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THE SECOND LAW OF THERMODYNAMICS

Thermodynamics is concerned with transformations of energy, and the laws of thermodynamics describe the bounds within which these transformations are observed to occur. The first law, stating that energy is conserved in any ordinary process, imposes no restriction on the process direction. Yet all experience indicates the existence of such a restriction, the concise statement of which constitutes the second law.

The differences between the two forms of energy, heat and work, provide some insight into the second law. In an energy balance, both work and heat are included as simple additive terms, implying that one unit of heat, a joule, is equivalent to the same unit of work. Although this is true with respect to an energy balance, experience teaches that there is a difference in quality between heat and work. This experience is summarized by the following facts.

Work is readily transformed into other forms of energy: for example, into potential energy by elevation of a weight, into kinetic energy by acceleration of a mass, into electrical energy by operation of a generator. These processes can be made to approach a conversion efficiency of 100 percent by elimination of friction, a dissipative process that transforms work into heat. Indeed, work is readily transformed completely into heat, as demonstrated by Joule's experiments.

On the other hand, all efforts to devise a process for the continuous conversion of heat completely into work or into mechanical or electrical energy have failed. Regardless of improvements to the devices employed, conversion efficiencies do not exceed about 40 percent. Evidently, heat is a form of energy intrinsically less useful and hence less valuable than an equal quantity of work or mechanical or electrical energy.

Drawing further on our experience, we know that the flow of heat, between two bodies always takes place from the hotter to the cooler body, and never in the reverse direction. This fact is of such significance that its restatement serves as an acceptable expression of the second law.

STATEMENTS OF THE SECOND LAW

The observations just described are results of the restriction imposed by the second law on the directions of actual processes. Many general statements may be made which describe this restriction and, hence, serve as statements of the second law.

Two of the most common are:

- No apparatus can operate in such a way that its only effect (in system and surroundings) is to convert heat absorbed by a system completely into work done by the system.
- No process is possible which consists solely in the transfer of heat from one temperature level to a higher one.

Statement 1 does not say that heat cannot be converted into work; only that the process cannot leave both the system and its surroundings unchanged. Consider a system consisting of an ideal gas in a piston/cylinder assembly expanding reversibly at constant temperature. The work produced can be evaluated from $\int P dV$, and for an ideal gas $\Delta U = 0$. Thus, according to the first law, the heat absorbed by the gas from the surroundings is equal to the work produced by the reversible expansion of the gas. At first this might seem a contradiction of statement 1, since in the surroundings the only result is the complete conversion of heat into work. However, the second-law statement requires in addition that there be no change in the system, a requirement which is not met.

This process is limited in another way, because the pressure of the gas soon reaches that of the surroundings, and expansion ceases.- Therefore, the continuous production of work from heat by this method is impossible. If the original state of the system is restored in

order to comply with the requirements of statement 1, energy from the surroundings in the form of work is needed to compress the gas back to its original pressure. At the same time energy as heat is transferred to the surroundings to maintain constant temperature. This reverse process requires at least the amount of work gained from the expansion; hence no net work is produced. Evidently, statement 1 may be expressed in an alternative way, viz.:

1a. It is impossible by a cyclic process to convert the heat absorbed by a system completely into work done by the system.

The word cyclic requires that the system be restored periodically to its original state. In the case of a gas in a piston/cylinder assembly the expansion and compression back to the original state constitute a complete cycle. If the process is repeated, it becomes a cyclic process. The restriction to a cyclic process in statement 1a amounts to the same limitation as that introduced by the words only effect in statement 1.

The second law does not prohibit the production of work from heat, but it does place a limit on the fraction of the heat that may be converted to work in any cyclic process. The partial compression of heat into work is the basis for nearly all commercial production of power. The development of a quantitative expression for the efficiency of this conversion is the next step in the treatment of the second law.

HEAT ENGINES

The classical approach to the second law is based on a macroscopic viewpoint of properties independent of any knowledge of the structure of matter or behavior of molecules. It arose from -study of the heat engine, a device or machine that produces work from heat in a cyclic process. An example is a steam power plant in which the working fluid (steam) periodically returns to its original state. In such a power plant the cycle (in simple form) consists of the following steps:

- Liquid water at approximately ambient temperature is pumped into a boiler at a high pressure.
- Heat from a fuel (heat of combustion of a fossil fuel or heat from a nuclear reaction) is transferred in the boiler to the water, converting it to high- temperature steam at the boiler pressure.
- Energy is transferred as shaft work from the steam to the surroundings by a device such as a turbine, in which the steam expands to reduced pressure and temperature.
- Exhaust steam from the turbine is condensed at low temperature and pressure by the transfer of heat to cooling water, thus completing the cycle.

Essential to all heat-engine cycles are the absorption of heat at a high temperature, the rejection of heat at a lower temperature, and the production of work. In the theoretical treatment of heat engines, the two temperature levels which characterize their operation are maintained by heat reservoirs, bodies imagined capable of absorbing or rejecting an infinite quantity of heat without temperature change. In operation, the working fluid of a heat engine absorbs heat $|Q_H|$ from a hot reservoir produces a net amount of work $|W|$ discards heat to $|Q_C|$ cold reservoir, and returns to its initial state. The first law therefore reduces to

$$|W| = |Q_H| - |Q_C| \dots\dots\dots 1$$

Defining the thermal efficiency of the engine as

$$\eta = \frac{\text{net work out put}}{\text{heat input}}$$

Water and wind power arc of course not included.

We get,

$$\eta = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|}$$

or

$$\eta = 1 - \frac{|Q_C|}{|Q_H|} \dots\dots\dots 2$$

Absolute-value signs are used to make the equations independent of the sign convention- V for Q and W. We note that for η to be unity (100 percent thermal efficiency) $|Q_C|$ must be zero. No engine has ever been built for which this is true; some heat 'always rejected to the cold reservoir. This result of engineering experience is the basis for statements 1 and 1a of the second law.

If a thermal efficiency of 100 percent is not possible for heat engines, what then determines the upper limit? One would certainly expect the thermal efficiency of a heat engine to depend on the degree of reversibility of its operation. Indeed, a heat engine operating in a completely reversible manner is very special, and is called a Carnot engine. The characteristics of such an ideal engine were first described by N. L. S. Carnot² in 1824. The four steps that make up a Carnot cycle are performed in the following order:

- A system initially in thermal equilibrium with a cold reservoir at temperature T_C undergoes a reversible adiabatic process that causes its temperature to rise to that of a hot reservoir at T_H .
- The system maintains contact with the hot reservoir at T_H and undergoes a reversible isothermal process during which heat $|Q_H|$ is absorbed from the hot reservoir.
- The system undergoes a reversible adiabatic process in the opposite direction of step 1 that brings its temperature back to that of the cold reservoir at T_C .
- The system maintains contact with the reservoir at T_C , and undergoes a reversible isothermal process in the opposite direction of step 2 that returns it to its initial state with rejection of heat $|Q_C|$ to the cold reservoir.

A Carnot engine operates between two heat reservoirs in such a way that all heat absorbed is absorbed at the constant temperature of the hot reservoir and all heat rejected is rejected at the constant temperature of the cold reservoir. Any reversible engine operating between two heat reservoirs is a Carnot engine; an engine operating on a different cycle must necessarily transfer heat across finite temperature differences and therefore cannot be reversible.

Since a Carnot engine is reversible, it may be operated in reverse; the Carnot cycle is then traversed in the opposite direction, and it becomes a reversible refrigeration cycle for which the quantities $|Q_H|$, $|Q_C|$, and $|W|$ are the same as for the engine cycle but are reversed in direction.

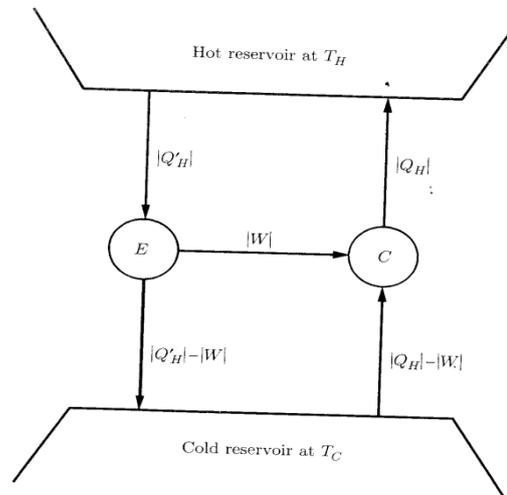


Figure : Engine E operating a Carnot refrigerator C.

Carnot's theorem states that for two given heat reservoirs no engine can have a higher thermal efficiency than a Carnot engine. Such an engine absorbs heat $|Q_H|$ from a hot reservoir, produces work $|W|$, and discards heat $|Q_C| = |Q_H| - |W|$ to a cold reservoir. Assume an engine E with a greater thermal efficiency than a Carnot engine for the same heat reservoirs, absorbing heat $|Q'_H|$, producing work $|W|$, and discarding heat $|Q'_H| - |W|$. Then

$$\frac{|w|}{|Q'_H|} > \frac{|w|}{|Q_H|}$$

When,

$$|Q_H| > |Q'_H|$$

Let engine E drive the Carnot engine backward as a Carnot refrigerator, as shown schematically in Fig.1. For the engine/refrigerator combination, the net heat extracted from the cold reservoir is

$$|Q_H| - |W| - (|Q'_H| - |W|) = |Q_H| - |Q'_H|$$

The net heat delivered to the hot reservoir is also $|Q_H| - |Q'_H|$. Thus, the sole result of the engine/refrigerator combination is the transfer of heat from temperature T_c to the higher temperature T_H . Since this is in violation of statement 2 of the second law the original premise that engine E has a greater thermal efficiency than the Carnot engine is false, and Carnot's theorem is proved.

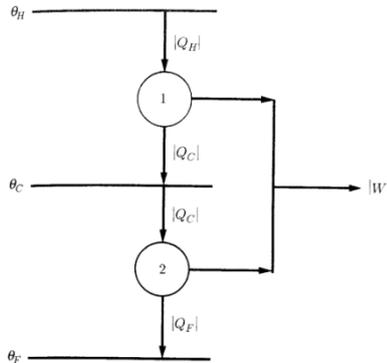


Figure 2: Carnot engines 1 and 2 constitute a third Carnot engine.

In similar fashion, one can prove a corollary to Carnot's theorem: All Carnot engines operating between heat reservoirs at the same two temperatures have the same thermal efficiency. These results show that the thermal efficiency of a Carnot engine depends only on the temperature levels T_H and T_c and not upon the working substance of the engine.

THERMODYNAMIC TEMPERATURE SCALES

In the preceding discussion we identified temperature levels by the Kelvin scale, established with ideal-gas thermometry. This does not preclude our taking advantage of the opportunity provided by the Carnot engine to establish a thermodynamic temperature scale that is truly independent of any material properties. Let θ represent temperature on some empirical scale that unequivocally identifies temperature levels. Consider now two Carnot engines, one operating between a hot reservoir at θ_H and a cold reservoir at temperature θ_c , and a second operating between the reservoir at θ_c and a still colder reservoir at θ_F , as shown in Figure 2. The heat rejected by the first engine $|Q_c|$ is absorbed by the second; therefore the two engines working together constitute a third Carnot engine absorbing heat $|Q_H|$ from the reservoir at θ_H and rejecting heat $|Q_F|$ to the reservoir at θ_F . According, to Carnot's theorem, the thermal efficiency of the first engine is a function of θ_H and θ_c :

$$\eta = 1 - \frac{|Q_c|}{|Q_H|} = \phi(\theta_H, \theta_c)$$

Rearrangement gives

$$\frac{|Q_H|}{|Q_c|} = \frac{1}{1 - \phi(\theta_H, \theta_c)} = f(\theta_H, \theta_c) \dots\dots\dots 3$$

Where, f is an unknown function.

For the second and third engines, equations of the same functional form apply.

$$\frac{|Q_c|}{|Q_F|} = f(\theta_c, \theta_F)$$

and

$$\frac{|Q_H|}{|Q_F|} = f(\theta_H, \theta_F)$$

Division of the second of these equations by the first gives

$$\frac{|Q_H|}{|Q_c|} = \frac{f(\theta_H, \theta_F)}{f(\theta_c, \theta_F)}$$

Comparison of this equation with Eq. (3) shows that the arbitrary temperature θ_F must cancel from the ratio on the right, leaving

$$\frac{Q_H}{Q_c} = \frac{\psi(\theta_H)}{\psi(\theta_c)} \dots\dots\dots 4$$

where ψ is another unknown function.

The right-hand side of Equation (4) is the ratio of ψ evaluated at two thermodynamic temperatures; the ψ 's are to each other as the absolute values of the heats absorbed and rejected by a Carnot engine operating between reservoirs at these temperatures, quite independent of the properties of any substance. However, Equation (4) still leaves us arbitrary choice of the empirical temperature represented by θ : once this choice is made, we must determine the function ψ . If θ is chosen as the Kelvin temperature T , then Equation (4) becomes

$$\frac{Q_H}{Q_C} = \frac{\psi(T_H)}{\psi(T_C)} \dots\dots\dots 5$$

THERMODYNAMIC TEMPERATURE AND THE IDEAL-GAS SCALE

The cycle traversed by an ideal gas serving as the working fluid in a Carnot engine is shown by a PV diagram in Figure 3. It consists of four reversible steps;

- a → b Adiabatic compression until the temperature rises from T_C to T_H .
- b → c Isothermal expansion to arbitrary point c with absorption of heat $|Q_H|$.
- c → d Adiabatic expansion until the temperature decreases to T_C .
- d → a Isothermal compression to the initial state with rejection of heat $|Q_C|$.

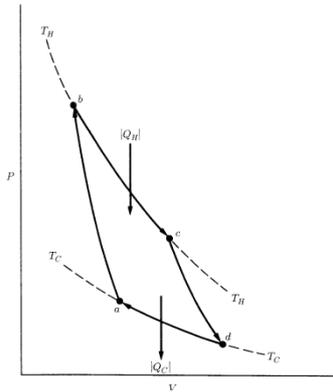


Figure 3: PV diagram showing Carnot cycle for an ideal gas.

For the isothermal steps b → c and d → a,

$$|Q_H| = RT_H \ln \frac{V_c}{V_b} \quad \text{and} \quad |Q_C| = RT_C \ln \frac{V_d}{V_a}$$

Therefore

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C} \frac{\ln(V_c/V_b)}{\ln(V_d/V_a)} \dots\dots\dots 6$$

For an adiabatic process

$$-\frac{C_v}{R} \frac{dT}{T} = \frac{dV}{V}$$

For step a → b, integration gives

$$\int_{T_C}^{T_H} \frac{C_v}{R} \frac{dT}{T} = \ln \frac{V_a}{V_b}$$

Similarly, for step c → d,

$$\int_{T_C}^{T_H} \frac{C_v}{R} \frac{dT}{T} = \ln \frac{V_d}{V_c}$$

Since the left-hand sides of these two equations are same,

$$\ln \frac{V_a}{V_b} = \ln \frac{V_d}{V_c}$$

This may also be written

$$\ln \frac{V_c}{V_b} = \ln \frac{V_d}{V_a}$$

Equation (6) now becomes,

$$\frac{|Q_H|}{|Q_C|} = \frac{|T_H|}{|T_C|} \dots\dots\dots 7$$

Comparison of this result with Equation (5) yields the simplest possible functional relation for namely. $\psi(T) = T$. We conclude that the Kelvin temperature scale, based on the properties of ideal gases, is in fact a thermodynamic scale, independent of the characteristics of any particular substance. Substitution of Equation (7) into Equation (2) gives

$$\eta = 1 - \frac{T_C}{T_H} \dots\dots\dots 8$$

Equations (7) and (8) are known as Carnot's equations. In equation (7) the smallest possible value of $|Q_C|$ is zero; the corresponding value of T_C is the absolute zero of temperature on the Kelvin scale. As mentioned earlier this occurs at -273.15°C . Equation (8) shows that the thermal efficiency of a Carnot engine can approach unity only when T_H approaches infinity or T_C approaches zero. Neither of these conditions is realized on earth: all heat engines therefore operate at thermal efficiencies less than unity. The cold reservoirs naturally available are the atmosphere, lakes and rivers, and the oceans, for which $T_C = 300$ K. Hot reservoirs are objects such as furnaces where the temperature is maintained by combustion of fossil fuels and nuclear reactors where the temperature is maintained by fission of radioactive elements. For these practical heat sources. $T_H = 600$ K. With these values.

$$\eta = 1 - \frac{300}{600} = 0.5$$

This is a rough practical limit for the thermal efficiency of a Carnot engine: actual heat engines are irreversible, and their thermal efficiencies rarely exceed 0.35.

Example : A central power plant, rated at 800.000 kW. generates steam at 585 K and discards heat to a river at 295 K. If the thermal efficiency of the plant is 70 percent of the maximum possible value, how much heat is discarded to the river at rated power?

SOLUTION: The maximum possible thermal efficiency is given by equation (8). Taking T_H as the steam- generation temperature and T_C as the river temperature, we get

$$\eta_{\max} = 1 - \frac{295}{585} = 0.4957$$

The actual thermal efficiency is then

$$\eta = (0.7)(0.4957) = 0.3470$$

By definition

$$\eta = \frac{|W|}{|Q_H|}$$

Substituting for $|Q_H|$ by Eq. (5.1) gives

$$\eta = \frac{|W|}{|W| + |Q_C|}$$

Which may be solved for $|Q_C|$

$$|Q_C| = \left(\frac{1-\eta}{\eta} \right) |W|$$

Now,

$$|Q_C| = \left(\frac{1-0.347}{0.347} \right) (800,000) = 1,505,500 \text{ kW}$$

or

$$|Q_C| = 1,505,500 \text{ kJ s}^{-1}$$

this amount of heat would raise the temperature of a moderate-size river several degrees Celsius.

ENTROPY

Equation (7) for a Carnot engine may be written

$$\frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C}$$

If the heat quantities refer to the engine (rather than to the heat reservoirs), the numerical value of $|Q_H|$ is positive and that of $|Q_C|$ is negative. The equivalent equation written without absolute-value signs is therefore

$$\frac{Q_H}{T_H} = \frac{-Q_C}{T_C}$$

or

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0 \dots\dots\dots 9$$

Thus for a complete cycle of a Carnot engine, the two quantities Q/T associated with the absorption and rejection of heat by the working fluid of the engine sum to zero. Since the working fluid of a Carnot engine periodically returns to its initial state, such properties as temperature, pressure, and internal energy return to their initial values even though they vary from one part of the cycle to another.

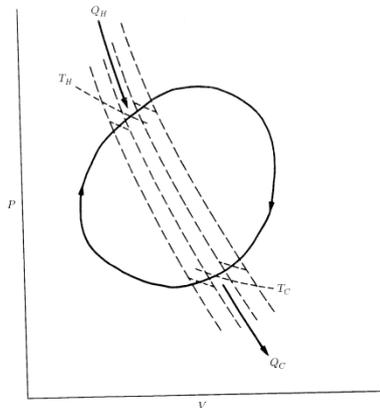


Figure 4: An arbitrary cyclic process drawn on a PV diagram.

The principal characteristic of a property is that the sum of its changes is zero for any complete cycle. Thus equation (9) suggests the existence of a property whose changes are here given by the quantities Q/T .

Further insight may be gained through study of a reversible cyclic process as shown by the PV diagram of Figure 4 where the closed curve represents an arbitrary path taken by an arbitrary fluid. We divide the entire enclosed area by a series of reversible adiabatic curves; since such curves cannot intersect (see statement of 2nd law), they may be drawn arbitrarily close to one another. A few of these curves are shown on the figure as long dashed lines. We connect adjacent adiabatic curves by two short reversible isotherms which approximate the curve of the general cycle as closely as possible. The approximation clearly improves as the adiabatic curves are more closely spaced, and by making the separation arbitrarily small, we may approximate the original cycle as closely as we please. Each pair of adjacent adiabatic curves and their isothermal connecting curves represent a Carnot cycle for which equation (9) applies.

Each cycle has its own pair of isotherms T_H and T_C and associated heat quantities Q_H and Q_C . These are indicated on figure 4 for a representative cycle. When the adiabatic curves are so closely spaced that the isothermal steps are infinitesimal, the heat quantities become dQ_H and dQ_C , and equation (9) is written

$$\frac{dQ_H}{T_H} + \frac{dQ_C}{T_C} = 0$$

In this equation T_H and T_C are the absolute temperatures at which the quantities of heat dQ_H and dQ_C are transferred to or from the fluid of the cyclic process. Integration gives the sum of all quantities dQ/T for the entire cycle:

$$\oint \frac{dQ_{rev}}{T} = 0 \dots\dots\dots 10$$

Where, the circle in the integral sign signifies that integration is over a complete cycle and the subscript "rev" indicates that the equation is valid only for reversible cycles.

Thus the quantities dQ_{rev}/T sum to zero for any series of reversible processes that causes a system to undergo a cyclic process. We therefore infer the existence of a property of the system whose differential changes are given by these quantities. The property is called entropy (en'-tro-py), and its differential changes are

$$dS^t = \frac{dQ_{rev}}{T} \dots\dots\dots 11$$

where, S^t is the total (rather than molar) entropy of the system. Alternatively,

$$dQ_{rev} = TdS^t \dots\dots\dots 12$$

We represent by points A and B on the PV diagram of Figure 5 two equilibrium states of a particular fluid, and show two arbitrary reversible processes connecting these points along paths ACB and ADB. Integration of equation (11) for each path gives

$$\Delta S^t = \int_{ACB} \frac{dQ_{rev}}{T}$$

or

$$\Delta S^t = \int_{ADB} \frac{dQ_{rev}}{T}$$

Where, in view of equation (10) the two integrals must be equal. We therefore conclude that ΔS^t is independent of path and is a property change given by $S^t_B - S^t_A$.

If the fluid is changed from state A to state B by an irreversible process, the entropy change must still be $\Delta S^t = S^t_B - S^t_A$, but experiment shows that this result is not given by $\int dQ/T$ evaluated for the irreversible process itself, because the calculation of entropy changes by this integral must in general be along reversible paths.

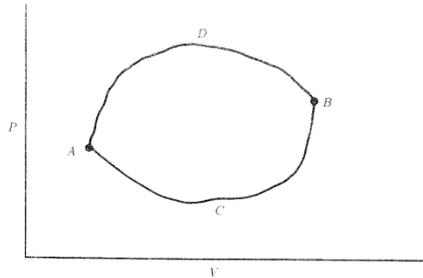


Figure 5: Two reversible paths joining equilibrium states A and B.

The entropy change of a heat reservoir, however, is always given by Q/T . Where Q is the quantity of heat transferred to or from the reservoir at temperature T , whether the transfer is reversible or irreversible. The reason is that the effect of heat transfer on a heat reservoir is the same regardless of the temperature of the source or sink of the heat.

When a process is reversible and adiabatic, $dQ_{rev} = 0$; then by equation (11), $dS^t = 0$. Thus the entropy of a system is constant during a reversible adiabatic process, and the process is said to be isentropic.

This discussion of entropy can be summarized as follows:

- The change in entropy of any system undergoing a reversible process is found by integration of equation (11):

$$dS^t = \frac{dQ_{rev}}{T} \dots\dots\dots (A)$$

- When a system undergoes an irreversible process from one equilibrium state to another, the entropy change of the system ΔS^t must be evaluated by application of equation (A) to an arbitrarily chosen reversible process that accomplishes the same change of state as the actual process. Integration is not carried out for the irreversible path. Since entropy is a state function, the entropy changes of the irreversible and reversible processes are identical.
- Entropy is useful precisely because it is a state function or property. It owes its existence to the second law. From which it arises in much the same way as internal energy does from the first law.

In the special case of a mechanically reversible process the entropy change of the system is correctly evaluated from $\int dQ/T$ applied to the actual process even though the

heat transfer between system and surroundings is irreversible. The reason is that it is immaterial, as far as the system is concerned whether the temperature difference causing the heat transfer is differential (making the process reversible) or finite. The entropy change of a system caused by the transfer of heat can be calculated by $\int dQ/T$, whether the heat transfer is accomplished reversibly or irreversibly. However, when a process is irreversible on account of finite differences in other driving forces, such as pressure, the entropy change is not caused solely by the heat transfer, and for its calculation one must devise a reversible means of accomplishing the same change of state.

This introduction to entropy through a consideration of heat engines is the classical approach, closely following its actual historical development. A complementary approach based on molecular concepts and statistical mechanics.

ENTROPY CHANGES OF AN IDEAL GAS

The first law, written for one mole or a unit mass of fluid, is

$$dU = dQ + dW$$

For a reversible process, this becomes

$$dU = dQ_{rev} - PdV$$

By the definition of enthalpy,

$$H = U + PV$$

whence

$$dH = dU + PdV + VdP$$

Substitution for dU gives

$$dH = dQ_{rev} - PdV + PdV + VdP$$

or

$$dQ_{rev} = dH - Vdp$$

For an ideal gas, we make the substitution $dH = c_{igP} dT$ and $V = RT/P$; then division by T gives

$$\frac{dQ_{rev}}{T} = C_{igP} \frac{dT}{T} - R \frac{dP}{P}$$

As a result of Eq. (5.11), this may be written

$$dS = C_{igP} \frac{dT}{T} - R \frac{dP}{P}$$

$$\frac{dS}{R} = \frac{C_{igP}}{R} \frac{dT}{T} - d \ln P \dots\dots\dots 13$$