

Lecture 7 & 8

Thermodynamics

Part-II

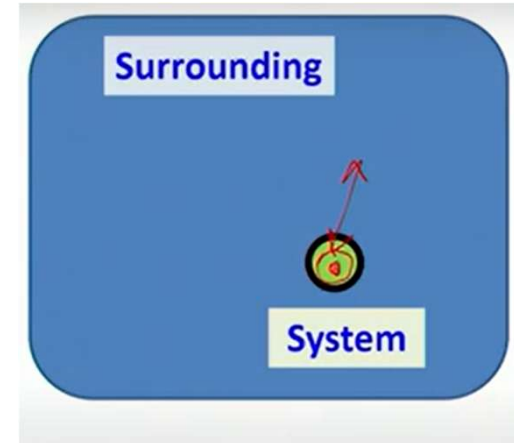
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1st Law and Its Limitations

- The concept of **internal energy, U** and **enthalpy, H**
- **Assumption:**
 - ✓ Universe: **system + surrounding**
 - ✓ Universe is **isolated**
- During any **change in state of the system**

1st law states that if due to heat flow, q amount of heat is lost by A then exactly q amount of heat will be gained by B



Limitations of 1st Law

- Whether heat-flow or such change in state would occur or not ?
- If the heat flow/ change in state occurs what will be the spontaneous direction?
- What will be the new equilibrium state and under which condition will the change stop ?

- From the 1st law, when $\Delta U = 0$, $q = -w$.

So heat supplied to a system can be **completely** converted to work!!

- Such possibility is tested by the construction of **heat engines**

The perfect heat engine

Efficiency of the heat engine

$$\eta = \frac{|w|}{Q_h}$$

1st law predicts that construction of such an engine is possible

Construction of a heat engine

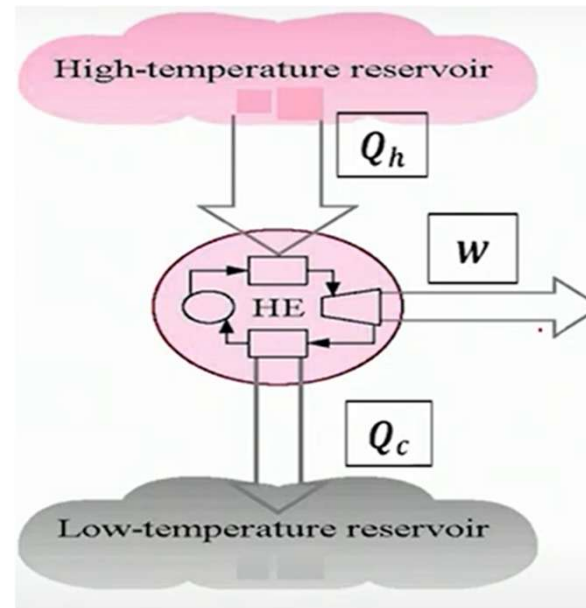
An engine is a device (system) that converts energy to work.

A heat engine

- draws heat from a hot reservoir,
- converts some heat to work, and
- releases some heat to a cold reservoir.

The engine itself is a system that undergoes a cyclic process

A reservoir is a large body whose temperature does not change when it absorbs or release heat



Efficiency of the heat engine

$$\eta = \frac{|w|}{Q_h}$$

For a cyclic process,

$$\Delta U = 0 \Rightarrow$$

$$w = -Q = -(Q_h + Q_c)$$

$$\Rightarrow \eta = \frac{|w|}{Q_h} = \frac{Q_h + Q_c}{Q_h} = 1 + \frac{Q_c}{Q_h}$$

$$\therefore \eta < 1 \text{ as } Q_c < 0$$

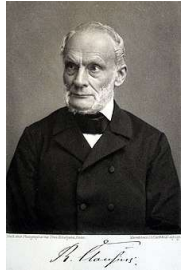
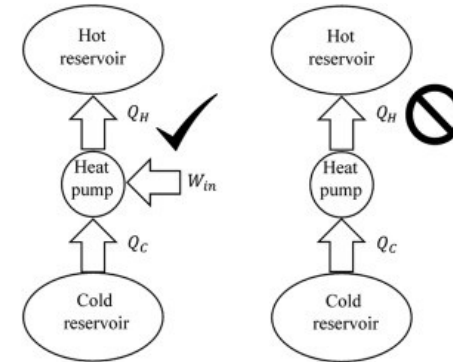
Origin of 2nd Law of Thermodynamics

1. Clausius Statement (Heat Transfer Perspective)

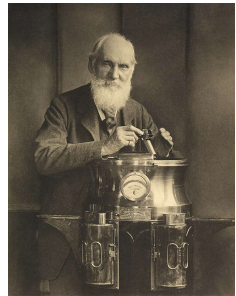
"It is impossible to construct a device that operates in a cycle and transfers heat from a colder body to a hotter body without external work being done on the system."

This means that **heat cannot spontaneously flow from a cold body to a hot body** without external work. This is the principle behind refrigerators and heat pumps, which require an external power source to transfer heat against the natural direction.

Example: A refrigerator requires electricity to move heat from its cooler interior to the warmer surroundings.



Rudolf Clausius



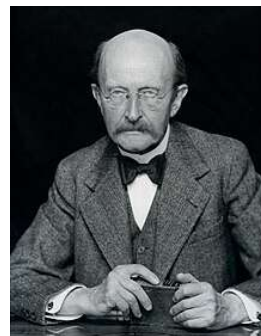
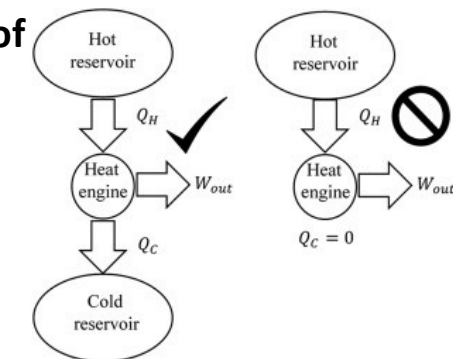
Sir William Thomson, Baron Kelvin (Lord Kelvin)

2. Kelvin-Planck Statement (Work and Efficiency Perspective)

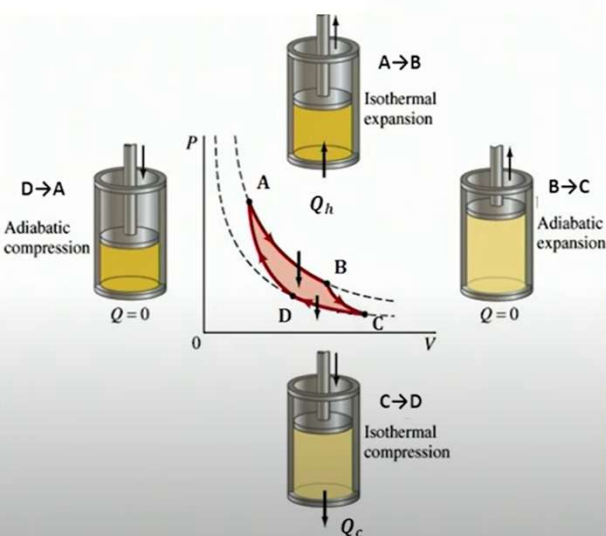
"It is impossible to construct a heat engine that operates in a cyclic process and converts all the heat energy absorbed from a heat source into an equal amount of work, without any loss of energy."

This means that **no heat engine can have 100% efficiency**—some energy will always be lost as waste heat to a lower-temperature reservoir.

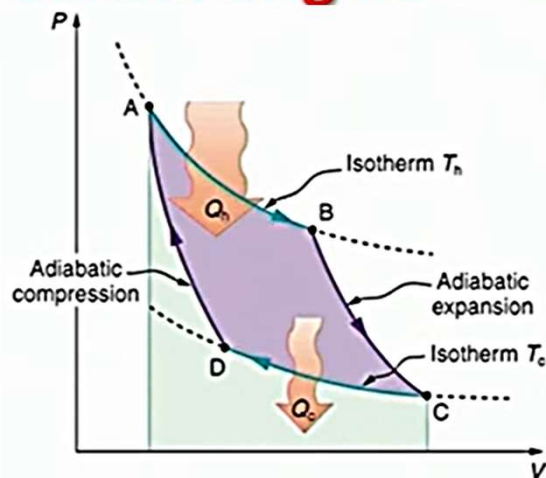
Example: A car engine cannot convert all fuel energy into useful work; some energy is always lost as heat.



Max Planck



Carnot Engine



$$TV^{\gamma-1} = \text{const.};$$

$$T_h V_B^{\gamma-1} = T_c V_C^{\gamma-1} \quad T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1}$$

$$\left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1} \quad \left(\frac{V_B}{V_A}\right) = \left(\frac{V_C}{V_D}\right)$$

$$\ln(V_D/V_C) = -\ln(V_B/V_A)$$

Step	1 (A → B)	2 (B → C)	3 (C → D)	4 (D → A)	Total (A → B → C → D → A)
w	$-nRT_h \ln\left(\frac{V_B}{V_A}\right)$	$C_V (T_c - T_h)$	$-nRT_c \ln\left(\frac{V_D}{V_C}\right)$	$C_V (T_h - T_c)$	$-nR(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right)$
q	$nRT_h \ln\left(\frac{V_B}{V_A}\right)$	0	$nRT_c \ln\left(\frac{V_D}{V_C}\right)$	0	$nR(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right)$
ΔU	0	$C_V (T_c - T_h)$	0	$C_V (T_h - T_c)$	0
$\frac{q_{rev}}{T}$	$nR \ln\left(\frac{V_B}{V_A}\right)$	0	$nR \ln\left(\frac{V_D}{V_C}\right)$	0	0

For any cyclic engine, $\Delta U = 0 \Rightarrow \underline{|w|} = \underline{|Q|} = \underline{|Q_h + Q_c|}$

Thus, by definition $\eta = \frac{|w|}{Q_h} = \frac{Q_h + Q_c}{Q_h}$ i.e. $\boxed{\eta = 1 + \frac{Q_c}{Q_h}}$

As the Carnot engine works **reversibly** and employs **an ideal gas**,

$$Q_H = nRT_h \ln\left(\frac{V_B}{V_A}\right) \quad \text{and} \quad |w| = nR(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right)$$

$$\therefore \eta = \frac{|w|}{Q_H} = \frac{T_h - T_c}{T_h} \quad \text{i.e.} \quad \boxed{\eta = 1 - \frac{T_c}{T_h}}$$

Note: $1 + \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h} \Rightarrow \frac{Q_h}{T_h} + \frac{Q_c}{T_c} = 0$

Critical discussion on η

- (i) Explanation of perpetual motion machine of 1st kind- If no heat is supplied then $Q=0$, then $w=0$, i.e. the engine cannot produce any work if heat is not supplied to it.
- (ii) Explanation of perpetual motion machine of 2nd kind- If $T_h=T_c$, i.e., same heat source is used, then $w=0$, i.e. the engine cannot produce any work by extracting heat from a single reservoir.
- (iii) Unattainability of absolute zero temp and incomplete conversion of heat into work by an engine.

We have $\eta = 1 - \frac{T_c}{T_h}$. Thus, η can only be unity if either $T_c = 0^\circ \text{A}$, or $T = \infty \text{A}$, which is impossible in practice. Again, as $\eta < 1$; i.e., heat cannot be completely converted into work, T_c cannot be 0°A . This means $T_c = 0^\circ \text{A}$ is unattainable.

Thermodynamic
Scale/Kelvin Scale of
Temperature



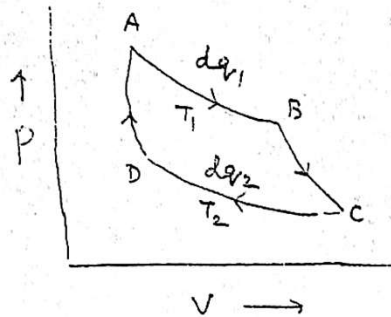
Suppose we have an engine that is working reversibly between a hot source at a temperature T_h and a cold sink at a temperature T , then we know

$$T = (1 - \eta)T_h$$

This expression enabled Kelvin to define the **thermodynamic temperature scale** in terms of the efficiency of a heat engine: we construct an engine in which the hot source is at a known temperature and the cold sink is the object of interest. The temperature of the latter can then be inferred from the measured efficiency of the engine. The **Kelvin scale** (which is a special case of the thermodynamic temperature scale) is defined by using water at its triple point as the notional hot source and defining that temperature as 273.16 K exactly. For instance, if it is found that the efficiency of such an engine is 0.20, then the temperature of the cold sink is $0.80 \times 273.16 \text{ K} = 220 \text{ K}$. This result is independent of the working substance of the engine.

Concept of Entropy from Carnot Cycle

Concept of entropy from
Carnot cycle



The Carnot cycle operates in rev. paths.
Let it take dq_1 heat from HTR at T_1
and rejects dq_2 heat to LTR at T_2 .

The indicator diagram is shown here.

From the efficiency of the cycle, $\eta = \frac{dq_1 - dq_2}{dq_1}$

$$\text{or } \frac{dq_1}{T_1} = \frac{dq_2}{T_2} = \frac{T_1 - T_2}{T_1}$$

Now let us consider the quantity, $\frac{\text{heat change}}{\text{temp.}}$

The quantity, $\frac{\text{heat change}}{\text{temp}}$ for the state $A \rightarrow C$.

$A \rightarrow C$ via B, $\frac{\text{heat change}}{\text{temp}} = \frac{dq_1}{T_1} + 0 = \frac{dq_1}{T_1}$ Again for,

$A \rightarrow C$ via D, $\frac{\text{heat change}}{\text{temp}} = 0 + \frac{dq_2}{T_2} = \frac{dq_2}{T_2}$ But Carnot cycle states $\frac{dq_1}{T_1} = \frac{dq_2}{T_2}$

hence, we can conclude that $\frac{\text{heat change}}{\text{temp}}$ term is same for the change of two definite states & independent of path of change.
Again for the whole cycle of operation,

$$\oint \frac{\text{heat change}}{\text{temp}} = \frac{dq_1}{T_1} + 0 - \frac{dq_2}{T_2} + 0 = \frac{dq_1}{T_1} - \frac{dq_2}{T_2} = 0.$$

Therefore, $\frac{\text{heat change}}{\text{temp}}$ is a fundamental property & it refers to a property that is state function.

**In search of a new system property
that decides the direction and endpoint
of a spontaneous process**

Entropy

- A state function called entropy, S is identified such that

➤ $dS = \frac{\delta q_{rev}}{T}$ is an exact differential

➤ $\Delta S = S_b - S_a = \int_a^b dS = \int_a^b \frac{\delta q_{rev}}{T}$ is independent of the path.

Critical Questions about Entropy

- **Can we estimate the change in entropy, ΔS for different processes?**
- Can we use Entropy to determine/predict the following:
 - ✓ the direction of spontaneous change
 - ✓ the condition of equilibrium
- Can we use entropy to explain why the heat engines do not have the ideal efficiency?

Change in Entropy of the System for Different Processes

By definition

$$dS = \frac{\delta q_{rev}}{T}$$

For an adiabatic process

$$\delta q_{rev} = 0 \Rightarrow \textcolor{red}{dS} = \textcolor{red}{0} \text{ for non-zero temperatures}$$

$$\therefore \int_1^2 dS = S_2 - S_1 = \textcolor{red}{\Delta S} = \textcolor{red}{0} \Rightarrow \textcolor{green}{S_2} = \textcolor{green}{S_1}$$

For any isothermal process

$$\Delta S = \int_1^2 \frac{\delta q_{rev}}{T} = \frac{1}{T} \int_1^2 \delta q_{rev}$$

$$\therefore \textcolor{red}{\Delta S} = \frac{\textcolor{red}{Q}_{rev}}{\textcolor{red}{T}}$$

For an isothermal expansion of an ideal gas

$$\Delta U = 0 \Rightarrow Q_{rev} = -w_{rev} = RT \ln \left(\frac{V_2}{V_1} \right)$$

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

Change in Entropy of the System for Different Processes

For a **reversible** process involving changes in T and V of 1 mole of an ideal gas

$$\delta q_{rev} = dU + p dV \quad \Rightarrow \quad \frac{\delta q_{rev}}{T} = \frac{dU}{T} + \frac{p}{T} dV$$

$$dS = \frac{C_V}{T} dT + \frac{R}{V} dV$$

$$\int_1^2 dS = S_2 - S_1 = \Delta S = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

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

Change in Entropy of the System for Different Processes

- For a **reversible** process $(T_1 \ V_1 \ N) \rightarrow (T_2 \ V_2 \ N)$

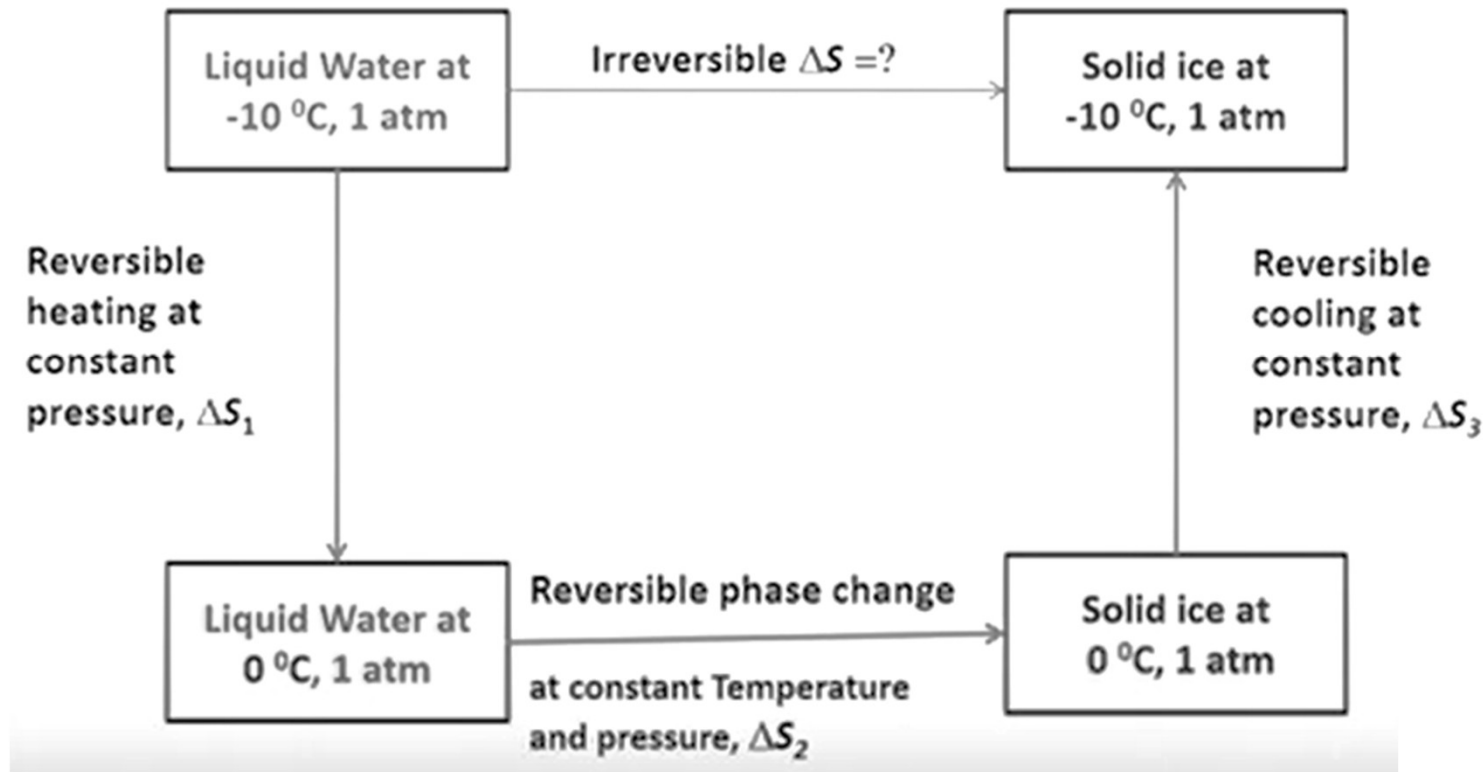
$$\Delta S = C_V \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right)$$

- For an **irreversible** process between $(T_1 \ V_1 \ N) \rightarrow (T_2 \ V_2 \ N)$

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

Reversible Process	ΔS
Adiabatic	0
Isothermal	$\Delta S = \frac{Q_{rev}}{T}$
Isothermal expansion of an ideal gas	$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$
Isochoric heating	$\Delta S = C_V \ln \left(\frac{T_2}{T_1} \right)$
Heating with volume change	$\Delta S = C_V \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right)$
Heating at constant pressure	$\Delta S = C_p \ln \left(\frac{T_2}{T_1} \right)$ (No phase change)
	$\Delta S = \frac{\Delta H}{T}$ (Phase change)

Construction of reversible steps to describe an irreversible process



Homework

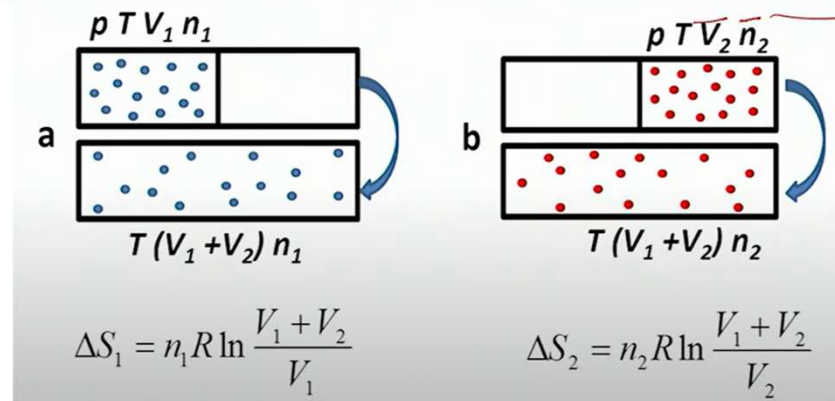
Construction of reversible steps to describe an irreversible process

Entropy of Mixing

Experiment-1



Experiment-2



$$\Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1}$$

$$\Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2}$$

$$\frac{V_1}{V_1 + V_2} = \frac{n_1}{n_1 + n_2} = x_1$$

$$\frac{V_2}{V_1 + V_2} = x_2$$

$$\Delta S_{\text{mixing}} = \Delta S_1 + \Delta S_2$$

$$\Delta S_{\text{mixing}} = -n_1 R \ln x_1 - n_2 R \ln x_2$$

$$\Delta S_{\text{mixing}} = -nR (x_1 \ln x_1 + x_2 \ln x_2)$$

Entropy at Very Low Temperatures

- Nernst heat theorem

The **entropy change** for any chemical or physical transformation **approaches zero** as **T approaches zero**;

$S \rightarrow 0$ as $T \rightarrow 0$ if all the substances involved are **perfectly ordered**.

Experimental evidence

$$S(\beta) \rightarrow S(\alpha)$$

$$\Delta S_{tr} = S_m(\alpha) - S_m(\beta)$$

$$\Delta H_{tr} = -402 \text{ J mol}^{-1} \text{ at } 369 \text{ K}$$

$$\Delta S_{tr} = -1.09 \text{ J K}^{-1} \text{ mol}^{-1}$$

Also,
$$\left. \begin{array}{l} S_m(\alpha) = S_m(\alpha, 0) + 37 \\ S_m(\beta) = S_m(\beta, 0) + 38 \end{array} \right\} \text{ J K}^{-1} \text{ mol}^{-1} \Rightarrow \Delta S_{tr} = S_m(\alpha, 0) - S_m(\beta, 0) - 1$$

$$S_m(\alpha, 0) \approx S_m(\beta, 0) \approx 0$$

It follows from the Nernst theorem that, if we arbitrarily ascribe the value zero to the entropies of elements in their perfect crystalline form at $T = 0$, then all perfect crystalline compounds also have zero entropy at $T = 0$ (because the change in entropy that accompanies the formation of the compounds, like the entropy of all transformations at that temperature, is zero).

This conclusion is summarized by the Third Law of thermodynamics:

	$S_m^\ominus \text{ (J K}^{-1} \text{ mol}^{-1})$
Diamond (s)	2.4
Water (l)	69.9
Benzene (l)	173.3
CO ₂ (g)	213.7

Third Law of Thermodynamics:

The entropy of all perfect crystalline substances is zero at $T = 0$.

Key points: The entropy acts as a signpost of spontaneous change

- (a) Entropy change is defined in terms of heat transactions (the Clausius definition).
- (b) Absolute entropies are defined in terms of the number of ways of achieving a configuration (the Boltzmann formula: $S = k_B \ln w$, where w is number of possible arrangements).
- (c) The Carnot cycle is used to prove that entropy is a state function.
- (d) The efficiency of a heat engine is the basis of the definition of the thermodynamic temperature scale and one realization, the Kelvin scale.
- (e) The Clausius inequality is used to show that the entropy increases in a spontaneous change and therefore that the Clausius definition is consistent with the Second Law.