

7. The Second Law and the Concept of Entropy

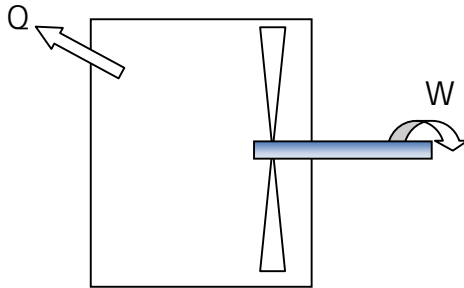
- 7.1. The Direction of Energy Flow
- 7.2. Reversible and Irreversible Processes
- 7.3. Observations
- 7.4. Heat Engines and Refrigerators
- 7.5. Efficiency and Coefficient of Performance
- 7.6. The Carnot Cycle and Carnot Cycle Efficiency
- 7.7. The Thermodynamic Temperature Scale
- 7.8. The Clausius Inequality and Entropy
- 7.9. The Thermodynamic Property Entropy
- 7.10. The T-s Diagram and the Isentropic Process
- 7.11. The Principle of the Increase of Entropy
- 7.12. Two Important Thermodynamic Relations
- 7.13. Entropy Change of a Compressed Liquid or Solid
- 7.14. References

The second law, like the First Law, is characterized by both qualitative concepts and quantitative analysis (mathematics). These two approaches are interwoven in this presentation to present a complete picture of this essential thermodynamic principle. In the quantitative sense, there are many observations of the Second Law which now may appear obvious but were logical steps to the development and understanding of energy in the eighteenth century. Quantitatively the Second Law is presented mathematically through the concept of entropy which now forms the basis of engineering analysis. Interestingly, the Second Law and the concept of entropy have far ranging philosophical implications that extend beyond engineering applications into fundamental physics and beyond, into the creation and existence of the universe.

7.1. The Direction of Energy Flow. Energy is a quantity measured in the dimensions of $[F][L]$ and, in the SI system, in units of Joule or, because the joule is a relatively small quantity in engineering applications, the kilojoule. Thus, the flow of energy is characterized by direction. Intuitively we know that heat flows naturally from a warm body to a cooler body; it does not flow naturally from a cooler body to a warmer body. Unlike the First Law, a direction is established.

Consider a container, a closed system, with a paddle wheel rotating at high velocity as shown below.

As the paddle wheel is rotated energy is added to the system and the internal energy of the substance contained within the system increases in temperature. If the surroundings are at a lower temperature, then energy moves through the containment in the form of heat. This is an intuitively correct phenomenon observed in a variety of typical applications. On the other hand however, if we add energy in the form of heat to the containment we do not expect the paddle wheel to turn. Thus energy has a functional direction.



substance contained within the system increases in temperature. If the surroundings are at a lower temperature, then energy moves through the containment in the form of heat. This is an intuitively correct phenomenon observed in a variety of typical applications. On the other hand however, if we add energy in the form of heat to the containment we do not expect the paddle wheel to turn. Thus energy has a functional direction.

Another example, typical in everyday life, is a brake for a bicycle or automobile. When a brake caliper contacts a rotating disk as the brake is applied the result is a slowing of the disk and the creation of heat energy in the contact surfaces of the caliper. Kinetic energy of the rotating disk is converted to heat energy. However, if we add energy in the form of heat to the caliper (heat the caliper) then we intuitively know that the disk will not rotate.

While both of these examples obey the First Law regardless of the direction of energy flow, the second law provides explanation as to what can and what cannot occur in the physical world.

7.2 Reversible and Irreversible Processes. Energy accountability in the science of thermodynamics is described through the logical concepts of state and process. A process occurs when the thermodynamic system undergoes a change in state or an energy transfer at steady state. A process can be perfect or reversible or imperfect and irreversible.

A reversible process occurs when the process can be completely reversed and leave no change on the surroundings.

Reversible processes occur in an ideal world and help define how close real world applications approach the ideal. Consider a steel ball (a ball bearing) dropped from a height of 2 meters onto a very hard steel plate. The ball bearing bounces off the plate and almost returns to its original drop point of 2 meters. It does not return exactly to its drop point because of aerodynamic losses from the air and hysteresis losses (internal frictional losses due to molecular interaction within the bearing) from the almost elastic collision with the plate. If it did return then this simple process would be reversible. Consider this same scenario with a soft rubber ball. The rubber ball would not come close to its original drop point because of greater aerodynamic losses and hysteresis losses. Thus the rubber ball has greater irreversibility than the steel ball. The steel ball approaches the ideal.

There are several physical factors that render a process irreversible or less than perfect. Some of these factors most often encountered in engineering applications are:

- Friction – No surface, no matter how finely polished, is void of irregularities at the molecular level. As two surfaces come together and moved with a velocity difference

relative to each other these irregularities and surface protrusions are displaced from the parent material and give rise to discernable wear over time. Too, molecular and atomic attractions between surfaces act in similar fashion. Wear over time without lubricant the effect can be pronounced. Of course, this phenomenon occurs even with the finest lubricant and most finely machined bearing. As the molecules collide and tear from the parent material the kinetic energy due to relative velocity between surfaces is transferred to vibrational, rotational, and electronic energy on the molecular level. This increase in molecular energy is thus transferred to the surroundings in the form of heat.

- Unrestrained expansion – When a gas, liquid, or solid is held in place and suddenly released unrestrained expansion occurs which cannot be easily reversed. Consider a gas held under high pressure within a vessel and then allowed to expand by opening a throttling valve. No matter how long we wait it is impossible for this gas to return to the vessel and regain its original pressure.
- Heat transfer through a finite temperature difference – This is one factor of irreversibility which causes the most confusion amongst student scholars of thermodynamics because heat is one of only two ways of energy transfer. The heat transfer process due to a temperature difference is highly irreversible. Recall heat transfer from a warm body to a cooler body was used as a basic premise or observation of the second law. The process is clearly directional and cannot be reversed without change to the surroundings. The greater the temperature difference, the greater the irreversibility which will be illustrated with the mathematics of entropy. In the real world we are surrounded by the heat transfer process, hence we are surrounded by irreversibility which in the philosophical sense can be construed as synonymous with the passage of time, from the birth of the universe to its ultimate end.
- Mixing of two or more different substances – When two substances are completely separated and are allowed to mix due to molecular motion (e.g. Brownian motion) then the expectation that they will eventually separate is unrealistic and outside of the realm of statistical behavior. Consider two gasses separated by a diaphragm and then the diaphragm suddenly removed. The two gases will eventually mix even if the pressure of both gases is identical. These two gases will never separate again under ordinary means.

There are, of course, other irreversible factors too numerous to mention here. Chemical reactions such as combustion, oxidation, reduction, etc. are irreversible. Once having taken place, they cannot be reversed and leave no change the surroundings. Electrical resistance as current flows through a wire due to a potential voltage difference is yet another example. Irreversibility is quantified through the use of the thermodynamic property entropy which is introduced later in this discussion.

7.3. Observations. There are several fundamental observations of the second law. Historically in thermoscience literature, two observations have been noted as of significance. One of these observations has already been stated and is obvious to anyone in today's world. This observation is often referred to as the Clausius statement named after German scientist Rudolf

Clausius (1822-1888) in honor of his achievements in the understanding of heat , work, and the Second Law.

No process is possible whose sole result is the transfer of heat from a body of lower temperature to a body of higher temperature.

Spontaneously, heat cannot flow from cold regions to hot regions without external work being performed on the system, which is evident from ordinary experience of refrigeration, for example. In a refrigerator, heat flows from cold to hot, but only when forced by an external agent, a compressor, which requires work.

The second observation may not be as obvious and was more difficult to accept. Even today the second observation often will require some thought before acceptance. This observation is referred to the Kelvin Planck statement named after two scientists William Thomson, 1st Baron Kelvin, Lord Kelvin (1824 –1907) and Max Karl Ernst Ludwig Planck (1858 –1947) for their contributions to the science of thermodynamics.

No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

Thus it is impossible to extract energy by heat from a high-temperature energy source and then convert all of the energy into work. At least some of the energy must be passed on to heat a low-temperature energy sink. Thus, a heat engine with 100% efficiency is thermodynamically impossible. From an engineering applications view:

Work is much more valuable than heat since work can be completely and continuously turned into heat (through friction, electrical resistance heating, etc) but not the other way around.

The concept of energy quality, called availability by some or exergy by others is the subject of further reading. Work like heat is energy transferred but has much greater usefulness because it can be turned into heat with relative ease. Heat on the other hand requires a thermodynamic cycle to produce work and since the efficiency of a thermodynamic cycle cannot achieve 100% thus more heat is required to produce work and some sort of mechanical device (a heat engine) is required.

7.4. Heat Engines and Refrigerators. It cannot be stressed enough that heat engines are essential to modern civilization. Gasoline and diesel engines for transportation and utility use, jet engines for air transport, stationary gas and steam turbines for electrical power generation are all examples of heat engines. In a thermodynamic sense, work is more valuable than heat because heat can be obtained from a variety of sources including solar, petroleum, coal, natural gas and uranium (through radioactive decay). Work, on the other hand, requires a thermodynamic cycle (heat to work). Work cannot easily be obtained from natural energy

sources in the quantities needed to sustain production and transportation (although wind and hydroelectric generation are good examples of work to work conversion).

Of historical interest . . .

The first practical heat engine appeared in the coal regions of Dudley north and slightly east of Cornwall, the southwestern tip of England about 1710 invented and constructed by Thomas Newcomen (1664 –1729) who was an ironmonger (iron and metal merchant) by trade and a Baptist lay preacher by calling. The depth of coal and mineral mining in England, essential to the onset and success of the industrial revolution, was limited because of flooding. Newcomen created the first practical steam engine for pumping water combining the ideas of Thomas Savery and Denis Papin. Savery had devised a relatively crude (ineffective beyond a depth of about 30 feet) 'fire engine' in which steam was admitted to an empty container and then condensed with cold water allowing the vacuum created by the condensation process to suck water from a sump at the bottom of a mine.

Newcomen replaced the receiving vessel (where the steam was condensed) with a cylinder containing a piston. Instead of the vacuum drawing in water, it drew down the piston. This was used to work a beam engine, which was attached by chain to a pump at the base of the mine. The Newcomen engine held its place without material change for about three-quarters of a century, spreading gradually to more and more areas of the UK and to mainland Europe. At first brass cylinders had been used but these were expensive and limited in size. New iron casting techniques allowed larger cylinders to be used, up to about 6 feet (1.8 m) in diameter by the 1760s, and experience gradually led to better construction and minor refinements in layout. By 1775 about 600 Newcomen engines had been built, although many of these had worn out before then, and been abandoned or replaced.

The Newcomen Engine was by no means an efficient machine. Significant heat was lost when condensing the steam in the power cylinder. Therefore, Newcomen's engine was gradually replaced after 1775 by an improved design, invented by James Watt, in which the steam was condensed in a separate condenser outside of the power cylinder. The Watt steam engine aided by better engineering techniques was much more fuel efficient. Despite Watt's improvements, Common Engines (as they were then known) remained in use for a considerable time, and many more Newcomen engines than Watt ones were built even during the period of Watt's patent (up to 1800), as they were cheaper and less complicated: of over 2,200 engines built in the eighteenth century, only about 450 were Watt engines.

A simple thermodynamic cycle that produces useful work then must incorporate a heat addition process and a heat rejection process as shown in Figure XX. The heat rejection process cannot be eliminated as it is a consequence of the Second Law. The cycle shown in Figure XX involves a piston-cylinder mechanism commonly used in internal combustion engines although the cycle processes are different and with an internal combustion engine flow into and out of the cylinder is open by nature of the combustion process. Common cycles are discussed later.

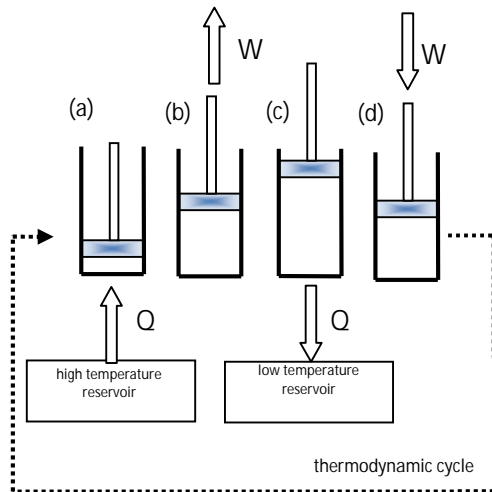


Figure XX. A simple thermodynamic cycle incorporating closed system.

All thermodynamic cycles must incorporate a heat rejection process to a lower temperature reservoir. The heat rejection process is necessary to complete the cycle. Without a heat rejection process the cycle is not complete.

Heat engines can, of course, incorporate steady state steady flow processes as illustrated in Figure XX below. Note that the cycle in its entirety is closed. Only heat and work cross the system boundary.

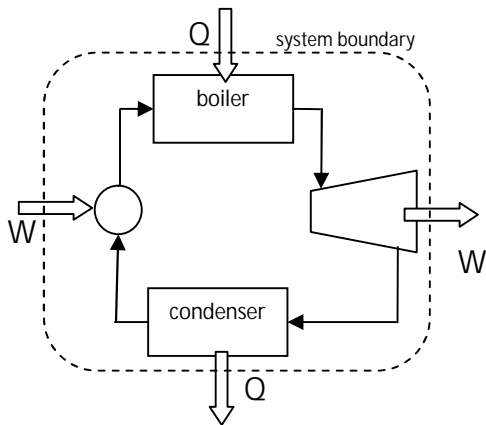


Figure XX. A heat engine involving steady state steady flow processes.

Figure XX is illustrative of a Rankine cycle commonly used for electrical power generation.

7.5. Efficiency and Coefficient of Performance. Efficiency is an important goal of engineering applications. Efficiency is defined as the desired output divided by the required input. For a thermodynamic cycle the thermal efficiency is:

$$\eta_t = \frac{\text{Work Output}}{\text{Heat Input}} = \frac{W_{net}}{Q_{added}}$$

Drawing the hypothetical boundary around the cycle, and by definition of the cycle $\Delta U=0$:

$$Q_{net} - W_{net} = \Delta U = 0$$

$$Q_H - Q_L = Q_{net} = W_{net}$$

Then:

$$\eta_t = \frac{Q_H - Q_L}{Q_H}$$

Where Q_H is the heat added from the higher temperature reservoir and Q_L is the heat rejected from the lower temperature reservoir.

Coefficient of performance, COP) is used for refrigeration systems. Unlike efficiency which can never be greater than one (or 100%), larger COP is desirable:

$$\begin{aligned} COP &= \frac{\text{desired output}}{\text{required input}} \\ &= \frac{\text{heat absorbed by the evaporator}}{\text{work of the compressor}} \\ &= \frac{Q_L}{W_{pump}} \end{aligned}$$

W_{net} is the work of the pump (work input) since expansion work (accomplished through a throttling valve) is by definition zero.

7.6. The Carnot Cycle and Carnot Cycle Efficiency. (incomplete - see text)

7.7. The Thermodynamic Temperature Scale. (incomplete - see text)

7.8. The Clausius Inequality and Entropy. The concept of entropy is an essential component to the Second Law. Entropy is a property and hence a function of other thermostatic properties. Entropy is a quantitative feature, a mathematical and physical entity, of the Second Law. While familiar devices such as thermometers and pressure gauges measure temperature and pressure, there is no 'entropy meter'. Instead, differences or changes in the property entropy

are calculated through mathematical relationships¹ and the absolute value of entropy is described by the Third Law left for another discussion:

The entropy of a substance is zero at absolute zero.

Rudolf Clausius, a German born nineteenth century mathematician and physicist, in his work to further quantify the concept of heat mathematically derived entropy by dividing a quantity of heat by temperature T:

$$\Delta S = \int \frac{\partial Q}{T}$$

or in the special case where T = constant:

$$= \frac{\Delta Q}{T}$$

T is an integrating factor. In mathematics, an integrating factor is a function that is used in multivariable calculus that allows an inexact differential to be made into an exact differential which can then be integrated to give a scalar result.

In his mathematical analysis of a cycle, Clausius revealed that the summation of entropy change for all processes in the thermodynamic cycle yielded the inequality

$$\int \frac{\partial Q}{T} \Big|_{cycle} \leq 0$$

where the summation of entropy change is equal to zero for the ideal cycle involving ideal processes and less than zero for a real cycle involving less than ideal processes. The above statement is referred to as the Clausius inequality.

Consider the following example, a simple Rankine cycle:

¹ Maxwell's relations after James Clerk Maxwell (1831 –1879), a Scottish physicist and mathematician, who some say his outstanding work paralleled that of Sir Isaac Newton and Albert Einstein.

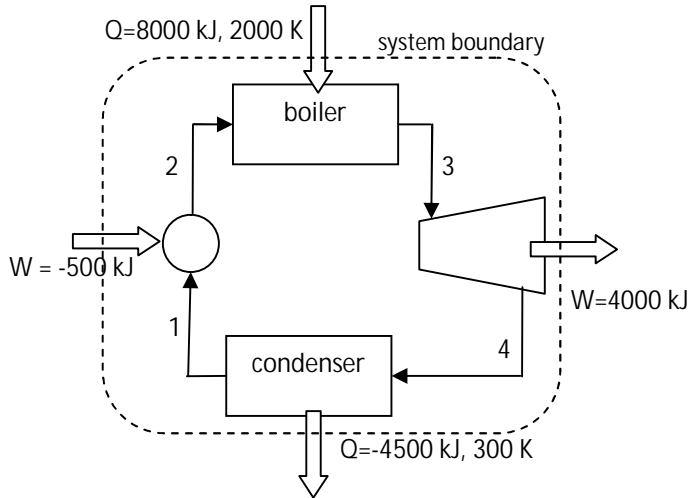


Figure X. A heat engine involving steady state steady flow processes.

In the cycle above, process 1-2 occurs adiabatically. Since q is zero, the change in entropy is zero:

$$\Delta s|_1^2 = \int_1^2 \frac{\partial Q}{T} = 0$$

In process 2-3, 12000 kJ of heat is transferred from an infinite reservoir (the boiler) to the working fluid at the boiler temperature of 2000 K. The entropy change is:

$$\Delta s|_2^3 = \int_2^3 \frac{\partial Q}{T} = \frac{\Delta Q}{T} = \frac{8000 \text{ kJ}}{2000 \text{ K}} = 4 \frac{\text{kJ}}{\text{K}}$$

Similar to process 1-2, process 3-4 occurs adiabatically. Since q is zero, the change in entropy is zero:

$$\Delta s|_3^4 = \int_3^4 \frac{\partial Q}{T} = 0$$

Finally, in process 4-1, 3000 kJ of heat is transferred from the working fluid to an infinite reservoir (the surroundings) at a temperature of 300 K. The entropy change is:

$$\Delta s|_4^1 = \int_4^1 \frac{\partial Q}{T} = \frac{\Delta Q}{T} = \frac{-4500 \text{ kJ}}{300 \text{ K}} = -15 \frac{\text{kJ}}{\text{K}}$$

Summing the entropy change throughout the cycle yields:

$$\Delta s = \Delta s|_1^2 + \Delta s|_2^3 + \Delta s|_3^4 + \Delta s|_4^1$$

$$\Delta s = 0 + 4 + 0 - 15 = -11 \frac{\text{kJ}}{\text{K}}$$

The cycle obeys the Clausius inequality of:

$$\int \frac{\partial Q}{T} \Big|_{\text{cycle}} \leq 0$$

The efficiency of the cycle is:

$$\eta_t = \frac{Q_H - Q_L}{Q_H} = \frac{W_{net}}{Q_H} = \frac{3500 \text{ kJ}}{8000 \text{ kJ}} = 0.438 = 43.8\%$$

In the cycle above work into the fluid by the pump and work out from the fluid are considered reversible and adiabatic or isentropic. An isentropic process is an ideal process.

7.9. The Thermodynamic Property Entropy. A property is a characteristic of the matter within the system. Entropy is a property. The use of tables, graphs, and equations can be used to determine entropy for a given substance like pressure, temperature, internal energy, and enthalpy. Entropy (in kJ/kg K) is tabulated in tables for pure substances (e.g., steam tables for water, etc) and is particularly useful for the two phase region. Entropy is tabulated in for many other substances. Since the change of entropy is important in engineering applications rather than the absolute value, the datum point of zero entropy is not essential. Entropy change can be calculated for ideal gases (re: Two Important Thermodynamic Relations below).

7.10. The T-s Diagram and the Isentropic Process. Like the pV diagram introduced earlier, a plot of temperature verses entropy reveals how various processes occur when there is a change of state. Also of importance is the area under the T-s process which mathematically represents the heat transferred since:

$$\Delta S = \int \frac{\partial Q}{T}$$

Then,

$$Q = \int T dS$$

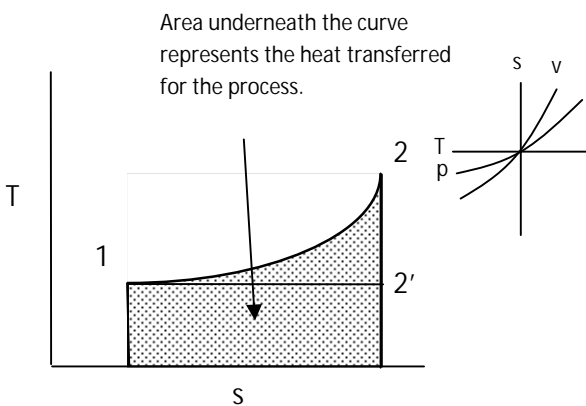


Figure XX. The T-s diagram and symbolic representation of various key processes on right. Note: Isentropic ($s=\text{const.}$) is a vertical line on the T-s diagram.

Comparing the area under the T-s curve for two or more processes between two given end-states illustrates the comparative heat transfer either to or from the system for the various processes considered. Note that the process 1-2 incorporates greater heat transfer than the process 1-2' although the entropy change is the same.

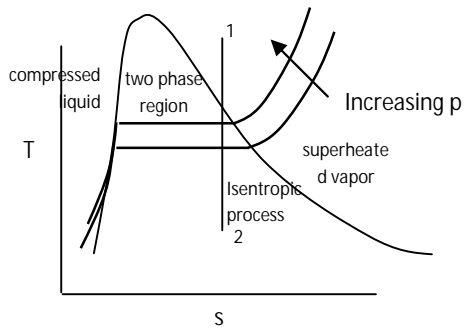


Figure XX. The T-s diagram for the two phase region (e.g. water).

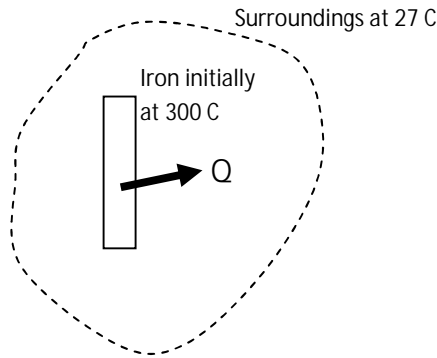
Figure XX above is a T-s diagram for a two phase substance such as water. The lines of constant pressure incline upward but remain horizontal in the two phase region because T and p are dependent in the mixture region, i.e., once the temperature is fixed the pressure is fixed as well like that in the pV diagram introduced earlier. The isentropic process (reversible adiabatic) is vertical (process 1-2 in the figure).

7.11. The Principle of the Increase of Entropy. One of the most significant features of the property entropy is that the change in entropy for both system and surroundings is a measure of the irreversibility of a process. That is, the total change of entropy is equal to zero in a reversible process and greater than zero in an irreversible process:

$$\Delta s|_{net} = \Delta s|_{system} + \Delta s|_{surroundings} \geq 0$$

A degree of irreversibility can be assigned as the greater the total (or net) entropy change then the greater the irreversibility for a given process.

Consider of heat energy transferred from a 100 kg mass of iron ($c_v=0.45$ kJ/kg K) as the iron cools from 300 C to the surrounding temperature of 27 C:



For the system (the iron):

$$Q_{1-2} - W_{1-2} = \Delta U = mc_v(T_2 - T_1) = (100 \text{ kg}) \left(\frac{0.45 \text{ kJ}}{\text{kgK}} \right) (300 - 573 \text{ K}) = -12285 \text{ kJ}$$

Since the work is zero: $Q_{1-2} = -12285 \text{ kJ}$

$$\Delta s|_{\text{iron}} = \int \frac{\partial Q}{T} = mc \ln \frac{T_2}{T_1} = (100 \text{ kg}) \left(0.45 \frac{\text{kJ}}{\text{kgK}} \right) \ln \frac{(27+273 \text{ K})}{(300+273 \text{ K})} = -29.12 \frac{\text{kJ}}{\text{kgK}}$$

For the surroundings which occurs at constant temperature as it is an infinite sink:

$$\Delta s|_{\text{surroundings}} = \int \frac{\partial Q}{T} = \frac{+12285 \text{ kJ}}{(27+273 \text{ K})} = +40.95 \frac{\text{kJ}}{\text{kgK}}$$

$$\Delta s|_{\text{net}} = \Delta s|_{\text{system}} + \Delta s|_{\text{surroundings}} = -29.12 \frac{\text{kJ}}{\text{kgK}} + 40.95 \frac{\text{kJ}}{\text{kgK}} = 11.83 \frac{\text{kJ}}{\text{kgK}} > 0$$

Heat from the iron is negative (loss) and heat to the surroundings is positive (gain). Note that as the temperature difference between system and surrounds approaches zero the entropy change approaches zero (ideal). Note also that entropy change can most certainly be negative for a process but when the surroundings are accounted the entropy change is always positive in a real world.

This has philosophical considerations in that the total entropy for the isolated system (the universe) increases with energy transfers that occur within the universe if it is assumed the universe is indeed isolated. Entropy is always increasing.

7.12. Two Important Thermodynamic Relations. Like physics, mathematical relationships are embedded throughout the science of thermodynamics. Applying these relationships allows the derivation of useful formulae that assist with calculations. In elementary entropy relationships, two important mathematical relationships are presented which will allow the calculation of entropy change of an ideal gas. The differential form of the first law:

$$\partial Q - \partial W = dU$$

Incorporating the definition of entropy and closed system work leads to:

$$TdS - pdV = dU$$

Dividing by T, substituting the ideal gas relationships $dU = c_v dT$ and $p = RT/V$, and integrating over a process from state 1 to state 2 yields:

$$\int dS = \int c_v \frac{dT}{T} + \int R \frac{dV}{V}$$

$$\Delta S = S_2 - S_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

The above relationship can be used to calculate the entropy change of an ideal gas. Similarly, by differentiating the definition of enthalpy $H = U + pV$:

$$dH = dU + dpV = pdV + Vdp$$

$$dU = dH - pdV - Vdp$$

Substituting the above for dU into the First Law, and incorporating the definition of entropy and work yields:

$$TdS - pdV = dH - pdV - Vdp$$

$$TdS = dH - Vdp$$

Similarly as above, dividing by T, substituting the ideal gas relationships $dU = c_v dT$ and $V = RT/p$, and integrating over a process from state 1 to state 2 yields:

$$\int dS = \int c_p \frac{dT}{T} - \int R \frac{dp}{p}$$

$$\Delta S = S_2 - S_1 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1}$$

As earlier, the above relationship can be used to calculate the entropy change of an ideal gas in slightly different format than that derived earlier. The only restriction is that both relationships are valid for ideal gas.

7.13. Entropy Change of a Compressed Liquid or Solid. The above relationships can be simplified in the case of compressed liquids that are nearly incompressible or solids that are essentially not compressible by dropping the work term since $dV = 0$ for incompressible substances. Then:

$$\partial Q - \partial W = dU$$

$$TdS - pdV = dU$$

$$\Delta S = S_2 - S_1 = c \ln \frac{T_2}{T_1}$$

Where c is the heat capacity, in dimensions of $[F][L]/[M][T]$ or in SI units of kJ/kgK . Here c_p and c_v have no meaning since the contribution of v (or p) to an incompressible substance is negligible, and the ideal gas relationships are not employed in this derivation.

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