Equilibrium and Non-equilibrium Thermodynamics: Concept of Entropy Part-2

- Entropy Production
- Onsager’s reciprocal relations

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Numerical:

Calculate the standard entropy change for the following process at 298 K:

$$H_2O(g) \longrightarrow H_2O(l)$$

The value of the standard entropy change at room temperature, $\Delta S^o{}_{298}$, is the difference between the standard entropy of the product, $H_2O(l)$, and the standard entropy of the reactant, $H_2O(g)$.

$$\Delta S^o{}_{298} = S^o{}_{298}(H_2O\ (l)) - S^o{}_{298}(H_2O(g))$$

$$(70.0\ Jmol^{-1}K^{-1}) - (188.8 Jmol^{-1}K^{-1})$$

$$= -118.8\ Jmol^{-1}K^{-1}$$

Use the data of Standard Molar Entropy Values of Selected Substances at 25°C to calculate ΔS° for each reaction.

1) $H_2(g) + 1/2O_2\ (g) \rightarrow H_2O(l)$
2) $CH_3OH(l) + HCl(g) \rightarrow CH_3Cl(g) + H_2O(l)$
3) $H_2(g) + Br_2(l) \rightarrow 2HBr(g)$
4) $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(s) + H_2(g)$

For standard molar entropy values see the following webpage:
https://www.chem.wisc.edu/deptfiles/genchem/netorial/modules/thermodynamics/table.htm

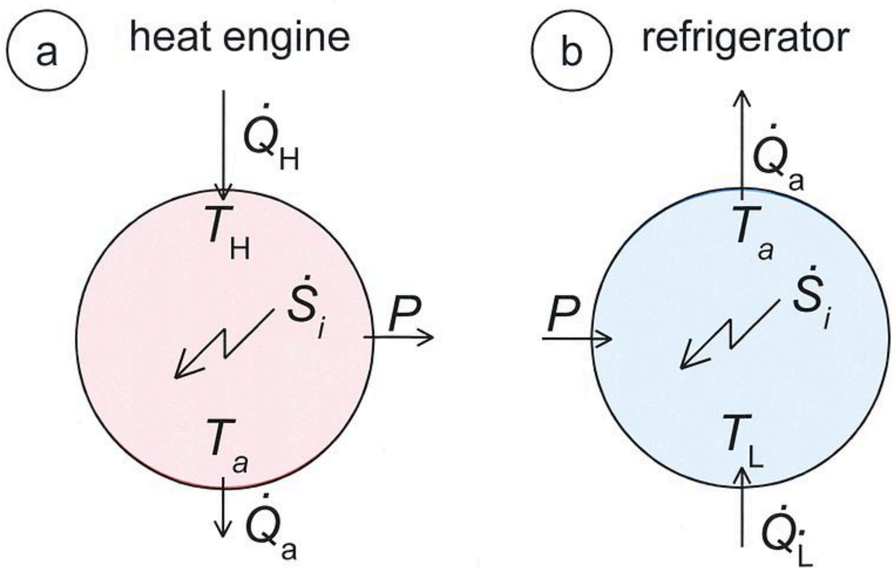
Note: Students should also try more numerical questions

Entropy Production: In a reversible process, net change in the entropy of the system and surroundings is zero therefore, it is only possible to produce entropy in an irreversible process. Entropy production (or generation) is the amount of entropy which is produced in any irreversible processes. This can be achieved via heat and mass transfer processes including motion of bodies, heat exchange, fluid flow, substances expanding or mixing, deformation of solids, and any irreversible thermodynamic cycle, including thermal machines such as power plants, heat engines, refrigerators, heat pumps, and air conditioners.

Entropy production in a heat engine and a refrigerator:

Heat engine: Heat Q_H enters the engine at temperature T_H and power P is generated. Heat Q_a leaves the system at T_a. Entropy S_i is generated.

Refrigerator: Cooling Q_L at a temperature T_L and power P is supplied. Heat Q_a leaves the system at T_a. Entropy S_i is generated.



Flux describes any effect that appears to pass or travel (whether it actually moves or not) through a surface or substance. In transport phenomena (heat transfer, mass transfer and fluid dynamics), flux is defined as the rate of flow of a property per unit area, which has the dimensions Quantity/Time·Area

There are different types of fluxes e.g., heat flux: rate of heat flow across a unit area (J/m^2s), diffusion flux: rate of moment of molecules per unit area (mol/ m^2s), energy flux: rate of energy flow per unit area (J/m^2s), etc.

Thermodynamics of irreversible processes

The thermodynamics of irreversible processes deals with systems which are not at equilibrium but are nevertheless stationary.

Note: For his discovery of these reciprocal relations, Lars Onsager was awarded the 1968 Nobel Prize in Chemistry

Onsager reciprocal relations: Onsager reciprocal relations express the equality of certain ratios between flows (fluxes) and forces in thermodynamic systems those are out of equilibrium, but with a local equilibrium.

Reciprocal relations are relation of mutual dependence or action or influence

Reciprocal relations occur between different pairs of forces and flows in a variety of physical systems. For example, consider fluid systems described in terms of temperature, matter density, and pressure. In this class of systems, it is known that temperature differences lead to heat flows from the warmer to the colder parts of the system; similarly, pressure differences will lead to matter flow from high-pressure to low-pressure regions. What is remarkable is the observation that, when both pressure and temperature vary, temperature differences at constant pressure can cause matter flow (as in convection) and pressure differences at constant temperature can cause heat flow. Perhaps surprisingly, the heat flow per unit of pressure difference and the density (matter) flow per unit of temperature difference are equal. This equality was shown to be necessary by Lars Onsager using statistical mechanics as a consequence of the time reversibility of microscopic dynamics (microscopic reversibility).

Note: Students should also go through the following website:
https://www.slideshare.net/SpringerIndia/non-equilibrium-thermodynamics-in-multiphase-flows

Onsager reciprocal relations

Onsager observed that when two or more irreversible transport processes, like heat conduction, electrical conduction and diffusion take place simultaneously in a macroscopic system, the processes may interfere with each other. The individual transport processes in the absence of the interference effects mentioned above, like mass transport (described by Fick's law) and heat transport (the Fourier law) are well described by a relation between the flux (J) and the force (X). However, the presence of the examples of coupled irreversible processes mentioned above (*the thermoelectric phenomena, the transference phenomena in electrolytes and heat conduction in an anisotropic medium*) clearly shows that the phenomenological laws to be generalized by including cross-terms.

Hence, for two such related processes, we need to write the transport laws as:

$J_i = \Sigma L_{ij} X_j$: (1)

where J_i and X_i are the flux and the force of the individual transport process '*i*'. L_{ij} is the proportionality coefficients. For the diagonal case, these are the transport properties like diffusion co-efficient and conductivity. However, nothing much was known for the off-diagonal coefficients.

Onsager established, using the principle of microscopic reversibility and the assumption of regression to show that

$L_{ij} = L_{ji}$ for $j \neq i$: (2)

The aove equation shows that the off-diagonal terms are equal and this is Onsager's reciprocal relations.

Note: Students should also go through the following website:
https://www.nobelprize.org/uploads/2018/06/onsager-lecture.pdf