Chapter 4: Second Law of Thermodynamics

4.1 Heat Engines and Second Law Statements

The First Law provides a constraint on the total energy contained in a system and its surroundings. If it disappears in one form from the system during any thermodynamic process of change, it must reappear in another form either within the system or in the surroundings. However, a pertinent question that one may often need to answer is: Is the process of change aimed at feasible? As may be evident, the first law provides *no constraint* on the possible direction a process may take place. Nevertheless, in the real world such constraints do exist. For example, heat always flows from a high temperature body to one at a lower temperature. Momentum flow is always prompted in the direction of a pressure gradient, and molecules always migrate from a region of higher to lower chemical potential. These observations clearly are indicative of the existence of a constraint on natural processes, which have never been found to be violated.

Further, it is common observation that work is readily transformed into other forms of energy, including heat. But all efforts to develop a device that may work in a continuous manner and convert heat completely into work or any other form of energy have proved impossible. Experimental observations show that typically no more than 40-50% of the total heat available may be converted to work or other energy forms. This finding has led to the conclusion that heat is a lower form of energy in that while it may be feasible to "degrade" work to heat, it is impossible to "upgrade" heat completely into work.

Heat may be seen as a more *primitive* form of energy, as it always has to be made available from matter (say by combustion) and subsequently converted to work for carrying out activities useful to humans. In this sense one never derives work *directly* from the energy locked in matter as enthalpy. This prompts the natural question: what determines the efficiency of such a conversion of heat to work? Evidently one needs a limiting principle that may help answer this question. These considerations provide the basis for formulating the Second Law of Thermodynamics.

2.1 Second Law Statements

It need be mentioned that the second law is a product of experiential observations involving *heat engines* that powered the Industrial Revolution of the 19th century. A heat engine is a machine that produces work from heat through a cyclic process. An example is a steam power plant in which the working fluid (steam) periodically goes through a series of steps in a cyclic manner as follows:

- *Step 1*: Liquid water at ambient temperature is pumped into a boiler operating at high pressure
- *Step 2:* Heat released by burning a fossil fuel is transferred in the boiler to the water, converting it to steam at high-temperature and pressure
- *Step 3:* The energy contained in the steam is then transferred as shaft work to a turbine; during this process steam temperature and pressure are reduced.
- *Step 4:* Steam exiting the turbine is converted to water by cooling it and transferring the heat released to the surroundings. The water is then returned to step 1.

Like the steam power plant all heat engines absorb heat at a higher temperature body (*source*) and release a fraction of it to a low temperature body (sink), the difference between the two quantities constitutes the net work delivered during the cycle. The schematic of a heat engine (for example: steam / gas power plant, automotive engines, etc) is shown in fig. 4.1. As in the case of the steam cycle, a series of heat and work exchanges takes place, in each case a specific hot source and a cold sink are implicated. A schematic of such processes is suggested inside the
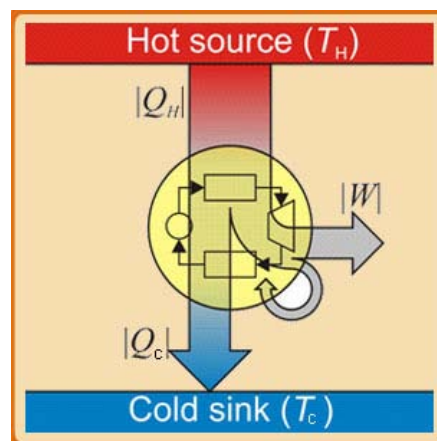

Fig. 4.1 Schematic of Heat Engine

yellow circle between the hot and cold sources. The opposite of a heat engine is called the heat pump (refrigerators being an example of such device) is shown in fig. 4.2. There are indeed a large number other types of practical heat engines and power cycles. Select examples include: Ericsson Cycle, Stirling cycle, Otto cycle (e.g. Gasoline/Petrol engine, high-speed diesel engine), Diesel cycle (e.g. low-speed diesel engine), etc. The Rankine cycle most closely reproduces the functioning of heat engines that use steam as the process fluid function (fig. 4.3); such heat engines are most commonly found in power generation plants. In such plants typically heat is derived from nuclear fission or the combustion of fossil fuels such as coal, natural gas, and oil. Detailed thermodynamic analysis of the various heat engine cycles may be found in a number of textbooks (for example: J.W. Tester and M. Modell, *Thermodynamics and its Applications*, 3rd ed., Prentice Hall, 1999).
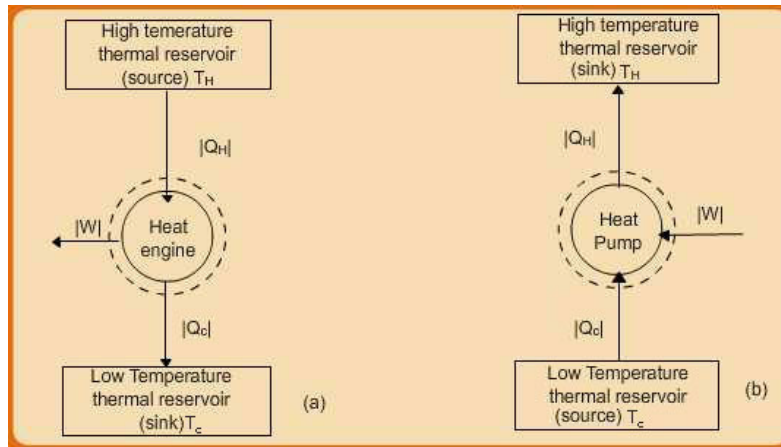

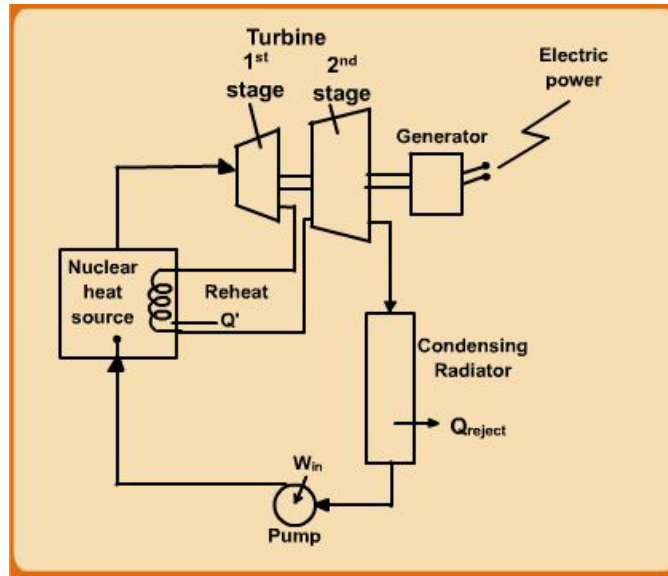Fig. 4.2 Comparison of Heat Engine and Heat Pump

Fig. 4.3 Schematic of a Power Plant (Rankine) Cycle

As evident, the operation of practical heat engines requires two bodies at *constant* differential temperature levels. These bodies are termed *heat reservoirs;* they essentially are bodies with – theoretically speaking – infinite *thermal mass* (i.e., $mC_P \to \infty$) which therefore do not undergo a change of temperature due to either release or absorption of heat. The above considerations may be converted to a set of statements that are *equivalent* descriptors of the second law (R. Balzheiser, M. Samuels, and J. Eliassen, *Chemical Engineering Thermodynamics*, Prentice Hall, 1972):

Kelvin-Planck Statement: It is impossible to devise a cyclically operating device, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work.

Clausius Statement: It is impossible to devise a cyclically operating device, the sole effect of which is to transfer energy in the form of heat from a low temperature body to a high temperature body.

2.2 Carnot Heat Engine Cycle and the 2nd Law

In theory we may say that a heat engine absorbs a quantity of heat $|Q_H|$ from a high temperature reservoir at T_H and rejects $|Q_C|$ amount of heat to a colder reservoir at T_H. It follows that the net work W delivered by the engine is given by:

$$W = |Q_H| - |Q_C| \qquad \qquad ..(4.1)$$

Hence the efficiency of the engine is:

$$\eta = \frac{W}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|} \qquad \qquad ..(4.2)$$

$$\eta = 1 - \frac{|Q_C|}{|Q_H|} \qquad \qquad ..(4.3)$$

Of the various forms of heat engines ideated, the *Carnot engine* proposed in 1824 by the French engineer Nicholas Leonard Sadi Carnot (1796-1832), provides a fundamental reference concept in the development of the second law. The so-called Carnot cycle (depicted in fig. 4.4) is a series of *reversible* steps executed as follows:

- **Step 1: A** system at the temperature of a cold reservoir T_C undergoes a *reversible* adiabatic compression which raises it temperature to that of a hot reservoir at T_H.

- **Step 2:** While in contact with the hot reservoir the system absorbs $|Q_H|$ amount of heat through an isothermal process during which its temperature remains at T_H.

- **Step 3:** The system next undergoes a *reversible* adiabatic process in a direction reverse of step 1 during which its temperature drops back to T_C.

- **Step 4:** A *reversible* isothermal process of expansion at T_C transfers $|Q_C|$ amount of heat to the cold reservoir and the system state returns to that at the commencement of step 1.
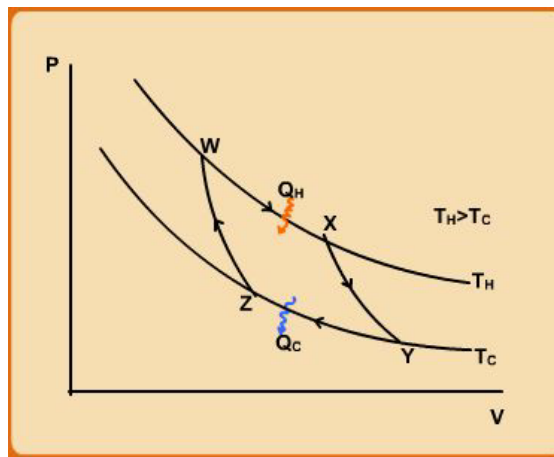

Fig. 4.4 Carnot Cycle Processes

The Carnot engine, therefore, operates between two heat reservoirs in such a way that all heat exchanges with heat reservoirs occur under isothermal conditions for the system and at the temperatures corresponding to those of the reservoirs. This implies that the heat transfer occurs under *infinitesimal* temperature gradients across the system boundary, and hence these processes are reversible (see last paragraph of section 1.9). If in addition the isothermal and adiabatic processes are also carried out under mechanically reversible (quasi-static) conditions the cycle operates in a fully reversible manner. It follows that any other heat engine operating on a different cycle (between two heat reservoirs) must necessarily transfer heat across finite temperature differences and therefore cannot be thermally reversible. As we have argued in section that irreversibility also derives from the existence of dissipative forces in nature, which essentially leads to waste of useful energy in the conversion of work to heat. It follows therefore the Carnot cycle (which also comprises *mechanically reversible* processes) offers the maximum efficiency possible as defined by eqn. 4.3. This conclusion may also be proved more formally (see K. Denbigh, *Principles of Chemical Equilibrium*, 4th ed., Cambridge University Press, 1981).

We next derive an expression of Carnot cycle efficiency in terms of macroscopic state properties. Consider that for the Carnot cycle shown in fig. 4.4 the process fluid in the engine is an ideal gas. Applying the eqn. 3.13 the heat interactions during the isothermal process may be shown to be:

$$\left|Q_H\right| = RT_H \ln\frac{V_x}{V_w} \qquad\qquad ..(4.4)$$

And $\left|Q_C\right| = RT_C \ln\dfrac{V_y}{V_z}$ $\qquad\qquad$ ..(4.5)

Further for the adiabatic paths *xy* and *zw* using eqn. 3.17 one may easily derive the following equality:

$$\ln\frac{V_x}{V_w} = \ln\frac{V_y}{V_z} \qquad\qquad ..(4.6)$$

Using eqns. 4.4 – 4.5 we may write:

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H \ln \frac{V_x}{V_w}}{T_C \ln \frac{V_y}{V_z}} \qquad \text{..(4.7)}$$

Finally applying eqn. (4.6) on obtains:

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C} \qquad \text{..(4.8)}$$

Hence, using eqn. 4.3: $\eta = 1 - \dfrac{T_C}{T_H}$ ..(4.9)

Also, $W = |Q_H| - |Q_C|$ ..(4.10)

Eqn. (4.8) may be recast as:

$$\frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C} \qquad \text{..(4.10)}$$

As heat Q_H enters the system it is *positive,* while Q_C leaves the system, which makes it negative in value. Thus, removing the modulus use, eqn. 4.10 may be written as:

$$\frac{Q_H}{T_H} = -\frac{Q_C}{T_C} \qquad \text{..(4.11)}$$

Or: $\dfrac{Q_H}{T_H} + \dfrac{Q_C}{T_C} = 0$ ..(4.12)

Or: $\displaystyle\sum \frac{Q}{T} = 0$ ..(4.13)

Consider now eqn. 4.9. For the Carnot efficiency to approach unity (i.e., 100%) the following conditions are needed: $T_H \rightarrow \infty$; or $T_C \rightarrow 0$. Obviously neither situation are practicable, which suggests that the efficiency must always be less than unity. In practice, the naturally occurring bodies that approximate a cold reservoir are: atmospheres, rivers, oceans, etc, for which a representative temperature T_C is ~ 300^0K. The hot reservoirs, on the other hand are typically furnaces for which T_H ~ 600^0K. Thus the Carnot efficiency is ~ 0.5. However, in practice, due to mechanical irreversibilities associated with real processes heat engine efficiencies never exceed 40%.

<u>Example 4.1</u>

An inventor claims to have devised a cyclic engine which exchanges heat with reservoirs at 27°C and 327°C, and which produces 0.6 kJ of work for each kJ of heat extracted from the hot reservoir. Is the claim believable? If instead he claimed that the delivered work would be 0.25kJ / kJ of extracted heat, would the engine be feasible?

(Click for solution)

It is interesting to note that the final step of thermodynamic analysis of Carnot cycle (i.e., eqn. 4.13) leads to the conclusion that there exists a quantity $\dfrac{Q}{T}$ which add up to zero for the complete cycle. Let us explore extending the idea to any general *reversible* cycle (as illustrated in fig.4.5) run by any working fluid in the heat engine.
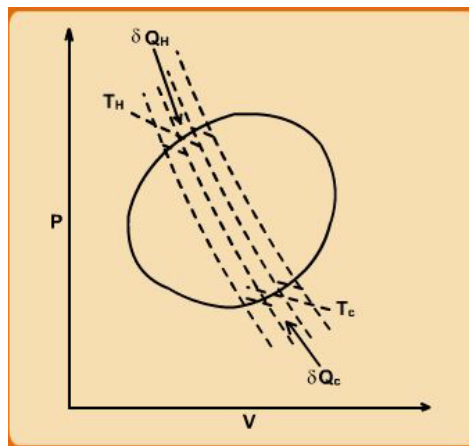

Fig. 4.5 Illustration of an arbitrary cycle decomposed into a series of small Carnot cycles

The complete cycle may, in principle, be divided into a number of Carnot cycles (shown by dotted cycles) in series. Each such Carnot cycle would be situated between two heat reservoirs. In the limit that each cycle becomes infinitesimal in nature and so the number of such cycles infinity, the original, finite cycle is reproduced. Thus for each infinitesimal cycle the heat absorbed and released in a *reversible* manner by the system fluid may be written as $\left|\delta Q_H\right|$ and $\left|\delta Q_C\right|$ respectively. Thus, now invoking eqn. 4.12 for each cycle:

$$\frac{\delta Q_H}{T_H} + \frac{\delta Q_C}{T_C} = 0 \qquad ..(4.14)$$

Hence, applying eqn. 4.13 to sum up the effects of series of all the infinitesimal cycles, we arrive at the following relation for the entire original cycle:

$$\oint \frac{\delta Q_{rev}}{T} = 0 \qquad ..(4.15)$$

Clearly, the relation expressed by eqn. 4.15 suggests the existence of a *state* variable of the form $\frac{\delta Q_{rev}}{T}$ as its sum over a cycle is zero. This state variable is termed as "Entropy" (S) such that:

$$dS = \frac{\delta Q_{rev}}{T} \qquad ..(4.16)$$

Thus: $\oint dS = 0$

Thus, for a *reversible* process: $dQ_{rev} = TdS$ \qquad ..(4.17)

If applied to a perfectly reversible *adiabatic* process eqn. 4.16 leads to the following result: $dS = 0.$ Thus, such a process is alternately termed as *isentropic*.

Since entropy is a state property (just as internal energy or enthalpy), even for irreversible process occurring between two states, the change in entropy would be given by eqn. 4.16. However since entropy is calculable directly by this equation one necessarily needs to construct a reversible process by which the system may transit between the same two states. Finite changes of entropy for irreversible processes *cannot* be calculated by a simple integration of eqn. 4.17. However, this difficulty is circumvented by applying the concept that regardless of the nature of the process, the entropy change is identical if the initial and final states are the same for each type of process. This is equally true for any change of state brought about by irreversible heat transfer due to finite temperature gradients across the system and the surroundings. The same consideration holds even for mechanically irreversibly processes.

With the introduction of the definition of entropy the Carnot engine cycle may be redrawn on a temperature-entropy diagram as shown in fig. 4.6.
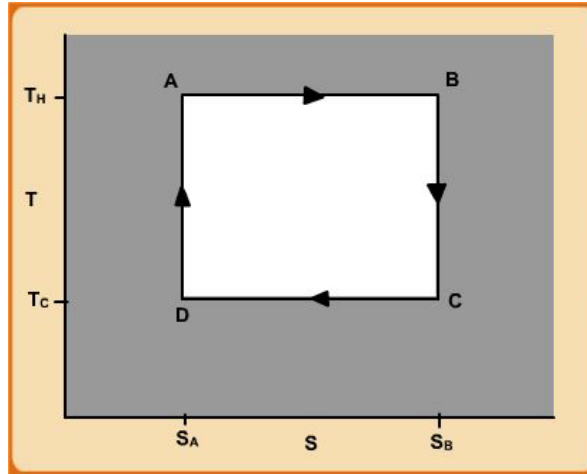
Fig. 4.6 Representation of Carnot cycle on T-S diagram

2.3 Entropy Calculations for Ideal Gases

For a closed system, the first law provides:

$$dU = dQ + dW$$

If the process of change occurs under reversible conditions then the above equation becomes:

$$d(H - PV) = TdS - PdV$$

$$dH - PdV - VdP = TdS - PdV \qquad ..(4.18)$$

However for an ideal gas: $dH = C_P^{ig} dT$ $\qquad ..(4.19)$

Thus combining eqns. 4.18 and 4.19:

$$C_P^{ig} dT = TdS + VdP$$

Or: $\dfrac{dS}{R} = \dfrac{C_P^{ig}}{R} \dfrac{dT}{T} - d\ln P \qquad ..(4.20)$

Integrating between an initial (T_0, P_0) and any final (T, P):

$$\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_P^{ig}}{R} \frac{dT}{T} - \ln \frac{P}{P_0}$$

Or: $\Delta S \big|_{P_0}^{P} = \displaystyle\int_{T_0}^{T} C_P^{ig} \frac{dT}{T} - R\ln \frac{P}{P_0} \qquad ..(4.21)$

The last equation provides a direct expression for computing entropy change between two states for an ideal gas.

For the special case of a reversible adiabatic $dQ = 0$; hence $dS = 0$. Thus:

$$\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_P^{ig}}{R} \frac{dT}{T} - \ln \frac{P}{P_0} = 0$$

For constant C_P^{ig}, it follows that: $T / T_0 = (P / P_0)^{R/C_P^{ig}} = (P / P_0)^{(\gamma-1)/\gamma}$ ..(4.22)

One may note that eqn. 4.22 provides the same relation as obtained by the Fist Law analysis as in eqn. 3.18.

2.4 Mathematical Statement of the 2nd Law:

Consider a mechanically irreversible adiabatic between two equilibrium states X and Y. In fig. 4.7 this path is reproduced as a broken line between points. Next the fluid is returned to the original state by means two sequential processes: (i) a mechanically reversible adiabatic process Y-Z, and then (ii) a reversible isobaric compression Z-X. Assuming that the mechanically irreversible process X-Y leads to an entropy change, heat transfer must occur during process Z-X (since none occurs on Y-Z). This is because for the reversible return path the same entropy change must occur as between X to Y. Since the return path is reversible we must get $dQ_{rev} = TdS$. Thus, integrating this expression for the return path:
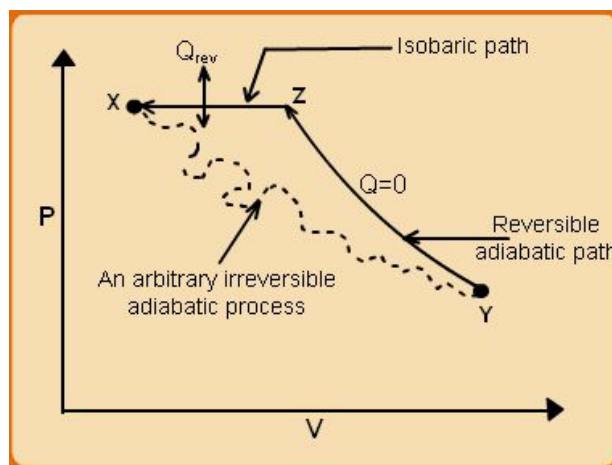
4.7 Cycle containing an irreversible adiabatic process A to B

$$\Delta S^t = \int_Y^X dS^t = S_X^t - S_Y^t = \int_Y^X \frac{dQ_{rev}}{T} \qquad ..(4.23)$$

For the entire cycle we must have $\Delta U^t = 0$. Thus, net total work during the cycle may be written as: $W^t = -Q_{rev}$. However, since (as depicted by the P-V diagram) a net work would need to be done *on* the system over the cycle, it follows that $W^t > 0$; hence $Q_{rev} < 0$. Therefore, using eqn. 4.23, it follows that: $S_X^t - S_Y^t = \int_Y^X \frac{dQ_{rev}}{T} < 0$, that is: $S_X^t < S_Y^t$. This implies that the entropy change for the original irreversible step A to B, we have: $\Delta S^t = S_Y^t - S_X^t > 0$. Therefore, we conclude that the original irreversible step is accompanied by a *positive* change of entropy. It may be additionally shown that if the original process occurred through *irreversible heat transfer* process an increase of entropy would result likewise.

It may be pointed out during the return reversible process, since the heat transfer (during the isobaric path) occurs under reversible conditions it must occur under infinitesimal temperature gradient between the system and surrounding. Thus for the system and the surrounding the net entropy change (gives by: Q_{rev}/T) is equal and opposite. Consequently the total entropy change of the universe (system + surrounding) is zero during this step. During the initial irreversible path X to Y, while entropy increases for the system, for the surrounding there is no change. Nevertheless, for the universe as such there is a positive change in entropy.

Since the above conclusion is not premised on any specific internal nature of the system, the above result may be generalized: all irreversible processes are accompanied by a positive change of entropy of the universe. This leads to a mathematical statement of the second law:

$$\Delta S^t \geq 0. \qquad ..(4.24)$$

At this point we can revert to the question that was stated at the beginning of this chapter: what change in a system is thermodynamically feasible? The second law provides answer to this, i.e., a process can only proceed in a direction that results in a positive change in the *total* entropy of the universe, the limiting value of zero being attained only by a fully reversible process. The corollary to this is: *no process is possible for which the total entropy of the universe decreases*.

Example 4.2

A rigid vessel of 0.06 m^3 volume contains an ideal gas, $C_V = (5/2)R$, at 500 K and 1 bar. (a) If 15 kJ of heat is transferred to the gas, determine its entropy change. (b) If the vessel is fitted with a stirrer that is rotated by a shaft so that work in the amount of 15 kJ is done on the gas, what is the entropy change of the gas if the process is adiabatic? What is ΔS^{total}?

Example 4.3

An ideal gas, $Cp = (7/2)R$, is heated in a steady-flow heat exchanger from 70°C to 190°C by another stream of the same ideal gas which enters at 320°C. The flow rates of the two streams are the same, and heat losses from the exchanger are negligible. Calculate the molar entropy changes of the two gas streams for both parallel and countercurrent flow in the exchanger. What is ΔS^{total} in each case?

2.5 Entropy Balance for Open Systems

As with energy balance for open systems, once can extend the equation 4.24 to a generalized entropy balance equation that may be written for the system shown in fig. 3.6. There is, however, an important point of departure from the first law. Unlike energy, entropy is *not* a conserved quantity for real world processes in which both mechanical and thermal irreversibilities are inevitable. Hence for such processes are attended by a positive entropy *generation rate,* $\dot{S}_G$. This conclusion may be expressed in mathematical terms as follows*:*

$$\begin{Bmatrix} Net \\ rate \\ of \\ entropy \\ change \\ through \\ flow \\ streams \end{Bmatrix} + {}_{-} \begin{Bmatrix} Rate \\ of \\ change \\ of \\ entropy \\ change \\ in \\ control \\ volume \end{Bmatrix} + \begin{Bmatrix} Rate \\ of \\ entropy \\ change \\ of \\ surrounding \end{Bmatrix} = \begin{Bmatrix} Total \\ rate \\ of \\ entropy \\ generation \end{Bmatrix}$$

$$\Delta (S \overset{\bullet}{m})_{fs} + \frac{d(mS)_{CV}}{dt} + \frac{dS^t_{surr}}{dt} = \overset{\bullet}{S}_G \geq 0 \qquad \qquad ..(4.25)$$

As with eqn. 4.24, for eqn. 4.25 too, the left side reduces to zero if the processes occurring in the open system are *totally* reversible; that is, both with respect to the system as well to the surroundings. Or else there is a net entropy generation.

A process is said to be *internally* reversible if all the processes occurring within the system are mechanically reversible, that is they are not subject to dissipative forces. *External* reversibility, on the other hand, signifies that all heat transfer between the system and surrounding occur under infinitesimal gradients and are therefore thermally reversible. In principle reversible heat transfer is possible if the surroundings have heat reservoirs with temperatures equal to those of the control surface or if reversible Carnot engines operate between the control-surface temperatures and the heat-reservoir temperatures.

We next expand eqn. 4.25 to a further level of detail. Let there be heat transfer at the rate $\overset{\bullet}{Q}_j$ at a particular part of the control surface of the open system where the surrounding temperature is given by $T_{\sigma, j}$.

Thus: $\dfrac{dS^t_{surr}}{dt} = -\sum_j \dfrac{\overset{\bullet}{Q}_j}{T_{\sigma, j}}$ \qquad \qquad ..(4.26)

Here, *j* runs over all the heat reservoirs associated with the system. The negative sign is used for the entropy term for the surroundings as heat transfer terms by convention are associated with the system.

Putting eqn. 4.26 in eqn. 4.25 one obtains:

$$\Delta(S\dot{m})_{fs} + \frac{d(mS)_{CV}}{dt} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0 \qquad\qquad ..(4.27)$$

For steady flows through the control volume eqn. 4.27 reduces to:

$$\Delta(S\dot{m})_{fs} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0 \qquad\qquad ..(4.28)$$

Further, for the simplest case of one inlet and exit, and one surrounding temperature:

$$\dot{m}(\Delta S)_{fs} - \frac{\dot{Q}}{T_\sigma} = \dot{S}_G \geq 0 \qquad\qquad ..(4.29)$$

Example 4.4

Ten kmol per hour of air is throttled from upstream conditions of 25°C and 10 bar to a downstream pressure of 1.2 bar. Assume air to be an ideal gas with $C_P = (7/2)R$. (a) What is the downstream temperature? (b) What is the entropy change of the air in J/molK? (c) What is the rate of entropy generation in W/K? (d) If the surroundings are at 20°C, what is the lost work?

Click for solution

2.6 Ideal and Lost Work for Flow Systems

We next derive the expressions for work exchange between system and surroundings for an open system operating under steady state by incorporating the idea of irreversibility. As we have discussed earlier, mechanical irreversibilities lead to *loss of work* due to dissipative conversion to heat. Thus, if work is to be delivered *by* an open system the *maximum* work obtains when the processes are mechanically reversible, we call that *ideal work*. Conversely, when work is done *on* the system the ideal work provides the *minimum* work needed to change the fluid state between the inlet and the exit. This is because an extra work would need to be provided beyond the ideal work against mechanical dissipative forces. From the considerations in the last section it may be

evident that ideal work obtains when the processes associated with the open system are both internally and externally reversible. For such a case one may write eqn. 4.29 as follows:

$$\dot{m}(\Delta S)_{fs} - \frac{\dot{Q}}{T_\sigma} = \dot{S}_G = 0 \qquad \qquad ..(4.30)$$

Thus: $\dot{Q} = T_\sigma \dot{m}(\Delta S)_{fs}$ ..(4.31)

From the 1st Law applied to the ideal case:

$$: \Delta \left[\left(H + \frac{1}{2}(u^2/g_c) + z(g/g_c) \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}_{ideal} \qquad \qquad ..(4.32)$$

Putting eqn. 4.31 into 4.32 and simplifying (assuming negligible kinetic and potential energy changes): $\dot{W}_{ideal} = \Delta \left[H \dot{m} \right]_{fs} - T_\sigma \Delta(S \dot{m})_{fs}$ ..(4.33)

Or: $\dot{W}_{ideal} = \dot{m}[\Delta H - T_\sigma \Delta S_{fs}]$

..(4.34)

In real processes however, actual work involved will depend on the extent of associated irreversibilities; hence we define *lost work* as follows:

$$\dot{W}_{lost} = \dot{W}_{actual} - \dot{W}_{ideal} \qquad \qquad ..(4.35)$$

Now from eqn. 4.32 for the simplest case where kinetic and potential energy changes are negligible:

$$\Delta \left[H \dot{m} \right]_{fs} = \dot{Q}_{actual} + \dot{W}_{actual} \qquad \qquad ..(4.36)$$

Using eqns. 4.34 and 4.35:

$$\dot{W}_{lost} = T_\sigma \Delta(S \dot{m})_{fs} - \dot{Q}_{actual} \qquad \qquad ..(4.37)$$

Applying eqn. 4.30, to a real process: $\dot{m}(\Delta S)_{fs} - \frac{\dot{Q}_{actual}}{T_\sigma} = \dot{S}_G$

..(4.38)

Or: $\dot{Q}_{actual} = T_\sigma \dot{m}(\Delta S)_{fs} - T_\sigma \dot{S}_G$ ..(4.39)

Thus from eqns. 4.37 and 4.39 it follows that:

$$\dot{W}_{lost} = T_\sigma \dot{S}_G \qquad\qquad\qquad ..(4.40)$$

Eqn. 4.40 suggests that greater the entropy generation rate $\dot{S}_G$ due to process irreversibility, greater is the lost work. Since irreversibilities implicit in a process cannot be calculated theoretically, it is indirectly expressed by a process efficiency factor, η. The expression for such efficiency is as follows.

For work done by system, $\eta = \dot{W}_{actual} / \dot{W}_{ideal}$ $\qquad\qquad\qquad$.(4.41)

For work done on a system, $\eta = \dot{W}_{ideal} / \dot{W}_{actual}$ $\qquad\qquad\qquad$ ..(4.42)

Example 4.5

A steady-flow adiabatic turbine (expander) accepts gas at conditions T_1 = 500 K, P_1 = 6 bar, and discharges at conditions T_2 = 371 K, P_2 = 1.2 bar. Assuming ideal gases, determine (per mole of gas) W_{actual}, W_{ideal}, W_{lost}, and entropy generation rate. T_{surr} = 300 K, C_P/R = 7/2.

Click for solution

Example 4.6

A steam turbine operates adiabatically at a power level of 3500 kW. Steam enters the turbine at 2400 kPa and 500°C and exhausts from the turbine at 20 kPa. What is the steam rate through the turbine, and what is the turbine efficiency?

Click for solution

Appendix: 4.1

Entropy: A Statistical Thermodynamic Interpretation

As with internal energy the concept of entropy may be provided a microscopic, molecular interpretation. However, it may be noted that unlike internal energy, molecules *do not* possess entropy. Entropy is purely a measure thermodynamic probability associated with the distribution of various positional and energy states that molecules of a substance may exist under given conditions of temperature and pressure. To understand this, consider a simple system comprised of a rigid, insulated vessel divided into two compartments of equal volume by a partition (of

negligible volume, fig. A.4.1). Initially, the left compartment contains gas at a temperature T_1 and pressure P_1, and the volume of each compartment is V_1^t; the right compartment is fully evacuated. The system is at equilibrium under the above conditions, and is described by the ideal
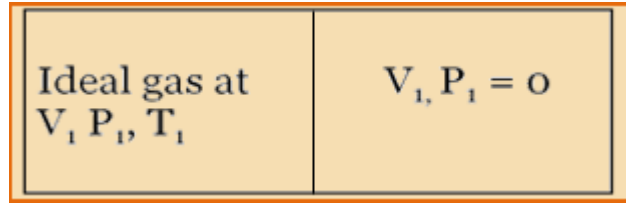

Fig. A.4.1 Ideal Gas Expansion into an evacuated chamber

gas EOS. At a certain point of time the partition is ruptured and the gas contained in the left compartment allowed to fill the entire system volume. Eventually the gas would reach a new equilibrium state (2) that is characterized by a pressure $P_1/2$ throughout. For the above process, applying the first law:

$\Delta U = Q + W$

But : $Q = W = 0$

Hence, $\Delta U = 0$ ..(A.4.1.1)

This implies that for the gas initially on the left side: $\Delta T = 0$; or $T_2 = T_1$

The entropy change per mole of the gas then is given by eqn. 4.21:

Thus, $\Delta S = C_P \dfrac{dT}{T} - R \dfrac{dP}{P} = -R \dfrac{dP}{P}$

$\Delta S = -R \ln \dfrac{P_2}{P_1} = R \ln \dfrac{V_2}{V_1} = R \ln 2$ ..(A.4.1.2)

From a microscopic point of view the molecular state variables are: position and energy. Since there is no change of temperature during the expansion process, the internal energy of each molecule does not change. There, is, however, a possible change in the position occupied a molecule. After the expansion a molecule may be located either on the left half or in the right half of the compartment at any point of time. We may say, in a simplified sense, there are two possible positions that it may have. Considering one mole of gas as basis, if there are, in general, j such states (either of position or energy) that a molecule may exist in, the total number of ways

that an Avogadro number of molecules $(N_A = 6.023 x 10^{23})$ may be distributed over all the available states is given by (with n_j molecules in the jth state):

$$\Omega = \frac{N_A!}{(n_1!)(n_2!)...(n_j!)} \; ; N_A = n_1 + n_2 + ... + n_j \quad ..(A.4.1.3)$$

The notation used for the right side of the above equation, Ω is called the *thermodynamic probability*. Thus for the system in question, in the initial state *all* the molecules are located in the left half of the compartment, so there is only 'one' positional state; thus:

$$\Omega_1 = \frac{N_A!}{(N_A!)(0!)} = 1 \quad ..(A.4.1.4)$$

However, in the final state as there are two possible positional states, the corresponding *maximum* thermodynamic probability is:

$$\Omega_2 = \frac{N_A!}{[(N_A/2)!][(N_A/2)!]} \quad ..(A.4.1.5)$$

The description 'maximum' is important, as the exact number of molecules that may be distributed between the two compartments at any point of time need not be as the same, as assumed in eqn. A.4.1.5. In general there could be many possible bifurcations of the total number molecules into the two compartments, each characterized by a corresponding thermodynamic probability. However, simple calculations suggest that Ω_2 has the *highest* possible value if each compartment contains equal number of molecules, i.e., $N_A/2$. Indeed, intuitively speaking, one would expect that to be the most *likely* distribution in the second equilibrium state. This implies that the system would tend to move to an equilibrium state that has the highest of all the possible values of the thermodynamic probability that one may attribute to the system. It was Ludwig Eduard Boltzmann (1844–1906) the Austrian physicist, who is credited with the development of the statistical concept of nature (now known as *statistical mechanics*), first proposed the relation between entropy and thermodynamic probability:

$$S = k \ln \Omega \quad ..(A.4.1.6)$$

k = *Boltzmann constant* = R / N_A

If one applies the equation to the expansion process, one obtains the following relation:

$$\Delta S = S_2 - S_1 = k \ln \Omega_2 - k \ln \Omega_1 = k \ln \frac{\Omega_2}{\Omega_1} \quad ..(A.4.1.7)$$

Thus: $\Delta S = k \ln\left[\dfrac{N_A!}{[(N_A/2)!][(N_A/2)!]}\right]$

Or: $\Delta S = k\left[\ln N_A! - 2\ln(N_A/2)!\right]$ ..(A.4.1.8)

By the well-known Stirling's formula, or large values of an integer N, one has:

$\ln N! = N \ln N - N$ ..(A.4.1.9)

On applying eqn. A.4.1.9 in A.4.1.8 and simplifying the following result obtains:

$\Delta S = kN_A\left[\ln\dfrac{N_A}{N_A/2}\right] = kN_A \ln 2 = R \ln 2$ ..(A.4.1.10)

Thus we see that the results of both eqns. A.4.1.2 and A.4.1.10 are identical. There is thus a convergence between the macroscopic and microscopic description of the concept of entropy.

It is particularly significant that the above result obtains if one assumes the highest value of Ω_2 as its most likely value. It may be argued that the highest value of Ω_2 corresponds to the most *disordered* state at the molecular level. Indeed extending the argument, since $\Omega_1 = 1$ the initial state is more ordered than state 2, as in the former all molecules are characterized by a single position coordinate, and therefore the probability of finding a molecule in that position is unity; in other words one has complete (or 'certain') information about position of any molecule. In contrast in the second state the probability of finding a molecule at any one position is half. This obtains if each compartment contains exactly half the total number of molecules. Any other distribution would be *less* disordered than this state, and also less probable! This is the reasoning which lies at the root of the popular description of entropy as a *measure* of disorder at the molecular level. It follows that a system at non-equilibrium state (say, at the point of rupture of the partition) always *tends* to the most disordered molecular state when it attains a new equilibrium. Since one has *less* microscopic *information* about a system with a greater degree of disorder, 'information' is also described as *negentropy*.

<mark>Assignment- Chapter 4</mark>