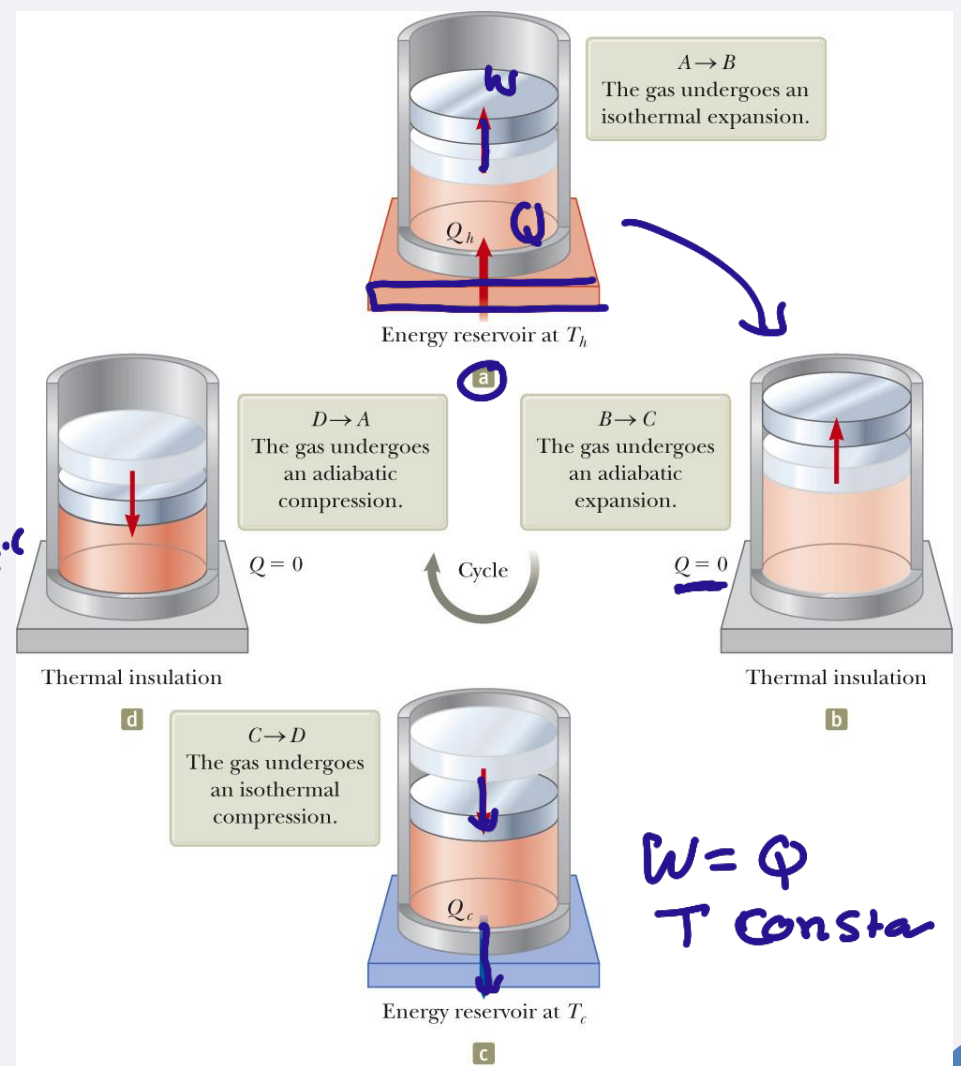
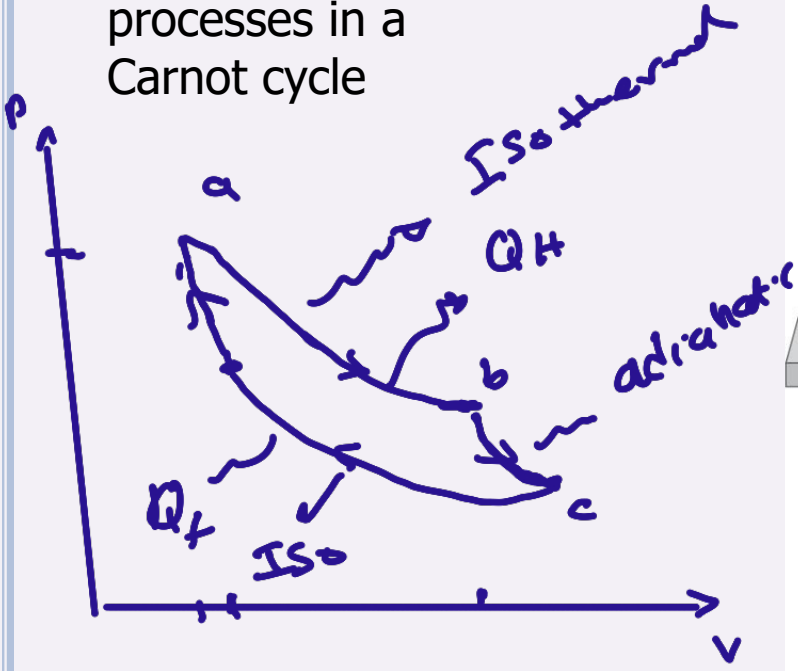
- All real engines are less efficient than a Carnot engine because they do not operate through a reversible cycle. المعرفات الاخرى قد تكون لانها لا تكون عملياً
- The efficiency of a real engine is further reduced by friction, energy losses through conduction, etc.



2 adiabatic  $Q=0$   
 2 Isothermal  $T=0$   $W=Q$

# CARNOT CYCLE

Overview of the processes in a Carnot cycle



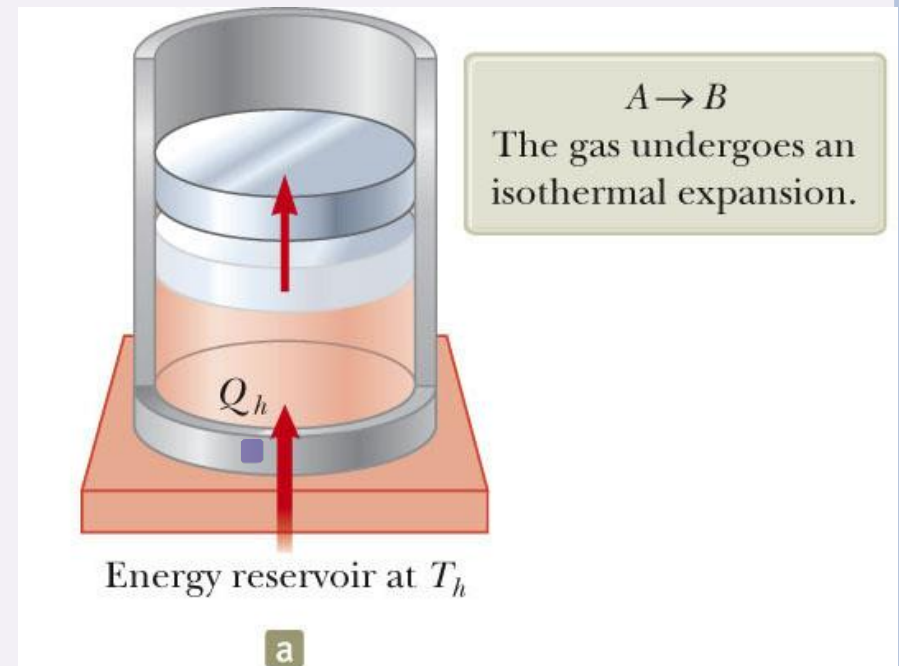
$W=Q$   
 $T \text{ const}$

# CARNOT CYCLE, A TO B

- $A \rightarrow B$  is an isothermal expansion.
- The gas is placed in contact with the high temperature reservoir,  $T_h$ .
- The gas absorbs heat  $|Q_h|$ .
- The gas does work  $W_{AB}$  in raising the piston.

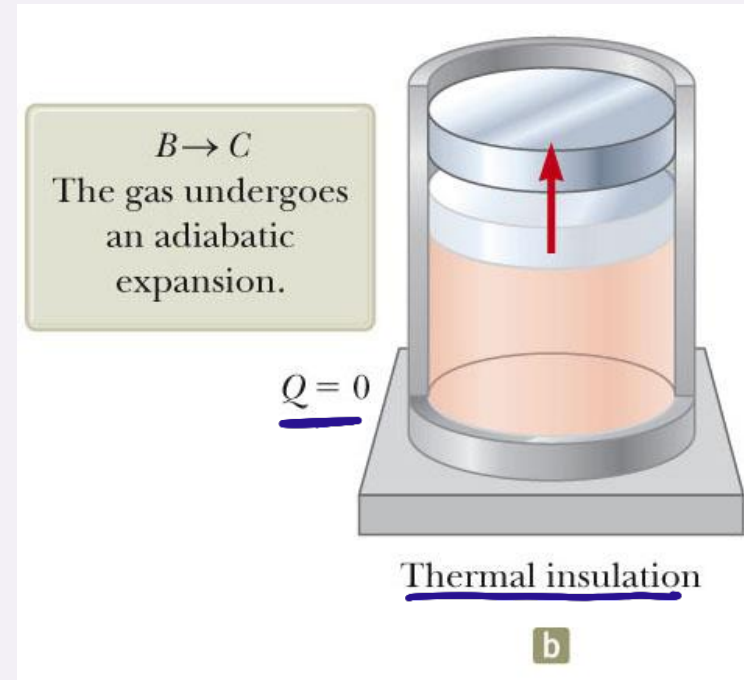
$$Q = W$$

$$T = \text{const}$$



# CARNOT CYCLE, $B$ TO $C$

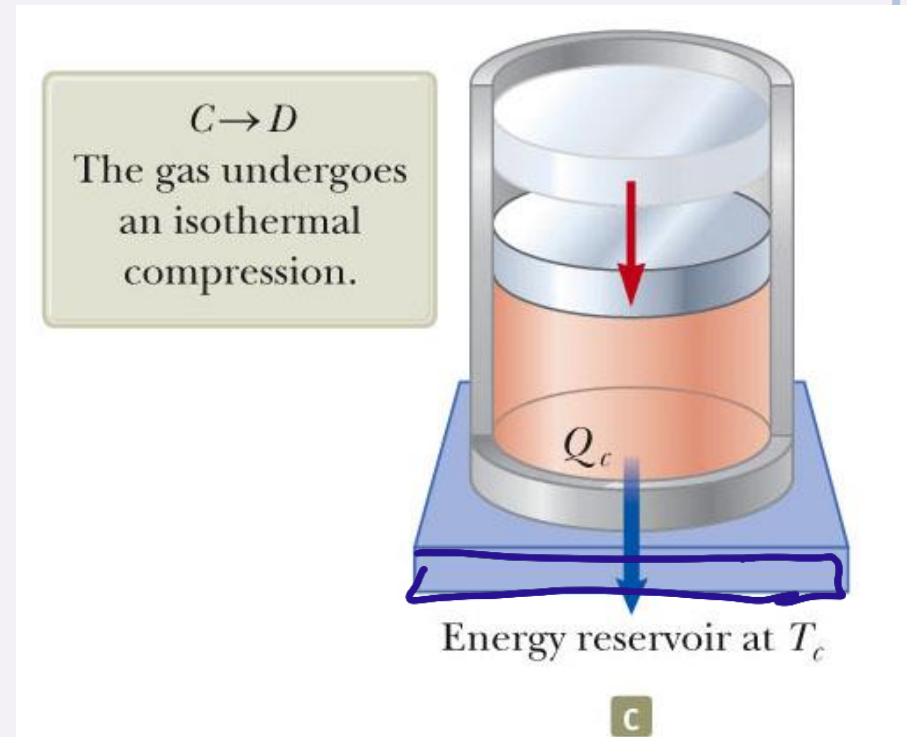
- $B \rightarrow C$  is an adiabatic expansion.
- The base of the cylinder is replaced by a thermally nonconducting wall. طبع عازل بالانضغ
- No energy enters or leaves the system by heat.  $Q = 0$
- The temperature falls from  $T_h$  to  $T_c$
- The gas does work  $W_{BC}$ .



# CARNOT CYCLE, $C$ TO $D$

- The gas is placed in thermal contact with the cold temperature reservoir.
- $C \rightarrow D$  is an isothermal compression.
- The gas expels energy  $|Q_c|$ .
- Work  $W_{CD}$  is done on the gas.

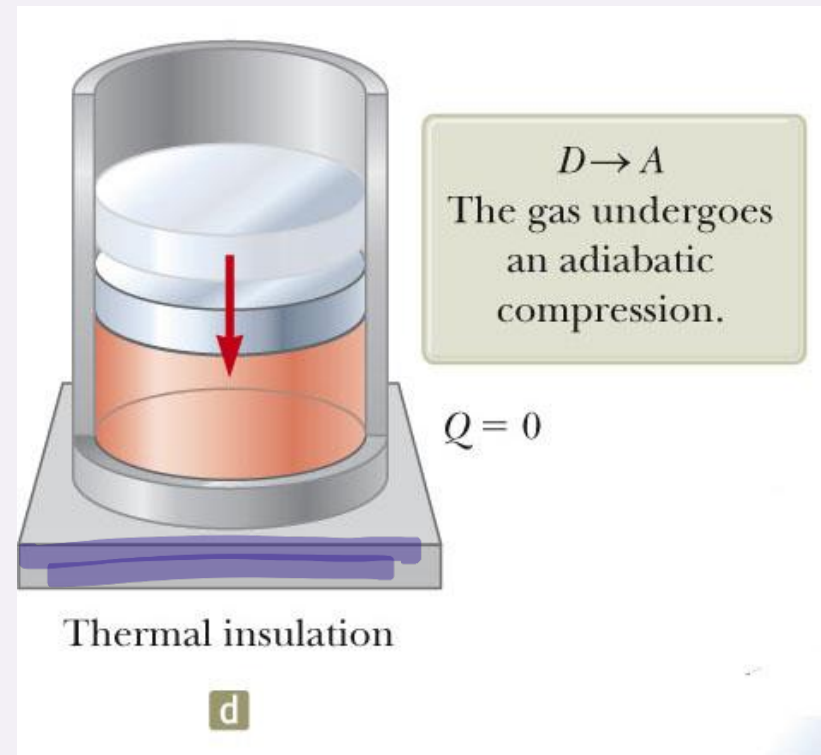
$$W = Q_c$$



# CARNOT CYCLE, $D$ TO $A$

- $D \rightarrow A$  is an **adiabatic compression**.
- The base is replaced by 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  $W_{DA}$ .

$$Q=0$$





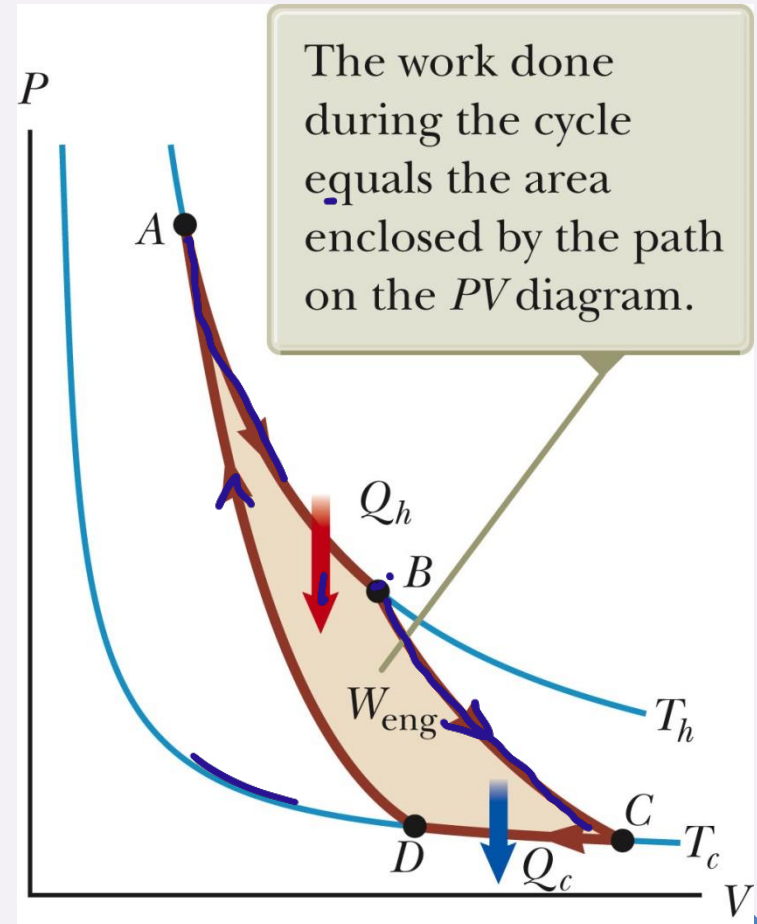
# CARNOT CYCLE, $PV$ DIAGRAM

- The work done by the engine is shown by the area enclosed by the curve,  $W_{\text{eng}}$ .
- The net work is equal to  $|Q_h| - |Q_c|$ .
- $\Delta E_{\text{int}} = 0$  for the entire cycle

$$W = \text{المساحة المحصورة}$$
$$\text{تحت المنحنى الدائري}$$

$$W = Q_h - Q_c$$

$$\Delta E_{\text{int}} = 0$$



# EFFICIENCY OF A CARNOT ENGINE

- Carnot showed that the efficiency of the engine depends on the temperatures of the reservoirs.

$$e = \frac{W_{eng}}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{T_c}{T_h}$$

- Temperatures must be in Kelvins
- All Carnot engines operating between the same two temperatures will have the same efficiency.

کفایت حرکت کارنوٹ تصدیق کی درجات الحرارة



# NOTES ABOUT CARNOT EFFICIENCY

- Efficiency is 0 if  $T_h = T_c$
- Efficiency is 100% only if  $T_c = \underline{0 \text{ K}}$ 
  - Such reservoirs are not available
  - Efficiency is always less than 100%
- The efficiency increases as  $T_c$  is lowered and as  $T_h$  is raised. كلما كانت الفروق أكبر كلما كانت الكفاءة أكبر.
- In most practical cases,  $T_c$  is near room temperature, 300 K
  - So generally  $T_h$  is raised to increase efficiency.



## CARNOT CYCLE IN REVERSE

○ Theoretically, a Carnot-cycle heat engine can run in reverse.

○ This would constitute the most effective heat pump available.  
اعد كفاءة

○ This would determine the maximum possible COPs for a given combination of hot and cold reservoirs.



# CARNOT HEAT PUMP COPs

- In heating mode: ✓

$$COP_C = \frac{|Q_h|}{W} = \frac{T_h}{T_h - T_c}$$

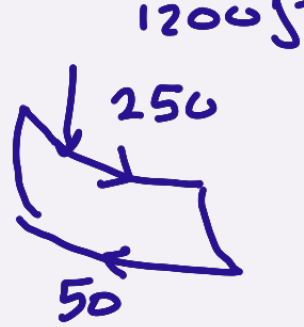
- In cooling mode: ✓

$$COP_C = \frac{|Q_c|}{W} = \frac{T_c}{T_h - T_c}$$

- In practice, the COP is limited to values below 10.



# EXAMPLE



An ideal gas is taken through a Carnot cycle. The isothermal expansion occurs at  $250^\circ\text{C}$ , and the isothermal compression takes place at  $50.0^\circ\text{C}$ . The gas takes in  $1200\text{ J}$  of energy from the hot reservoir during the isothermal expansion. Find (a) the energy expelled to the cold reservoir in each cycle and (b) the net work done by the gas in each cycle.

- Isothermal expansion at  $T_H = 523\text{ K}$
- Isothermal compression at  $T_L = 323\text{ K}$

$$e = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_C}{T_H}$$

$$(a) \quad \frac{Q_L}{Q_H} = \frac{T_C}{T_H} \quad \longrightarrow \quad Q_L = Q_H \frac{T_C}{T_H} \quad \longrightarrow \quad Q_L = 1200 \frac{323}{523} = 741\text{ J}$$

$$(b) \quad W = Q_H - Q_L \quad \longrightarrow \quad W = 1200 - 741 = 459\text{ J}$$

$$Q_L = Q_H \frac{T_C}{T_H} = 1200 \frac{323}{523} = 741\text{ J}$$

$$W = Q_H - Q_L = 1200 - 741 = 459\text{ J}$$

# Entropy

The zeroth law of thermodynamics involves the concept of temperature, and the first law involves the concept of internal energy.

Temperature and internal energy are both state variables; that is, the value of each depends only on the thermodynamic state of a system, not on the process that brought it to that state.

Another state variable—this one related to the second law of thermodynamics—is entropy.

متغيرات حالة ( state variable )  
energy ←  
Temperatur ←



# ENTROPY

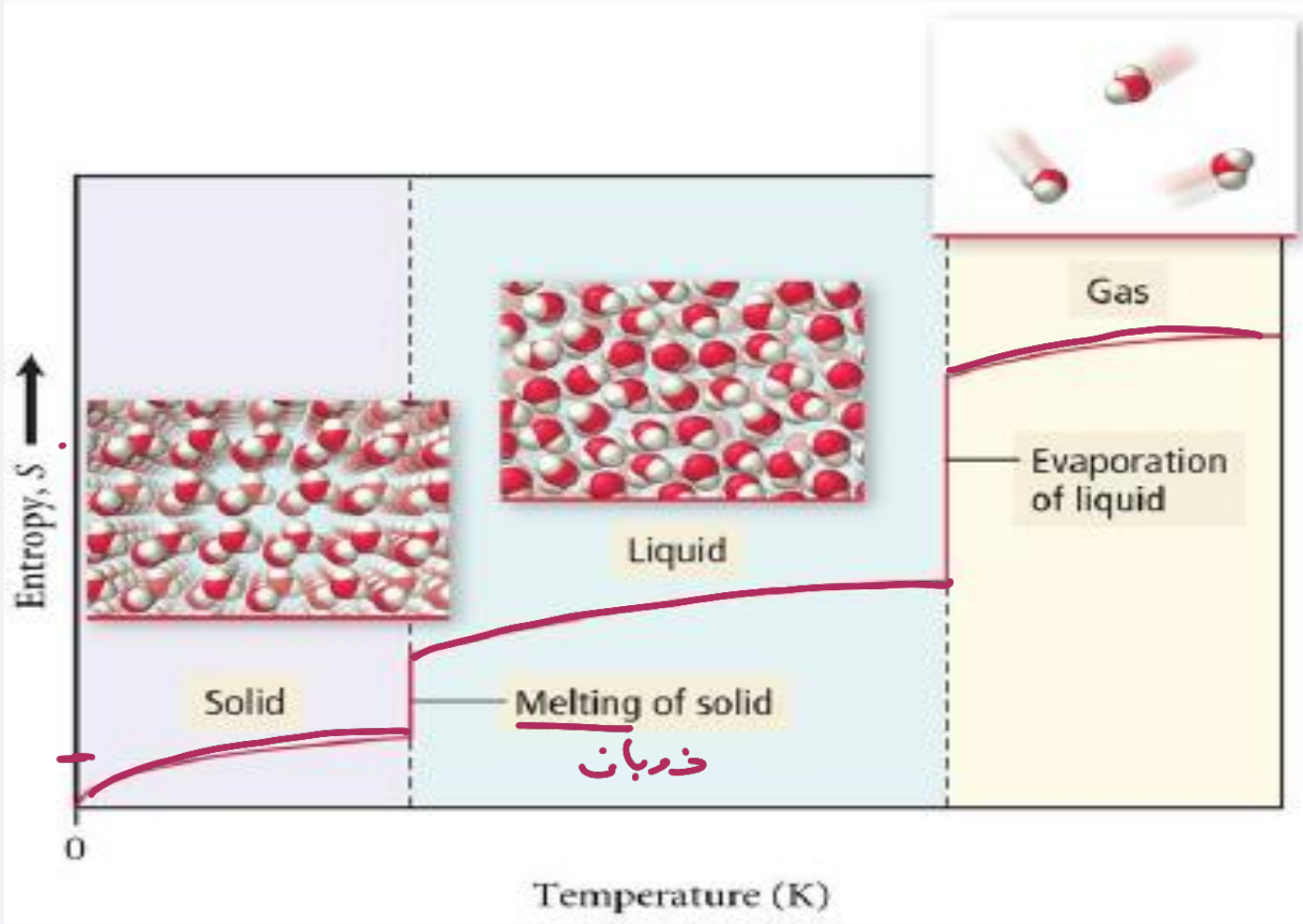
- The importance of entropy grew with the development of statistical mechanics.  
صياحي  
اصغانيه
- Entropy is a natural measure of the disorder.  
المقاييس الكميّة للمؤاينه

## The 2<sup>nd</sup> Law of Thermodynamics

In any spontaneous process there is always an increase in the entropy of the universe.

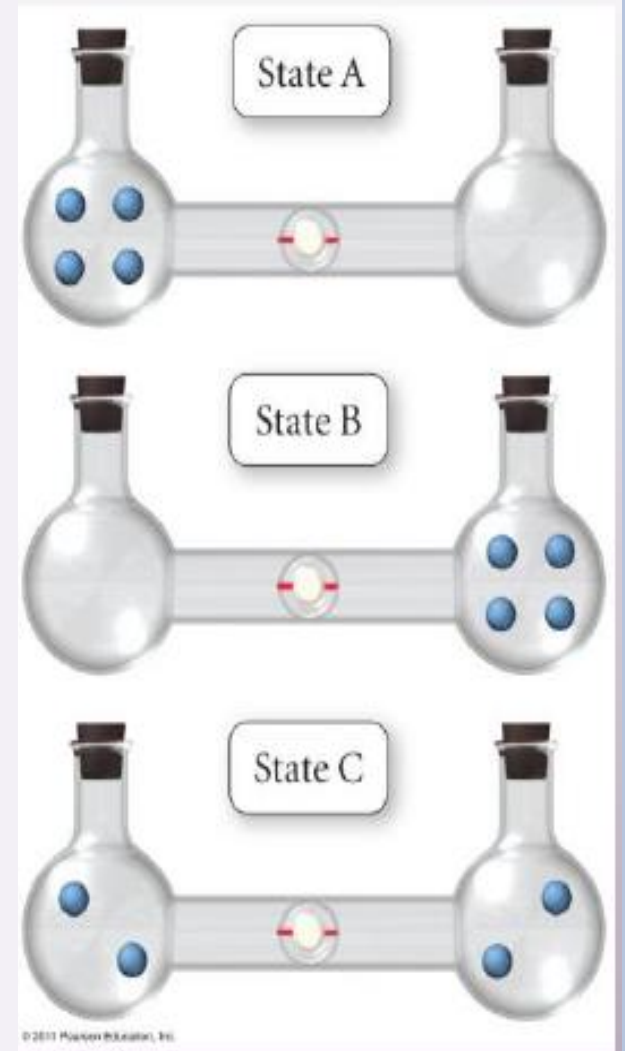
في عملية تلقائية دائما ليصاحب زياده في الاضطراب





# ENTROPY

Gases will spontaneously and uniformly mix because the mixed state has more possible arrangements (a larger value of macrostate and higher entropy) than the unmixed state.



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عند وضع جزئيات غازين معاً  
سوف يحدث خلط بشكل تلقائي  
لان عنصراً تلامس النوعين يكون هناك عدد

اعبرنا احتمالات الترتيب (وهذا مرتبط بزيادة إنتروبي

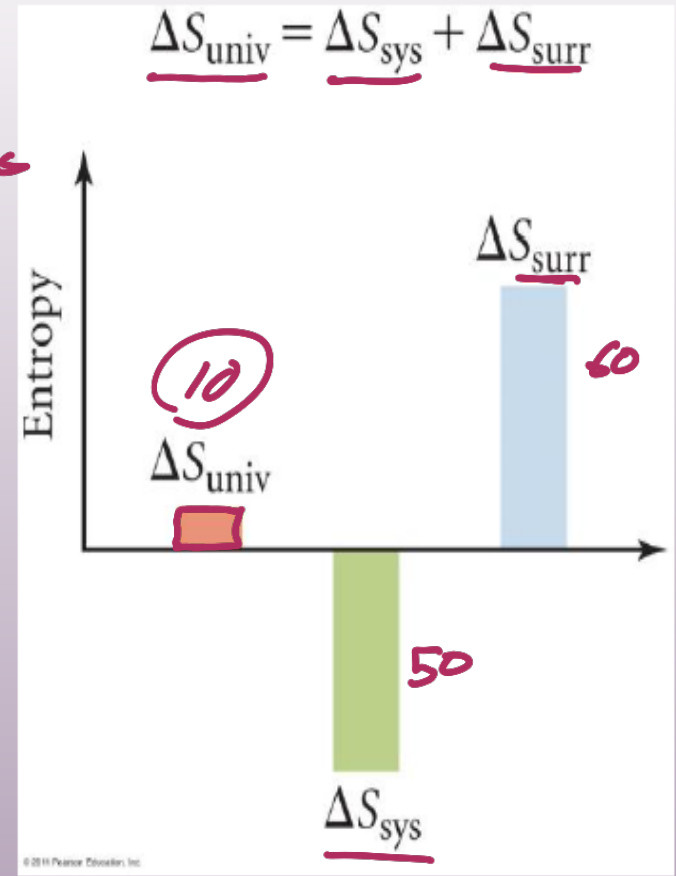
S

# Change in Entropy of the universe

Water spontaneously freezes at a temperature below 0°C. Therefore, the process increases the entropy of the universe!! عند تجميد الماء قلت الاضطرابي له الماء لانها ذات بانيه للنظام

- The water molecules become much more ordered as they freeze, and experience a decrease in entropy. The process also releases heat, and this heat warms gaseous molecules in air, and increases the entropy of the surroundings.
- Since the process is spontaneous below 0°C,  $\Delta S_{surr}$  must be greater in magnitude than  $\Delta S$  of the water molecules.

Entropy can be viewed as the dispersal or randomization of energy.



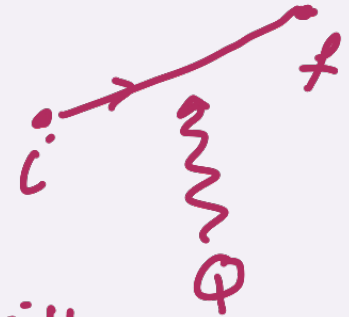
الاضطرابي زي عن تشتت وعوائيه الطاقة



# ENTROPY AND HEAT

- The original formulation of entropy dealt with the transfer of energy by heat in a reversible process.
- Let  $dQ_r$  be the amount of energy transferred by heat when a system follows a reversible path.
- The change in entropy,  $dS$  is

$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$$

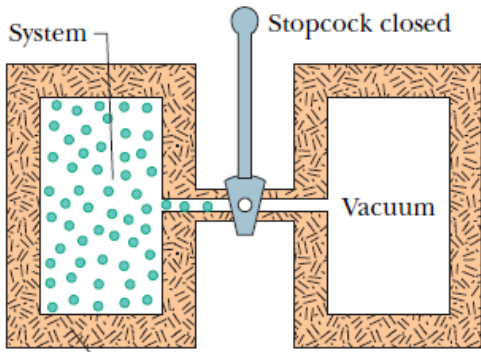


المتغيرين الامتروبي يعتمد فقط على نقطتي البداية والنهاية وليس

المتغيرين الامتروبي يعتمد فقط على نقطتي البداية والنهاية وليس  
○ The change in entropy depends only on the endpoints and is independent of the actual path followed.

○ The entropy change for an irreversible process can be determined by calculating the change in entropy for a reversible process that connects the same initial and final points.



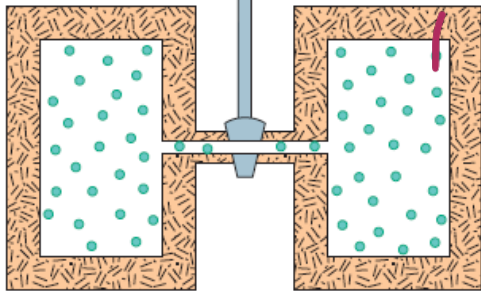


(a) Initial state  $i$

$S_i$



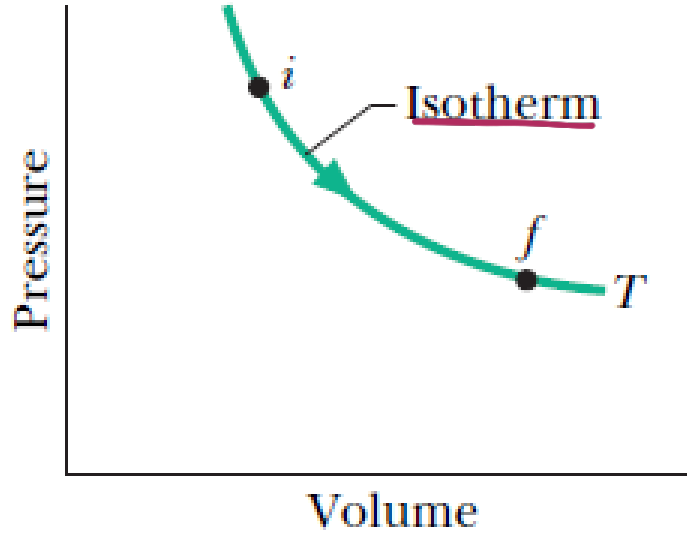
Stopcock open



(b) Final state  $f$

$S_f$

Entropy change of an irreversible process can be found with a reversible one connecting the initial and final states.



free expansion

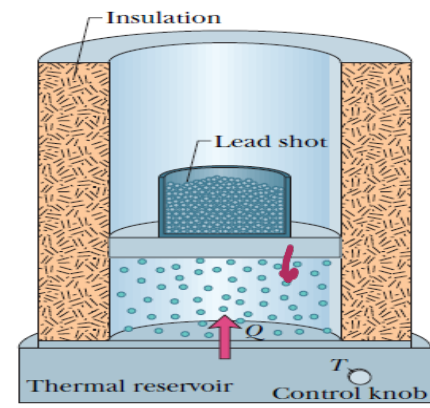
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$$\Delta S = S_f - S_i = \frac{1}{T} \int_i^f dQ.$$

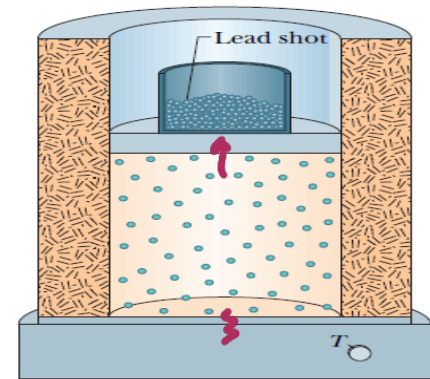
$$\int dQ = Q,$$

$$\Delta S = S_f - S_i = \frac{Q}{T}$$

(change in entropy, isothermal process).



(a) Initial state  $i$



(b) Final state  $f$

تساوي  
ت

an isothermal process

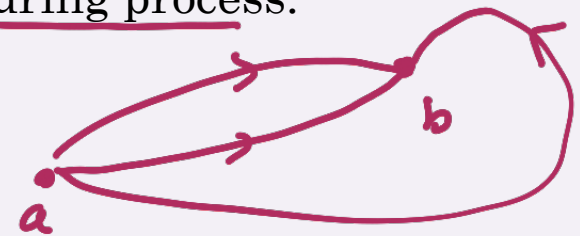
# MORE ABOUT CHANGE IN ENTROPY

○  $dQ_r$  is measured along a reversible path, even if the system may have followed an irreversible path.

○ The meaningful quantity is the change in entropy and not the entropy itself.

○ For a finite process, T is generally not constant during process.

$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$$



○ The change in entropy of a system going from one state to another has the same value for all paths connecting the two states.

حساب  $\Delta S$  لا يعتمد على المسار فقط البراهين والتهريب

□ If an **irreversible process** occurs in a closed system, the change in entropy  $\Delta S$  of the system always increases; it never decreases.

$$\Delta S \rightarrow J/K$$

□ Unit of  $\Delta S$  is J/K, The change in entropy depends only on the endpoints and is independent of the actual path followed.

في نظام مغلق دائماً  $\Delta S$  تزداد

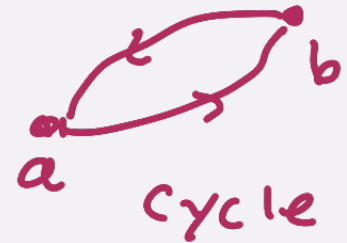


# $\Delta S$ FOR A REVERSIBLE CYCLE

- $\Delta S = 0$  for any reversible cycle
- In general,

$$\Delta S = S_f - S_i = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$$

- This integral symbol indicates the integral is over a closed path.

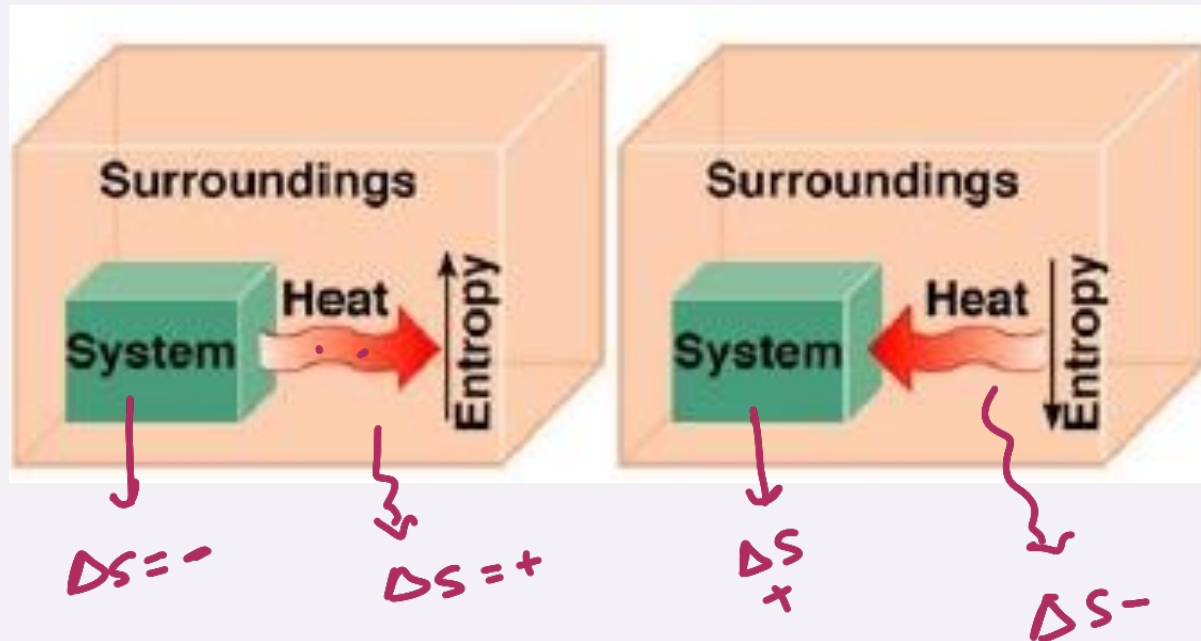


$$\Delta S = 0$$

$$\Delta S = \int_a^a \frac{dQ}{T} = 0$$



- When energy is absorbed by the system,  $dQ_r$  is positive and the entropy of the system increases.
- When energy is expelled by the system,  $dQ_r$  is negative and the entropy of the system decreases.





كيف نحس  $\Delta S$  في حالة تغير الحالة؟ ذوبان تبخر

$$\Delta S = \frac{m d_f}{T_m} \quad \text{ذوبان}$$

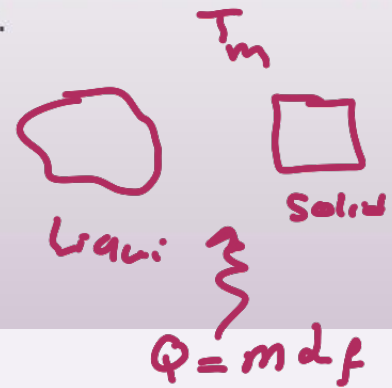
$$\Delta S = \frac{m d_v}{T_b} \quad \text{تبخير}$$

A solid that has a latent heat of fusion  $L_f$  melts at a temperature  $T_m$ . Calculate the change in entropy of this substance when a mass  $m$  of the substance melts.

$$\Delta S = \int_i^f \frac{dQ}{T}$$

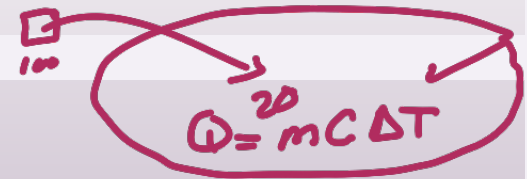
$$\Delta S = \frac{1}{T_m} \int_i^f dQ = \frac{Q}{T_m}$$

$$\Delta S = \frac{mL_f}{T_m}$$



A Styrofoam cup holding 125 g of hot water at 100°C cools to room temperature, 20.0°C. What is the change in entropy of the room? Neglect the specific heat of the cup and any change in temperature of the room.

$$\Delta S = \frac{\Delta Q}{T} = \frac{0.125 \times 4186 \times 80}{293} \quad Q_{\text{room}} = (mc|\Delta T|)_{\text{water}}$$

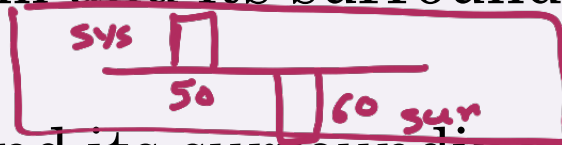


$$\Delta S = \frac{Q_{\text{room}}}{T} = \frac{(mc|\Delta T|)_{\text{water}}}{T} = \frac{0.125 \text{ kg}(4186 \text{ J/kg} \cdot ^\circ\text{C})(100 - 20)^\circ\text{C}}{293 \text{ K}} = \underline{143 \text{ J/K}}$$

احصلوا حساب التغير في الانتروبي للرفة

# ENTROPY CHANGES IN NON-ISOLATED SYSTEMS

○ The increase in entropy described in the second law is that of the system and its surroundings.



$$\Delta S_{uni} \neq 0$$

○ When a system and its surroundings interact in an irreversible process, the increase in entropy of one is greater than the decrease in entropy of the other.

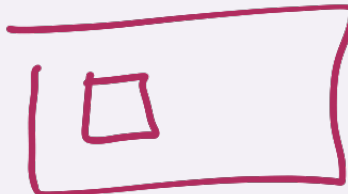
reversible



$$\Delta S = 0$$

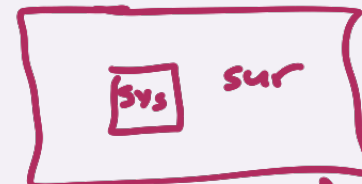
○ The change in entropy of the Universe must be greater than zero for an irreversible process and equal to zero for a reversible process.

$$\Delta S \neq 0$$



Irreversible

$$\Delta S = 0$$



reversible



# ENTROPY CHANGES IN IRREVERSIBLE PROCESSES

○ To calculate the change in entropy in a real system, remember that entropy depends only on the state of the system.

○ Do not use Q, the actual energy transfer in the process.

$$\Delta S = \int \frac{dQ_r}{T}$$

- Distinguish this from  $Q_r$ , the amount of energy that would have been transferred by heat along a reversible path.
- $Q_r$  is the correct value to use for  $\Delta S$ .

$Q_r$  الموجود في القانون لسيّة الطاقة المتحوّلة  
ولكن هي كمية الطاقة غير مرئية



# 20.3 Change in Entropy: Entropy is a State Function

Suppose that an ideal gas is taken through a reversible process, with the gas in an equilibrium state at the end of each step.

For each small step, the energy transferred as heat to or from the gas is dQ, the work done by the gas is dW, and the change in internal energy is dE<sub>int</sub>

We have:  $dE_{int} = dQ - dW$

$dE_{int} = dQ - dW$   
 $nC_v \Delta T = dQ - PdV$

Since the process is reversible,  $dW = p dV$  and  $dE_{int} = nC_v dT$ .

Therefore,  $dQ = p dV + nC_v dT$ .  
 $PV = nRT$   
 $P = \frac{nRT}{V}$

$\frac{dQ}{T} = \frac{PdV}{T} + \frac{nC_v dT}{T}$

Using ideal gas law, we obtain:  $\frac{dQ}{T} = nR \frac{dV}{V} + nC_v \frac{dT}{T}$ .

$\int \frac{dQ}{T} = \int \frac{nR dV}{V} + \int \frac{nC_v dT}{T}$

Integrating,  $\int_i^f \frac{dQ}{T} = \int_i^f nR \frac{dV}{V} + \int_i^f nC_v \frac{dT}{T}$ .

$\Delta S = nR \int_i^f \frac{dV}{V} + nC_v \int_i^f \frac{dT}{T}$

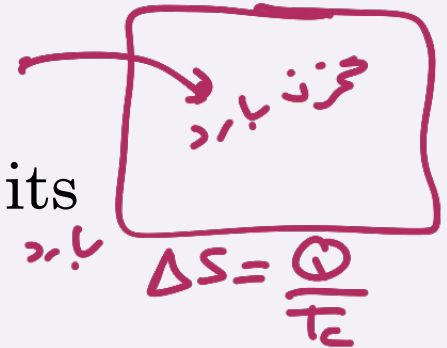
Finally,  $\Delta S = S_f - S_i = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_i}$ .

**The change in entropy  $\Delta S$  between the initial and final states of an ideal gas depends only on properties of the initial and final states;  $\Delta S$  does not depend on how the gas changes between the two states.**

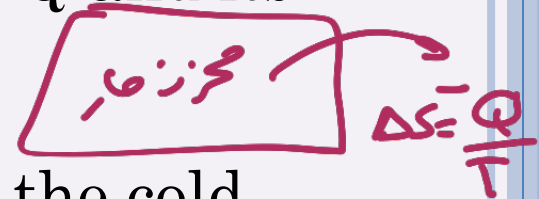
$\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_i}$

# $\Delta S$ IN THERMAL CONDUCTION

○ The cold reservoir absorbs energy  $Q$  and its entropy changes by  $\underline{Q/T_c}$ .



○ At the same time, the hot reservoir loses  $Q$  and its entropy changes by  $\underline{-Q/T_h}$ .



○ Since  $\underline{T_h} > \underline{T_c}$ , the increase in entropy in the cold reservoir is greater than the decrease in entropy in the hot reservoir.

$$\Delta S_{\text{بارده}} > \Delta S_{\text{جاري}}$$

○ Therefore,  $\underline{\Delta S_U} > 0$

- For the system and the Universe

$$\Delta S_U$$

موجب

الاتردي. يجب ان تزداد بالنتيجة لـ U



# EXAMPLE

$$\Delta S_u = +$$

An irreversible engine operating between the temperatures of 550 K and 300 K extracts 1200 J of heat from the hot reservoir and produces 450 J of work. How much is the change in entropy in the process?

$$\Delta S = \frac{Q_c}{T_c} - \frac{Q_h}{T_h}$$

$$Q_h = 1200\text{J}$$

$$T_h = 550\text{K}$$

$$T_c = 300\text{K}$$

$$W = 450\text{J}$$

$$550$$

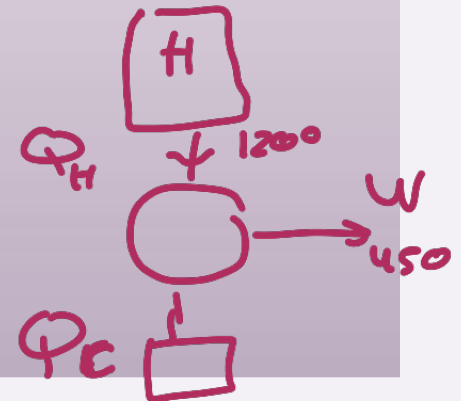
$$\Delta S = \frac{Q_h}{T_h}$$

$$300$$

$$\Delta S = \frac{Q_c}{T_c}$$

$$\therefore Q_c = 1200 - 450\text{J} = 750\text{J}$$

$$\Delta S = \frac{750}{300} - \frac{1200}{550} = \underline{+0.318\text{J/K}}$$



$$W = Q_H - Q_C$$

$$450 = 1200 - Q_C$$

$$Q_C = 1200 - 450 = 750$$

$$\Delta S_h = \frac{1200}{550}$$

$$\Delta S_c = \frac{750}{300}$$

$$\Delta S = \Delta S_c - \Delta S_h = \frac{750}{300} - \frac{1200}{550} = 0.318\text{K}$$

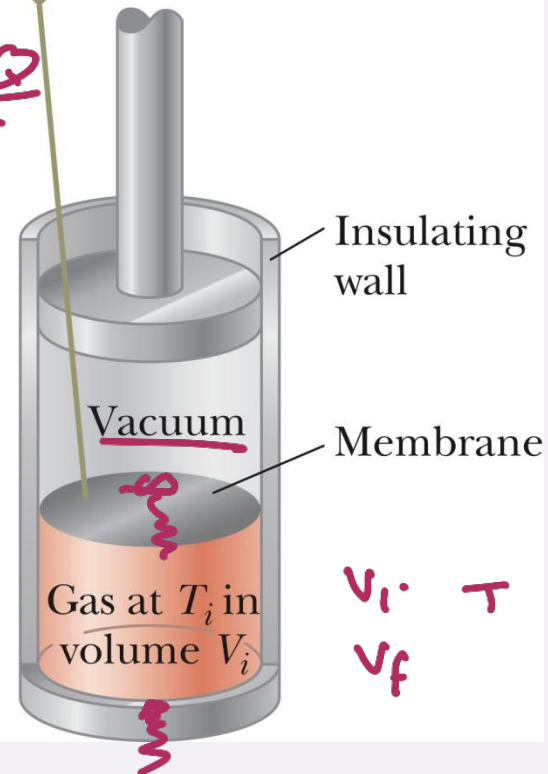
# $\Delta S$ IN A FREE EXPANSION

- Consider an adiabatic free expansion.
- This process is irreversible since the gas would not spontaneously crowd into half the volume after filling the entire volume .
- $Q = 0$  but we need to find  $Q_r$
- Choose an isothermal, reversible expansion in which the gas pushes slowly against the piston while energy enters from a reservoir to keep  $T$  constant.

$$\Delta S = \int_i^f \frac{dQ_r}{T} = \frac{1}{T} \int_i^f dQ_r$$

When the membrane is ruptured, the gas will expand freely and irreversibly into the full volume.

$$\Delta S = \int \frac{\Delta Q}{T}$$



## $\Delta S$ IN FREE EXPANSION, CONT

- For an isothermal process, this becomes

$$\Delta S = nr \ln \frac{V_f}{V_i}$$

- Since  $V_f > V_i$ ,  $\Delta S$  is positive

- This indicates that both the entropy and the disorder of the gas increase as a result of the irreversible adiabatic expansion.

$$\Delta S = nr \ln \frac{V_f}{V_i}$$

تغير الإنتروبي  
في التمدد الحثي





$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_i}$$

## EXAMPLE

One kilogram of water at 0°C is heated to 100°C. Compute its change in entropy.  $v_f = v_i$ .

$$\Delta S = \int_{T_i}^{T_f} \frac{dQ}{T}$$

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ}{T}$$

$$\Delta S = mc \ln \frac{T_f}{T_i}$$

$$dQ = mc dT$$

$$\Delta S = \int_{T_i}^{T_f} \frac{mc dT}{T}$$

$$\Delta S = mc \int_{T_1}^{T_2} \frac{dT}{T} = mc \ln \frac{T_2}{T_1}$$

تغییر فقط  
نبرد ۴۰۰، ۱۰۰

$$\Delta S = 1000 \times 4.168 \ln \frac{373}{273} = 1308 \text{ J/K}$$

$$mc \int_{T_i}^{T_f} \frac{dT}{T} = mc \ln \frac{T_f}{T_i} = 1000 \times 4.168 \ln \frac{373}{273}$$

$$= 1308 \text{ J/K}$$



# HEAT DEATH OF THE UNIVERSE

○ Ultimately, the entropy of the Universe should reach a maximum value.

○ At this value, the Universe will be in a state of uniform temperature and density.

○ All physical, chemical, and biological processes will cease.

في حالة التوازن لا يوجد طاقة متوفرة لا يمكن استخدامها

• The state of perfect disorder implies that no energy is available for doing work.

• This state is called the heat death of the Universe.



# ENTROPY AND THE SECOND LAW

- Entropy is a measure of disorder.
- The entropy of the Universe increases in all real processes.
  - This is another statement of the second law of thermodynamics.
    - It is equivalent to the Kelvin-Planck and Clausius statements.

