

From S

①

$$\frac{Q_c}{Q_H} = \frac{T_c}{T_H}$$

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$$(a) Q_c = Q_H \frac{T_c}{T_H}$$

$$= 2000 \times \frac{277+273}{(227+273)}$$

$$= 1400 J$$

(b) For all heat engines and refrigerators

$$W = Q_H - Q_c$$

$$W = 2000 - 1400$$

$$= 600 J$$

$$(c) e = 1 - \frac{T_c}{T_H}$$

$$= 1 - \frac{350}{500} = 0.3 = 30\%$$

For a Carnot refrigerator, the coefficient of performance is given as

$$K_{\text{Carnot}} = \frac{T_c}{T_H - T_c}$$

3.6 The Carnot Cycle and the Second Law.

No engine can be more efficient than a Carnot engine operating between the same two temperatures. In a similar way it can be shown that a refrigerator can have a greater coefficient of performance than a Carnot refrigerator operating between the same two temperatures. Thus, the statement that no engine can be more

$$\left(\frac{\delta M}{\delta y}\right)_x = \frac{\delta^2 z}{\delta x \delta y} \text{ and } \left(\frac{\delta N}{\delta x}\right)_y = \frac{\delta^2 z}{\delta y \delta x}$$

(2)

It can be seen that the two differentials above are identical:

$$\left(\frac{\delta M}{\delta y}\right)_x = \left(\frac{\delta N}{\delta x}\right)_y \quad \text{--- S.2}$$

Equation S.2 is an important relation for partial derivatives, and it is used in calculus to test whether a differential dz is exact or inexact. In thermodynamics, this relation forms the basis for the development of the Maxwell relations.

5.2 Gibbs Relations

To derive the Maxwell relations, we have to first derive the Gibbs relations which are also called the Tds relations.

We know that $\left(\frac{\delta Q}{T}\right)_{\text{int, rev}}$ corresponds to

a differential change in a property called entropy. When the temperature varies during a process, we have to have a relation between δQ and T to perform the integration for finding the entropy change. Finding such relation is what we intend to do in this section.

The differential form of the first law for closed stationary system (fixed mass) is

$$\delta Q - \delta U = dH \quad \text{--- S.3}$$

(3)

thus $Tds = du + Pdv$ — or 5.4

equation 5.4 is known as the first Gibbs or Gibbs equation.

The second Tds equation is obtained by eliminating du from equation 5.4 using the definition of enthalpy ($h = u + Pv$)

If $h = u + Pv$

$dh = du + Pdv + v dp$

from 5.4 $Tds = du + Pdv$ thus

$$Tds = dh - vdp \quad \text{—— S.5}$$

Equations 5.4 and 5.5 are extremely valuable since they relate entropy changes of a system to the changes in other properties.

5.3 The Maxwell Relations

The equations that relate the partial derivatives of properties P, V, T and s of a simple compressible system to each other are called the Maxwell relations. They are obtained from four Gibbs equations by exploiting the exactness of the differentials of thermodynamic properties.

Two of these Gibbs relations have been derived in section 5.2 as

$$du = Tds - Pdv \quad \text{—— S.6}$$

$$dh = Tds + vdp \quad \text{—— S.7}$$

Other two Gibbs relations are based on two

(B)

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The other two Gibbs relations are based on two new combination properties - the Helmholtz function "F" and the Gibbs function "G".

$$dU = Tds \quad (1) \quad S. 8$$

$$dH = Tds - sdt \quad S. 9$$

differentiating, we get

$$da = du - Tds - sdt$$

$$dg = dh - Tds - sdt$$

Simplifying using equations S.6 and S.7 we obtain the other two Gibbs relations for simple compressible systems as follows

$$da = -sdt - pdv \quad S. 10$$

$$dg = -sdt + vdp \quad S. 11$$

A Carefull examination of the four Gibbs relations reveals that they are of the form $dz = Mdx + Ndy$ such that

$$\left(\frac{\delta M}{\delta y}\right)_x = \left(\frac{\delta N}{\delta x}\right)_y \quad S. 2$$

Since U, H, a and g are properties and thus have exact differentials. Applying the above equation S.2 we obtain;

$$\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V \quad S. 12$$

$$\left(\frac{\delta T}{\delta P}\right)_S = \left(\frac{\delta V}{\delta S}\right)_P \quad S. 13$$

$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V \quad S. 14$$

$$\left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P \quad S. 15$$

S

These above equations S.12 → S.15 are called the Maxwell relations. They are extremely valuable in thermodynamics because they provide a means of determining the entropy change, which cannot be measured directly by simply measuring the changes in properties P, V and T.

NOTE: The Maxwell relations given above are limited to simple compressible systems. However other similar relations can be written just as easily for nonsimple systems such as those involving electrical, magnetic and other effects.

Example 5.1

Using the Maxwell relations determine a relation for $(\delta S/\delta P)_T$ for a gas whose equation of state is $P(v-b) = RT$

Solution 5.1

$$P(v-b) = RT \quad \text{--- (1)}$$

from Maxwell relations

$$\left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P$$

from (1)

$$V = \frac{RT}{P} + b$$

$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{R}{P}$$

$$\left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P = -\frac{R}{P}$$

S

equivalent statement of the second law. It also follows that all Carnot engines operating between the same two temperatures have the same efficiency, irrespective of the nature of the working substance.

Equation ⑥ is valid for any Carnot engine no matter what its working substance may be. The equation also sets an upper limit to the efficiency of a real engine such as a steam turbine. To maximise this upper limit and the actual efficiency of the real engine, the designer must make the intake temperature T_H as high as possible & the exhaust temperature T_C as low as possible.

CHAPTER 7

ENTROPY AND FOUR IRREVERSIBILITY

4.0 GENERAL INTRODUCTION

The second law of thermodynamics is not different in form from many familiar physical law but rather a statement of impossibility. However, the second law can be stated as a quantitative relationship with the concept of entropy which is the subject of this chapter.

We have talked about several processes that proceed naturally in the direction of increasing disorder. Irreversible heat flow increases disorder because the molecules are initially sorted in hotter and cooler regions; this sorting is lost when the system comes to thermal equilibrium. Adding heat to a body increases its disorder because it increases average molecular speed and therefore the randomness of molecular motion. Free expansion of a gas increases its disorder because the molecules have greater random of position after the expansion.

4.1 Entropy and Disorder

By definition Entropy is a quantitative measure of disorder in a system. To introd this concept, lets consider an infinitesimal isothermal expansion of an ideal gas. We add heat dQ and let the gas expand just enough to keep the temperature constant. Since the internal energy of an ideal gas depends only on its temperature, the internal energy is also constant for this process, thus, the work done by the gas is equal to the heat dW done

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$$dQ = dW = PdV$$

$$= \frac{nRT}{V} dV \text{ therefore; } \frac{dV}{V} = \frac{dQ}{nRT}$$

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The gas is in a more disordered state after the expansion than before because the molecules are moving in a larger volume and have more randomness of position. Thus the fractional volume change dV/V is a measure of the increase of disorder, and the above equation shows this is proportional to the quantity dQ/dT . We introduce the symbol S for the entropy of the system, and we define the infinitesimal entropy change dS during an infinitesimal reversible process at absolute temperature T .

$$dS = \frac{dQ}{T} \quad (\text{For infinitesimal reversible process})$$

For a reversible isothermal process, the total entropy change $\Delta S = S_2 - S_1 = Q/T$

Entropy is measured in J/K

Note that in entropy calculations we must always use absolute, or Kelvin temperature.

Example 4.1

One kilogram of ice at 0°C is melted and converted to water at 0°C . What is the entropy change if the melting is done reversibly as the heat of fusion of water is $L_f = 3.34 \times 10^5 \text{ J/kg}$

Solution

$$\text{Heat added to melt the ice } Q = mL_f = 1 \times 3.34 \times 10^5 \text{ J/K} \\ = 334,000 \text{ J}$$

$$\Delta S = S_2 - S_1 = \frac{Q}{T} = \frac{334,000}{273} = 1.22 \times 10^3 \text{ J/K}$$

The definition of entropy change can be generalized to include any reversible process leading from one state to another, whether it isothermal or not. We represent the process as a series of infinitesimal reversible steps. During a typical step, an infinitesimal quantity of heat dQ is added to the system at absolute temperature T . Then the sum of dQ/T , which is for the entire process is the integral

$$\Delta S = \int_1^2 dQ/T \quad \text{Entropy change in a reversible process}$$

The limits 1 and 2 refer to the initial and final states respectively. Entropy depends only on the state of the system.

Since entropy is a function of state only we can compute entropy changes in irreversible processes. We do this by simply inventing a path connecting the given initial and final states that does consist entirely of reversible equilibrium processes and compute the total entropy change for that path. As with internal energy, the above discussion does not tell us how to calculate entropy itself, but only the change in entropy in any given process.

Example 4:2

One kilogram of water at 0°C is heated to 100°C . Compute its change in entropy.

Solution

$$dQ = mc dT \quad \text{thus} \\ \Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} mc \frac{dT}{T}$$

$$= mc \ln\left(\frac{T_2}{T_1}\right)$$

$$= 1 \times 4183 \times \ln\left(\frac{100+273}{0+273}\right)$$

$$= 131 \times 10^3 \text{ J/K}$$

4.2 Reversible Adiabatic (Isentropic) process
In an adiabatic process, no heat enters or leaves the system. Hence $dQ = 0$ and there is change in entropy in this process. $\Delta S = 0$

Every reversible adiabatic process is a constant entropy process and is also called Isentropic process. The increase in disorder resulting from the gas occupying a greater volume is exactly balanced by the decrease in disorder associated with lowered temperature and reduced molecular speeds when a gas expands adiabatically and reversibly.

Also, the total entropy change during a reversible cyclic process is zero. A reversible cyclic process on a PV-diagram is a closed path, the total entropy change for the full cycle is the sum of the entropy changes for each small cycle, each of which is zero. Thus

$$\int \frac{dQ}{T} = 0 \quad (\text{reversible cyclic process})$$

It follows that for a reversible process, the entropy change of the system is independent of the path.

4.3 Entropy in Irreversible Processes

In an idealised, reversible process involving only equilibrium states the total entropy change of the system and its surroundings is zero. However, all irreversible processes involve an increase in entropy, thus, unlike energy, entropy is not a conserved quantity. The entropy of an isolated system can change but can never decrease.

Example 4.3

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Suppose 1.50 kg of water at 100°C is placed in thermal contact with 1.00 kg of water at 0°C. What is the total entropy change assuming that the specific heat capacity of water is constant at 4190 J/kg·K over this temperature range?

Solution

Since the both the hot and cold water are of equal mass and specific heat capacity, the final temperature of each will be 50°C

$$= 323 \text{ K}$$

- Entropy change of the hot water is

$$\Delta S_{\text{hot}} = mc \int_{T_1}^{T_2} \frac{dt}{T} \quad [ds = S \frac{dt}{T} = S_m dt]$$

$$= 1 \times 4190 \int_{373}^{323} \frac{dt}{T}$$

$$= 4190 \ln \left(\frac{323}{373} \right) = -603 \text{ J/K}$$

- Entropy change of the cold water is

$$\Delta S_{\text{cold}} = 4190 \int_{273}^{323} \frac{dt}{T} = 4190 \ln \left(\frac{323}{273} \right)$$

$$= 705 \text{ J/K}$$

∴ total entropy change of the system is

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{hot}} + \Delta S_{\text{cold}} \\ &= -603 + 705 \\ &= 102 \text{ J/K}\end{aligned}$$

4.4 Entropy and the Second Law

As demonstrated in Example 4.3, about the flow of heat from a higher to a lower temperature, or the mixing of substances at different temperatures, are characteristics of all natural (real, irreversible) processes.