

4.2 THE CONCEPT OF ENTROPY

According to the Clausius's inequality, the integral of the quantity dQ/T over a cycle is zero for all reversible cycles. The following arguments show that the integral of dQ/T between any two states of the system in a reversible cyclic process is independent of the path between the two points. Clausius realized that path-independence of the integral of dQ/T between two states can be used to introduced a new state variable in thermodynamics, which he called entropy, after the Greek phrase, “en trope”, meaning “in transformation”. Here we follow the two arguments of Clausius that led to the discovery of the property called entropy: (1) the path-independence of integral of dQ/T for a reversible process, and (2) the introduction of a property whose value depends on the state of the system.

(1) Path independence of integral over dQ/T

Consider two equilibrium states A and B on an arbitrary reversible cycle shown in Fig. 4.2. The integral of dQ/T for the cycle is equal to the sum of two integrals, one from A to B along path labeled I and another from B to A on path II .

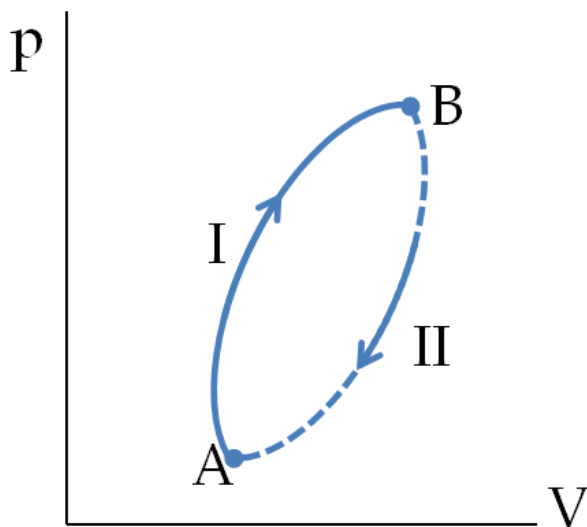


Figure 4.2: Two paths between states A and B on a cyclic process, A - B - A .

$$\oint \frac{dQ}{T} = \left(\int_A^B \frac{dQ}{T} \right)_{\text{path I}} + \left(\int_B^A \frac{dQ}{T} \right)_{\text{path II}} \quad (4.7)$$

The integral on the left side of this equation is equal to zero for a

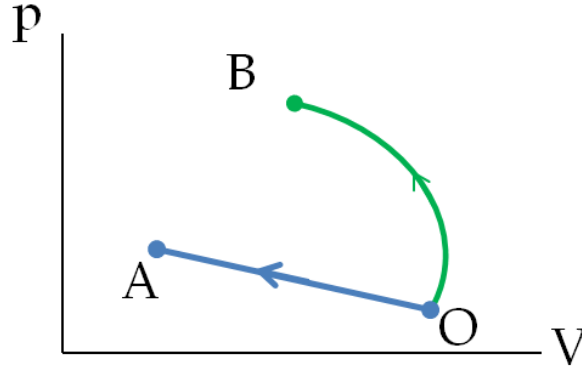


Figure 4.3: Representative paths for finding entropies of states A and B with respect to an arbitrarily chosen standard state O .

reversible cyclic process.

$$\left(\int_A^B \frac{dQ}{T} \right)_{\text{path I}} + \left(\int_B^A \frac{dQ}{T} \right)_{\text{path II}} = 0 \quad (\text{since reversible cycle}) \quad (4.8)$$

Moving the second integral to the other side of the equality, and writing it from A to B on path II rather than from B to A , we find that the integral has the same value for the two paths of reversible cyclic process.

$$\left(\int_A^B \frac{dQ}{T} \right)_{\text{path I}} = \left(\int_A^B \frac{dQ}{T} \right)_{\text{path II}} \quad (\text{reversible process}) \quad (4.9)$$

Since the paths between A and B were arbitrary, we conclude that the integral over dQ/T for any reversible process between two states is independent of the path and depends on the end states A and B only.

Introducing the state property entropy

The derivation given above allows us to define a state variable, whose change between two states does not depend on how the change was made. To accomplish that, we arbitrarily pick an equilibrium state O to serve as a reference, called the **standard state**, and define a new state variable, called **entropy** of an equilibrium state A , by the following integral of dQ/T over any reversible path from O to A as shown in Fig. 4.3.

$$S(A) = \left(\int_O^A \frac{dQ}{T} \right)_{\text{rev}} \quad (4.10)$$

Since the state O is a fixed reference for all states, and the integral depends only on the end states, the integral giving the entropy of

state A is a function of properties of state A only. By evaluating the integral from O to all possible macrostates of the system we determine the entropy function $S(A)$.

You can immediately show that the difference of entropy between two states A and B is equal to the integral of dQ/T between A and B , and is independent of the choice of the reference state O . Let $S(A)$ and $S(B)$ be entropies of states A and B , then their difference is given by the following.

$$\begin{aligned} S(B) - S(A) &= \left(\int_O^B \frac{dQ}{T} \right)_{\text{rev}} - \left(\int_O^A \frac{dQ}{T} \right)_{\text{rev}} \\ &= \left(\int_O^B \frac{dQ}{T} \right)_{\text{rev}} + \left(\int_A^O \frac{dQ}{T} \right)_{\text{rev}} \\ &= \left(\int_A^B \frac{dQ}{T} \right)_{\text{rev}} \end{aligned}$$

The arbitrariness of the reference state O does not matter when we are dealing with only the change of entropy from one state to another. But if we are interested in the entropy of a particular state, then the value will depend on the choice of the reference.

Third Law of Thermodynamics

The Third law of thermodynamics, also called the Nernst's theorem, is used to fix the choice of the reference state. The third law of thermodynamics asserts that,

“The entropy of every system at absolute zero of temperature is zero.”

We will assume that the standard state O corresponds to the state of the system at absolute zero temperature.

Example 4.2.1. Entropy Change in a Reversible Process.

Two kg water is heated reversibly from 20°C to 30°C at constant pressure of 1 atmosphere. What is the change in entropy?

Solution. We can heat the given water infinitesimally slowly so that the process is reversible. Therefore, heat in any infinitesimal step is given by

$$dQ = mc_p dT$$

Here c_p is constant, with a value of 1 calorie per gram. Therefore, the change in entropy is given by

$$\begin{aligned} \Delta S &= \int_{T_1}^{T_2} \frac{mc_p dT}{T} = mc_p \ln \left(\frac{T_2}{T_1} \right) \\ &= 2 \text{ kg} \times \frac{1000 \text{ cal}}{\text{kg} \cdot \text{K}} \times \ln \left(\frac{303 \text{ K}}{293 \text{ K}} \right) = 67 \frac{\text{cal}}{\text{K}}. \end{aligned}$$

Example 4.2.2. Entropy Change in an Isothermal Process of an Ideal Gas.

Five moles of a monatomic ideal gas is expanded isothermally and reversibly at 100°C from a volume of 10 L to three times the volume. What is the change in its entropy?

Solution. We can again use the definition of entropy change we used in example above. But, this time dQ is not give by specific heat definitions because temperature is constant. To find an appropriate formula for dQ we will appeal to first law of thermodynamics.

$$dQ = dU + pdV.$$

Since we have a monatomic ideal gas as the system, the change in internal energy is given by

$$dU = \frac{3}{2}nRdT.$$

Since, we have an isothermal process, $dT = 0$. This means that $dU = 0$. Therefore, we use $dQ = pdV$ in the definition of entropy. This gives

$$\Delta S = \int_{V_1}^{V_2} \frac{pdV}{T} \quad (\text{Note: integration is over volume now.})$$

Using the equation of state for the ideal gas we can replace p/T by nR/V , which can be integrated to give

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

Now, we put the numerical values to obtain the change in entropy.

$$\Delta S = 5 \text{ mol} \times \frac{8.3 \text{ J}}{\text{mol.K}} \times \ln(3) = 46 \text{ J/K}.$$