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Thermodynamics
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Lecture 70
Entropy Part 1

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for rev. cycle $\oint \frac{\delta Q}{T} = 0$
 for irrev. cycle $\oint \frac{\delta Q}{T} < 0$
 $\oint \frac{\delta Q}{T} \leq 0 \rightarrow$ Clausius' inequality

$\oint \delta Q = \int \delta W$
 $\delta Q - \delta W = \frac{dE}{dt}$



1-A-2-B-1-2
 $\oint \frac{\delta Q}{T} = 0 \Rightarrow \int_1^2 \frac{\delta Q_A}{T_A} + \int_2^1 \frac{\delta Q_B}{T_B} = 0$

1-A-2-C-1
 $\oint \frac{\delta Q}{T} = 0 \Rightarrow \int_1^2 \frac{\delta Q_A}{T_A} + \int_2^1 \frac{\delta Q_C}{T_C} = 0$

reversible paths

$\int_2^1 \frac{\delta Q_B}{T_B} = \int_2^1 \frac{\delta Q_C}{T_C} = \int_2^1 \frac{\delta Q_{rev}}{T} = \text{same}$

$\delta Q_{rev} = dS$
 $dS = \int \frac{\delta Q_{rev}}{T}$



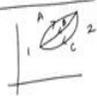



Figure 1.

1-A-2-B-1-2
 $\oint \frac{\delta Q}{T} = 0 \Rightarrow \int_1^2 \frac{\delta Q_A}{T_A} + \int_2^1 \frac{\delta Q_B}{T_B} = 0$

1-A-2-C-1
 $\oint \frac{\delta Q}{T} = 0 \Rightarrow \int_1^2 \frac{\delta Q_A}{T_A} + \int_2^1 \frac{\delta Q_C}{T_C} = 0$

reversible paths

$\int_2^1 \frac{\delta Q_B}{T_B} = \int_2^1 \frac{\delta Q_C}{T_C} = \int_2^1 \frac{\delta Q_{rev}}{T} = \text{same}$

$\delta Q_{rev} = dS$
 $dS = \int \frac{\delta Q_{rev}}{T}$



$dS_{rev} = \int \frac{\delta Q_{rev}}{T}$

S is a state function / property

$dS_{for B} = dS_{rev}$ as calculated for A

$dS_{for B} \neq \int \frac{\delta Q_{irrev}}{T}$ $\oint \frac{\delta Q}{T} < 0$

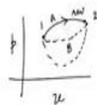



Figure 2.

We know that $\oint \frac{\delta Q}{T} = 0$ for a reversible cyclic process.

Two states, states 1 and 2, of a certain system are shown on a p-v diagram in Fig. 1. The system can change the state by three reversible paths, A, B or C.

For the reversible cycle 1-A-2-B-1, $\oint \frac{\delta Q}{T} = 0 \rightarrow \int_1^2 \frac{\delta Q_A}{T_A} + \int_2^1 \frac{\delta Q_B}{T_B} = 0 \dots (1)$

Similarly, for the reversible cycle 1-A-2-C-1, $\oint \frac{\delta Q}{T} = 0 \rightarrow \int_1^2 \frac{\delta Q_A}{T_A} + \int_2^1 \frac{\delta Q_C}{T_C} = 0 \dots (2)$

Subtracting (2) from (1),

$$\int_2^1 \frac{\delta Q_B}{T_B} = \int_2^1 \frac{\delta Q_C}{T_C}.$$

This is true for any reversible path between the states 1 and 2, i.e., $\int \frac{\delta Q}{T}$ is the same for any reversible path between the same initial and final state. In other words, $\int \frac{\delta Q}{T}$ is path independent for a reversible process. We know that for a fixed initial and final state, the difference in a property values at the initial and final state is independent of the path taken to reach from the initial state to final state. Also, the cyclic integral of a differential change in a property of a system undergoing a cyclic process is 0. Hence, $\frac{\delta Q}{T}$ must be representing a change in some property of a system undergoing a reversible process. We assign letter S to this property and write $\frac{\delta Q}{T_{rev}} = dS$ ('rev' is written to indicate that the process is reversible). After integrating, $\int \frac{\delta Q}{T_{rev}} = \Delta S$. Here, δQ is a path function, T is a state function or a property, but $\frac{\delta Q}{T}$ represents a change in a property for a reversible process. We call this property as entropy (S).

In mathematics, inexact differentials are converted to exact differentials by multiplying with integrating factors. Here, δQ is an inexact differential. By multiplying δQ with the integrating factor $1/T$, we get dS which is an exact differential.

From the first law of thermodynamics, we get the property called energy, while from the second law, we get entropy. Entropy is defined in a different way in statistical thermodynamics. In classical thermodynamics, it is the ratio of heat transferred to the temperature at which the heat was transferred in a reversible process.

What about an irreversible process?

An irreversible process cannot be plotted on any property diagram (e.g. p-v, p-T, etc.) because we don't know the properties of a system during this process. We cannot measure the heat transferred and the temperature for the system during such a process. Hence, we cannot find $\int \frac{\delta Q}{T}$ for an irreversible process.

Figure 2 shows states 1 and 2 of a certain system on a p-v diagram. The path A from the state 1 to 2 is reversible. It is shown with a solid line. The path B joining states 1 and 2 is irreversible. It is shown with a dotted line. Even though it is shown with a dotted line, it does not mean that property values (in this case, p and v) of the system during that process lie on that dotted line. We just don't know the system properties during the irreversible process. The dotted line could have been drawn to take any arbitrary path. Also, we cannot calculate the area below the dotted line.

For the reversible path A, $\int \frac{\delta Q_A}{T_{rev}} = \Delta S_{rev,A}$ = difference in the entropy values at the state 2 and the state 1 (ΔS may have a positive or a negative value depending on the values at the state 1 and 2, and the direction the path is traversed, i.e., whether the system goes from state 1 to 2 or from 2 to 1). The magnitude of ΔS is the same for the given initial and final states irrespective of the path taken. Hence, for the irreversible path B, $\Delta S_{irrev,B} = \Delta S_{rev,A}$. However, for the irreversible path B, $\Delta S_{irrev,B} \neq \int \frac{\delta Q_B}{T}$, because we cannot measure the heat transfer and the temperature for an irreversible process. Hence, for calculating ΔS_{irrev} for any irreversible process between the given states, we should calculate $\int \frac{\delta Q}{T}$ along any reversible path between the same states to get ΔS_{rev} which also equals ΔS_{irrev} . But $\Delta S_{irrev} \neq \int \frac{\delta Q}{T}$.

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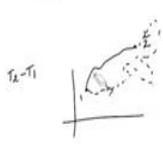
$S = \text{entropy } \frac{J}{K}$
 $s = \text{specific entropy } \int \frac{\delta Q_{rev}}{T} = \int \frac{s_{rev}}{m \cdot T}$
 $s = \frac{J}{kg \cdot K}$

$dS = \frac{\delta Q}{T}$

Third Law of Thermodynamics

$dE = \delta Q - \delta W$ ✓
 $\delta Q = dE + \delta W$ ✓ simple compressible substances
 $E = U + KE + PE$
 $\delta Q = dU + \delta W$
 $TdS = dU + pdV$
 $Tds = du + p dv$ } - *first relation*
 $Tds = dh - v dp$ }

$h = u + pv \Rightarrow dh = du + p dv + v dp$
 $du + p dv = dh - v dp$



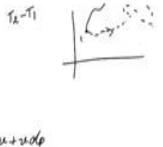



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$h = u + pv \Rightarrow dh = du + p dv + v dp$
 $du + p dv = dh - v dp$

Solid / liquid
 $Tds = du + p dv$ $v = \text{small}$
 $\frac{v}{T} \approx 0$

$Tds = du = C_v dT$
 $ds = C_v \frac{dT}{T}$
 $\Delta s = \int C_v \frac{dT}{T} = C_v \ln \frac{T_2}{T_1}$






The unit of entropy (S) is J/K (joule/kelvin). The unit of specific entropy (s) is $\frac{J}{kg \cdot K}$. $\Delta S_{rev} = \int \frac{\delta Q_{rev}}{mT}$ where m is the mass of the system.

In the context of this, it is also useful to look at the third law of thermodynamics. Again, there are various statements of this law to take into account some very specific things. However, for the purpose of this course, we have the following statement: for pure substances, if we reach a temperature of absolute 0, the entropy of the substance would be 0. This gives some reference to calculate entropy.

Let's see how to calculate changes in entropy for various substances. Consider simple compressible systems. The first law, by not considering changes in kinetic and potential energy, for a process is, $dU = \delta Q - \delta W$. There is only pdV type of work. Hence, $\delta Q = dU + pdV$. Now, for a reversible process, $\frac{\delta Q}{T} = dS$. Hence, $TdS = dU + pdV$. Dividing by mass of the system throughout, we get, $Tds = du + pdv$. We also know that $h = u + pv$. Hence, $dh = du + pdv + vdp$. Substituting for du , $Tds = dh - vdp$. $Tds = du + pdv$ and $Tds = dh - vdp$ are known as Gibb's relations. To calculate change in entropy even for an irreversible process, we can use Gibb's relations as these are property relations (?). Properties are independent of path. Change in a property depends only on the initial and the final state.

Let's use these relations to calculate entropy change for a solid or a liquid.

For a solid or a liquid, specific volume v is very small and it can be ignored. Changes in specific volume are even smaller during a process. We have $Tds = du + pdv$. Setting $dv=0$, $Tds = du$. Hence, $Tds = CdT$ (C is specific heat). Therefore, $ds = C \frac{dT}{T}$. Integrating, $\Delta s = s_2 - s_1 = C \ln\left(\frac{T_2}{T_1}\right)$ (T_2 - final temperature, T_1 - initial temperature). However, for a process of phase change, where temperature does not change, $T\Delta s = \Delta u =$ latent heat of vaporization.

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Δs for an ideal gas

$Tds = du + pdv$ ✓
 $Tds = C_v dT + pdv$
 $ds = \frac{C_v dT}{T} + \frac{pdv}{T}$
 $ds = C_v \frac{dT}{T} + R \frac{dv}{v}$
 Integrating, $\Delta s = \int C_v \frac{dT}{T} + R \int \frac{dv}{v}$
 $s_2 - s_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$ ✓

$Tds = dh - vdp$
 $ds = \frac{C_p dT}{T} - \frac{vdp}{T} \Rightarrow ds = \frac{C_p dT}{T} - \frac{R dp}{p}$
 $\Delta s = \int C_p \frac{dT}{T} - R \int \frac{dp}{p} \Rightarrow s_2 - s_1 = C_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1}$ ✓

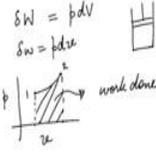



Integrating, $\Delta s = \int \frac{C_v dT}{T} + R \int \frac{dv}{v}$
 $s_2 - s_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$ ✓

$Tds = dh - vdp$
 $ds = \frac{C_p dT}{T} - \frac{vdp}{T} \Rightarrow ds = \frac{C_p dT}{T} - \frac{R dp}{p}$
 $\Delta s = \int C_p \frac{dT}{T} - R \int \frac{dp}{p} \Rightarrow s_2 - s_1 = C_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1}$ ✓

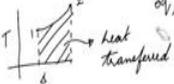



$\delta W = p dV$
 $\delta W = pdv$



work done

$ds = \frac{\delta Q_{rev}}{T}$ or $ds = \frac{\delta Q_{rev}}{T}$
 $\delta Q_{rev} = T ds$



heat transferred

We can use Gibb's relations to calculate the entropy change for an ideal gas. We have $Tds = du + pdv$. Now, $Tds = C_v dT + pdv \rightarrow ds = C_v \frac{dT}{T} + \frac{p}{T} dv$. We know, for an ideal gas, $pv = RT \rightarrow \frac{p}{T} = \frac{R}{v}$. Hence, $ds = C_v \frac{dT}{T} + \frac{R}{v} dv$. Integrating, $\Delta s = s_2 - s_1 = \int C_v \frac{dT}{T} + \int R \frac{dv}{v} = C_{v0} \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right)$ (C_v is assumed constant and written as C_{v0} . If it is not constant, it cannot be taken out of the integral).

We also have $Tds = dh - vdp = C_p dT - vdp \rightarrow ds = C_p \frac{dT}{T} - \frac{v}{T} dp = C_p \frac{dT}{T} - \frac{R}{p} dp$ (for an ideal gas, $\frac{v}{T} = \frac{R}{p}$). Integrating, $\Delta s = s_2 - s_1 = \int C_p \frac{dT}{T} - \int R \frac{dp}{p} = C_{p_0} \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{p_2}{p_1}\right)$ (C_p is assumed constant and written as C_{p_0} . If it is not constant, it cannot be taken out of the integral.).

We have been showing processes undergone by a system by drawing curves on a p-v diagram for quite some time now. We know that small displacement work is represented as $\delta w = pdv$ (on a unit mass basis). The term pdv represents the area under the infinitesimally small section of the curve representing a process on a p-v diagram with respect to v axis. Integrating, we get $w = \int \delta w = \int pdv =$ area with respect to v axis under the entire curve representing the process on a p-v diagram = amount of work done/received by the system. For calculating this area, the process must be quasi-static.

We know that, for a reversible process, $\frac{\delta q}{T} = ds$ (on a unit mass basis). Hence, $\delta q = Tds$ (this function looks similar to $\delta w = pdv$). Hence, in line with discussion above, $q = \int \delta q = \int Tds =$ area with respect to s axis under the entire curve representing the reversible process on a T-s diagram = amount of heat transfer to or from the system.