The second and third law of thermodynamics

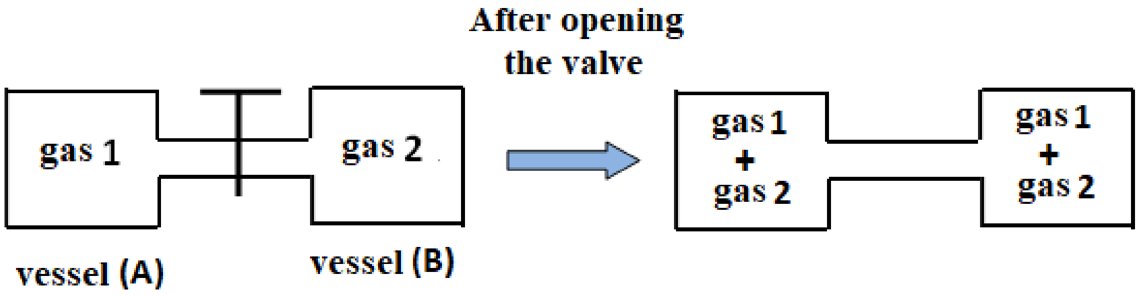
1- Introduction: All natural transformations in an isolated system are spontaneous and not influenced by the external environment. The spontaneous transformation is defined as a physical or chemical process that occurs on its own under certain conditions without the influence of any external factors. It is not necessary for this process (transformation) to be fast, as speed is not a crucial factor in determining spontaneity.

Examples:

- Heat transfer from a hot body to a cold one, but not the reverse.

- Rolling of objects from elevated positions to lower ones, but the reverse does not occur without external intervention.

- When two gases are placed in a vessel (A) and a vessel (B) after opening the valve, the two gases diffuse into the vessels spontaneously without the intervention of an external environment.



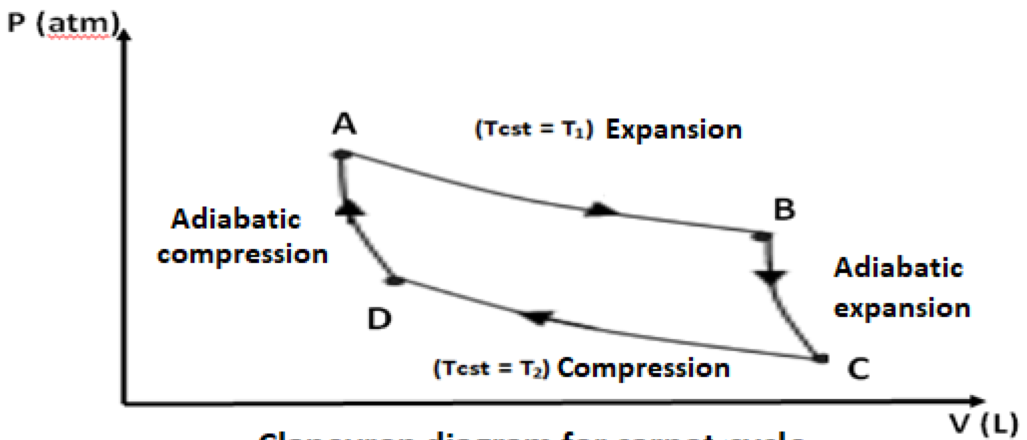
Conclusion: These examples illustrate that processes occurring spontaneously in a specific direction cannot occur spontaneously in the opposite direction, even though internal energy is conserved even in the reverse transformation. This necessitates the existence of a second law of thermodynamics, which specifies the spontaneous direction of the transformation.

2- Second Law Statement: An isolated system undergoing a transformation (evolution) cannot return to its initial state.

3-Carnot cycle of an ideal gas: (Principle of operation of some heat engines):

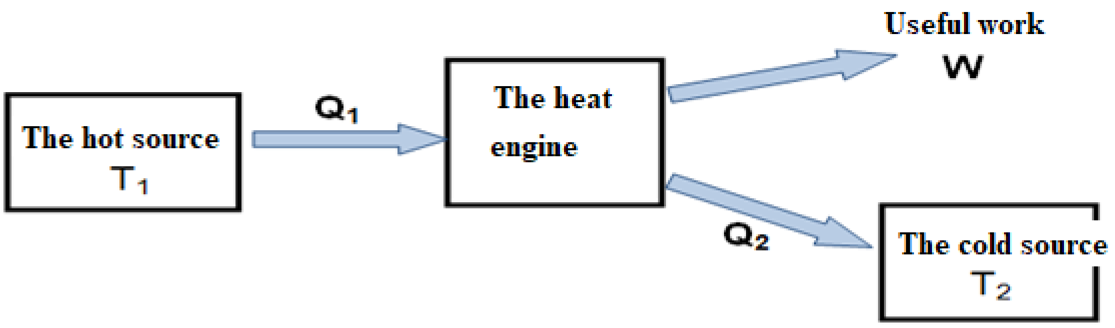
It is a set of reversible transformations undergone by an ideal gas such that the initial state corresponds to the final state, meaning these transformations form a cycle.

This cycle consists of four reversible transformations, two of which are isothermal and two are adiabatic.



Clapeyron diagram for carnot cycle

So, the heat engine takes a quantity of heat from the hot source, and from this heat, it produces useful work and transfers a quantity of heat to the cold source.



Within a certain period of time, the system returns to its initial state, thus completing a cycle or closed loop, where the loop consists of two transformations at constant temperature and two adiabatic transformations.

Studying the Carnot cycle:

• The transformation from A to B:

$$A \xrightarrow{T\ Cst} B \quad \Longrightarrow V_B > V_A (\text{ Gas expansion })$$

$$\Longrightarrow \Delta U_{AB} = Q_{AB} + W_{AB} = 0 \ (\text{According to the first law of Joul}) \Longrightarrow Q_{AB} = -W_{AB}$$

$$\text{Reversible transformation of an ideal gas} \Longrightarrow W_{AB} = -\int P\,dV = -nRT_1 Ln(\frac{V_B}{V_A})$$

$$Q_{AB} = -W_{AB} = nRT_1 Ln\left(\frac{V_B}{V_A}\right) = Q_1 > 0 \ (V_B > V_A)$$

$$Q_1 : (T_1) \text{ The amount of heat taken from the hot source}$$

$$Q_{AB} = Q_1 = nRT_1 Ln\left(\frac{V_B}{V_A}\right) = nRT_1 Ln\left(\frac{P_A}{P_B}\right) \ldots\ldots\ldots.. (1)$$

• The transformation from B to C:

$$B \xrightarrow{\text{Adiabatic}} C \quad \Rightarrow Q_{BC} = 0$$

$$V_C > V_B \left(\text{Gas expansion} \right)$$

Since the transformation is adiabatic $\Longrightarrow$ We can apply the relationships of Laplace

$$\Rightarrow PV^{\gamma} = Cst , TV^{\gamma-1} = Cst \quad \Rightarrow P_C V_C^{\gamma} = P_B V_B^{\gamma}$$ و $$T_C V_C^{\gamma-1} = T_B V_B^{\gamma-1}$$

$$\Rightarrow T_2 V_C^{\gamma-1} = T_1 V_B^{\gamma-1} \quad \ldots\ldots\ldots (2)$$

• The transformation from C to D:

$$C \xrightarrow{T\ Cst} D \quad \Rightarrow P_D > P_C$$ (إنضغاط الغاز)

$$\Rightarrow \Delta U_{CD} = Q_{CD} + W_{CD} = 0$$ (ح ق ج 1) $$\Rightarrow Q_{CD} = -W_{CD}$$

تحول عكوس لغاز مثالي $$\Rightarrow W_{CD} = -\int P\,dV = -nRT_2 Ln\left(\frac{V_D}{V_C}\right)$$

$$Q_{CD} = -W_{CD} = nRT_2 Ln\left(\frac{V_D}{V_C}\right) = Q_2 < 0 \ (V_D < V_C)$$

Q_2: (T_2) كمية الحرارة المعطاة من طرف الغاز إلى المنبع البارد

$$Q_{CD} = Q_2 = nRT_2 Ln\left(\frac{V_D}{V_C}\right) = nRT_2 Ln\left(\frac{P_C}{P_D}\right) \ldots\ldots\ldots (3)$$

• The transformation from D to A:

$$D \xrightarrow{\text{Adiabatic}} A \quad \Rightarrow Q_{DA} = 0$$

$$V_A < V_D$$ (إنضغاط الغاز) و $$P_A > P_D$$

Since the transformation is adiabatic $\Longrightarrow$ We can apply the relationships of Laplace

$$\Rightarrow PV^{\gamma} = Cst , TV^{\gamma-1} = Cst \Rightarrow P_D V_D^{\gamma} = P_A V_A^{\gamma}$$ و $$T_D V_D^{\gamma-1} = T_A V_A^{\gamma-1}$$

$$\Rightarrow T_1 V_A^{\gamma-1} = T_2 V_D^{\gamma-1} \quad \ldots\ldots\ldots (4)$$

From equations (2) and (4), we find:

$$\begin{cases} T_1 V_B^{\gamma-1} = T_2 V_C^{\gamma-1} \quad \ldots\ldots\ldots (2) \\ \\ T_1 V_A^{\gamma-1} = T_2 V_D^{\gamma-1} \quad \ldots\ldots\ldots (4) \end{cases} \quad \Longrightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

From equation (1), we find:

$$Q_1 = nRT_1 Ln\left(\frac{V_B}{V_A}\right) \Rightarrow \frac{Q_1}{T_1} = nRLn\left(\frac{V_B}{V_A}\right)$$

From equation (3), we find:

$$Q_2 = nRT_2 Ln\left(\frac{V_D}{V_C}\right) \Rightarrow \frac{Q_2}{T_2} = nRLn\left(\frac{V_D}{V_C}\right)$$

So:

$$\frac{Q_1}{T_1} = -\frac{Q_2}{T_2} \Rightarrow \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

It means:

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

The efficiency of the engine τ: It is the amount of work done by the engine on the external medium divided by the amount of heat taken from the external medium.

$$\tau = \frac{-W}{Q_1} = \left|\frac{W}{Q_1}\right|$$

The total internal energy remains conserved during the cyclic transformation.

$$\Delta U_{cycle} = W_{cycle} + Q_1 + Q_2 = 0 \Rightarrow W_{cycle} = -(Q_1 + Q_2)$$

$$\tau = \frac{-W_{cycle}}{Q_1} = \frac{(Q_1 + Q_2)}{Q_1} = 1 + \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$\tau\% = (1 - \frac{T_2}{T_1}) \times 100$$

T_2 **: The temperature of the cold source**

T_1 **: The temperature of the hot source**

Note:

To obtain work from a heat cycle, there must be at least two heat sources, one hot and the other cold. However, it's not possible to convert all the heat into work because the efficiency is less than one, and efficiency is better when the temperature difference between the two sources is greater.

Practical Example: A heat engine operates according to the Carnot cycle between two reservoirs, one hot with a temperature of T_1 = 630°C and the other cold with a temperature of T_2 = 45°C. Calculate the efficiency of the heat engine and the work done by the engine if the amount of heat taken from the hot reservoir Q1 is equal to 100 Kj.

Solution:

Calculating the efficiency of the engine:

$$\tau\% = \left(1 - \frac{T_2}{T_1}\right) \times 100 = \left(1 - \frac{45 + 273}{630 + 273}\right) \times 100 = 64.7\%$$

Calculating the work done:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \Rightarrow Q_2 = -\frac{T_2}{T_1} . Q_1 = -\left(\frac{45 + 273}{630 + 273}\right) . 100 = -35.22Kj$$

$$W = -(Q_1 + Q_2) = -\big(100 + (-35.22)\big) = -64.78Kj$$

4- Entropy:

Through the previous relationship: $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$

Proven in the Carnot cycle, this result can be generalized to any reversible cycle for any ideal gas. We define a new function called entropy, represented by: S, and its differential expression is:

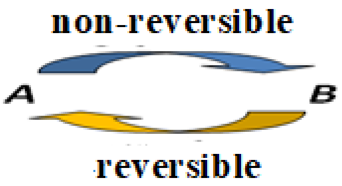
$$dS = \frac{dQ_{rev}}{T}$$

Entropy is a perfect differential (the integral of this quantity over a cyclic transformation is zero), and this relationship is the differential expression of the second law. Thus, during a reversible transformation from initial state A to final state B along a reversible path, the change in entropy is path-independent, where:

$$\Delta S = S_B - S_A = \int_A^B \frac{dQ_{rev}}{T}$$

And its unit is: J/mol. K or cal/mol. K

Studying the cycle ABA in the case of non-reversible transformation: We consider the evolution from the initial state A to the final state B through a non-reversible (real) path.



We assume the existence of a reversible path that returns the system from state B to state A. Therefore, the ABA cycle is non-reversible, and the Clausius inequality can be applied:

$$\oint_{ABA}\frac{dQ}{T} < 0$$

So:

$$\int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ_{rev}}{T} < 0$$

Knowing that:

$$S_A - S_B = \int_B^A dS = \int_B^A \frac{dQ_{rev}}{T}$$

So:

$$\int_A^B \frac{dQ}{T} + (S_A - S_B) < 0 \Longrightarrow S_B - S_A > \int_A^B \frac{dQ}{T}$$

If the system is isolated during the non-reversible path (from A to B), there is no heat exchange with the external surroundings.
So:

$$\int_A^B \frac{dQ}{T} = 0 \Longrightarrow \Delta S = S_B - S_A > 0$$

Through the non-reversible ABA cycle, we observe that the entropy of an isolated system increases during a real (non-reversible) transformation and remains constant during a reversible transformation.

Isolated system → **reversible transformation** $\Delta S = 0$
Isolated system → **non-reversible transformation** $\Delta S > 0$

Conclusion:

- During a real (non-reversible) transformation, the entropy of an isolated system increases.
- During a reversible transformation, the entropy of an isolated system remains constant.
- The universe is an example of an isolated system; therefore, the entropy of the universe remains constant during a reversible transformation and increases for a non-reversible transformation. The entropy of the universe cannot decrease.

$$\Delta S_{univers} \geq 0$$

The entropy of a system or a closed system: The entropy of a system or a closed system is defined by the following relationship:

$$\Delta S = \Delta\sigma + \Delta_e S = S_f - S_i$$

Where:

ΔS : The change in entropy (state function) of a system as it evolves, is the same for both reversible and irreversible transformations.

Δσ : The entropy generated within the system or the system, and based on its value, we can determine the nature or type of transformation.

$$\textbf{reversible transformation} \implies \Delta\sigma = 0$$

$$\textbf{Irreversible transformation}\ (\textbf{real transformation}) \implies \Delta\sigma > 0$$

$\Delta_e S$: The change in entropy acquired from the external surroundings, known as the exchange entropy, is not a state function. And it equals the ratio of the amount of heat gained by the system to the temperature of the source (the temperature of the external surroundings), where:

$$\Delta_e S = \frac{Q}{T_{source}}$$

- The sign of $\Delta_e S$ is related to the sign of the exchanged heat quantity.
- To determine the value of Δσ, it is necessary to know the values of ΔS and $\Delta_e S$, where:

$$\Delta\sigma = \Delta S - \Delta_e S$$

$$\Delta S = \int \frac{dQ_{rev}}{T}$$

$$\Delta_e S = \frac{Q}{T_{source}}$$

Special case (isolated system): In this case, there is no heat exchange.

$$\Delta S = \Delta_e S + \Delta\sigma$$

$$\Delta_e S = \frac{Q}{T_{source}} = 0 \implies \Delta S = \Delta\sigma \geq 0$$

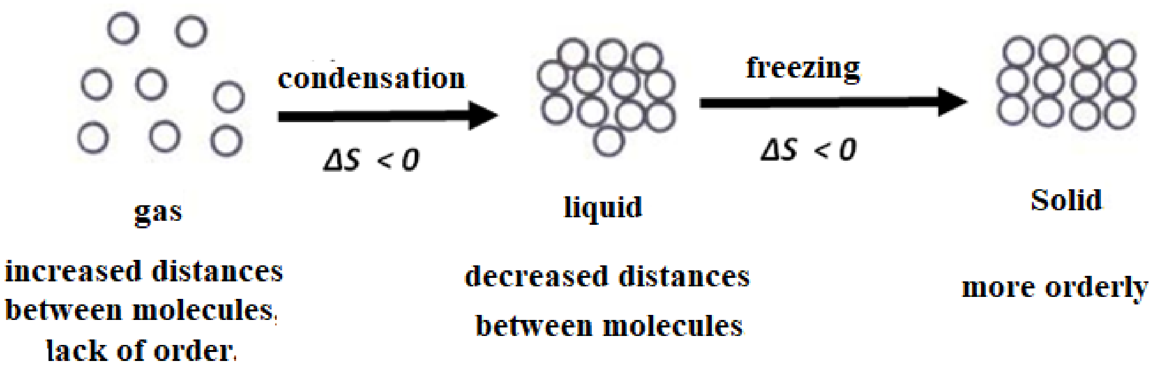
$$\Delta\sigma = 0 \implies \textbf{reversible transformation}$$

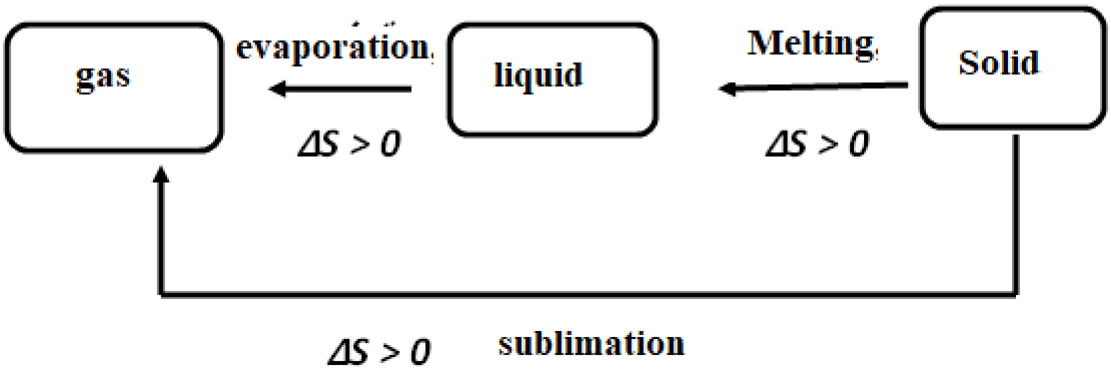
$$\Delta\sigma > 0 \implies \textbf{Irreversible transformation}\ (\textbf{real transformation})$$

The physical interpretation of entropy: Entropy S is a thermodynamic state function and is considered a measure of the degree of disorder or randomness of the system.

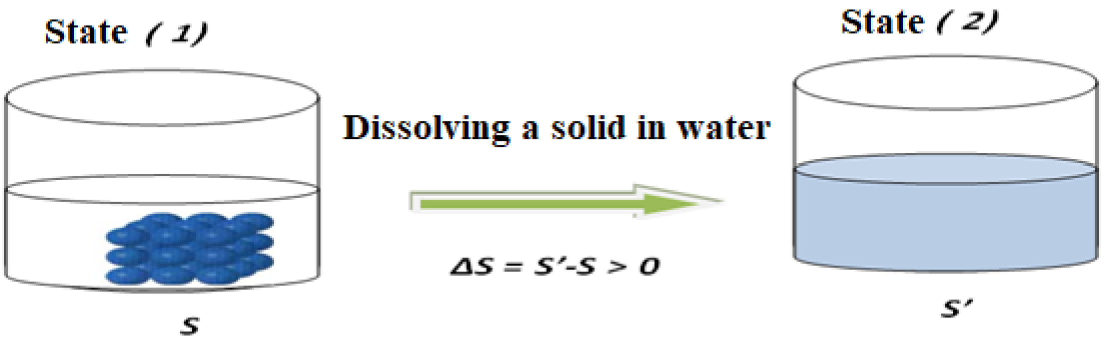
$$\Delta S = S_f - S_i$$

ΔS for physical changes:



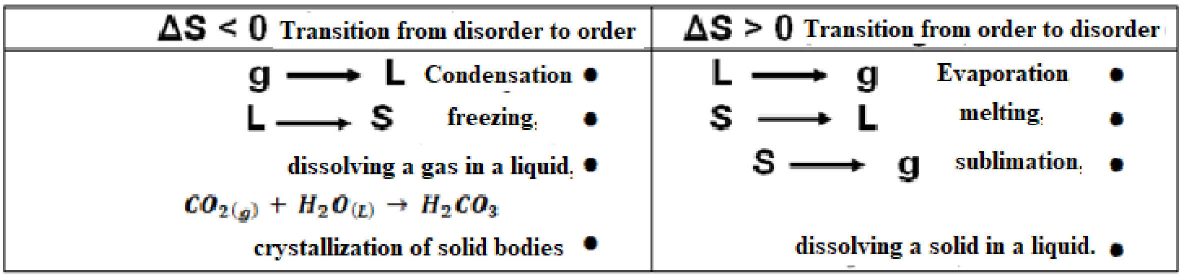


The process of dissolving a solid in a liquid:



The transition from state (1) orderly to state (2) less orderly.

So entropy describes the extent of disorder or randomness of the particles in the system and the dispersion of energy associated with these particles. We summarize in the following table the different physical transformations and the sign of the corresponding entropy change.



$\Delta S < 0$ Transition from disorder to order	$\Delta S > 0$ Transition from order to disorder
$g \longrightarrow L$ Condensation •	$L \longrightarrow g$ Evaporation •
$L \longrightarrow S$ freezing •	$S \longrightarrow L$ melting •
dissolving a gas in a liquid •	$S \longrightarrow g$ sublimation •
$CO_{2(g)} + H_2O_{(L)} \rightarrow H_2CO_3$	
crystallization of solid bodies •	dissolving a solid in a liquid •

Applying the second law to ideal gases during reversible transformations:

1- Entropy expression in terms of T and V:

According to the first law:

$$dU = dW + dQ$$

$$dS = \frac{dQ}{T} \Rightarrow dU = dW + TdS$$

$$dW = -P_{ext}dV = -PdV \Rightarrow dU = -PdV + TdS$$

$$dS = \frac{dU}{T} + \frac{P}{T}\,dV$$

$$PV = nRT \Rightarrow P = \frac{nRT}{V} \Rightarrow \frac{P}{T} = \frac{nR}{V}$$

$$dS = \frac{dU}{T} + \frac{nR}{V}\,dV = nC_V\frac{dT}{T} + nR\frac{dV}{V}$$

$$\Delta S = nC_V\int_{T_1}^{T_2}\frac{dT}{T} + nR\int_{V_1}^{V_2}\frac{dV}{V}$$

$$\Delta S = nC_V Ln\left(\frac{T_2}{T_1}\right) + nRLn\left(\frac{V_2}{V_1}\right)$$

Note:

If $T\ Cst \Rightarrow \Delta S = nRLn\left(\frac{V_2}{V_1}\right)$

If $V\ Cst \Rightarrow \Delta S = nC_V Ln\left(\frac{T_2}{T_1}\right)$

2- Entropy expression in terms of T and P:

$$H = U + PV \Rightarrow dH = dU + VdP + PdV$$
$$dH = dQ + dW + VdP + PdV$$
$$dW = -PdV$$
$$dS = \frac{dQ}{T} \Rightarrow dQ = TdS$$
$$dH = dQ + dW + VdP + PdV = TdS - PdV + VdP + PdV = TdS + VdP$$
$$PV = nRT \Rightarrow \frac{V}{T} = \frac{nR}{P}$$
$$dS = \frac{dH}{T} - nR\frac{dP}{P}$$
$$\Delta S = \int_{T_1}^{T_2} \frac{dH}{T} - \int_{P_1}^{P_2} nR\frac{dP}{P}$$

$$\Delta S = nC_P \int_{T_1}^{T_2} \frac{dT}{T} - nR\int_{P_1}^{P_2} \frac{dP}{P}$$
$$\Delta S = nC_P Ln\left(\frac{T_2}{T_1}\right) - nRLn\left(\frac{P_2}{P_1}\right)$$

Note:

If $T\ Cst \Rightarrow \Delta S = -nRLn\left(\frac{P_2}{P_1}\right)$

If $P\ Cst \Rightarrow \Delta S = nC_P Ln\left(\frac{T_2}{T_1}\right)$

3- Entropy expression in terms of P and V:

$$dS = nC_V\frac{dT}{T} + nR\frac{dV}{V} \dots\dots\dots\dots\dots (1)$$
$$dS = nC_P\frac{dT}{T} - nR\frac{dP}{P} \dots\dots\dots\dots\dots (2)$$
$$(1) = (2) \Rightarrow nC_V\frac{dT}{T} + nR\frac{dV}{V} = nC_P\frac{dT}{T} - nR\frac{dP}{P}$$

$$n(C_P - C_V)\frac{dT}{T} = nR\left(\frac{dV}{V} + \frac{dP}{P}\right) \Rightarrow nR\frac{dT}{T} = nR\left(\frac{dV}{V} + \frac{dP}{P}\right)$$

$$\frac{dT}{T} = \frac{dV}{V} + \frac{dP}{P} \dots\dots\dots\dots.(3)$$

By substituting (3) into (1), we find:

$$dS = nC_V(\frac{dV}{V} + \frac{dP}{P}) + nR\frac{dV}{V}$$

$$dS = nC_V\frac{dP}{p} + n(C_V + R)\frac{dV}{V}$$

$$dS = nC_V\frac{dP}{p} + nC_P\frac{dV}{V}$$

$$\Delta S = nC_V\int_{P_1}^{P_2}\frac{dP}{p} + nC_P\int_{V_1}^{V_2}\frac{dV}{V} \Rightarrow \Delta S = nC_V Ln\left(\frac{P_2}{P_1}\right) + nC_P Ln\left(\frac{V_2}{V_1}\right)$$

Note:

If $P\ Cst \Rightarrow \Delta S = nC_P Ln\left(\frac{V_2}{V_1}\right)$

If $V\ Cst \Rightarrow \Delta S = nC_V Ln\left(\frac{P_2}{P_1}\right)$

We can summarize all the previous relationships in the following tables for the reversible transformation of n moles of an ideal gas:

Isothermal transformation	
$Q = nRTLn\left(\frac{V_2}{V_1}\right) = nRTLn\left(\frac{P_1}{P_2}\right)$	**Q**
$W = -nRTLn\left(\frac{V_2}{V_1}\right) = -nRTLn\left(\frac{P_1}{P_2}\right)$	**W**
$\Delta U = 0 \quad 1\ according\ to\ the\ first\ law\ of\ Joul$	**ΔU**
$\Delta H = 0\ \ according\ to\ the\ second\ law\ of\ Joul$	**ΔH**
$\Delta S = nRLn\left(\frac{V_2}{V_1}\right)$ $\Delta S = -nRLn\left(\frac{P_2}{P_1}\right)$	**ΔS**

Isochoric transformation	
$Q = Q_V = \Delta U = nC_V(T_2 - T_1)$	**Q**
$W = 0$	**W**
$\Delta U = nC_V(T_2 - T_1)$	**ΔU**
$\Delta H = nC_P(T_2 - T_1)$	**ΔH**
$\Delta S = nC_V Ln\left(\frac{T_2}{T_1}\right)$	**ΔS**

Isobaric transformation	
$Q = Q_P = \Delta H = nC_P(T_2 - T_1)$	**Q**
$W = -P_2(V_2 - V_1)$ $W = \Delta U - \Delta H$	**W**
$\Delta U = nC_V(T_2 - T_1)$	**ΔU**
$\Delta H = nC_P(T_2 - T_1)$	**ΔH**
$\Delta S = nC_P Ln\left(\frac{T_2}{T_1}\right)$	**ΔS**

Adiabatic transformation	
$Q = 0$	Q
$W = \Delta U = nC_V(T_2 - T_1)$ $W = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	W
$\Delta U = nC_V(T_2 - T_1)$	ΔU
$\Delta H = nC_P(T_2 - T_1)$	ΔH
$\Delta S = 0$	ΔS

Types of Entropy:

1- Entropy Change of State: At constant pressure (P Cst) and constant temperature (T Cst). During a phase change of a pure substance, the pressure remains constant and equals atmospheric pressure, and likewise, the temperature of the phase change remains constant. In this case, the change in entropy equals:

$$dS = \frac{dQ_{rev}}{T} \Rightarrow \Delta S = \int \frac{dQ_{rev}}{T} = \frac{1}{T}\int dQ_{rev} = \frac{Q_{rev}}{T}$$

$$\Delta S = \frac{n\Delta H_{Transformation}}{T_{Transformation}}$$

$$\Delta S_{fusion} = \frac{n\Delta H_{fusion}}{T_{fusion}} \; ; \; \Delta S_{vaporization} = \frac{n\Delta H_{vaporization}}{T_{vaporization}}$$

$$\Delta H_{fusion} = L_{fusion}; \quad \Delta H_{vaporization} = L_{vaporization}$$

L: Latent heat (J/mol ; cal/mol)

Example :

Calculate the change in entropy ΔS corresponding to this transformation:

$$H_2O_{(L)} \longrightarrow H_2O_{(g)}$$

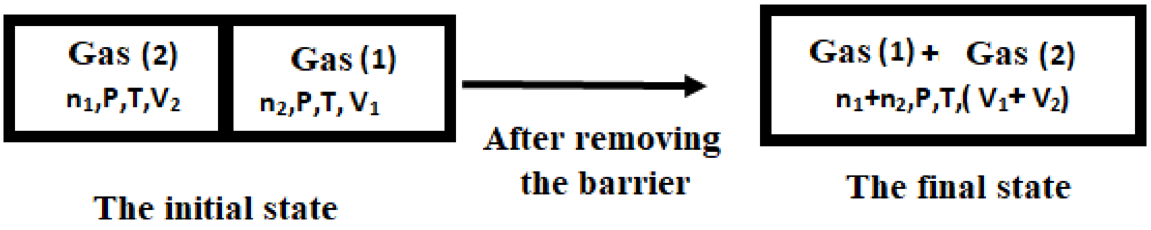
$$T_{vaporization} = 100°C$$

$$\Delta H_{vaporization} = 40,4Kj/mol$$

$$\Delta S_{vaporization} = \frac{n\Delta H'_{vaporization}}{T_{vaporization}} = \frac{40,4 \times 10^3}{100 + 273} = 108,3\ J/K$$

2- Mixture Entropy:

2-1) Two different gases at constant temperature: Let's consider two different gases present in separate containers, insulated from each other by a heat-insulating cover, as systems under the same pressure and temperature.



$$dS = \frac{dQ}{T} = \frac{dU - dW}{T} = \frac{dU}{T} - \frac{dW}{T} = nC_V\frac{dT}{T} + P\frac{dV}{T} = nC_V\frac{dT}{T} + nR\frac{dV}{V}$$

$$T\ Cst \Longrightarrow \Delta S = nRLn\left(\frac{V_f}{V_i}\right) \Longrightarrow \Delta S_{Tot} = \Delta S_1 + \Delta S_2$$

$$\Delta S_1 = n_1RLn\left(\frac{V_1 + V_2}{V_1}\right);\ \Delta S_2 = n_2RLn\left(\frac{V_1 + V_2}{V_2}\right)$$

$$\Delta S_{Tot} = n_1RLn\left(1 + \frac{V_2}{V_1}\right) + n_2RLn\left(1 + \frac{V_1}{V_2}\right)$$

$$P\ Cst;\ T\ Cst \Longrightarrow PV_1 = n_1RT\ ;\ PV_2 = n_2RT \Longrightarrow \frac{V_1}{V_2} = \frac{n_1}{n_2}$$

$$\Delta S_{Tot} = n_1RLn\left(1 + \frac{n_2}{n_1}\right) + n_2RLn\left(1 + \frac{n_1}{n_2}\right)$$

$$\Delta S_{Tot} = n_1RLn\left(\frac{n_1 + n_2}{n_1}\right) + n_2RLn\left(\frac{n_2 + n_1}{n_2}\right)$$

$$\Delta S_{Tot} = -n_1RLn\left(\frac{n_1}{n_1 + n_2}\right) - n_2RLn\left(\frac{n_2}{n_2 + n_1}\right)$$

$$\Delta S_{Tot} = -n_1RLn(X_1) - n_2RLn(X_2) = -R[n_1Ln(X_1) + n_2Ln(X_2)]$$

$$\Delta S_{Tot} = -R\sum_{i=1}^{n} n_iLn(X_i)$$

Where :

n_i : the number of moles of gas i.

x_i : The molar fraction of gas i.

Example:

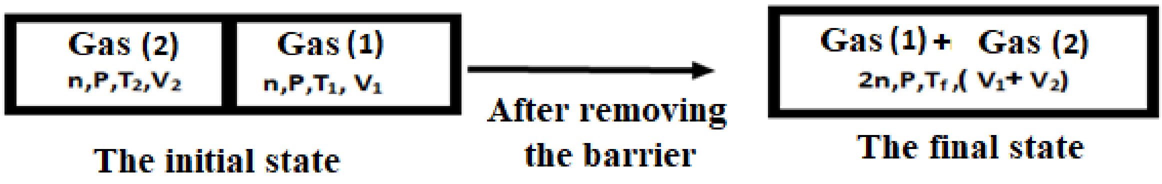
Calculate ΔS corresponding to the preparation of a mixture consisting of 1 mole of oxygen gas and 2 moles of hydrogen gas, assuming no chemical reaction between them and that it is reversible.

solution:

$$\Delta S = -R\sum_{i=1}^{n} n_i Ln(X_i) = -R\left[1.\,Ln\left(\frac{1}{3}\right) + 2.\,Ln\left(\frac{2}{3}\right)\right]$$

$$\Delta S = -8,314.\left[1.\,Ln\left(\frac{1}{3}\right) + 2.\,Ln\left(\frac{2}{3}\right)\right] = 15,87\ J/K$$

2-2) Two gases of the same nature at different temperatures:



After removing the barrier and at thermal equilibrium, we have:

$$T_f = \frac{T_1 + T_2}{2}$$

Assuming the gas is an ideal gas and C_P is constant, then:

$$\Delta S_{Tot} = \Delta S_1 + \Delta S_2$$

$$dS_1 = nC_P\frac{dT}{T} - nR\frac{dP}{P}$$

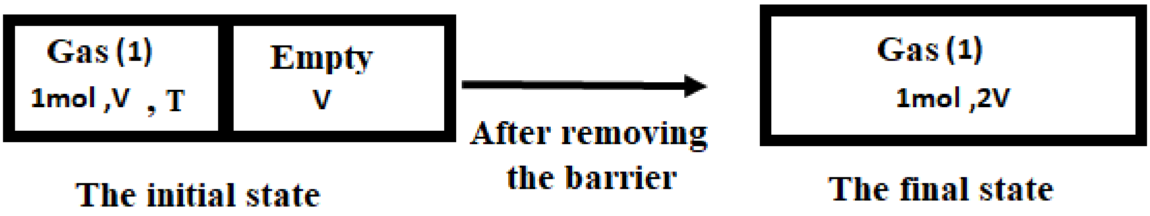
$$P\ Cst \Rightarrow dS_1 = nC_P\frac{dT}{T} \Rightarrow \Delta S_1 = nC_P Ln\left(\frac{T_f}{T_1}\right)$$

$$\Delta S_2 = nC_P Ln\left(\frac{T_f}{T_2}\right) \Rightarrow \Delta S_{Tot} = nC_P Ln\left(\frac{T_f}{T_1}\right) + nC_P Ln\left(\frac{T_f}{T_2}\right)$$

$$\Delta S_{Tot} = nC_P\left[Ln\left(\frac{T_f}{T_1}\right) + Ln\left(\frac{T_f}{T_2}\right)\right] = nC_P\ Ln\left(\frac{T_f^{\ 2}}{T_1 \times T_2}\right)$$

$$\Delta S_{Tot} = nC_P\ Ln\left(\frac{(T_1 + T_2)^2}{4(T_1 \times T_2)}\right)$$

Practical Example 1: A setup consists of two equally sized insulated containers connected by a valve. We place 1 mole of gas in one of them and completely evacuate the other. Calculate the change in entropy when the valve is opened between the containers, allowing the gas to spread throughout the entire volume. (Temperature remains constant).



$$V_f = 2V \,;\, n_{Tot} = 1\text{mol} \,;\, T_f = T_i = Cst$$

$$\Delta S = nC_V Ln\left(\frac{T_f}{T_i}\right) + nRLn\left(\frac{V_f}{V_i}\right) = nRLn\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = 1 \times 8{,}314 Ln\left(\frac{2V}{V}\right) = 5{,}76\, J/K$$

Practical Example 2:

Calculate the change in entropy and the work done for a gas compression process at constant temperature from the initial state ($T_1 = 15°C$; $V_1 = 0.03\ m^3$; $P_1 = 1.05$ atm) to the final state ($P_2 = 4.2$ atm).

Solution:

Calculate n:

$$P_1V_1 = nRT_1 \Rightarrow n = \frac{P_1V_1}{RT_1} = \frac{1{,}05 \times 0{,}03 \times 10^3}{0{,}082 \times (273 + 15)} = 1{,}334\ mol$$

$$\Delta S = nC_P Ln\left(\frac{T_f}{T_i}\right) - nRLn\left(\frac{P_f}{P_i}\right)$$

$$TCst \Rightarrow \Delta S = -nRLn\left(\frac{P_f}{P_i}\right) = -1{,}334 \times 8{,}314 Ln\left(\frac{4{,}2}{1{,}05}\right) = -15{,}37\, J/K$$

Let's calculate the work:

$$TCst \Rightarrow \Delta U = 0 \Rightarrow W + Q = 0 \Rightarrow w = -Q$$

$$\Delta S = \frac{Q}{T} \Rightarrow Q = T\Delta S \Rightarrow W = -T\Delta S = -288 \times (-15{,}37) = 4426{,}56 J$$

Second method :

$$W = -\int PdV = -\int nRT\frac{dV}{V} = -nRTLn\left(\frac{V_f}{V_i}\right) = -nRTLn\left(\frac{V_2}{V_1}\right)$$

$$P_1V_1 = nRT; P_2V_2 = nRT \Longrightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$W = -nRTLn\left(\frac{P_1}{P_2}\right) = -1,334 \times 8,314 \times 288Ln\left(\frac{1,05}{4,2}\right) = 4428,06\,J$$

The third Law of thermodynamics:

Introduction: **The experiments conducted by both Nernst and Planck on solid bodies at low temperatures have demonstrated that the specific heat of solid bodies decreases significantly.**

Text of the third law principle:

The entropy of a pure crystalline solid in its most stable form is zero at absolute zero, and we write:

$$S_{0\,°K} = 0$$

From the results of this principle, the following are observed:

1- The specific heat of all bodies tends towards zero as the temperature approaches absolute zero.

2- At absolute zero, the internal motion of molecules becomes nonexistent, thus the crystalline body is in a state of maximum regularity and its corresponding entropy is zero. After raising the temperature, molecules begin to move randomly, increasing the state of disorder and consequently increasing entropy.

3- This principle allows us to calculate absolute entropy at temperatures other than absolute zero using the aforementioned relationships.

Example:

$$\underset{0\,°\mathrm{K}}{H_2O_{(s)}} \rightarrow \underset{\mathrm{T}\,°\mathrm{K}}{H_2O_{(s)}}$$

At absolute zero, water exists in a solid state, and from it:

$$\Delta S = S_f - S_i = S°_{T\,°K} - S°_{0\,°K} = S°_{T\,°K}$$

$S°_{T\,°K}$ **: The absolute molar entropy at** $T\,°K$

$S°_{0\,°K}$ **: The absolute molar entropy at** $0\,°K$

The absolute entropy of a pure substance at T °K: **We consider 1 mole of a pure substance and raise its temperature from 0 °K to T °K at constant pressure:**

$$\begin{array}{cccccc} A_{(S)} \xrightarrow{\Delta S_1} & A_{(S)} \xrightarrow{\Delta S_2} & A_{(L)} \xrightarrow{\Delta S_3} & A_{(L)} \xrightarrow{\Delta S_4} & A_{(g)} \xrightarrow{\Delta S_5} & A_{(g)} \\ 0\ ^\circ K & T_{fus} & T_{fus} & T_{ébu} & T_{ébu} & T\ ^\circ K \end{array}$$

$$\Delta S = S_f - S_i = \Delta S = S^\circ_{T\,^\circ K} - S^\circ_{0\,^\circ K} = S^\circ_{T\,^\circ K}$$

$$dS = \frac{dQ_{rev}}{T}$$

$$\Delta S = S^\circ_{T\,^\circ K} = \int_{0\,^\circ K}^{T_{fus}} C_P(A)_S \frac{dT}{T} + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_{ébu}} C_P(A)_L \frac{dT}{T} + \frac{\Delta H_{vap}}{T_{ébu}} + \int_{T_{ébu}}^{T\,^\circ K} C_P(A)_g \frac{dT}{T}$$

Special cases:

1- Calculation of the absolute entropy under standard conditions S°$_{298\ K}$: If the solid remains solid under standard conditions, then:

$$\Delta S = S^\circ_{298^\circ K} - S^\circ_{0\,^\circ K} = S^\circ_{298^\circ K} = \int_{0\,^\circ K}^{298^\circ K} n\, C_P(A)_S \frac{dT}{T}$$

The following table provides some values of absolute entropy under standard conditions for some elements:

The compound	$C_{graphite}$	$CuO_{(S)}$	$H_2O_{(L)}$	$O_{2(g)}$
$S^\circ_{298^\circ K}$ (cal/mol.K)	0,6	10,4	16,7	49

2- Calculation of the absolute entropy at temperature T °K:

$$S^\circ_{T\,^\circ K} = S^\circ_{298^\circ K} + \int_{298^\circ K}^{T\,^\circ K} n\, C_P(A).\frac{dT}{T}$$

In case there is no change in physical state during the temperature change from 298 °K to T °K.

Chemical reaction entropy:

- **The change in entropy for a chemical reaction at constant temperature is calculated using Hess's law.**
- **In standard conditions (P = 1 atm, T = 298 °K), the change in entropy for a reaction is given by the following equation:**

$$\Delta S^\circ_{R,298\,^\circ K} = \sum \alpha_i S^\circ_i(\text{ Products}) - \sum \beta_i S^\circ_i(\text{ Reactants })$$

$$\alpha_i, \beta_i : \text{ stoichiometric coefficients}$$

- **In the case of variable temperature, the change in entropy is calculated using Kirchhoff's law (assuming no change in physical state for the reactants and products during the temperature change):**

$$\text{In the case } C_P \neq f(T) \Longrightarrow \Delta S^\circ_{R,\ T\,^\circ K} = \Delta S^\circ_{R,298\,^\circ K} + \Delta C_P \int_{298}^{T} \frac{dT}{T}$$

$$\text{In the case } C_P = f(T) \Longrightarrow \Delta S^\circ_{R,\ T\,^\circ K} = \Delta S^\circ_{R,298\,^\circ K} + \int_{298}^{T} \Delta C_P \frac{dT}{T}$$

$$\Delta C_P = \sum \alpha_i C_{P_i}(\text{ Products}) - \sum \beta_i C_{P_i}(\text{ Reactants })$$

$$\alpha_i, \beta_i : \text{ stoichiometric coefficients}$$

Examples:

1- Let the chemical reaction be:

$$C_4H_{10(g)} \rightarrow 4C_{grahite} + 5H_{2(g)}$$

$$S^\circ_{298\,^\circ K}(C_{grahite}) = 5,74J/molK$$

$$S^\circ_{298\,^\circ K}(H_{2(g)}) = 130\,,68\,J/molK$$

$$S^\circ_{298\,^\circ K}(C_4H_{10(g)}) = 320,23\,J/molK$$

The change in entropy for this reaction is:

$$\Delta S^\circ_{R,298\,^\circ K} = 4S^\circ_{298\,^\circ K}(C_{grahite}) + 5S^\circ_{298\,^\circ K}(H_{2(g)}) - S^\circ_{298\,^\circ K}(C_4H_{10(g)})$$

$$\Delta S^\circ_{R,298\,^\circ K} = 4(5,74) + 5(130,68) - 320,23 = 356,13\,J/molK$$

$$\Delta S^\circ_{R,298\,^\circ K} > 0 \text{ . because } \quad n_{gi} < n_{gf}$$

2 - Let the chemical reaction be:

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

$$S^\circ_{298\,^\circ K}(N_{2(g)}) = 191,61J/molK$$

$$S^\circ_{298\,^\circ K}(H_{2(g)}) = 130\,,68\,J/molK$$

$$S^\circ_{298\,^\circ K}(NH_{3(g)}) = 192,45\,J/molK$$

The change in entropy for this reaction is:

$$\Delta S^{\circ}_{\mathrm{R},298\,^{\circ}\mathrm{K}} = 2S^{\circ}_{298\,^{\circ}\mathrm{K}}(NH_{3(g)}) - S^{\circ}_{298\,^{\circ}\mathrm{K}}(N_{2(g)}) - 3S^{\circ}_{298\,^{\circ}\mathrm{K}}(H_{2(g)})$$

$$\Delta S^{\circ}_{\mathrm{R},298\,^{\circ}\mathrm{K}} = 2(192,45) - (191,61) - 3(130\,,68)$$

$$= -198,75\ J/molK$$

$\Delta S^{\circ}_{\mathrm{R},298\,^{\circ}\mathrm{K}} < 0$ لأن $n_{gi} > n_{gf}$ **The final state is more ordered than the initial state.**

Practical Example 1:

1- Calculate the standard molar absolute entropy of water at 298 °K, where:

$$\Delta H_{fus,273}\,(H_2O)_S = 1440\ cal/mol\ ;\ S^{\circ}_{273}(H_2O)_S = 10,28\ cal/mol.k$$

$$C_P(H_2O)_L = (11,2+7,17.10^{-3}T)$$

2- Calculate the change in standard molar entropy for the formation of water at 298 °K, where:

$$S^{\circ}_{298}(H_2)g = 31,21\ cal/mol.K\ ;\quad S^{\circ}_{298}(O_2)g = 49\ cal/mol.K$$

Solution:

1- Calculating the standard molar absolute entropy of water at 298 °K:

$$\begin{tikzcd} \begin{array}{c} H_2O_{(s)} \\ 273\ \mathrm{K} \end{array} \arrow[r, "\Delta S_1"] \arrow[rr, bend right, "\Delta S^{\circ}_{Tot} = \Delta S_1 + \Delta S_2"'] & \begin{array}{c} H_2O_{(l)} \\ 273\ \mathrm{K} \end{array} \arrow[r, "\Delta S_2"] & \begin{array}{c} H_2O_{(l)} \\ 298\ \mathrm{K} \end{array} \end{tikzcd}$$

$$\Delta S^{\circ}_{Tot} = S^{\circ}_{298^{\circ}K}(H_2O_L) - S^{\circ}_{273^{\circ}K}(H_2O_S) = \Delta S_1 + \Delta S_2$$

$$S^{\circ}_{298^{\circ}K}(H_2O_L) = S^{\circ}_{273^{\circ}K}(H_2O_S) + \Delta S_1 + \Delta S_2$$

$$\Delta S_1 = \frac{n\Delta H_{fus}}{T_{fus}} = \frac{1 \times 1440}{273} = 5,27\ cal/molK$$

$$\Delta S_2 = \int_{273}^{298} nC_P(H_2O_L)\frac{dT}{T} = \int_{273}^{298} 1\left(\frac{11,2}{T} + 7,17 \times 10^{-3}\right)dT$$

$$\Delta S_2 = 11,2Ln\left(\frac{298}{273}\right) + 7,17 \times 10^{-3}(298 - 273) = 1,1606\ cal/molK$$

$$S^{\circ}_{298^{\circ}K}(H_2O_L) = S^{\circ}_{273^{\circ}K}(H_2O_S) + \Delta S_1 + \Delta S_2 = 10,28 + 5,27 + 1,606$$

$$S^{\circ}_{298^{\circ}K}(H_2O_L) = 16,71\ cal/molK$$

2- Calculating the change in standard molar entropy for the formation reaction of water at 298 °K.

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(L)}$$

$$\Delta S^\circ_{R,298\,^\circ K} = S^\circ_{298\,^\circ K}\left(H_2O_{(L)}\right) - S^\circ_{298\,^\circ K}\left(H_{2(g)}\right) - \frac{1}{2}S^\circ_{298\,^\circ K}\left(O_{2(g)}\right)$$

$$\Delta S^\circ_{R,298\,^\circ K} = 16,71 - 31,21 - \frac{1}{2}(49) = -39\ J/molK$$

$$\Delta S^\circ_{R,298\,^\circ K} < 0\ (\text{ Increase in orderliness })$$

Practical Example 2:

Let the following chemical reaction be: $2NH_{3(g)} + \frac{3}{2}O_{2(g)} \rightarrow N_{2(g)} + 3H_2O_{(L)}$

Calculate ΔS° for this reaction at:

- **Temperature 298 °K.**
- **Temperature 300 °K where water is in the liquid state.**
- **Temperature 400 °K where water is in the gaseous state.**

Given: at T = 25 °C and P = 1 atm.

The compound	$H_2O_{(L)}$	$H_2O_{(g)}$	$N_{2(g)}$	$O_{2(g)}$	$NH_{3(g)}$
S° (J/molK)	69,94	188,72	191,5	205,0	192,6
C_p (J/molK)	75,30	33,58	29,12	29,37	35,1

$\Delta Hvapo(H_2O_{(L)})$ = 40,5 KJ/mol

Solution:

- **Calculating ΔS° at a temperature of 298 °K:**

$$\Delta S^\circ_{R,298\,^\circ K} = 3S^\circ_{298\,^\circ K}\left(H_2O_{(L)}\right) + S^\circ_{298\,^\circ K}\left(N_{2(g)}\right) - 2S^\circ_{298\,^\circ K}\left(NH_{3(g)}\right) - \frac{3}{2}S^\circ_{298\,^\circ K}\left(O_{2(g)}\right)$$

$$\Delta S^\circ_{R,298\,^\circ K} = 3(69,94) + 191,5 - 2(192,6) - \frac{3}{2}(205,0)$$

$$\Delta S^\circ_{R,298\,^\circ K} = -291,38\ J/molK$$

- **Calculating ΔS° at a temperature of 300 °K**

There is no change in the physical state for the reactants or the products during the temperature change from 298 °K to 300 °K. Therefore, according to Kirchhoff's law:

$$\Delta S^{\circ}_{R,\ 300\,°K} = \Delta S^{\circ}_{R,298\,°K} + \int_{298}^{300} \Delta C_P \frac{dT}{T}$$

$$\Delta C_P = C_P(N_{2(g)}) + 3C_P(H_2O_{(L)}) - 2C_P(NH_{3(g)}) - \frac{3}{2}C_P(O_{2(g)})$$

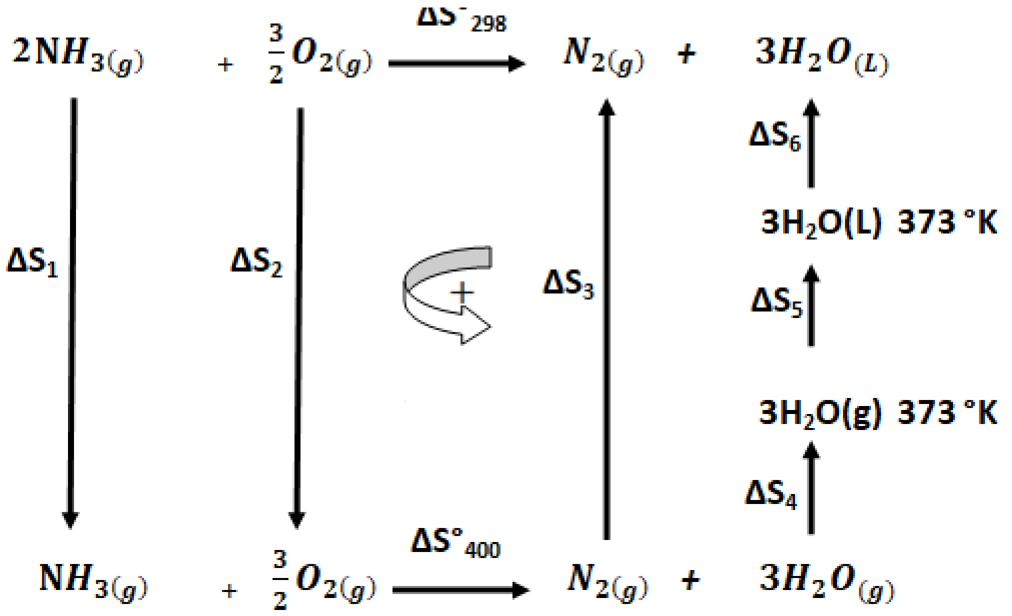
$$\Delta C_P = 29,12 + 3(75,30) - 2(35,1) - \frac{3}{2}(29,37) = 140,765\ J/molK$$

$$\Delta S^{\circ}_{R,\ 300\,°K} = \Delta S^{\circ}_{R,298\,°K} + \int_{298}^{300} \Delta C_P \frac{dT}{T} = -291,38 + \mathrm{Ln}(\frac{300}{298})$$

$$\Delta S^{\circ}_{R,\ 300\,°K} = -290,43\ J/mol.K$$

• Calculating ΔS° at a temperature of 400 °K.

When the temperature is raised to 400 °K, water converts to the gaseous state.



$$\Delta S_{\text{cycle}} = 0 \Rightarrow \Delta S_1 + \Delta S_2 + \Delta S^\circ{}_{400} + \Delta S_3 + \Delta S_4 + \Delta S_5 + \Delta S_6 - \Delta S^\circ{}_{298} = 0$$

$$\Delta S^\circ{}_{400} = \Delta S^\circ{}_{298} - \Delta S_1 - \Delta S_2 - \Delta S_3 - \Delta S_4 - \Delta S_5 - \Delta S_6$$

$$\Delta S_1 = \int_{298}^{400} 2C_P(NH_{3(g)})\frac{dT}{T} = 2 \times 35,1Ln\left(\frac{400}{298}\right) = 20,664\, J/K$$

$$\Delta S_2 = \int_{298}^{400} \frac{3}{2}C_P(O_{2(g)})\frac{dT}{T} = \frac{3}{2} \times 29,37Ln\left(\frac{400}{298}\right) = 12,96\, J/K$$

$$\Delta S_3 = \int_{400}^{298} C_P(N_{2(g)})\frac{dT}{T} = 29,12Ln\left(\frac{298}{400}\right) = -8,57\, J/K$$

$$\Delta S_4 = \int_{400}^{373} 3C_P(H_2O_{(g)})\frac{dT}{T} = 3 \times 33,58Ln\left(\frac{373}{400}\right) = -7,040\, J/K$$

$$\Delta S_5 = \frac{-3\Delta H_{vap}}{T_{vap}} = \frac{-3 \times 40,5 \times 10^3}{373} = -325,73\, J/K$$

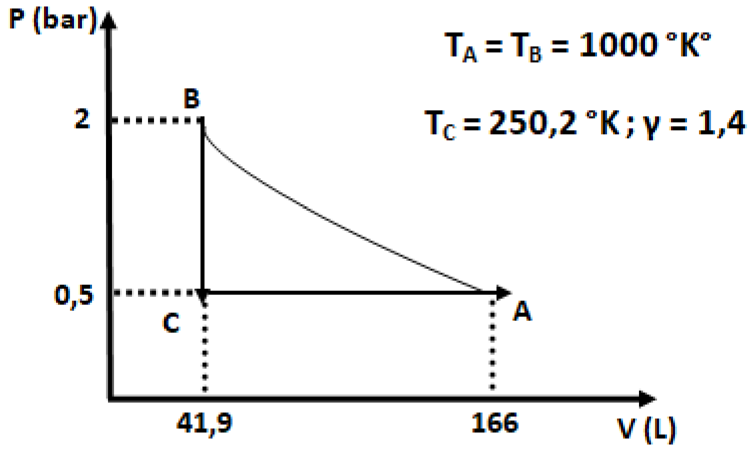
$$\Delta S_6 = \int_{373}^{298} 3C_P(H_2O_{(L)})\frac{dT}{T} = 3 \times 75,30Ln\left(\frac{298}{373}\right) = -50,71\, J/K$$

$$\Delta S^\circ{}_{400} = -291,38 - (20,664) - (12,96) - (-8,57) - (-7,040) - (-325,73) - (-50,71) = 67,046\, J/K$$

$\Delta S^\circ{}_{400} > 0$ Increasing the number of gas moles

Practical Example 3:

The following figure represents a Clapeyron diagram for the three transformations undergone by 1 mole of an ideal gas, forming a closed cycle.



Calculating ΔS for the cycle:

$$A \xrightarrow{T\ Cst} B \;\Rightarrow\; \Delta S_{AB} = nRLn\left(\frac{V_B}{V_A}\right) = 1 \times 8,314Ln\left(\frac{41,9}{166}\right)$$

$$\Delta S_{AB} = -11,45\, J/K$$

$$C_V = \frac{R}{\gamma - 1}\ ;\ C_P = \frac{\gamma R}{\gamma - 1}$$

$$B \xrightarrow{V\ Cst} C \;\Rightarrow\; \Delta S_{BC} = nC_V Ln\left(\frac{T_C}{V_B}\right) = 1 \times \frac{8,314}{1,4-1} Ln\left(\frac{250,2}{1000}\right)$$

$$\Delta S_{BC} = -28,8\, J/K$$

$$C \xrightarrow{P\ Cst} A \;\Rightarrow\; \Delta S_{CA} = nC_P Ln\left(\frac{T_A}{V_C}\right) = 1 \times \frac{1,4 \times 8,314}{1,4-1} Ln\left(\frac{1000}{250,2}\right)$$

$$\Delta S_{BC} = 40,32\, J/K$$

$$\Delta S_{\text{cycle}} = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CA} = -11,45 + (-28,8) + 40,32 \approx 0$$