

## 4.3 ENTROPY CHANGE FOR IRREVERSIBLE PROCESSES

The definition of entropy gives us only an inequality for irreversible processes. For an irreversible process that takes a system from state A to state B, we have the following inequality.

$$S(B) - S(A) > \left( \int_A^B \frac{dQ}{T} \right)_{\text{irr}} \quad (4.11)$$

Here the right side may not be calculable since we may not know  $dQ$  and  $T$  during the process. A reversible process between the same two states gives us an equality for entropy change.

$$S(B) - S(A) = \left( \int_A^B \frac{dQ}{T} \right)_{\text{rev}} \quad (4.12)$$

Since entropy is a state function, the difference of entropy between states  $A$  and  $B$  does not depend on how the change was made. It should be the same for any process between  $A$  and  $B$ . Therefore, if the actual process performed between states  $A$  and  $B$  is an irreversible process, then, to find the entropy change, we can invent some convenient reversible process that starts with state  $A$  and ends with state  $B$ . The entropy change over the imagined reversible process will equal the entropy change over the irreversible process in question. I will now present two examples to make this point clearer.

**Example 4.3.1. Entropy Change for Heating Water Irreversibly.** A glass beaker of mass 600 g contains 800 g of water at 20°C. The beaker is put in a microwave and heated. At the end the temperature of water and beaker becomes 80°C. What is the change in entropy of the beaker and water? Use  $c = 0.2 \text{ cal/g.K}$  for glass.

**Solution.** Note that water is not heated slowly enough to be quasi-static and reversible. Therefore we have an irreversible process between two states: beaker+water at 20°C (state  $A$ ) and same at 80°C (state  $B$ ). We do not have any formula for directly evaluating entropy for this process. We need to imagine a reversible process or processes that will cause state  $A$  to change to state  $B$ . One way this can be done is as follows. We can imagine an infinite number of heat baths of different temperatures between 20°C and 80°C. The system at temperature  $T$  is then dipped into a bath at temperature  $T + dT$  so that the temperature of the system rises by an infinitesimally amount quasi-statically and reversibly. The change of entropy

in one such infinitesimal reversible process is

$$dS = \left( mc_p \frac{dT}{T} \right)_{beaker} + \left( mc_p \frac{dT}{T} \right)_{water}$$

Integrating from  $T_1 = 20 + 273 = 293$  K to  $T_2 = 80 + 273 = 353$  K we find the following.

$$\Delta S = \left( mc_p \ln \frac{T_2}{T_1} \right)_{beaker} + \left( mc_p \ln \frac{T_2}{T_1} \right)_{water} = 171 \text{ cal/K}.$$

**Example 4.3.2. Entropy Change for an Ideal Gas in an Irreversible Process.** Two moles of a monatomic ideal gas at  $-50^\circ\text{C}$  is in one chamber of a two chamber insulated container where the chambers are equal in volume and are connected by a stopcock. The other chamber is evacuated to a perfect vacuum. When the stopcock is opened the gas rushes into the second chamber without any effort. Since gas does not move any piston or wall no work is done in the process. Find the entropy change.

**Solution.** Note that, even though no heat enters or exits the system, the entropy change is not necessarily zero. We cannot use  $dQ/T$  of an irreversible process to find the entropy change. We have to imagine a reversible process between the initial and final state to carry out the calculation of entropy change. Let us first be clear about the initial and final states  $A$  and  $B$  respectively. Since no work is done and no heat is exchanged, the internal energy of the gas does not change. As internal energy of an ideal gas is only a function of temperature, this means that final state's temperature is same as that of the initial state.

State  $A$  :  $T = 223$  K, volume  $V$ , pressure  $p_A$ .

State  $B$  :  $T = 223$  K, volume  $2V$ , pressure  $p_B$ .

By using the ideal gas law, we can show that  $p_B = p_A/2$ . Now we can imagine some convenient reversible processes for calculation of entropy.

**Imagined reversible process: Isothermal process between  $A$  and  $B$ .** As the system is an ideal gas, the internal energy is only a function of temperature, which makes  $dU = 0$  on this process. Therefore, from the first law of thermodynamics we get

$$dQ = pdV = (nRT/V)dV$$

Hence the change in entropy is

$$\Delta S = nR \int_{V_A}^{V_B} \frac{dV}{V} = nR \ln \frac{V_B}{V_A} = 2 \text{ mol} \times \frac{8.31 \text{ J}}{\text{mol.K}} \ln(2) = 11.5 \text{ J/K}.$$

This says that even when  $(\Delta Q)_{irr} = 0$ ,  $\Delta S \neq 0$ .