KINGDOOM OF SAUDI ARABIA
Ministry of Education
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College of Science
Department of Physics

المملكة العربية السعودية
وزارة التعليم
جامعة الإمام محمد بن سعود الإسلامية
كلية العلوم
قسم الفيزياء

Chapter 4

Applications of the second Law of Thermodynamics

المفهوم الرياضي للانتروبي

THE MATHEMATICAL CONCEPT OF ENTROPY

دلالة على العشوائية

The Clausius's definition of the entropy S is given by: $dS = \frac{dQ_r}{T}$

Where dQ_r is the heat flow into the system for reversible process, and T is the absolute temperature. When we substitute the precedent equation and the first law of thermodynamic, we obtain, for reversible process: $dU = T\,dS - P\,dV$

$du = dq - W$

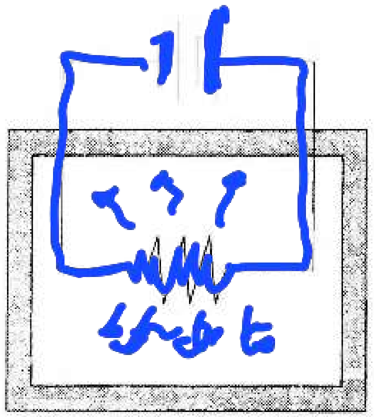
$du = dsT - pdv$

العمليات غير العكسية

IRREVERSIBLE PROCESSES

Consider the following processes and the results observed in nature:

عندما يمر تيار في مقاومه فان الطاقة تنضب في المقاومه ويؤدي الى تفريغ البطارية

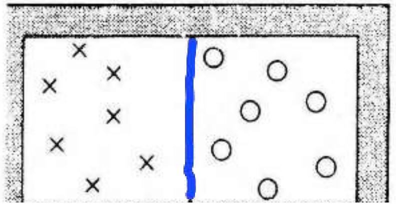


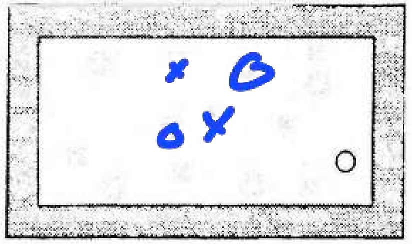
1- A battery will discharge through a resistor, releasing energy. The reverse will not happen adding energy to the resistor by heating will not cause the battery to charge itself.

لا يمكن عكس هذه العملية (Irreversible)

خلط الغازات عمليه غير عكسية

2- Two gases, initially in separate adjoining chambers, will mix uniformly





تعريف Clausius's

$$dS = \frac{dQ_r}{T} \qquad dQ_r = dS\,T$$

dQ_r : التدفق الحراري في العملية العكسية

T : درجة الحرارة المطلقة

عند التعويض في القانون الاول نحصل على

$$dU = dQ - W$$

$$dU = TdS - PdV \quad ✓$$

- نص القانون الثاني في الديناميكا الحرارية

* اي تغير تلقائي يجب ان ترافقه زيادة في الانتروبي

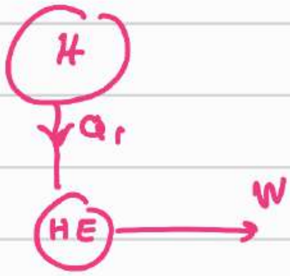
- نص كلاسيوس

من المستحيل استعمال اي عملية دائرية لنقل الحرارة من جسم بارد الى جسم ساخن بشكل تلقائي

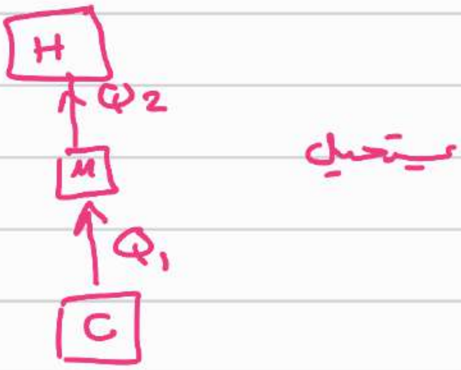
- نص كلفن

من المستحيل تشغيل جهاز حراري يعمل على التبادل الحراري مع مستودع حراري واحد

Kelvin



Clausius



IRREVERSIBLE PROCESSES

لن يضغط الغاز نفسه من جديد
اى الوضع الاصلي Irreversible

3- A gas in one portion of a chamber is allowed to undergo a free expansion into an evacuated section of the chamber.

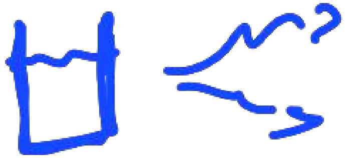
The gas will not compress itself back into its original volume.

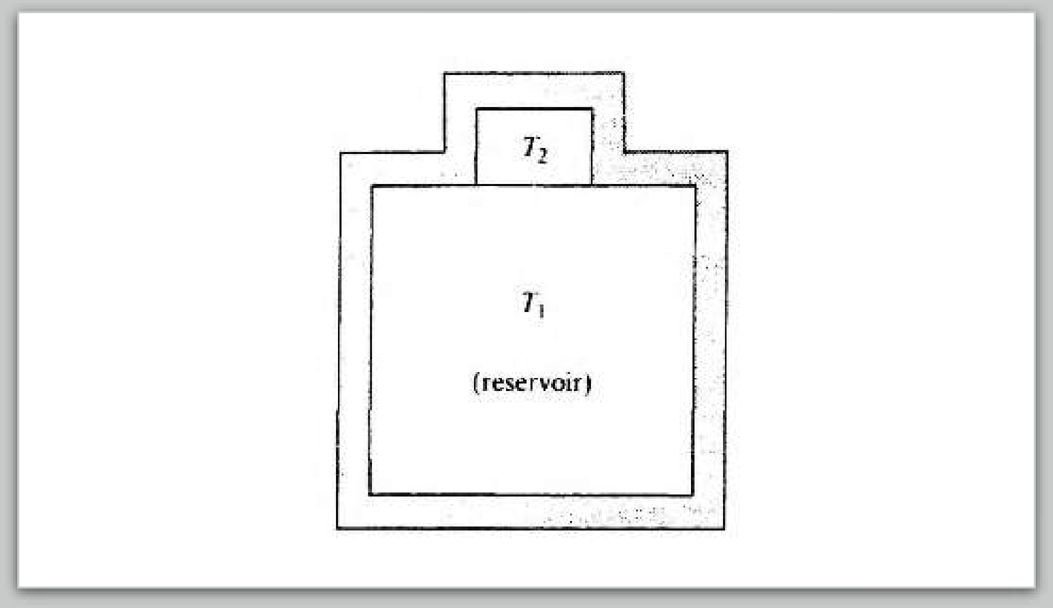
4- Heat flows from a high temperature body to a low temperature reservoir in the absence of other effects.

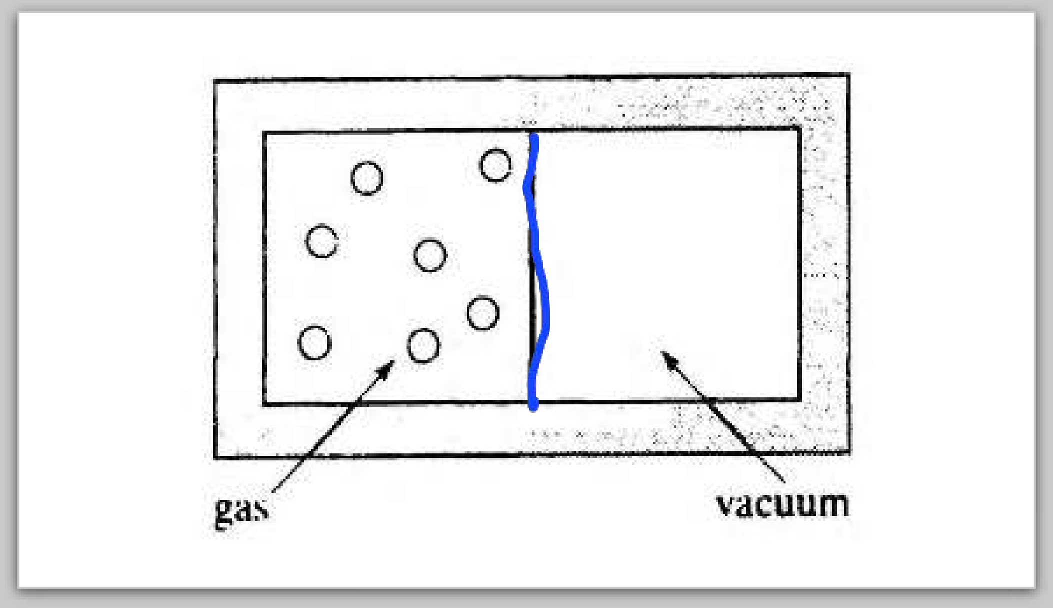
The reverse process does not take place.

If T2 > T1 initially, the body comes to temperature T1

لا تنتقل الحرارة تلقائياً
من الجسم البارد الى الساخن





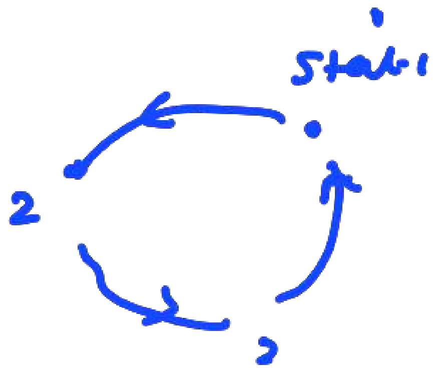


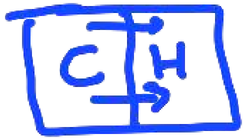
IRREVERSIBLE PROCESSES

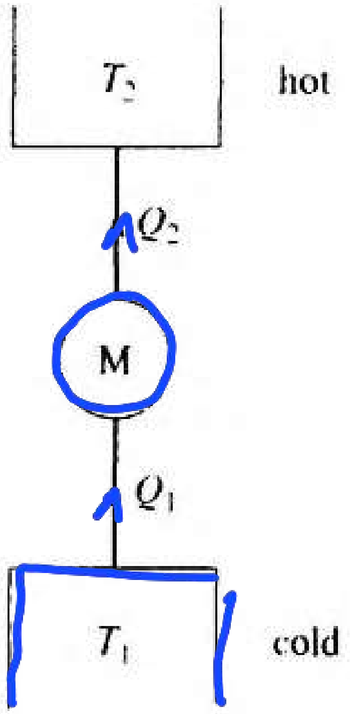
In process such as these, the impossibility of the occurrence of the reverse process was first encountered in two famous statements:

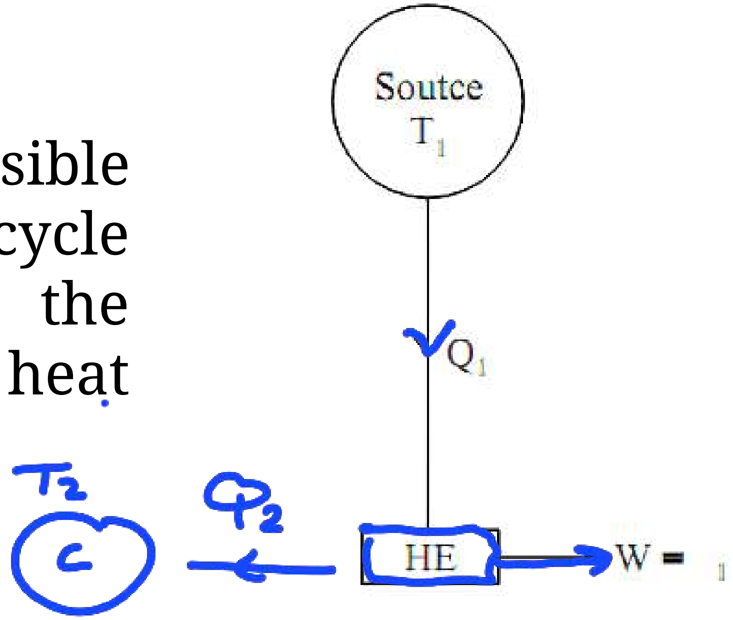
Clausius Statement: its impossible to construct a device that operates in cycle and whose sole effect is to transfer heat from a cooler body to hotter body.

Kelvin - Plank Statement: It is impossible to construct a device that operates in a cycle and produces no other effect than the performance of work and exchange of heat with a single reservoir





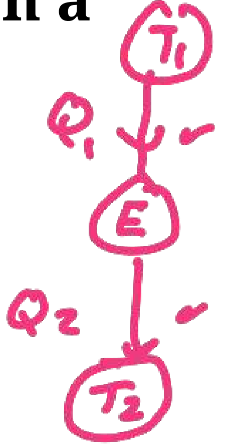




CARNOT'S THEOREM

اكثر محرك كفاءة بين خزانين حراريين هو محرك Carnot

No engine operating between two reservoirs can be more efficient than a Carnot engine operating between those same two reservoirs.



THE CLAUSIUS INEQUALITY AND THE SECOND LAW

For a Carnot cycle we have seen that: $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$

$\frac{Q}{T}$ معامل Carnot

The quantity Q/T is known as the Carnot ratio. From this we deduced the efficiency $\eta = 1 - \frac{T_1}{T_2}$, and proved that the efficiency of all reversible cycles has this value.

كفاءة

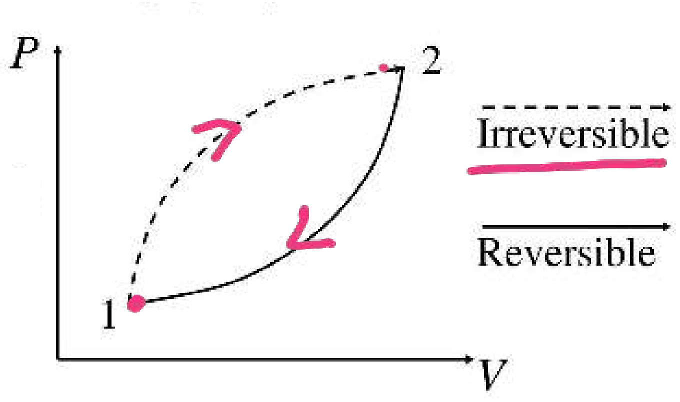
$\eta = 1 - Q_1/Q_2$

We consider an arbitrary reversible cycle and represent it as a continuous contour in a P-V diagram.

We have: $\oint \frac{dQ}{T} \leq 0$

where the equal sign holds for reversible processes. The precedent equation is sometimes taken as a statement of the second law.

Finally, we consider the change in entropy in an irreversible process. Let 1--2 be an irreversible change and 2--1 be any reversible path connecting the two states in the P- V diagram of Figure . Then the precedent equation becomes:



$$\oint \frac{dQ}{T} = \int_1^2 \frac{dQ}{T} + \int_2^1 \frac{dQ_r}{T} \leq 0$$

Changing the order of integration and the sign of the second term we have:

$$\int_1^2 \frac{dQ}{T} \leq \int_2^1 \frac{dQ_r}{T} = S_2 - S_1$$

Thus: $\Delta S = S_2 - S_1 \geq \int_1^2 \frac{dQ}{T}$ Or $dS \geq \frac{dQ}{T}$

For an isolated system: $dQ = 0$ and $dS \geq 0$ Or $\Delta S = S_2 - S_1 \geq 0$

for a finite process. We conclude that:

The entropy of an isolated system increases in any irreversible process and is unaltered in any reversible process.

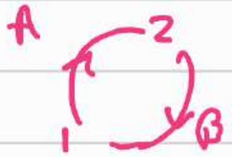
This is the principle of increasing entropy. It is to be noted that this statcn1cnt refers to net entropy changes.

Carnot cycle $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$

$\frac{Q}{T} \Rightarrow$ carnot ration

Efficiency (الكفاءة) $\Rightarrow \eta = 1 - \frac{T_1}{T_2}$

Clausius enquality



$$\oint \frac{dQ}{T} \leq 0$$

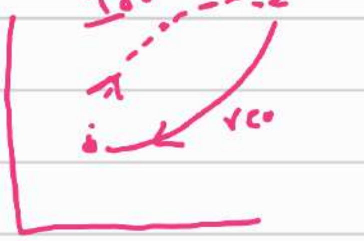
تنطبق على جميع العمليات الحرارية

for reversible process $\Rightarrow \oint \frac{dQ_r}{T} = 0$

for irreversible process $\Rightarrow \oint \frac{dQ}{T} < 0$

$$\underline{\oint ds} = \oint \frac{dQ}{T}$$

$$\oint \frac{dQ}{T} = \int_1^2 \frac{dQ}{T} + \int_2^1 \frac{dQ_r}{T} \leq 0$$



$|dW_r| \geq |dW|$

$$\int_2^1 \frac{dQ_r}{T} \geq \int_1^2 \frac{dQ}{T}$$

$$\int_2^1 \frac{dQ_r}{T} = S_2 - S_1 = \Delta S$$

for Isolated system $dQ = 0$:

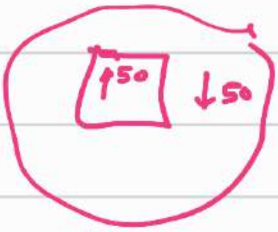
$\Delta S = S_2 - S_1$ ← موجبه

ds

الانتروبي لاي نظام معزول دائما تزداد لاي عمليه غير عكسية.

الانتروبي في الكون دائما في تزايد

Reversible



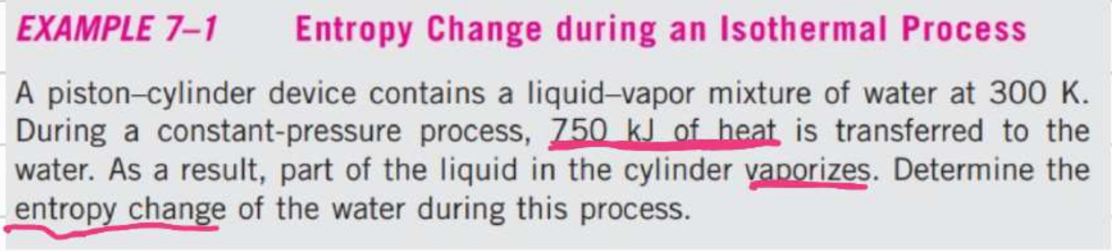
$$\Delta S = 0 = \Delta S_{system} + \Delta S_{surrounding}$$

Irrversible

$$\Delta S > 0 \Rightarrow \Delta S_{system} + \Delta S_{surroun.} > 0$$

adiabitic process $dQ = 0$

$$\Delta S = 0$$

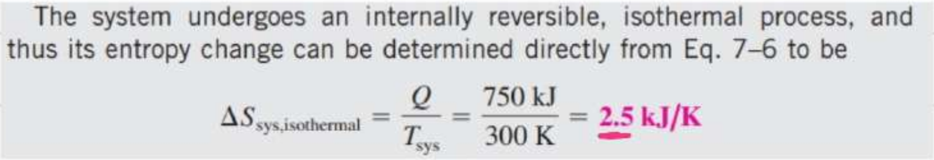


EXAMPLE 7–1 **Entropy Change during an Isothermal Process**

A piston–cylinder device contains a liquid–vapor mixture of water at 300 K. During a constant-pressure process, 750 kJ of heat is transferred to the water. As a result, part of the liquid in the cylinder vaporizes. Determine the entropy change of the water during this process.

$Q = 750 KJ$

$\Delta S = ??$



The system undergoes an internally reversible, isothermal process, and thus its entropy change can be determined directly from Eq. 7–6 to be

$$\Delta S_{\text{sys,isothermal}} = \frac{Q}{T_{\text{sys}}} = \frac{750 \text{ kJ}}{300 \text{ K}} = 2.5 \text{ kJ/K}$$

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

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

$$\Delta S = 2.5K/K$$

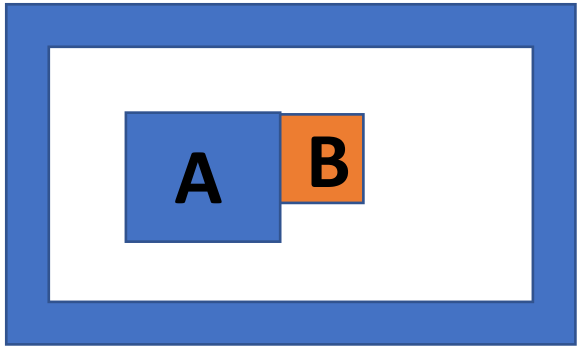
Example:

dQ=0

Consider ~~tow~~ two body in thermal contact in an adiabatic enclosure.
If the heat flows from body A to body B at a lower temperature, with both bodies contained in an adiabatic enclosure, ΔS_A is then negative but: $\Delta S = \Delta S_A + \Delta S_B$ will still be positive

If then, our universe consists of a system and its surroundings, it follows that:

$$\Delta S_{univers} = \Delta S_{System} + \Delta S_{sourinding} \geq 0$$



Enclosure Adiabatic

ABSOLUTE TEMPERATURE

$$\frac{|Q_1|}{|Q_2|} = \frac{T_1}{T_2}$$

The Carnot cycle together with Carnot’s theorem can serve as the basis for defining an absolute temperature scale. Carnot's theorem shows that the ratio Q_1/Q_2 has the same value for all reversible engines that operate between the same temperatures. The special fact about a reversible Carnot cycle is that the efficiency is independent of the nature of the working substance. It can therefore be used to define an absolute scale of temperature as follows.

لا تعتمد على نوع

The definition of the Kelvin scale is completed by assigning to T_1 in Equation: $\frac{|Q_1|}{|Q_2|} = \frac{T_1}{T_2}$ $T = \frac{\boxed{T_1 Q_1}}{Q_2}$

لماذ الدرجة الثلاثية

the value of 273.16 K, the temperature of the triple point of water.

For a Carnot engine operating between temperatures T and T_1, we have: $\boldsymbol{T = 273.16 \frac{Q}{Q_1}}$

The smallest value of Q is zero and the corresponding value of T is zero, called absolute zero. In a Carnot cycle, heat is transferred during the isothermal processes. Hence, if a system undergoes a reversible isothermal process without heat transfer, the temperature at which the process takes place is absolute zero. This is a fundamental definition of absolute zero.

absolute Temp

تعريف

COMBINED FIRST AND SECOND LAWS

$$\boxed{dU = dq_r - dW_r}$$

$$du = Tds - Pdv$$

We saw early in the chapter that for a reversible process,

$$\underline{dU = dQ_r - dW_r} = \underline{TdS} - Pdv \qquad (1)$$

In its most general form, the first law can be written:

$$du = \underline{dQ + \varepsilon} - dW_r$$

$$\underline{dU = dQ - dW} \qquad (2) \qquad \underline{(general)}$$

The second law states that: $\underline{T\,dS = dQ_r} > \underline{dQ}$ for an irreversible process.

We can write: $\underline{dQ_r} = \underline{dQ + \varepsilon}$ (3) $\qquad \varepsilon > 0$

$$du = dQ_r - \varepsilon - dW$$

(3) In (1) → $\quad dU = dQ + \varepsilon - dW_r \qquad (4)$

From (2) and (4) we have: $\underline{dW} = \underline{dW_r} - \underline{\varepsilon}$

We conclude that, the total work done by the system is the reversible configuration work (the useful mechanical work) plus the (negative) dissipative work associated with frictional forces.

$$dU = dQ - dW = dQ_r - \varepsilon - (dW_r - \varepsilon)$$

Or: $\quad \underline{dU = TdS - Pdv} \quad$ (general) $\qquad$ (5)

The equation (5) is most important equation in classical thermodynamics

$$dU = dQ_r - \varepsilon - (dW_r - \varepsilon)$$

سالضايع في الطاقة

الضايع من الشغل

Calculation of the Entropy ~~Change~~ Changes

ENTROPY CHANGES IN REVERSIBLE PROCESSES

To illustrate the calculation of the entropy change, we first consider reversible processes:

$$dQ_r = dU + Pdv \qquad or \qquad \frac{dQ_r}{T} = \frac{dU}{T} + \frac{P}{T}dv = dS$$

We shall examine some special cases.

a) **Adiabatic process**: $dQ_r = 0, dS = 0$ $and\ S = constant.$

A reversible adiabatic process is an isentropic (constant entropy) process. We note in passing that an irreversible adiabatic process is not isentropic.

b) Isothermal process: $S_2 - S_1 = \int_1^2 \frac{dQ_r}{T} = \frac{Q_r}{T}$

c) Isothermal (and isobaric) change of phase: $S_2 - S_1 = \frac{l}{T}$

Here l is the Latent heat of transformation

d) Isochoric process: We assume that u = u(v, T) in general. Since v = constant in an isochoric process, u = u(T), as for an ideal gas, $dU = c_v dT$. Thus: $S_2 - S_1 = \int_1^2 c_v \frac{dT}{T}$

If c_v, is constant over the temperature range $T_2 - T_1$, we have: $S_2 - S_1 = c_v \ln\frac{T_2}{T_1}$

ENTROPY CHANGES IN REVERSIBLE PROCESSES

e- Isobaric process: It is convenient to use the specific enthalpy in an isobaric process.

Since: $h = U + Pv$ and $dQ_r = dU + Pdv \quad \dashrightarrow \quad dh = dU + Pdv + vdP$

$dh = dQ_r + vdP \quad \dashrightarrow \quad \boldsymbol{dS = \frac{dQ_r}{T} = \frac{dh}{T} - \frac{v}{T}\, dP}$

In general $h = h(T, P)$, here P = constant then $h = h(T)$ and $dh = c_p\, dT$

Then: $\boldsymbol{\Delta S = S_2 - S_1 = \int_1^2 c_p \frac{dT}{T} = c_p \ln\frac{T_2}{T_1}}$ $(if\ c_p\ is\ constant)$

① Isochoric process $dV=0$

$$dQ = dU = C_{\underline{v}}\, dT \quad ✓$$

$$\Delta S = \int dS = \int \frac{dQ}{T} = \int \frac{C_v\, dT}{T}$$

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

$$\Delta S = C_v \ln \frac{T_2}{T_1}$$

② Isobaric process $dP=0$

$$dQ = dU + PdV = C_{\underline{p}}\, dT$$

$$\Delta S = \int \frac{dQ}{T} = \int \frac{C_p\, dT}{T} = C_p \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta S = C_p \ln \frac{T_2}{T_1}$$

③ Isothermal process $dU=0$

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$dQ = P\, dV$$

$$\Delta S = \int \frac{dQ}{T} = \int \frac{P\, dV}{T} = \int \frac{nR\cancel{T}}{V\cancel{T}}\, dV = nR \ln \frac{V_2}{V_1}$$

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

④ adiabatic process $dQ = 0$

$$\Delta S = \int \frac{dQ}{T} = 0$$

$$\Delta S = 0$$

⑤ for an Ideal gas

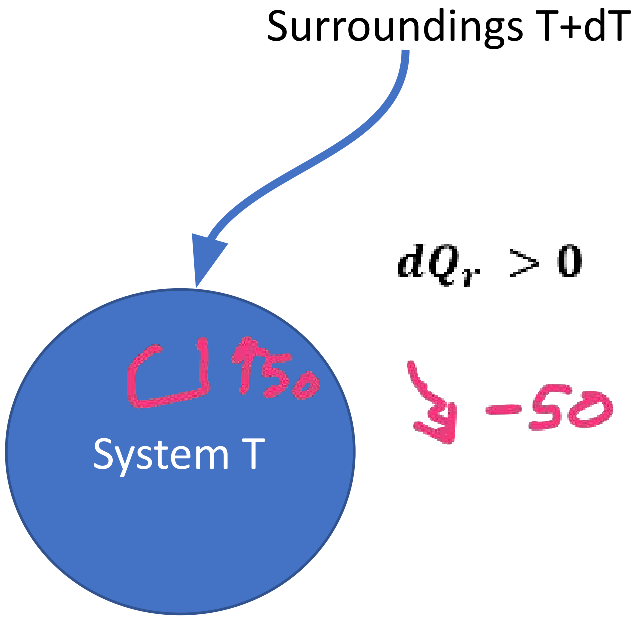
$$\Delta S = C_2 \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

ENTROPY CHANGE OF TH E SURROUNDINGS FOR A REVERSIBLE PROCESS

The heat flow into a system from its surroundings in reversible process is shown in the figure

Thus: $dS_{System} + dS_{surrondinds} = dS_{univers}$

As: $|dS_{system}| = -|dS_{surronding}|$ *and* $dS_{univers} = 0$



In any reversible process, the entropy change of the universe is always zero. This means that any change in entropy of the system will be accompanied by an entropy change in the surroundings equal in magnitude but opposite in sign.

Entropy is conserved in a reversible process. Of course, only idealized -processes are reversible; all natural processes are irreversible, and entropy is not conserved in general.

$dS = +50 - 50$
$= 0$

جمع العمليات الطبيعيه هي عمليات غير عكسيه (الانتروبيا غير محفوظه).

ENTROPY CHANGE FOR AN IDEAL GAS

$pv = nRT$ ✓

$du = dQ + Pdv$

With: $dU = c_v dT$ and $\frac{dQ_r}{T} = \frac{dU}{T} + \frac{P}{T} dv = dS$

Then: $\frac{dQ_r}{T} = \frac{c_v dT}{T} + \frac{P}{T} dv = dS$

for a reversible process. For an ideal gas: $\frac{P}{T} = \frac{R}{v}$

$P = \frac{nRT}{v}$

So: $dS = \frac{c_v dT}{T} + \frac{R}{v} dv$

If c_v is constant, we have: $\Delta S = S_2 - S_1 = c_v \ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}$

$ds = \frac{dQ}{T}$

$dQ = ds\,T$

$du = Tds - pdv$

$du = Tds - \frac{nRT}{v}dv$

$\frac{\cancel{T}ds}{\cancel{T}} = \frac{du}{T} + \frac{nR\cancel{T}dv}{\cancel{T}v}$

$ds = \frac{du}{T} + \frac{R\,dv}{v} \Rightarrow \int_{s_1}^{s_2} dS = \int_{T_1}^{T_2} \frac{C_v dT}{T} + \int_{v_1}^{v_2} \frac{R dv}{v} = S_2 - S_1 = C_v \ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}$

$= S_2 - S_1 = C_p \ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}$

ENTROPY CHANGE IN IRREVERSIBLE PROCESSES

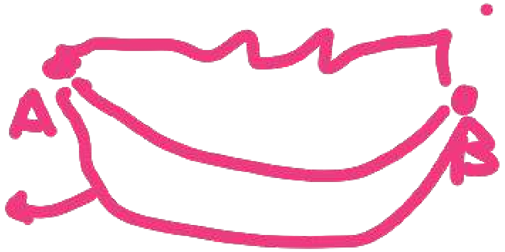
How do we calculate the entropy change for an irreversible process when the entropy is only defined in terms of reversible heat flow?

We resort again to an earlier argument. The entropy is a state variable. and the entropy difference is the same between any two equilibrium states regardless of the nature of the process.

Thus, we can find ΔS as for an irreversible process by choosing any convenient reversible path from the initial to the final state and be certain that it is equal to the change produced by the actual irreversible path.

$\Delta S = S_2 - S_1$

ΔS مثل ΔU لاتعتمد عل العمليه، المسار



EXAMPLE

Suppose that 0.5 kg of water at 90°C is cooled to 20°C, the temperature of the surrounding room. The specific heat capacity at constant pressure of water is 4180 $JKg^{-1}K^{-1}$. The change in entropy of the system (the water) is the change that would occur if the water were cooled reversibly from:

90 $T_1 = 363\,K$ and $T_2 = 293\,K$. → 20

Calculate the change in entropy of the system (water) ,the change in entropy of the surrounding and the change in entropy of the universe.

ΔS

$T_1 = 363k$ $T_2 = 293k$ $c_p = 4180$

$m = 0.5 kg$

$$\Delta S = m c_p \ln \frac{T_2}{T_1}$$

$$\Delta S_{water} = 0.5(4184) \ln\left(\frac{293}{363}\right)$$

$$= -448 \ J/K$$

$$\Delta S_{universe} = 0$$

$$0 = \Delta S_{water} + \Delta S_{surrding}$$

$$\Delta S_{sur} = 448 \ J/K$$

Free expantion of an Ideal gas

$$\Delta S = R \ln\left(\frac{V_2}{V_1}\right) + C_v \cancel{\ln\left(\frac{T_2}{T_1}\right)}$$

Isothermal $\Delta T = 0$

$$\Delta S = R \ln\left(\frac{V_2}{V_1}\right)$$

$W_r = Q_r$ $\Delta Q = T \Delta S$

$$W = R T_0 \ln \frac{V_2}{V_1}$$

In Free expantion no work done, reversible isothermal

$W = \Delta S T$

FREE EXPANSION OF AN IDEAL GAS

in the free expansion of an ideal gas, du = 0 and dQ = 0 so that dW = 0 also.
Referring to the figure, we observe that the equations describing the equilibrium end states are:

$P_1V_1 = nRT_1$

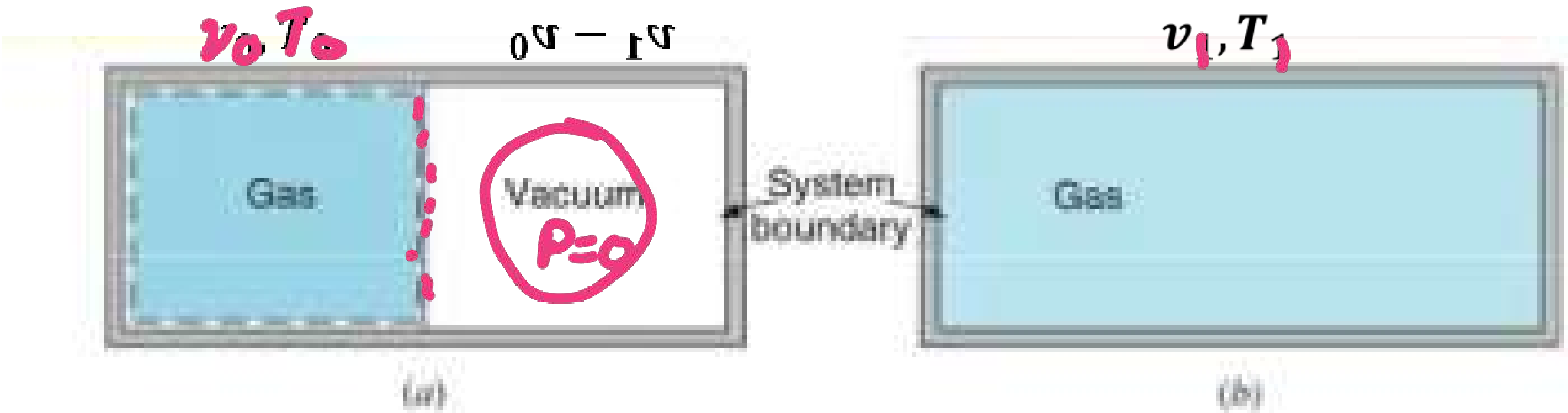
$P_2V_2 = nRT_2$

$$P_0 = \frac{RT_0}{v_0}\,; and\ P_1 = \frac{RT_1}{v_1}$$

A reversible isothermal process would be described by the equation Pv = constant or $P_0v_0 = P_1v_1$. However, the latter equation does not describe the free expansion because P_1 is initially zero and the process is irreversible.

$P_0V_0 = P_1V_1$

X



FREE EXPANSION OF AN IDEAL GAS

$pv = nRT$

Nonetheless, the entropy change can be calculated by assuming that a reversible, isothermal expansion takes place between the initial and final states of the system. Thus,

$du = dQ - pdv$

$du = Tds - pdv$

$\frac{du}{T} = ds - \frac{nR}{v} dv$

$$\mathbf{dS} = c_v \frac{dT}{T} + R\frac{dv}{v}$$ ✓ **(isothermal → dT =0)**

So: $$(\Delta S)_{System} = S_2 - S_1 = \int_1^2 R\frac{dv}{v} = \mathrm{R} \ln\left(\frac{v_2}{v_1}\right)$$

$(\Delta S)_{surronding} = -(\Delta S)_{System} > \mathbf{0}$; the system is isolated (adiabatically insulated).

In an irreversible free expansion, the available energy levels become more closely spaced leading to greater randomness and increased entropy.

$ds = \frac{C_v dT}{T} + \frac{R dv}{v}$

✓ ✓ ✓

$\Delta S = \cancel{C_v \ln \frac{T_2}{T_1}} + R \ln \frac{V_2}{V_1}$

For a reversible isothermal expansion, the work done would be:

$$W_r = \mathrm{R}T_0 \ln\left(\frac{v_2}{v_1}\right)$$

Since: $dU = 0$; $Q_r = W_r$ *so that*: $\Delta S = \frac{Q_r}{T} = R\ln\left(\frac{v_2}{v_1}\right)$

In a free expansion no work is done but the change in entropy in the irreversible process is as if work were done in a reversible, isothermal process between the same end points.

The Tds Equations

$du = dQ - PdV$

$\underline{Tds} = du + PdV$

From the combined first and second laws expressed as:

$$TdS = dU + P\,dv$$

We can obtain some powerful results known as the "TdS equation".

They envolve writing the specific entropy as function of two independent coordinates, that is, two of the three fundamental state variable P, T and v. the equations are:

$$TdS = c_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_v dv = c_v\,dT + \frac{T\beta}{K}\,dv; \quad S = S(T,v)$$

متغيرين مستقلين T,V
متغير تابع P

$$T\,dS = c_P\,dT - T\left(\frac{\partial v}{\partial T}\right)_P dP = c_p\,dT - Tv\,\beta\,dP; \quad S = S(T,P)$$

متغيرين مستقلين P,T
متغير تابع V

$$T\,dS = c_p\left(\frac{\partial T}{\partial v}\right)_P dv + c_v\left(\frac{\partial T}{\partial P}\right)_v dP = \frac{c_p}{\beta v}\,dv + \frac{c_v K}{\beta}\,dP; \quad S = S(P,v)$$

كتابه معادله Tds باستخدام عاملين مستقلين وعامل ١ تابع

The Tds Equations

$$ds = \frac{dQ_r}{T}$$

The Tds equations have a variety of uses:

1) they give the heat transferred in a reversible process $dQ_r = TdS$.
2) the entropy can be obtained by dividing by T and integrating.
3) the equations express the heat flow or entropy in terms of measurable properties such as: c_p, β, K, T, ect ...
4) they can be used to determine the difference in the specific heat capacities cp and cv
5) the equations can provide relations between pairs of coordinates in a reversible adiabatic process in which ds = 0.

$$du = C_v dT$$

$$du = C_p dT$$

$$du = dQ - PdV$$

$$dQ = du + PdV$$

$$ds = \frac{du}{T} + \frac{PdV}{T}$$

ENTROPY CHANGE FOR A LIQUID OR SOLID

The equation of state of a liquid or solid is, to a first approximation

$$\boxed{v = v_0[1 + \beta(T - T_0) - k\cancel{(P - P_0)}]}$$

المعادله الثانيه من معادلات Tds

The second TdS equation: $T\,dS = c_P\,dT - T\left(\frac{\partial v}{\partial T}\right)_P dP$

Setting: $\left(\frac{\partial v}{\partial T}\right)_P = \beta v_0$

We obtain:

$$\int dS = \int c_P \frac{dT}{T} - \int \beta v_0\,dP$$

التغير في S في حالة الاجسام الصلبة والسائلة

Integrating we have:

$$\boxed{\Delta S = S_2 - S_1 = c_p \ln\left(\frac{T}{T_0}\right) - \beta v_0(P - P_0)}$$

The entropy increases if the temperature increases and decreases if the pressure Increases.

تزداد S اذا زادت درجة الحرارة وتقل عندما يزداد الضغط

Tds equation

$$Tds = du + pdv$$

① باخذ العاملين $S(T, v)$

$$Tds = c_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv \qquad \beta = k\frac{\partial p}{\partial T}$$

$$Tds = c_v dT + T\frac{\beta}{k} dv$$

② ناخذ العاملين $\underline{T, P}$

$$Tds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dP$$

$$\frac{\partial v}{\partial T} = v\beta$$

$$Tds = c_p dT - Tv\beta dP$$

③ باخذ العاملين $S = S(P, v)$

$$Tds = c_p\left(\frac{\partial T}{\partial v}\right)_p dv + c_v\left(\frac{\partial T}{\partial P}\right)_v dP$$

$$= \frac{c_p}{\beta v} dv + \frac{c_v k}{\beta} dP$$