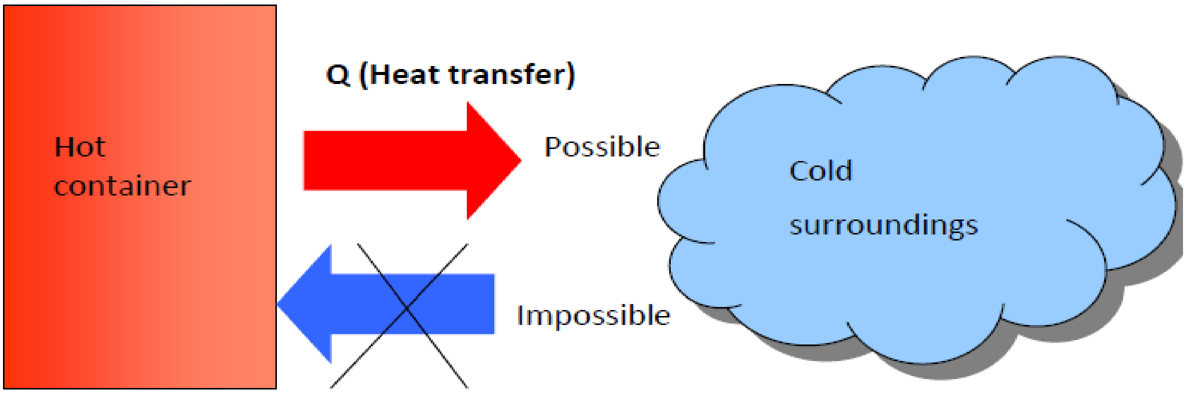
The Second Law of Thermodynamics

The first law places no restriction on the direction of a process, and satisfying the first law does not guarantee that the process will occur. Thus, we need another general principle (second law) to identify whether a process can occur or not.

The second law of thermodynamics asserts that processes occur in a certain direction and that the energy has *quality* as well as *quantity*.



- Heat transfer from a hot container to the cold surroundings is possible; however, the reveres process (although satisfying the first law) is impossible.
- It is impossible to construct a machine working in cycles which will transfer heat from a lower temperature to a higher temperature.
- Heat cannot be completely converted into work without leaving changes either in the system or in the surroundings.
- Heat cannot be pass from a colder to a warmer body.
- No machine has yet been made with efficiency of a unity.

A process can occur when and only when it satisfies both the first and the second laws of thermodynamics.

The second law is also used in determining the theoretical limits for the performance of commonly used engineering systems, such as heat engines and refrigerators etc.

Thermal Energy Reservoirs

Thermal energy reservoirs are hypothetical bodies with a *relatively* large thermal energy capacity (mass x specific heat) that can supply or absorb finite amounts of **heat without undergoing any change in temperature**. Lakes, rivers, atmosphere, oceans are example of thermal reservoirs.

A two-phase system can be modeled as a reservoir since it can absorb and release large quantities of heat while remaining at constant temperature.

A reservoir that supplies energy in the form of heat is called a **source** and one that absorbs energy in the form of heat is called a **sink.**

Heat Engines

Heat engines convert heat to work. There are several types of heat engines, but they are characterized by the following:

1-They all receive heat from a high-temperature source (oil furnace, nuclear reactor, etc.)

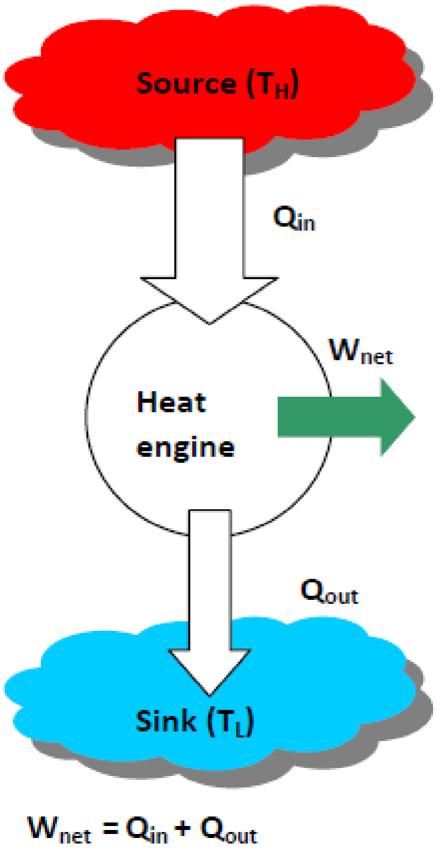
2-They convert part of this heat to work.

3-They reject the remaining waste heat to a low-temperature sink

4-They operate in a cycle.

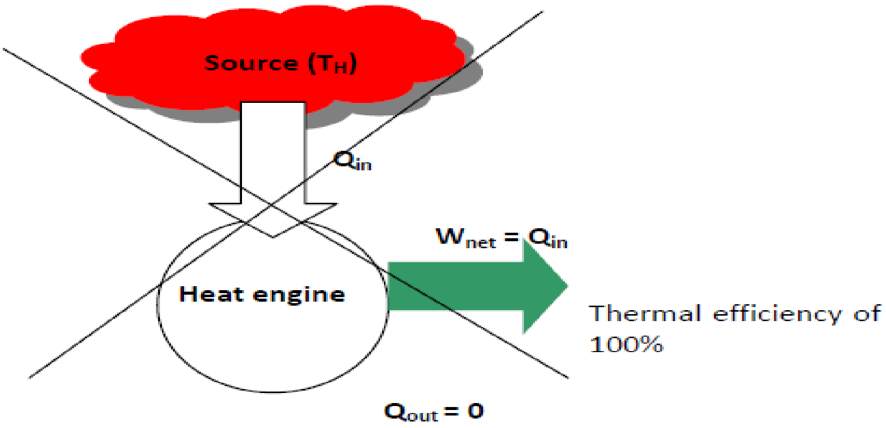
The efficiency: is the fraction of the heat input that is converted to the net work output.

$$\eta = \frac{W_{net,out}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$



The Second Law: Kelvin-Planck Statement

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work. In other words, no heat engine can have a thermal efficiency of 100%.



Refrigerators and Heat Pumps

In nature, heat flows from high-temperature regions to low-temperature ones. The reverse process, however, cannot occur by itself. The transfer of heat from a low temperature region to a high-temperature one requires special devices called ***refrigerators***. Refrigerators are cyclic devices, and the working fluids used in the cycles are called refrigerant.

Heat pumps transfer heat from a low-temperature medium to a high-temperature one some work is done on it by the surrounding and rejects heat at the higher temperature. It thus functions as a refrigerator, that is, it extracts heat from a cold reservoir and passes it to a hot reservoir. The ratio of work done on the engine to the heat absorbed at lower temperature is the coefficient of performance of the engine and is given as:

$$\frac{W}{Q_1} = \frac{(T_2 - T_1)}{T_2}$$

$$W = Q_1 \frac{(T_2 - T_1)}{T_2}$$

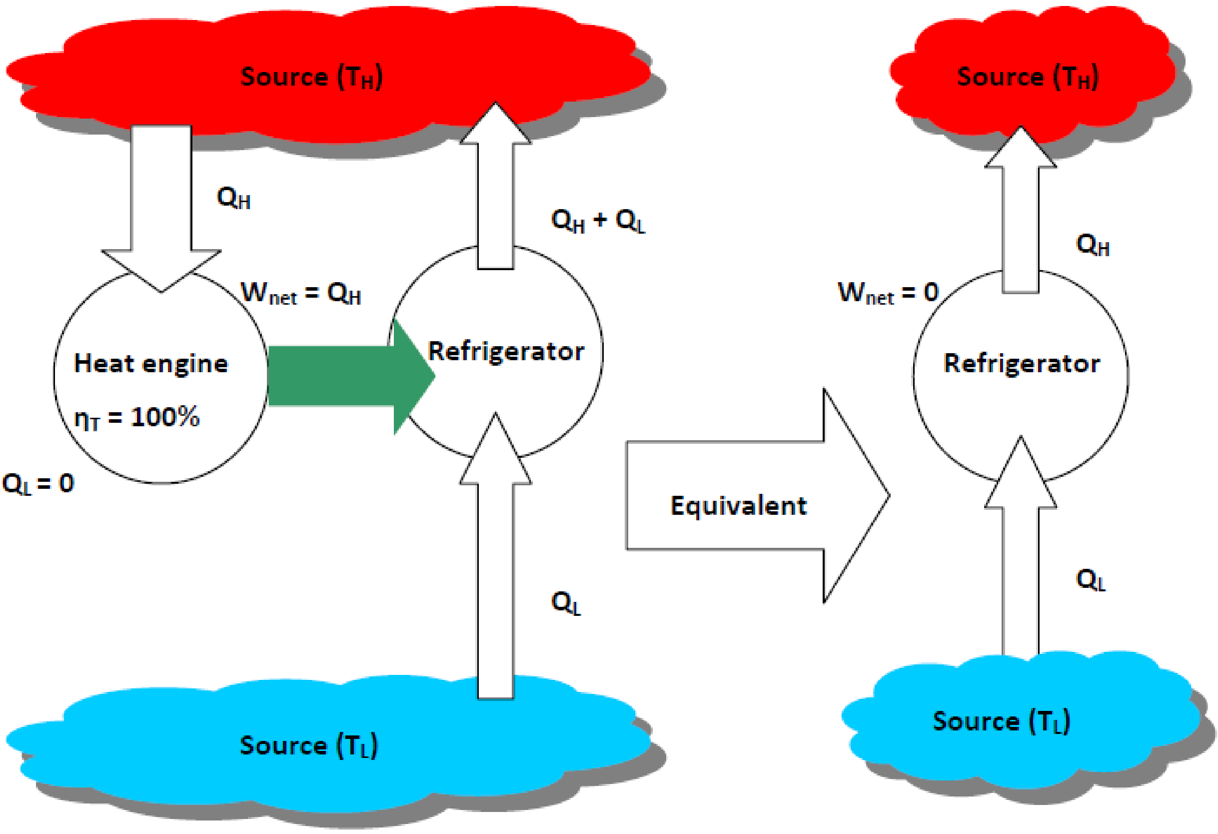
This equation represents the minimum amount of work which must be done to remove a quantity of heat (Q_1) at T_1 and giving it at higher temperature T_2.

The Second Law of Thermodynamics: Clausius Statement

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to higher-temperature body. In other words, a refrigerator will not operate unless its compressor is driven by an external power source.

Kelvin-Planck and Clausius statements of the second law are negative statements, and a negative statement cannot be proved. So, the second law, like the first law, is based on experimental observations.

The two statements of the second law are equivalent. In other words, any device violates the Kelvin-Planck statement also violates the Clausius statement and vice versa.



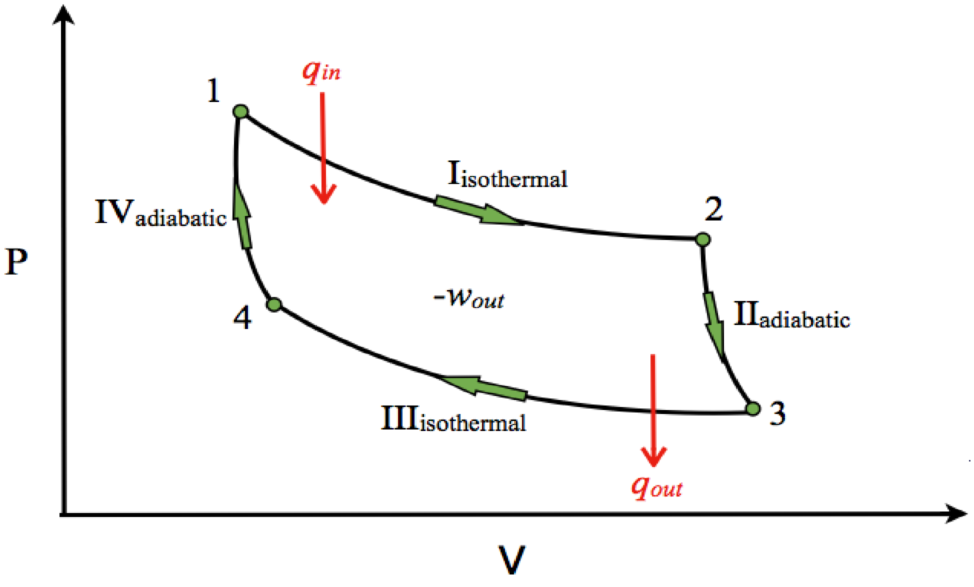
- Clausius introduced the function of entropy (S). Entropy function is a measure of randomness.
- Spontaneous processes are the processes which take place of their own without the external intervention of any kind.
- Spontaneous processes happen in one direction and are irreversible.
- Spontaneous processes pass from a less probable to more probable.

The Carnot Cycle

The efficiency of a heat-engine cycle greatly depends on how the individual processes that make up the cycle are executed. The net work (or efficiency) can be maximized by using reversible processes. The best known reversible cycle is the *Carnot cycle*.

Note that the reversible cycles cannot be achieved in practice because of irreversibility associated with real processes. But, the reversible cycles provide upper limits on the performance of real cycles.

- Consider a gas in a cylinder-piston (closed system). The Carnot cycle has four processes:



Carnot Cycle

(Step 1)Reversible isothermal expansion: The cylinder containing the gas is placed in contact with the reservoir T_2. It absorbs a certain quantity of heat q_2. The gas expands slowly, doing work on the surrounding; it expands isothermally and reversibly at the temperature T_2 of the source. The volume changes from V_1 to V_2. So there is no change in the internal energy $\Delta U=0$

$$\Delta U = 0 \rightarrow q_2 = -W_1 = nRT_2 \, ln \frac{V_2}{V_1}$$

(Step 2)Reversible adiabatic expansion: The cylinder is removed from the source. It is surrounding by a thermally insulated enclosure and the gas is allowed to expand reversibly and adiabatically from its volume V_2 to V_3 until its temperature drops to T_1, the temperature of the sink. The expansion is adiabatic: no heat enters or leaves the system. $q = 0$

$$W_2 = C_V (T_1 - T_2)$$

(Step 3)Reversible isothermal compression: The gas is allowed to exchange heat with a sink at temperature T_1 as the gas is being slowly compressed. So, the surrounding is doing work (reversibly) on the system and heat is transferred from the system to the surroundings (reversibly) such that the gas temperature remains constant at T_1 until it volume changes from V_3 to V_4.

$$\Delta U = 0 \rightarrow q_2 = -W_3 = nRT_1 \, ln \frac{V_4}{V_3}$$

(Step 4)Reversible adiabatic compression: the cylinder is removed from the sink, surrounded by the thermal insulation and compressed adiabatically and reversibly until its temperature rises to that of source and volume decrease from V_4 to V_1.

$$W_4 = C_V (T_2 - T_1)$$

$$W = W_1 + W_2 + W_3 + W_4$$

$$W = -nRT \, ln \frac{V_2}{V_1} + C_V (T_1 - T_2) - nRT \, ln \frac{V_4}{V_3} + C_V (T_2 - T_1)$$

$$C_V(T_1 - T_2) = -C_V(T_2 - T_1)$$

$$W = -RT_2\ ln\frac{V_2}{V_1} + RT_1\ ln\frac{V_4}{V_3}$$

V_2, V_3 lie on the adiabatic I, V_1, V_4 on the adiabatic II.

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\left[\frac{V_3}{V_2} = \frac{V_4}{V_1}\right] \div \frac{V_2}{V_4} \rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

The net work is:

$$-W = RT_2\ ln\frac{V_2}{V_1} - RT_1 ln\frac{V_3}{V_4} = R(T_2 - T_1)\ln\frac{V_2}{V_1}$$

The efficiency of the engine is thus:

$$\eta = \frac{-W}{q_2} = \frac{R(T_2 - T_1)ln\frac{V_2}{V_1}}{RT_2\ ln\frac{V_2}{V_1}} = \frac{(T_2 - T_1)}{T_2} = 1 - \frac{T_1}{T_2}$$

Mathematical Formulation of Entropy

We now from Carnot cycle:-

$$\frac{-W}{q_2} = \frac{q_1 + q_2}{q_2} = \frac{(T_2 - T_1)}{T_2} = 1 + \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

$$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

In the Carnot cycle, heat is exchanged only in the isothermal steps and the sum of q/T terms represents a definite thermodynamic property of the system. It is called entropy which for an infinitesimally small changes in the state of the system is defined as the heat absorbed isothermally and reversibly divided by the temperature at which the absorption of heat takes place,

$$dS = \frac{q}{T}$$

$$for\ a\ finite\ changes\ in\ the\ state\ of\ the\ sstem\quad \Delta S = \frac{q}{T}$$

$$\Delta S_{cycle} = \sum \frac{q_{rev}}{T} = 0$$

$$\oint dS\ is\ zero$$

Relation between energy, enthalpy and entropy- combined form of the first law and the second law

$$\Delta U = q - w = q - PdV$$

$$dS = \frac{dq}{T} \rightarrow dq = TdS$$

$$\Delta U = TdS - PdV$$

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$dH = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

Entropy changes in reversible process (noncyclic process)

$$\Delta S_{sys} = \frac{q_{rev}}{T}\quad , \quad \Delta S_{surr} = -\frac{q_{rev}}{T}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$$

(i) Isothermal reversible process

$$\Delta S_{sys} = \frac{q_{rev}}{T}$$

$$q = -w = nRT_2\ ln\frac{V_2}{V_1} = nRT\ ln\frac{P_1}{P_2}$$

$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{nRT\ ln\frac{V_2}{V_1}}{T} = nR\ ln\frac{V_2}{V_1} = nR\ ln\frac{P_1}{P_2}$$

$$\Delta S_{sys} = -\Delta S_{surr}$$

(ii) Isobaric Reversible process involving changes in Temperature

$$\Delta S_{sys} = \sum \left(\frac{q_{rev}}{T}\right)_P \quad , \quad q_P = \Delta H = C_P \Delta T$$

When C_p is independent on temperature

$$\Delta S_{sys} = \sum \frac{C_P \Delta T}{T}$$

By integration

$$\Delta S_{sys} = \int_{T_1}^{T_2} \frac{C_P \Delta T}{T} = C_P ln \frac{T_2}{T_1} = 2.303\, C_P ln \frac{T_2}{T_1}$$

(iii) Isochoric Reversible process involving changes in Temperature

$$\Delta S_{sys} = \sum \left(\frac{q_{rev}}{T}\right)_V \quad , \quad q_V = \Delta U = C_V \Delta T$$

$$\Delta S_{sys} = \int_{T_1}^{T_2} \frac{C_V \Delta T}{T} = C_V ln \frac{T_2}{T_1} = 2.303\, C_V ln \frac{T_2}{T_1}$$

(iv)Entropy changes in vacuum or against zero opposing pressure.

In this process no work is done by the system and the expansion is isothermally

$$\Delta U = 0 \rightarrow q_{free} = W = nRT\, ln \frac{V_2}{V_1} = nRT\, ln \frac{P_1}{P_2}$$

$$\Delta S_{sys} = \frac{q_{free}}{T}$$

As no heat is exchange between the system and the surrounding

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

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = nR\, ln \frac{V_2}{V_1} = nR\, ln \frac{P_1}{P_2}$$

(v) Reversible phase Transition

Transformation of substance from one phase to another can be carried out reversibly at constant temperature and constant pressure usually 1 atm.

$$q_{trans} = \Delta H_{trans}$$

$$\Delta S_{trans} = \frac{q_{trans}}{T}$$

Example:

$$(+) \qquad \Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} \qquad \textit{Entropy of vaporization}$$

$$(+) \qquad \Delta S_{fus} = \frac{\Delta H_{fus}}{T_{fus}} \qquad \textit{Entropy of fusion}$$

$$(+) \qquad \Delta S_{sub} = \frac{\Delta H_{sub}}{T_{sub}} \qquad \textit{Entropy of sublimation}$$

$$(-) \qquad \Delta S_{frez} = \frac{\Delta H_{frez}}{T_f} \qquad \textit{Entropy of freezing}$$

Tronton's Rule

A wide range of liquids give approximately the same standard entropy of vaporization (about 85 JK^{-1} mol^{-1})

$$\Delta_{vap} S^{\circ} \approx 85\, JK^{-1} mol^{-1}$$

It is used to predict the standard molar enthalpy of vaporization $\Delta_{vap}H°$ at boiling point.

$$\Delta_{vap} S^{\circ} = \frac{\Delta_{vap} H^{\circ}}{T}$$

$$\Delta_{vap} H^{\circ} = \Delta_{vap} S^{\circ} \times T_b = T_b \times 85\, JK^{-1} mol^{-1}$$

Variation of entropy with Temperature and volume

Considering entropy as a function of volume and temperature. For infinitesimal changes, dS can be written as:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \;\ldots..(1)$$

Considering U= f(V,T) we get:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$= n\,C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Substituting this value of dU in this equation

$$TdS = dU + PdV$$

$$dS = \frac{n\,C_V}{T} dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \;\ldots\ldots(2)$$

This equation is general and applicable to all substances solids, liquids, and gases. The first term on the right hand side of the equation gives the change in entropy due to change in temperature and the second expression denotes the contribution to entropy changes due to variation in volume. Comparing equation (1) and equation (2)

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{n\,C_V}{T} \;\ldots\ldots\ldots..(3)$$

$$and \qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \;\ldots\ldots\ldots(4)$$

For ideal gases $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{P}{T}$$

For one mole of ideal gas $\frac{P}{T} = \frac{R}{V}$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{R}{V}$$

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

For a mole of an ideal gas equation (2) reduces to:

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

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{n\, C_V}{T}$$

Integration yields the total change in entropy resulting from simultaneous changes in volume and temperature. The expression is:

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

For one mole of ideal gas $V = \frac{T}{P}$

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}\frac{T_2}{T_1}$$

$$\Delta S = (C_V + R) \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

$$\Delta S = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

Entropy of Mixing of Ideal gas

Mixing of two or more gases is irreversible and accompanied by an increase of entropy. We shall derive an expression for the entropy of mixing of ideal and nonreacting gases

Let consider two gases A and B, n_A is the number of moles of A and n_B is the number of moles of B. $n_t = n_A + n_B$

$V = V_A + V_B$

$$\Delta S_{mixing} = n_A R\, ln \frac{V}{V_A} + n_B R\, ln \frac{V}{V_B}$$

$$\Delta S_{mixing} = -n_A R\, ln\, \frac{V_A}{V} - n_B R\, ln\, \frac{V_B}{V}$$

$$\frac{V_A}{V} = \frac{n_A}{n_t} = X_A \quad , \quad \frac{V_B}{V} = \frac{n_B}{n_t} = X_B$$

$$\Delta S_{mixing} = -n_A R\, ln\, X_A - n_B R\, ln\, X_B$$

$$\Delta S_{mixing} = -R \sum n_i \; ln\, X_i$$

The entropy of mixing per mole of the mixture is obtained by dividing both sides of the above equation by n_i , the total number of moles;

$$\Delta S_{mixing} = -R \sum X_i \; ln\, X_i$$

The Third Law of thermodynamics

Variation of entropy of a substance with temperature at constant pressure is given by:

$$dS = \frac{C_P}{T} dT$$

Integrating this equation from T=0K to some temperature T below the melting point of the substance we get:

$$T_1 = 0K$$

$$T_2 = T$$

$$S_T - S_0 = \int_0^T \frac{C_P}{T}\, dT = C_P\, d\ln T$$

Where S_0 is the hypothetical value of entropy at absolute zero. C_P/T is positive, the entropy at some higher temperature must be greater than that at the absolute zero. In 1913, Plank suggested that entropy of a pure and perfectly crystalline substance is zero at the absolute zero of temperature. This known as the third law of thermodynamics.

If S_0 is taken to be zero at zero Kelvin:

$$S_T = \int_0^T \frac{C_P}{T}\, dT$$

Knowing the temperature dependence of heat capacity, entropy of a substance at any specified temperature can be calculated using the above equation. In evaluating the absolute value of entropy contributions to entropy due to phase transformations such as melting, vaporization, sublimation and transition from one allotropic form into other must be taken into account.

The entropy of a substance at any temperature above its boiling point is then given as:

$$S_T = \int_{trans}^{T_m} \frac{C_{P(s)}}{T}\, dT + \frac{\Delta H_{fus}}{T_m} + \int_{Tm}^{T_s} \frac{C_{P(l)}}{T}\, dT + \frac{\Delta H_{vap}}{T_b} + \int_{Tb}^{Tm} \frac{C_{P(g)}}{T}\, dT$$

Some Fundamental relation based on the second law of thermodynamics:

Prove that:

(1) $$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{T\left(\frac{\partial V}{\partial T}\right)_P}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial V}{\partial T}\right)_P = \frac{C_P}{T}$$

$$dH = VdP + TdS$$

$$\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial P}{\partial T}\right)_S$$

Replacing $\left(\frac{\partial S}{\partial V}\right)_P$ by $\left(\frac{\partial P}{\partial T}\right)_S$

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{T\left(\frac{\partial V}{\partial T}\right)_P}$$

(2) For an ideal gas

$$\boldsymbol{\left(\frac{\partial P}{\partial V}\right)_S = \frac{\gamma\, P}{V}}$$

Consider $S = f(P.V)$

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

If $dS = 0 \quad then$:

$$\left(\frac{\partial S}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_P$$

$$\left(\frac{\partial P}{\partial V}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial P}{\partial S}\right)_V$$

$$= \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V$$

$$= -\frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P \frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V$$

$$= -\frac{C_P}{C_V}\,\frac{R}{V}\,\frac{P}{R} = \boldsymbol{\gamma}\,\frac{P}{V}$$

(3) $\boldsymbol{\left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial H}{\partial P}\right)_S = -R \left(\frac{\partial U}{\partial S}\right)_V}$

$$dU = TdS - PdV$$

$$dT = TdS + VdP$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad and \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

The left hand side is thus –PV which is equal to RT. The right hand side is:

$$-R\left(\frac{\partial U}{\partial V}\right)_S = -R\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V$$

$$= -RC_V\frac{T}{C_V} = -RT$$

Solved Examples

Example1: Two moles of an ideal monoatomic gas C_P=5/2 R initially at 1 atm and 300 K are subjected through the following reversible cycle:

(1) isothermal compression to 2 atm.

$$\Delta S_{sys} = -nR\ln\frac{P_2}{P_1} = -2\times 8.314\ln\frac{2}{1} = -11.52JK^{-1}$$

(2) isobaric temperature increase to 400K.

$$\Delta S = nC_P\ \ln\frac{T_2}{T_1} = 2\times\frac{5}{2}\times 8.314\ln\frac{400}{300} = 11.97JK^{-1}$$

(3) Return to the initial state by a different path.

$$\Delta S_{cycl} = 0 = \Delta S_1 + \Delta S_2 + \Delta S_3 = -11.52 + 11.97 + \Delta S_3$$

$$\Delta S_{cycl} = -0.45JK^{-1}$$

Example2: One mole of an ideal gas C_V= 12.55 JK^{-1} mol^{-1} is transferred from 298K and 2 atm to 233K and 0.4 atm. Calculate for the change in the state of the system.

Solution:

$$C_V = 12.55JK^{-1}mol^{-1} \rightarrow C_P = 12.55 + 8.314 = 20.86JK^{-1}mol^{-1}$$

$$\Delta S = nC_P\ \ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1}$$

$$\Delta S = (1mol)(20.864)\ln\frac{233}{298} - (1mol)(8.314)\ln\frac{0.4}{2}$$

$$= -3.308 + 13.40 = 10.092JK^{-1}mol^{-1}$$

Example3: the temperature of an ideal monoatomic gas is increase from 273K to 819K. Calculate the pressure change in order that the entropy of the gas remains unchanged in the process?

$$\Delta S_{sys} = nC_P\ \ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1}$$

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

$$nC_P \ln\frac{T_2}{T_1} = nR\ln\frac{P_2}{P_1}$$

$$\frac{5}{2}R\ln\frac{T_2}{T_1} = R\ln\frac{P_2}{P_1}$$

$$\frac{5}{2}\ln\frac{819}{273} = \ln\frac{P_2}{P_1}$$

$$\ln\frac{P_2}{P_1} = 2.74 \rightarrow \frac{P_2}{P_1} = 15.588$$

Example4: One mole of hydrogen and nine moles of nitrogen are mixed at 298K and 1 atm pressure. Assuming ideal behavior for the gases, calculate the entropy of mixing per mole of the mixture formed.

For ideal gases, the entropy of mixing per mole of mixture is given by:

$$\Delta S_{mix} = -R\sum X_i \; ln\, X_i$$

$$X_{H_2O} = 0.1 \;\; and \; X_{N_2} = 0.9$$

$$\Delta S_{mix} = -R\,[0.1\ln 0.1 + 0.9\ln 0.9]$$

$$= -8.314 \times -0.3248 = 2.704 JK^{-1}mol^{-1}$$

Example4: Predict the enthalpy of vaporization of ethane from its boiling point, −88.6°C.

$$\Delta_{vap}H^{\circ} = \Delta_{vap}S^{\circ} \times T_b$$

$$\Delta_{vap}H^{\circ} = 85\, JK^{-1}mol^{-1} \times (-88.6 + 273)K = 15.6\; kJ\; mol^{-1}$$

Example 5: A reversible heat engine absorbs 40kJ of heat at 500 K and performs 10kJ of work rejecting the remaining amount to the sink at 300K. Calculate the entropy change for the source, sink and universe.

$$q_2 = 40000J$$

$$\Delta S_{source} = -\frac{40000}{500} = -80JK^{-1}$$

$$q_1 = 40kJ - 10kJ = 30000J$$

$$\Delta S_{sink} = \frac{30000\,J}{300K} = 100JK^{-1}$$

$$\Delta S_{univ} = \Delta S_{source} + \Delta S_{sink} = -80 + 100 = 20\,JK^{-1}$$

Exercises

(1) Calculate ΔS (for the system) when the state of 3.00 mol of perfect gas atoms, for which $C_{p,\mathrm{m}} = 5/2R$, is changed from 25°C and 1.00 atm to 125°C and 5.00 atm.

(2) Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,\mathrm{m}} = 7/2R$, is changed from 25°C and 1.50 atm to 135°C and 7.00 atm.

(3) A sample consisting of 3mol of diatomic perfect gas molecules at 200 K is compressed reversibly and adiabatically until its temperature reaches 250 K. Given that $C_{V,\mathrm{m}} = 27.5\ \mathrm{J\ K^{-1}\ mol^{-1}}$, calculate q, w, ΔU, ΔH, and ΔS.

(4) A carnot engine whose low temperature reservoir is at 280 K has an efficiency of 40%. It is desired to increase this to 50 %. By how much many degrees must the temperature of the low temperature reservoir be decreased if that of the high temperature reservoir remains constant.

(5) 2 moles of an ideal monoatomic gas at 300K and 10 atm pressure is expanded to 20 times its original volume by (i) isothermal reversible path and (ii) adiabatic reversible path.

(6) 10 moles of an ideal monoatomic gas ($C_{P,\mathrm{m}} = 28.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$) at 400K and 10 atm are expanded adiabatically to 2 atm. Calculate the entropy change for the system, surrounding and universe if the process is (1) reversible (2) expansion is a free expansion.