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Study of Entropy change in Irreversible Processes in co-relation with second law of thermodynamics

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Abstract : As per definition, calculation of the change in entropy requires information about a reversible path connecting the initial and final equilibrium states. To calculate changes in entropy for real (irreversible) processes, we must remember that entropy (like internal energy) depends only on the state of the system. That is, entropy is a state function. Hence, the change in entropy when a system moves between any two equilibrium states depends only on the initial and final states. We can show that if this were not the case, the second law of thermodynamics would be violated.

We now calculate the entropy change in some irreversible process between two equilibrium states by devising a reversible process (or series of reversible processes) between the same two states and computing $\Delta S = \int dQ_r / T$ for the reversible process. In irreversible processes, it is critically important that we distinguish between Q, the actual energy transfer in the process, and Q_r, the energy that would have been transferred by heat along a reversible path. Only Q_r is the correct value to be used in calculating the entropy change.

As we observe, the change in entropy for a system and its surroundings is always positive for an irreversible process. In general, the total entropy - and therefore the disorder - always increase in an irreversible process. Keeping these considerations in mind, we can state the second law of thermodynamics as follows:

"The total entropy of an isolated system that undergoes a change can never decrease."

Furthermore, if the process is irreversible, then the total entropy of an isolated system always increases. In a reversible process, the total entropy of an isolated system remains constant.

When dealing with a system that is not isolated from its surroundings, remember that the increase in entropy described in the second law is that of the system and its surroundings. When a system and its surroundings interact in an irreversible process, the increase in entropy of one is greater than the decrease in entropy of the other. Hence, we conclude that the change in entropy of the Universe must be greater than zero for an irreversible process and equal to zero for a reversible process. Ultimately, the entropy of the Universe should reach a maximum value. At this value, the Universe will be in a state of uniform temperature and density. All physical, chemical, and biological processes will cease because a state of perfect disorder implies that no energy is available for doing work. This gloomy state of affairs is sometimes referred to as the heat death of the Universe.

Entropy change in Thermal Conduction

Let us now consider a system consisting of a hot reservoir and a cold reservoir in thermal contact with each other and isolated from the rest of the Universe. A process occurs during which energy Q is transferred by heat from the hot reservoir at temperature T_h to the cold reservoir at temperature T_c . Because the cold reservoir absorbs energy Q , its entropy increases by Q / T_c . At the same time, the hot reservoir loses energy Q , and so its entropy change is $-Q / T_h$. Because $T_h > T_c$, the increase in entropy of the cold reservoir is greater than the decrease in entropy of the hot reservoir. Therefore, the change in entropy of the system (and of the Universe) is greater than zero:

$$\Delta S_U = \frac{Q}{T_c} + \frac{-Q}{T_h} > 0$$

Equation 1

Let us again consider the adiabatic free expansion of a gas occupying an initial volume V_i . A membrane separating the gas from an evacuated region is broken, and the gas expands (irreversibly) to a volume V_f . Let us find the changes in entropy of the gas and of the Universe during this process. The process is clearly neither reversible nor quasi-static. The work done by the gas against the vacuum is zero, and because the walls are insulating, no energy is transferred by heat during the expansion. That is, W = 0 and Q = 0. Using the first law, we see that the change in internal energy is zero. Because the gas is ideal, E_{int} depends on temperature only, and we conclude that $\Delta T = 0$ or $T_i = T_f$.

To apply Equation 1 we cannot use Q = 0, the value for the irreversible process, but must instead find Q_r; that is, we must find an equivalent reversible path that shares the same initial and final states. A simple choice is an isothermal, reversible expansion in which the gas pushes slowly against a piston while energy enters the gas by heat from a reservoir to hold the temperature constant. Because T is constant in this process, Equation below gives

$$\Delta S = \int_i^f \frac{dQ_r}{T} = \frac{1}{T}\int_i^f dQ_r$$

Equation 2

For an isothermal process, the first law of thermodynamics specifies that $\int f_i \, dQ_r$ is equal to the work done by the gas during the expansion from V_i to V_f, which is given by Equation 20.13. Using this result, we find that the entropy change for the gas is

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

Equation 3

Because $V_f > V_i$, we conclude that ΔS is positive. This positive result indicates that both the entropy and the disorder of the gas increase as a result of the irreversible, adiabatic expansion. Because the free expansion takes place in an insulated container, no energy is transferred by heat from the surroundings. (Remember that the isothermal, reversible expansion is only a replacement process that we use to calculate the entropy change for the gas; it is not the actual process.) Thus, the free expansion has no effect on the surroundings, and the entropy change of the surroundings is zero. Thus, the entropy change for the Universe is positive; this is consistent with the second law.

Entropy change in Calorimetric Processes

A substance of mass m_1, specific heat c_1, and initial temperature T_1 is placed in thermal contact with a second substance of mass m_2, specific heat c_2, and initial temperature $T_2 > T_1$. The two substances are contained in a calorimeter so that no energy is lost to the surroundings. The system of the two substances is allowed to reach thermal equilibrium. What is the total entropy change for the system? First, let us calculate the final equilibrium temperature T_f. Using Equation 2, $Q_{\text{cold}} = -Q_{\text{hot}}$, and Equation 3, $Q = mc\,\Delta T$, we obtain

$$m_1c_1\,\Delta T_1 = -\,m_2c_2\,\Delta T_2$$

$$m_1c_1(T_f - T_1) = -\,m_2c_2(T_f - T_2)$$

Solving for T_f, we have

$$T_f = \frac{m_1c_1T_1 + m_2c_2T_2}{m_1c_1 + m_2c_2}$$

Equation 4

The process is irreversible because the system goes through a series of nonequilibrium states. During such a transformation, the temperature of the system at any time is not well defined because different parts of the system have different temperatures. However, we can imagine that the hot substance at the initial temperature T_2 is slowly cooled to the temperature T_f as it comes into contact with a series of reservoirs differing infinitesimally in temperature, the first reservoir being at T_2 and the last being at T_f. Such a series of very small changes in temperature would approximate a reversible process. We imagine doing the same thing for the cold substance. Applying Equation 1 and noting that $dQ = mc\,dT$ for an infinitesimal change, we have

$$\Delta S = \int_1 \frac{dQ_{\text{cold}}}{T} + \int_2 \frac{dQ_{\text{hot}}}{T} = m_1c_1\int_{T_1}^{T_f}\frac{dT}{T} + m_2c_2\int_{T_2}^{T_f}\frac{dT}{T}$$

Equation 5

where we have assumed that the specific heats remain constant. Integrating, we find that

$$\Delta S = m_1 c_1 \ln \frac{T_f}{T_1} + m_2 c_2 \ln \frac{T_f}{T_2}$$

Equation 6

where T_f is given by Equation 5. If Equation 6 is substituted into Equation 6, we can show that one of the terms in Equation 6 is always positive and the other is always negative. (You may want to verify this for yourself.) The positive term is always greater than the negative term, and this results in a positive value for ΔS. Thus, we conclude that the entropy of the Universe increases in this irreversible process.

Finally, we noted that Equation 6 is valid only when no mixing of different substances occurs, because a further entropy increase is associated with the increase in disorder during the mixing. If the substances are liquids or gases and mixing occurs, the result applies only if the two fluids are identical.

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