

A PRIMER ON THERMODYNAMICS FOR USE IN ENERGY ANALYSIS OF BUILDING STOCK

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ABSTRACT

This working paper is a primer on thermodynamics for use in energy analysis of building stock, a field of study which estimates the direct and indirect energy required to sustain building stock. The principles of classical thermodynamics that underpin energy analysis are explained starting with the concepts of thermal equilibrium, work, heat, and energy, the conservation of energy, and the conversion of heat into work. The concepts of irreversible and reversible processes lead on to the Carnot cycle in a heat engine and finally to a derivation of the law of entropy. The state functions of enthalpy, availability (exergy), and Gibbs free energy are then defined and the grading of energy sources is explained.

Keywords: thermodynamics, energy, entropy, enthalpy, availability, Gibbs free energy.

1. INTRODUCTION

1.1 Classical thermodynamics and statistical mechanics

The principles and laws of classical thermodynamics were formalised in 1867 by Clausius who based his work on the earlier writings of Rumford, Mayer, Joule, and Carnot. Statistical mechanics was developed in parallel to classical thermodynamics during the latter part of the 19th century and early part of the 20th century by Maxwell, Boltzmann, and Gibbs. In setting up a primer on thermodynamics for use in energy analysis, it is neither necessary nor desirable for a full analysis of statistical mechanics and probability theory. The concepts of classical thermodynamics were derived and defined as the results of experiments in which macroscopic properties of classical thermodynamics such as temperature, pressure, and volume could be measured directly. Statistical mechanics, by way of contrast, is a microscopic approach based on an abstract molecular model of matter that invokes constructs that are not readily related to everyday experience. Although the properties of a large macro system assembly of molecules can be predicted with great accuracy by the statistical mechanics approach, the assumptions concerning the structure of nature cannot be measured directly and nor can

be justified until compared with similar deductions based on the macroscopic viewpoint of classical thermodynamics. Statistical mechanics therefore provides a qualitative and supplementary understanding of the laws of classical thermodynamics, but does not supplant or replace the fundamental principles and laws initiated by classical thermodynamics.

1.2 Thermodynamic equilibrium

A thermodynamic system consists of the contents of a definite region in space of sufficient volume and mass to allow macroscopic properties, such as pressure and temperature, of the system to be defined. Everything outside of the thermodynamic system that directly influences the system is called the surrounding. The thermodynamic use of the term ‘universe’ excludes any cosmic or celestial connotation, but instead denotes that portion of space that encompasses a thermodynamic system and its surroundings.

Macroscopic properties that have a bearing on the internal state of a system are called thermodynamic coordinates. When a thermodynamic coordinate changes, the system undergoes a thermodynamic process and a change in state. Classical thermodynamics is restricted to the study of the equilibrium states of macroscopic systems and a system in a state of thermodynamic equilibrium can be described by equations of macroscopic coordinates called equations of state. Each equation of state does not involve time and connects each thermodynamic coordinate in terms of one independent coordinate. A system in a state of non-equilibrium cannot be described by a single set of thermal coordinates due to unbalanced forces, such as acceleration, turbulence and eddies, being present in the interior of a system or between the system and its surroundings or another system.

Although neutral, unstable, and meta-stable states of equilibrium, as represented in Figure 1, can be disturbed by temporary changes in the surroundings, stable states can be disturbed only by permanent finite changes in the surroundings.

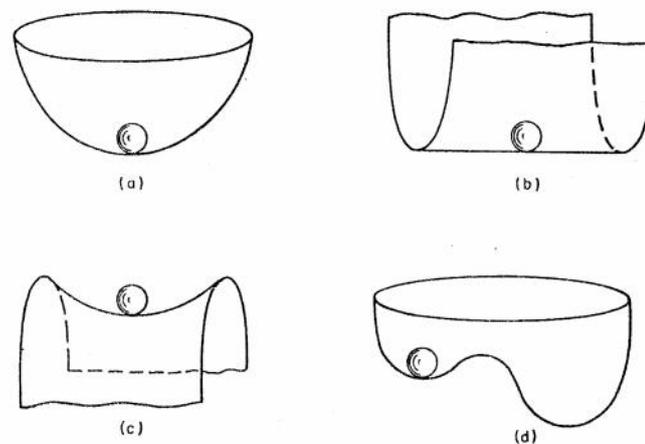


Figure 1. Representation of equilibrium states
(a) stable, (b) neutral, (c) unstable, (d) metastable

Restraints are required to be imposed at the boundary between a system and its surroundings in order to maintain separate states of equilibrium. Two systems separated by an adiabatic wall can coexist independently where the thermodynamic coordinates of each system may vary unconstrained by the other system. An adiabatic wall is an idealization that cannot be realized perfectly, but may be closely approximated by thermally insulating materials capable of withstanding pressure differences across the wall. A diathermic wall, on the other hand, allows the thermodynamic coordinates of one system to influence that of another. A thin sheet of copper is a practical example of a diathermic wall. The thermodynamic coordinates of two systems in actual contact, or separated by a diathermic wall will change spontaneously until thermal equilibrium has been reached – the state at which the thermodynamic coordinates of both systems are the same at all points. An isolated system in non-equilibrium also changes spontaneously until an internal state of thermal equilibrium has been reached.

The zeroth law of thermodynamics, the law of thermal equilibrium, states:

When two systems are in thermal equilibrium with a third system, then the two systems are in thermal equilibrium with each other.

It is the property of temperature T that determines whether any system is in thermal equilibrium with another. Each system has the same temperature at thermal equilibrium. When two systems are at different temperatures, the energy of heat always flows spontaneously from the hotter system to the colder system until each system has the same temperature. A heat reservoir, such as the environment, is able to exchange heat with a system without appreciable changes in its thermodynamic coordinates by virtue of its sheer size compared to any system contained within.

1.3 Work and heat

Energy may be defined as 'the ability to do work on other bodies' or as 'stored work'. In classical mechanics, positive work is said to be done on a system if that system experiences a displacement as the result of a force parallel to, and in the same direction as that force. In thermodynamics, work W is a macroscopic concept that refers to an interchange of energy between a system and its surroundings. There is a decrease in energy of a system when positive work is done by that system unless there is some other energy transfer. External work, or that work done on or by a system as a whole, has no unique value and is not a property of a system. It is meaningless to talk of 'work in a system' or 'work of a system'. Work depends on the particular process by which a system is taken from a reference state to a second state. A result of mechanical work on, or by, a system can be a change in kinetic energy, a change in potential energy of the system as in the case of compressing a spring, or dissipation into heat as in the case of boring out the centre of a cannon.

Heat Q is defined as that energy which is transferred between a system and its surroundings solely by

virtue of a temperature difference. An early 19th century theory incorrectly regarded heat as a liquid called ‘caloric’. It is also incorrect to refer to ‘heat in a body’ because heat is not a substance. Instead, heat is energy in transit. The unit of heat energy is the calorie which is defined as that amount of heat whose absorption by 1 gm of water at constant atmospheric pressure is accompanied by a temperature rise from 14.5 to 15.5 °C. The mechanical equivalent of heat $J = 4.185$ joules/calorie is that amount of mechanical work required to effect the same change in state as that produced by the absorption of one calorie of heat.

1.4 Conservation of energy

A fundamental hypothesis of thermodynamics states that when a system undergoes a process that involves a flow of heat or transfer of energy in the performance of work, the resulting change in the energy of that system is dependent only on the initial and end states of the system and not on the process itself.

When a system carries out work under adiabatic conditions, the system is completely enclosed by an adiabatic envelope to prevent exchange of heat with the surroundings. The system may still be coupled to the outside so that work can be done on, or by, the system. Indirect experiments indicate that although there may be an infinite number of paths by which a system may be transferred from some initial state to some final state by the performance of adiabatic work only, the work done is the same for all adiabatic paths. On the basis of these results, it was concluded that there exists a function of the coordinates of a thermodynamic system whose value at the final state minus its value at the initial state is equal to the adiabatic work in going from one state to the other. This function was called the internal energy function designated by U . The change in internal energy of the system after work is done *on* the system by its surroundings is given by

$$-W \text{ (adiabatic)} = U_{\text{final}} - U_{\text{initial}}. \quad (1)$$

The total internal energy E , or total energy of the system is related to the intrinsic internal energy U , or internal energy as follows:

$$E = U + E_{\text{kinetic}} + E_{\text{fields}} + E_{\text{other}}. \quad (2)$$

The system is said to be a simple system when $E_{\text{fields}} = 0$ and $E_{\text{other}} \approx 0$, and the system is said to be a simple system at rest when, in addition, $E_{\text{kinetic}} = 0$ in which case $E = U$. The internal energy U fully comprises the energy of molecular motion that cannot be differentiated or separated into energy of work or heat. The terms ‘work’ and ‘heat’ have meaning only in connection with a *flow* or interchange of energy.

The definition of the change in total internal energy $E_2 - E_1$ is expressed by

$$E_2 - E_1 = Q - W \quad (3)$$

where Q is positive when heat goes into the system and W is positive when force exerted by the system and the displacement have the same sign. All quantities are expressed in the same energy units with no distinction between different qualities of energy.

For a simple system at rest the change in internal energy is expressed by

$$U_2 - U_1 = Q - W. \quad (4)$$

The principle of the conservation of energy states that the total energy of an isolated system remains constant. In an isolated system where there is no exchange of energy or matter with the outside there is neither external work done by the system nor any flow of heat. The result is $W = Q = 0$. By Equation 3, $E_2 - E_1 = 0$ or, for a simple system at rest, $U_2 - U_1 = 0$. There is a zero change in internal energy, regardless of any process taking place within the system.

The first law of thermodynamics, the law of energy, states:

Energy can be changed in form but can be neither created nor destroyed.

The first law of thermodynamics rules out any possibility of a perpetual motion machine of the first kind – a machine that will put out more energy in the form of work than is absorbed in the form of heat. Many attempts have been made to construct a perpetual motion machine and have failed. The hypothesis that the internal energy of a system is a function of its state only, and not of its past history, continues to be upheld.

A distinction between exact and inexact differentials is necessary in formulating thermodynamic equations that describe the relationship between thermodynamic coordinates. By definition, the integral of an exact differential is a function of the limits of integration only and is independent of the path. This is not true for the integral of an inexact differential. It is impossible to assign any unique value to work W because the work done by a system depends on the path of the process. The inexact differential W used in this paper represents a small *quantity* of work as opposed to the exact differential dW which denotes a small *change* in the value of W . Thermodynamic equations are also usually written in terms of intensive variables to avoid dependence on any particular system. The value of an intensive variable – pressure, temperature, and density – is independent of the mass of a system, whereas volume is an extensive variable being proportional to the mass of the system.

For an infinitesimal process the first law becomes

$$dE = uQ - uW \quad (5)$$

or, for a simple system at rest

$$dU = uQ - uW \quad (6)$$

where Q and W are both inexact differentials. That Q is an inexact differential follows from the consideration of a cyclic process where the final and initial energy states are the same. In this case the first law reduces to $Q = W$ where the total work done by the system equals the net heat absorbed by the system. Because W is path dependent, it follows that Q is also path dependent. E and U are referred to as state functions because they are both independent of any previous history of a system.

1.5 Conversion of heat into work

In the process of converting heat into work, a heat engine absorbs heat Q_h from a high temperature reservoir, performs mechanical work, and rejects heat Q_c to a lower temperature reservoir that is usually the atmosphere. In a cyclic process, as encountered in a heat engine, the initial and final energies are equal. Therefore, from the first law of thermodynamics

$$E_2 - E_1 = 0 = Q - W \quad (7)$$

$$Q = W.$$

The net heat Q flowing into the engine per cycle is equal to the net work done by the engine. This net heat Q per cycle is the sum of the heat absorbed Q_h and the heat rejected Q_c .

$$W = Q = Q_h - Q_c. \quad (8)$$

The thermal efficiency η of a cycle is defined as the ratio of useful work to the heat absorbed

$$\eta = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}. \quad (9)$$

For a heat engine to be 100% thermally efficient, the engine is required to reject no heat Q_c to a reservoir. This requirement has proved to be a physical impossibility. The energy of heat comprises the internal energy of random molecular motion, as opposed to the ordered kinetic motion of mechanical work. It is not feasible to completely convert the random molecular motion of heat to ordered molecular motion of mechanical work because the motions of each individual molecule would need to be fully controlled. Furthermore, part of the portion of heat that can be converted into mechanical work dissipates to the heat form of energy due to the unavoidable friction present in all machines. The physical impossibility of totally converting heat into work has resulted in the Kelvin-Planck statement of the second law:

It is impossible to construct an engine that, operating in a cycle, will produce no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of heat.

The second law of thermodynamics is not deduced from the first law, but stands as a separate law of nature. The first law denies the possibility of creating or destroying energy, but does not preclude the

possibility of running a power station that extracts heat from the atmosphere. The second law denies any possibility of perpetual motion of the second kind whereby a machine utilizes the internal energy of one, and only one, heat reservoir.

A refrigerator is an engine which operates in the reverse direction to a heat engine. Work is applied to the refrigerator which absorbs heat Q_c from the cold reservoir and rejects heat Q_h to a hot reservoir. The ability of a refrigerator to extract as much heat as possible from a cold reservoir with at little expenditure of work is called the coefficient of performance (COP) given by

$$\text{COP} = \frac{Q_c}{W} = \frac{Q_h - W}{W} = \frac{Q_h}{W} - 1. \quad (10)$$

Work is always necessary to transfer heat from a cold reservoir to a hot reservoir. This physical requirement leads to the Clausius statement of the second law:

It is impossible to construct a device that, operating in a cycle, will produce no effect other than the transfer of heat from a cooler to a hotter body.

The Kelvin-Planck and Clausius statements of the second law of thermodynamics are equivalent and differ only in that the application of one statement may be more appropriate than the other, depending on the situation being examined.

Although work is always necessary to transfer heat from a cold reservoir to a hot reservoir, it is possible for the coefficient of performance of a refrigerator to be much greater than unity. Lord Kelvin in 1852 first pointed out the advantages of heating a house by refrigerating the outdoors. A reverse cycle heat engine used primarily for heating purposes is called a heat pump. The COP for commercial heat pumps can be as high as 4. If the source of heating energy is electrical then, from Equation 10 a heat pump system with a COP of 4 is able to provide the same heat as an electrical radiator for one-fifth of the electrical input. The capitals costs of a heat pump versus an electrical radiator as well as the running costs should be taken into account. From an energy analysis point of view, the decision to use high-grade energy to provide low-grade heat should also be examined. The use of low-grade solar energy for heating purposes may be more appropriate.

1.6 Irreversible and reversible processes

An irreversible process occurs spontaneously within a system that is not in thermodynamic equilibrium, resulting in both the system and the local surroundings being unable to be restored to their initial states without producing change in the rest of the universe. Examples of irreversible processes include viscosity, friction, inelasticity, electrical resistance, and magnetic hysteresis, all of which involve the dissipation of work into internal energy of the system or the reservoir. In these examples the process is said to exhibit external mechanical irreversibility. Internal mechanical irreversibility is

the transformation of internal energy into mechanical energy then back again into internal energy. Examples include an ideal gas rushing into a vacuum (free expansion) or the snapping of a stretched wire after it is cut. Further examples of irreversible processes include chemical irreversibility – the formation of new chemical constituents, mixing of two different substances (mixing of alcohol and water), and sudden change in phase or transport of matter between phases in contact (osmosis). The conduction of heat from a system to a cooler reservoir is an example of external thermal irreversibility, while the transfer of heat within parts of same system due to non-uniformity of temperature is an example of internal thermal irreversibility. With the exception of life processes, all natural processes are irreversible.

In a reversible process a change in direction of the driving force results in a reversal in the direction of the process. Reversibility can take place only under those conditions where there are no effects that may drive the process away from equilibrium, such as a finite temperature difference or dissipative effects like friction and electrical resistance.

The concept of a quasi-static equilibrium is applied in order to handle finite unbalanced forces that cause systems to pass through non-equilibrium states. In a quasi-static process finite external forces on a system are varied infinitesimally so that the system is maintained at all times near a state of thermodynamic equilibrium. A quasi-static process can be approached to a significant degree of precision under laboratory conditions with the proviso that the time required for a process to reach equilibrium is small compared to the time for the system to change its thermodynamic coordinates.

A geometrical representation of a quasi-static process, such as an isothermal process which takes place at constant temperature, can be drawn on a Pressure (p) - Volume (V) -Temperature (T) surface by tracing a path through a succession of intermediate equilibrium states which join the initial and final equilibrium states. In order to maintain the system at a constant temperature, changes in the other coordinates – pressure and volume – are carried out slowly and heat is transferred. The equation of state for an ideal gas, $pV = nRT$ defines the nature of the pVT thermodynamic surface as shown in Figure 2. By definition, the relationship $pV = nRT$ holds true at all pressures for an ideal gas.

The internal energy of an ideal gas system does not change under isothermal conditions because the internal energy U of an ideal gas depends only upon temperature. Work W done by an ideal gas system in expanding at a constant temperature T under isothermal conditions is therefore equal to the heat absorbed by the system, or

$$W \text{ (isothermal)} = Q. \quad (11)$$

The requirement that a reversible process is unaccompanied by any dissipative effects can be satisfied when a quasi-static process takes place infinitely slowly. Under these conditions there is no dissipation of energy due to friction. Upon completion of the process, both the system and the local surroundings can be restored to their initial states without producing any changes in the rest of the universe. How-

ever, an infinitely slow process would take an infinite time to complete and would correspond to no known technology. A reversible process, therefore, represents an idealization that can never be perfectly realised.

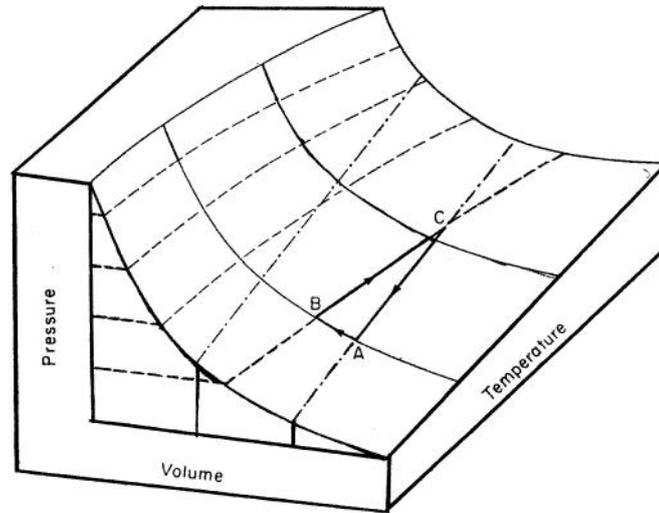


Figure 2. pVT surface for an ideal gas

An approximation of a reversible process can be achieved whenever a quasi-static process exchanges heat with a heat reservoir. Changes that do occur within the reservoir take place very slowly without dissipative effects and are the same as would be for a reversible process exchanging heat with the reservoir.

1.7 Carnot cycle

A Carnot cycle is a set of reversible processes that can be performed in a forward or reverse cycle by any thermodynamic system between two reservoirs at temperatures T_1 and T_2 . At the start of a forward cycle the system, or working substance that may be solid, liquid, or gas, is in thermal equilibrium with the cold reservoir at temperature T_2 . Figure 3 shows a Carnot cycle for a real gas. A reversible adiabatic process is performed in such a direction that the temperature of the working substance rises to that of the hotter reservoir T_1 . In the second process the working substance is maintained in contact with the hot reservoir at T_1 . A reversible isothermal process is performed so that heat Q_1 is absorbed from the reservoir.

A reversible adiabatic process is then performed in the opposite direction to the first reversible adiabatic process resulting in the temperature of the working substance dropping to that of the cold reservoir at temperature T_2 . In the final process the working substance is maintained in contact with the cold reservoir at temperature T_2 . A reversible isothermal process is carried out in the opposite direction to that of the first reversible isothermal process resulting in heat Q_2 being rejected to the cold reservoir. The cycle is complete and the working substance is back to its initial state.

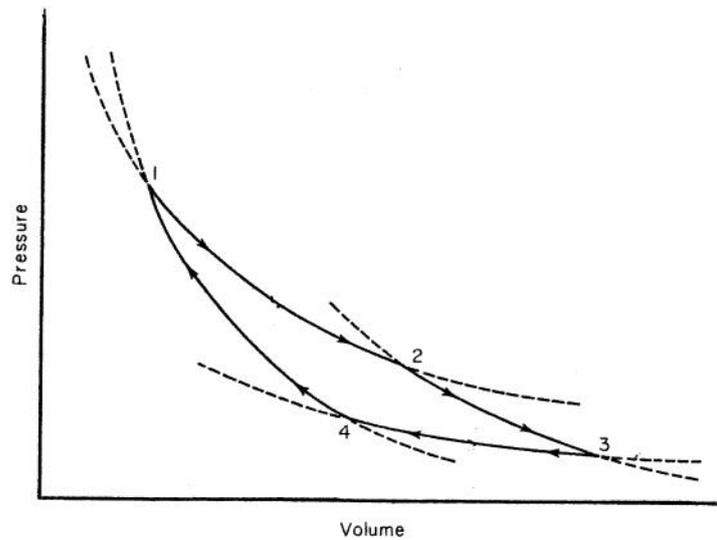


Figure 3. Carnot cycle of an ideal gas.

1.8 Carnot engine

A Carnot engine is an example of an idealized heat engine that uses an ideal gas as a working substance and which operates under a Carnot cycle. When operating in a reverse refrigeration cycle, work is applied to the Carnot engine which absorbs heat from the cold reservoir at a single temperature T_2 and rejects heat to the hot reservoir at a single temperature T_1 .

By linking together a forward and a reverse cycle Carnot engine, Sadi Carnot was able to prove that no engine operating between two given reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs. A corollary of Carnot's theorem is that all Carnot engines operating between the same two reservoirs have the same efficiency. It follows that the efficiency of a Carnot engine operating between two reservoirs is a function only of the temperatures T_1 and T_2 of the reservoirs. The thermal efficiency η of a Carnot engine may be written in terms of an unknown function $F(T_1, T_2)$. From Equation 9

$$\eta = 1 - \frac{Q_2}{Q_1} = F(T_1, T_2) \quad (12)$$

and, by rearrangement

$$\frac{Q_1}{Q_2} = \frac{1}{1 - F(T_1, T_2)} = f(T_1, T_2) \quad (13)$$

where $f(T_1, T_2)$ is also an unknown function. Lord Kelvin proposed that the ratio Q_1/Q_2 , which is constant for all Carnot engines, be defined as being equal to the ratio of two Kelvin scale temperatures of the reservoirs denoted by T_1 and T_2 so that

$$\frac{Q_1}{Q_2} = \frac{\mathcal{E}(1)}{\mathcal{E}(2)} = \frac{T_1}{T_2}. \quad (14)$$

The Kelvin temperature scale is an absolute scale in that the scale is independent of the characteristics of any particular substance. The triple point of water is that temperature and pressure (4.58 mm of Hg) at which solid, liquid and vapour phases can coexist in equilibrium. The triple point of water is set at 273.16°K in the Kelvin scale (0.01°C in the Celsius scale) with each degree division of the Kelvin and Celsius scales being equal.

The efficiency of a Carnot engine may be rewritten as

$$\eta = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}. \quad (15)$$

For a Carnot engine to be 100% efficient, the temperature of the colder reservoir is required to be at absolute zero (0°K). The molecules of a substance at absolute zero still have a finite amount of kinetic energy called zero-point energy. The unattainability of absolute zero in temperature is known as the unattainability statement of the third law of thermodynamics. This unattainability of absolute zero is demonstrated by considering a Carnot refrigerator operating between a reservoir at a fixed temperature T_2 and a colder reservoir at temperature T_1 . The mechanical work W required to take in heat Q_1 from the reservoir at temperature T_1 and reject heat Q_2 to the reservoir at fixed temperature T_2 is given by Equation 10.

$$\text{COP} = \frac{Q_2}{W} = \frac{Q_1 - W}{W} \quad \text{or} \quad W = Q_2 - Q_1. \quad (16)$$

From the definition of the Kelvin temperature given by Equation 14

$$Q_2 = Q_1 \frac{T_2}{T_1}. \quad (17)$$

Hence

$$W = Q_1 \frac{T_2}{T_1} - Q_1 \quad (18)$$

and

$$T_1 = T_2 \left(\frac{Q_1}{W + Q_2} \right). \quad (19)$$

The more work W there is put into the Carnot refrigerator, the lower can be the temperature T_1 of the cold reservoir. Absolute zero can be approached, but infinite work is required to reach absolute zero.

The unattainability of absolute zero follows directly from the definition of the Kelvin temperature scale.

One definition of absolute zero is that temperature at which a system may undergo a reversible isothermal process without transfer of heat. At absolute zero an isothermal process and an adiabatic process are identical. The classical thermodynamics definition of absolute zero holds for macroscopic scale effects of all systems, but does not account for, or refer to, molecular energy at the microscopic scale.

A Carnot engine with a 100% efficiency is a practical impossibility, as nature does not provide a reservoir at absolute zero. The exhaust temperature T_2 of an engine is usually that of the atmosphere in the range of 273°K to 303°K. In order to achieve a high thermal efficiency, given this range of exhaust temperatures, the difference between the intake temperature T_1 and the exhaust temperature T_2 is required to be as large as possible. The use of extremely high intake temperatures is limited by metallurgical technology. In practice, thermal efficiency is not the sole criterion for designing an engine. Size, weight, and cost also need to be taken into consideration. The full potential thermal efficiency is compromised as a result.

2. ENTROPY

2.1 Derivation

In a process during which the temperature may change in any manner, any reversible paths between two states can be replaced by a series of alternate adiabatic and isothermal paths such that the heat transferred during the sum of the isothermals paths is the same as the original process. This is shown in Figure 4.

The smooth closed curve represents the reversible cycle on a work diagram. A series of adiabatic and isothermal lines can divide the cycle into a number of strips, each of which forms a Carnot cycle. A zigzag path of alternate adiabatic and isothermal paths can follow the path of the smooth closed curve over the complete zigzag path.

For a single Carnot cycle

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2}. \quad (20)$$

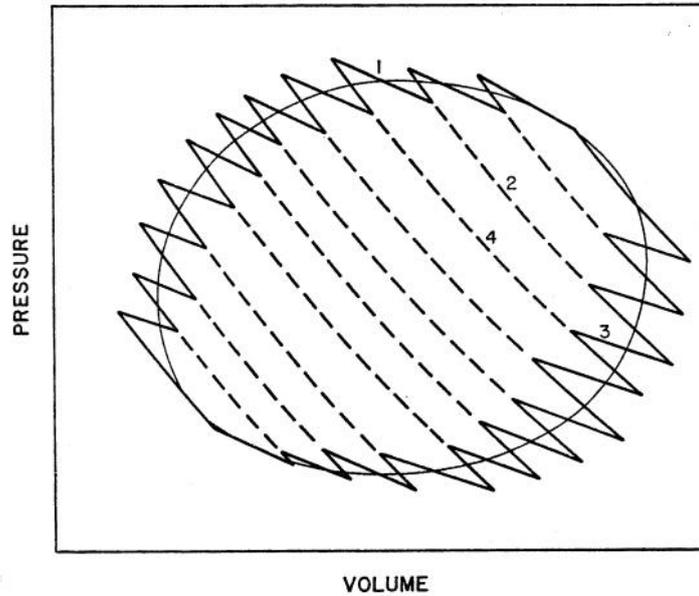


Figure 4. Representation of a reversible cycle.

By adopting the sign convention that Q is positive for heat absorbed and negative for heat rejected

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0. \quad (21)$$

For a series of Carnot cycles as shown in Figure 4

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \dots = 0. \quad (22)$$

By definition there is no transfer of heat during the adiabatic processes of a single, or series of Carnot cycles, so

$$\sum \frac{Q}{T} = 0 \quad (23)$$

As the isothermal processes become infinitesimal, the ratio Q/T for an infinitesimal isothermal step between two adjacent adiabatics is equal to the ratio Q/T for the same infinitesimal portion of the original smooth cycle. In the limit Clausius' theorem states

$$\oint_R \frac{Q}{T} = 0 \quad (24)$$

The circle through the integral signifies that the integration takes place over the complete cycle. The letter R emphasises that the equation is true only for a reversible cycle. For any reversible cycle, the sum along the total path of the heat added at each point of the path divided by the absolute temperature of the system at that point has the same value irrespective of the reversible path taken or the heat

added. It is therefore possible to take the system from an initial state 1 to a final state 2 along any number of reversible paths denoted by R_1 and return to state 1 by any reversible path denoted by R_2 . Inserting this random reversible path cycle in Clausius' theorem results in

$$\oint_{R_1 R_2} \frac{uQ}{T} = 0 = \int_{R_1}^2 \frac{uQ}{T} + \int_{R_2}^1 \frac{uQ}{T} \quad (25)$$

or

$$\int_{R_1}^2 \frac{uQ}{T} = - \int_{R_2}^1 \frac{uQ}{T}. \quad (26)$$

R_2 is a reversible path, therefore

$$\int_{R_1}^2 \frac{uQ}{T} = \int_{R_2}^2 \frac{uQ}{T}. \quad (27)$$

From Clausius' theorem it is inferred that there exists a function of the thermodynamic coordinates of a system whose value at the final state 2 minus its value at the initial state 1 equal the integral

$$\int_R^2 \frac{uQ}{T} \quad (28)$$

where this function is independent of the reversible path connecting two states 1 and 2.

The concept of internal energy was made possible by the experimental fact that the difference between the heat added and the work done by a system, $Q - W$, has the same value for all paths. The change in internal energy is defined and measured by the quantity $Q - W$. In the same way, the above integral is called the entropy function denoted by S .

If S_1 is the entropy at the initial state and S_2 the entropy at the final state then

$$S_2 - S_1 = \int_R^2 \frac{uQ}{T} \quad (29)$$

where $S_2 - S_1$, the change in entropy, is a state function defined only for equilibrium states. The unit of entropy is cal/°K.

If two equilibrium states are infinitesimally close, the quantity Q/T is an exact differential of the entropy function

$$\frac{uQ_R}{T} = dS \quad (30)$$

where the subscript R written along with Q indicates that the above equation is true only if Q is transferred reversibly.

The entropy function is a mathematical formulation of the second law of thermodynamics that was inferred on the basis of the Clausius theorem. In 1909 the mathematician Carathéodory independently inferred the existence of the entropy function and an integrating factor connected with the Kelvin temperature by stating the second law in terms of the inaccessibility of certain states via adiabatic paths and by using a mathematical theorem.

Provided the initial and final state of a system are equilibrium states, the change in entropy for an irreversible process can be computed by computing the same for any reversible process which takes that system from the same initial state to the same final state. When either the initial or final state is in a non-equilibrium state, it is impossible to find a reversible process by which the system may be brought from the same initial state to the same final state. Special methods must be used to calculate the change in entropy of a non-equilibrium system. A standard approach is to define an infinite number of reversible processes by considering the system to be composed of an infinite number of subsystems, each of which are at equilibrium. By this approach the system may be taken from a non-equilibrium state to an equilibrium state and the entropy change defined as the result of integrating Q_R/T over all of the reversible processes.

The change in entropy for an irreversible process is greater than zero as the following demonstrates. From Equations 9 and 15 the thermal efficiency for a Carnot engine is given by

$$y = \frac{W}{Q_h} = 1 - \frac{T_2}{T_1}. \quad (31)$$

If T_0 is the temperature of the coldest reservoir at hand, then the maximum work which can be achieved by the Carnot engine is given by

$$W \text{ (maximum)} = Q \left(1 - \frac{T_0}{T} \right) \quad (32)$$

which represents the maximum amount of energy available for work when Q units of heat are extracted from a reservoir at temperature T .

Given two reservoirs, one at higher temperature T_1 and the other at a lower temperature T_2 connected by a heat conducting bar, the maximum work that can be obtained by extracting Q units of heat from the higher temperature reservoir before conduction is given by

$$W \text{ (maximum before conduction)} = Q \left(1 - \frac{T_0}{T_1} \right). \quad (33)$$

The maximum work that can be obtained from the same unit of Q after conduction is given by

$$W \text{ (maximum after conduction) } = Q \left(1 - \frac{T_0}{T_2} \right). \quad (34)$$

The amount of energy E that has become unavailable for work, or has become degraded as the result of irreversible process of the conduction of heat under a finite temperature gradient, is the difference

$$\begin{aligned} E &= Q \left(1 - \frac{T_0}{T_1} \right) - Q \left(1 - \frac{T_0}{T_2} \right) \\ &= T_0 \left(\frac{Q}{T_2} - \frac{Q}{T_1} \right) \\ &= T_0 \Delta S \text{ (universe)}. \end{aligned} \quad (35)$$

A general form of the above result is given by

$$dE = T_0 dS \quad (36)$$

where dS is the change in entropy of the universe.

In a low entropy system the energy is free in the sense that it is available for producing mechanical work, while in a high entropy system the energy is said to be bound. Lord Kelvin first developed the principle of the degradation of energy that states because all natural processes dissipate energy to heat, energy is continually becoming unavailable for work. Within the isolated system of the universe there is a continuous and irrevocable degradation of free into bound energy.

The change in entropy for reversible and irreversible processes is formalized by the second law of thermodynamics, the law of entropy, which states:

When all systems taking part in a process are included, the entropy of the total system either remains constant or increases.

In mathematical terms

$$\Delta S \text{ (universe) } \geq 0. \quad (37)$$

An open system may exchange both energy and matter with the outside whereas a closed system exchanges only energy and not matter with the outside. Although the entropy of an isolated system remains either constant or increases, the entropy of open sub-systems may decrease. Life forms are an example of low entropy systems which, in order to retain the form of low entropy, need to continually take in energy and matter in the form of food and consume more than one unit of food in order to gain one unit in weight. During periods of increase in size and numbers the entropy of living organisms decreases while the entropy of the combined system, which includes their life support systems, simul-

taneously increases. Contrary to being a violation to the law of entropy, life forms comprise systems that hasten the increase of entropy in the universe.

2.2 Entropy as a measure of order and disorder

There are many different forms and interpretations of the law of entropy that incorporate the statistical mechanics concept of entropy as comprising a measure of order and disorder. In developing the kinetic theory of gases, Maxwell set up a model depicting the molecules of a gas as bounding in all directions and velocities off each other and the walls of a perfectly elastic container. Along with Boltzmann, he developed an equation that showed that the distribution of molecular velocities of a gas at a particular temperature comprised a few molecules moving very slowly or very quickly with the larger percentages moving at intermediate velocities. A rise in temperature causes the average velocity of the molecules to rise an increase in the kinetic energy of the molecules while a drop in temperature caused the average velocity to fall. Mechanical work, as opposed to the haphazard motions of individual molecules against intermolecular forces, involves the orderly motion of molecules. Whenever mechanical work is dissipated into heat, the temperature of the system rises and the disorderly motion of molecules increases. The kinetic theory of gases pictures temperature and heat as involving molecular movement and an interpretation of the second law as being a tendency for nature to proceed from a state of order to disorder thus providing a qualitative and supplementary understanding of the laws of classical thermodynamic.

Statistical mechanics is a further development of the kinetic theory of gases in which the microstate of each molecule is regarded as being completely defined by a specification of six coordinates for each molecule x, y, z, v_x, v_y, v_z , in terms of position, velocity and direction. A fundamental hypothesis of statistical mechanics is that all microstates are equally probable. The disorder of a system may be calculated by the theory of probability and expressed by a quantity w known as the thermodynamic probability. Boltzmann was able to show that the state of maximum entropy corresponds to the thermodynamic equilibrium state and that the most probable macrostate corresponds to the thermodynamic equilibrium state. This relationship between entropy and the thermodynamic probability is described by the equation

$$S = k \ln w \quad (38)$$

where k is a proportionality constant called the Boltzmann constant.

The law of entropy may be restated

In spontaneous processes, concentrations tend to disperse, structure tends to disappear, and order becomes disorder.

There is a degree of similarity between statistical mechanics and quantum theory. Both theories have

an explanatory and predictive value relating to microscopic phenomena and utilise the theory of probability. However, by making use of probability theory, statistical mechanics allows the possibility of water being able to spontaneously separate into a hotter and colder region. Human experience denies this possibility. According to statistical mechanics, even though this possibility is very small and may not occur within the time frame of any human experience, nonetheless the possibility exists.

Shannon and Weaver (1949) also used the theory of probability in the development of information theory in response to a study of how to most efficiently transmit a signal through telephone lines subject to noise interference. Shannon used the term 'entropy' to describe the measure of the 'amount' of information in the transmission of a signal perhaps on the basis of similarity in mathematical form to Boltzmann's equation for thermodynamic entropy. The use of the term 'entropy' would seem to be metaphorical rather than a relationship of process because entropy is a measure of order and disorder in statistical mechanics, whereas the meaning of a message is irrelevant in information theory. The concept of entropy has also been utilised to define the arrow of time as being in the same direction as followed by all natural processes due to dictates of the second law.

Georgescu-Roegen (1971) regards that Boltzmann's statistical approach to entropy opens the door to vacuous interpretations of what entropy means and that statistical mechanics is logically flawed by being underpinned by classical mechanics that denies qualitative change in the universe. The position adopted by Georgescu-Roegen is that entropy is neither reducible to locomotion nor to probability nor any subjective element. According to Georgescu-Roegen (1971)

The entropic phenomenon of a piece of coal burning irrevocably into ashes is neither a flow of probability from a lower to a higher value, nor an increase in the onlooker's ignorance, nor man's illusion of temporal succession.

The law of entropy was derived as a physics of the economic use of heat in an engine and not from the principles of classical mechanics that reduces all phenomena to reversible locomotion. As Georgescu-Roegen (1971) emphasises

...the discovery of the Entropy Law brought the downfall of the mechanistic dogma of classical physics which held that everything which happens in any phenomenal domain whatsoever consists of locomotion alone and, hence, there is no irrevocable change in nature.

The first law of thermodynamics does not contradict the laws of mechanics. The second law however, the law of entropy, is in direct contradiction with the laws of classical mechanics in that the law of entropy introduces the element of an irrevocable qualitative change when systems undergo any process.

3. STATE FUNCTIONS

3.1 Enthalpy

While total energy E and internal energy U form the foundations of classical thermodynamic, these state functions are not well suited for the analysis of many thermodynamic processes. Additional state functions are necessary in order to determine the energy requirements of processes carried out within systems. In energy analysis use is made of the additional state functions - enthalpy H , availability A , and Gibbs free energy G . Exergy is a recent term that has the same meaning as availability in this paper. These state functions are directly related to total energy E and internal energy U and are referred to as thermodynamic potentials with the same dimension of energy.

From the first law as formulated by Equation 5

$$dE = \delta Q - \delta W. \quad (39)$$

For a simple system, and only for a reversible process, the infinitesimal work δW of the system is given by

$$\delta W = p dV \quad (40)$$

where p is the pressure and dV is the corresponding change in volume. Equation 39 becomes

$$dE = \delta Q_R - p dV \quad (41)$$

or, in the case of a simple system at rest

$$dU = \delta Q_R - p dV. \quad (42)$$

From Equation 30 for a reversible process

$$\delta Q_R = T dS \quad (43)$$

so that Equation 41 becomes

$$dE = T dS - p dV. \quad (44)$$

By adding and subtracting $V dp$ to the right hand side of Equation 4, this gives

$$dE = T dS + V dp - p dV - V dp. \quad (45)$$

The last two terms form a complete integral

$$- p dV - V dp = - d(pV). \quad (46)$$

Transferring $d(pV)$ to the left side of Equation 45 leaves

$$d(E + pV) = T dS + Vdp. \quad (47)$$

The total enthalpy H_T of a system is defined as

$$H_T = E + pV \quad (48)$$

where

$$dH_T = TdS + Vdp. \quad (49)$$

For a simple system at rest the total energy E can be replaced by the internal energy U as follows

$$H = U + pV \quad (50)$$

and

$$dH = TdS + Vdp. \quad (51)$$

From the definition $H = U + pV$

$$dH = dU + pdV + Vdp. \quad (52)$$

But, from equation 42

$$u Q_R = dU + pdV. \quad (53)$$

Therefore

$$dH = u Q_R + Vdp. \quad (54)$$

During an isobaric process which is carried out at constant pressure this applies to any reversible process open to the environment the term $Vdp = 0$ leaving

$$dH = u Q_R. \quad (55)$$

The change in enthalpy for an isobaric process is equal to the heat that is transferred by the system. Enthalpies of formation H_u for simple systems at rest open to the atmosphere, or heat energy released during chemical reactions are tabulated in tables of standard enthalpies of formation for a number of individual sub-reactions. In a complex reaction that involves the equivalent of a number of separate steps, the change in enthalpy of formation H_u of the total reaction is the algebraic sum of the changes in enthalpy of formation of the individual steps. The use of these tables is made possible by standardising the conditions under which the tabled components react. These standard conditions are defined as the temperature of 298.15 °K (25 °C) and the pressure of 101.325 KPa (1 atmosphere).

3.1 Availability (Exergy)

The state function availability A is a development of the Helmholtz free energy state function F which in turn is derived in a similar way as for enthalpy. From Equation 44

$$dE = TdS - pdV. \quad (56)$$

By adding and subtracting SdT on the right hand side of Equation 56, this gives

$$dE = TdS + SdT - SdT - pdV. \quad (57)$$

The first pair of terms forms a complete integral

$$TdS + SdT = d(TS). \quad (58)$$

Transferring $d(TS)$ to the left side of Equation 58 leaves

$$d(E - TS) = -SdT - pdV. \quad (59)$$

The Helmholtz free energy F is defined as

$$F = E - TS \quad (60)$$

where

$$dF = -SdT - pdV. \quad (61)$$

For an isothermal process, where T is held constant,

$$dF = dE - TdS. \quad (62)$$

When a system exchanges heat with a single thermal reservoir, such as the environment, the work done during any reversible process between fixed end states is always the same.

$$\text{For reversible processes } \int_1^2 \delta W_R = K = \text{const.} \quad (63)$$

$$\text{For irreversible processes } \int_1^2 \delta W_I < K. \quad (64)$$

In order to extract maximum work from any process — mechanical, thermal, or chemical — the process that moves a system from its initial state to final state must be reversible. To bring into effect a reversible change may require one, or a series of auxiliary Carnot engines to be interposed between the system and the environment. The work done by an auxiliary Carnot engine W_N during an infinitesimal reversible process is given by a combination of Equations 9 and 15

$$\delta W_N = \frac{T_e - T}{T} \delta Q_N = T_e \frac{\delta Q_N}{T} - \delta Q_N \quad (65)$$

where T_e is the temperature of the environment.

The total work W_R is the work done by the system W plus the work done by the auxiliary Carnot

engines

$$uW_R = uW - uQ_N + \frac{T_e}{T} uQ_N. \quad (66)$$

From the first law and Equation 5

$$uQ_N - uW = dE. \quad (67)$$

From the second law and Equation 30 for a reversible process

$$TdS = uQ_N. \quad (68)$$

By substitution into Equation 66

$$uW_R = (uW - uQ_N) + T_e \frac{uQ_N}{T} = -(dE - T_e dS). \quad (69)$$

The infinitesimal work done by a system in a reversible isothermal process equals the decrease in its Helmholtz free energy. In an irreversible isothermal process only part of the decrease in free energy is transformed into work.

The total work done by a system that exchanges heat with a single reservoir, such as the environment, in a reversible process going from state 1 to state 2 is given by

$$\int_1^2 uW_R = \int_1^2 -(dE - T_e dS) = (E_1 - T_e S_1) - (E_2 - T_e S_2). \quad (70)$$

For a simple system at rest the total energy E can be replaced by the internal energy U

$$\int_1^2 uW_R = \int_1^2 -(dU - T_e dS) = (U_1 - T_e S_1) - (U_2 - T_e S_2) \quad (71)$$

where the quantity $(U - T_e S)$ is known as the non-flow availability function.

The maximum useful work that an active system can transfer to a passive system as both systems move to a final state of equilibrium within the closed system of the environment is called the available work A , or exergy, of that system. Availability A is always measured with respect to a standard rest state. The standard temperature of 25 °C and pressure of 1 atmosphere as agreed by convention for thermodynamicists commonly use enthalpy of formation H_u . The energy of the system at this rest state, or dead state, is written as U_0 because the kinetic energy and all other energy terms are measured zero relative to the environment. The maximum work that can be obtained from a system between the initial state 1 and the dead state 0 is given by

$$\begin{aligned} Q_{\max} &= (E_1 - T_0 S_1) - (U_0 - T_0 S_0) \\ &= (E_1 - U_0) - T_0 (S_1 - S_0). \end{aligned} \quad (72)$$

Some of this work is used to displace the environment and cannot be included as useful work. The maximum useful work W_{uR} that can be obtained from an active sub-system within the atmosphere at temperature T_o and pressure p_o is the total work W_R less the work produced against atmospheric pressure.

$$uW_{uR} = uW_R - p_o dV = -(dE + p_o dV - T_o dS) = d\Phi \quad (73)$$

where, by definition, the availability function

$$\Phi = (E + p_o V - T_o S). \quad (74)$$

The maximum useful work W_{uR} for a system changing between states 1 and 2 when T_o and p_o are constant is given by

$$\begin{aligned} W_{uR} &= (E_1 + p_o V_1 - T_o S_1) - (E_2 + p_o V_2 - T_o S_2) \\ &= \Phi_1 - \Phi_2. \end{aligned} \quad (75)$$

W_{uR} has a maximum value when state 2 corresponds to the dead state. The availability A of the system is defined as

$$\begin{aligned} A &= (W_u)_{\max} = \Phi - \Phi_0 \\ &= (E + p_o V - T_o S) - (U_0 + p_o V_0 - T_o S_0) \\ &= (E - U_0) + p_o (V - V_0) - T_o (S - S_0). \end{aligned} \quad (76)$$

For a simple system at rest, the change in total energy $E - U_o$ of the system, which includes kinetic energy, may be replaced by the change in internal energy $U - U_o$.

The above expression is a restricted definition of available work by not including a diffusion term where the system may exchange matter with the environment. IFIAS (1974) recommends this restricted definition of available work because there are practical difficulties in harnessing any diffusion contribution to available work.

The atmosphere does work on the system when the volume of the system decreases. If the entropy of the system increases under reversible conditions, the atmosphere transfers heat to the system. In both cases, energy from the atmosphere may be passed on as useful work.

A system undergoes a monothermal process if heat can be transferred to or from a single reservoir only which does not necessarily have to be at the same temperature as the system. When a process undergoes a reversible and monothermal change from an initial state 1 to a final state 2 which is not the rest state of the atmosphere, the system experiences a change in availability. The maximum useful work obtainable from such a transition is a function of the change in availability and entropy of the

system and the temperature of the atmosphere as shown in the following expression:

$$\begin{aligned}
 \Delta \Phi &= \Phi_1 - \Phi_2 \\
 &= (E_1 - E_2) + (p_1 V_1 - p_2 V_2) - T_e (S_1 - S_2) \\
 &= \Delta E + \Delta(pV) - T_e (\Delta S) \\
 &= \Delta H - T_e \Delta S.
 \end{aligned}
 \tag{77}$$

Under reversible conditions the total entropy of the system plus the environment does not change resulting in the difference between the incoming and outgoing flows of availability being equal to the work flow from the system. For this reason availability, or exergy, is a measure of the quality of the energy supply of the system. Energy forms that have high availability are called high-grade energy because of their greater ability to perform useful work.

One quantitative measure of availability is the temperature of a heat source. The larger is the temperature difference between a heat source and a reservoir, the more useful work can be extracted. This is demonstrated by the efficiency function for a Carnot heat engine which absorbs heat Q_s from a source and rejects heat Q_r to a reservoir as given by Equation 15

$$\text{Carnot Efficiency} = 1 - \frac{T_r}{T_s}
 \tag{78}$$

where T_s and T_r are the intake and exhaust temperatures respectively. The exhaust temperature T_r is usually that of the atmosphere. The above expression shows that the higher is the source temperature T_s at the intake, the greater is the efficiency of the Carnot engine. Conversely, as the intake temperature T_s approaches the exhaust temperature T_r , the thermal efficiency of a Carnot engine approaches zero in the limit. Because thermal efficiency is the ratio of useful work extracted to the heat absorbed by the system, it follows that the availability of low-grade heat at ambient temperature is zero.

3.3 Gibbs free energy

Gibbs free energy G is generated from enthalpy H and is defined as

$$G = H - TS.
 \tag{79}$$

A change in Gibbs free energy gives

$$\Delta G = \Delta H - \Delta(TS).
 \tag{80}$$

This can be expressed as:

$$\begin{aligned}\Delta G &= \Delta(E + pV) - \Delta(TS) \\ &= \Delta E + \Delta(pV) - \Delta(TS).\end{aligned}\tag{81}$$

In the case of a combined isothermal and isobaric process at fixed pressure p_0 and temperature T_0 , the change in Gibbs free energy is expressed by:

$$\begin{aligned}\Delta G &= \Delta E + p_0 \Delta V - T_0 \Delta S \\ &= (E_1 - E_2) + p_0(V_1 - V_2) - T_0(S_1 - S_2) \\ &= \Delta \Phi.\end{aligned}\tag{82}$$

The Gibbs free energy function for a combined isothermal and isobaric process at atmospheric pressure and temperature is identical to the availability function and, provided the same standard state of rest is applied in each function, the numerical value of each is the same. The change in Gibbs free energy in the above example, however, is a measure of work extractable from an isothermal and isobaric change of state, whereas availability measures the work extractable from any change in state. In addition, the definition of availability includes the temperature and pressure of the atmosphere only, and not that of the system, so can therefore be defined for a non-equilibrium state. As pointed out by Connolly and Spraul (1975):

At first glance the availability function varies only subtly from the Gibbs free energy, but in reality accounts for all of the possible energy that could be converted into work when the system interacts with the environment.

Availability, as opposed to the change in Gibbs free energy, is the more general function. In the opinion of Peet and Baines (1986) the availability function provides the best assessment of the quality of a fuel for comparative efficiency studies.

4. ENERGY

4.1 The grading of an energy source

The grading of an energy source can be classified in terms of the energy level of the source – a measure of its energy intensity in terms of energy per unit mass – and its energy grade that is a measure of energy quality. A high energy level system has the characteristics of high temperature, pressure, or enthalpy. The energy grade of a source can be separated into either work forms or heat forms of energy. Work forms of energy include mechanical work, electrical energy, waterpower, wind power, and the kinetic energy of a jet stream. Because work can be completely transformed into heat

the reverse transformation heat cannot completely transform heat into work due to the second law work forms of energy are given a higher classification than heat forms, though this distinction becomes less significant with high temperature sources of energy. Heat forms of energy heat from fusion/fission, heat from combustion, and heat from friction are graded in descending order according to the temperature of the source. The energy grade of a source serves to qualify the energy level. When two energy sources have the same level but different grades, the ordering of the lower grade source can be adjusted downwards to reflect a lower availability.

4.2 Efficiency of energy conversion

When energy is transformed from one form to another, each transformation is accompanied by a degradation of energy due to the second law. The efficiency of energy conversion is the ratio of the desired output energy, or work, to the necessary input energy, a ratio that can range from about 5% for an incandescent. Moore (1981) recommends the following guidelines to ensure that the conservation of free or available energy is maximised when energy is supplied in a converted form in order to carry out a task. Firstly, there should be a minimum number of energy conversion steps. Each unnecessary energy conversion step involves an unnecessary loss in free energy, as there is a severe penalty in transforming the energy of heat into mechanical work. Secondly, heat should be converted into work at the highest possible temperature and should be undertaken only once. Thirdly, the direction of any series of energy conversion processes should proceed from those with maximum conversion efficiencies to those with a lower efficiency of conversion. Finally, energy should ideally be stored in work reservoirs such as compressed air, mechanical springs, and pressurised liquids as such devices provide the potential for minimal energy storage loss.

4.3 First and second law efficiencies

The first and second law efficiencies are measure of the efficiency in carrying out a specific task such as heating or lighting a building or providing a transportation network. The first law efficiency is the ratio of the energy delivered by the process in the form and location necessary to achieve that task to the amount of energy supplied to the process. Although the first law can be used as a measure of energy conservation in carrying out a task, it should be noted that the quality of energy conserved is not taken into account. Nor is there any differentiation between energy losses caused by imperfections in the energy conversion process and energy losses due to the second law that cannot be avoided even by perfect technology.

These factors are included in the second law efficiency which is the ratio of the minimum amount of available energy required to carry out a task to the actual amount of available energy used. The second law efficiency is a measure of how much the performance of a task falls short of what is theoretically possible and can be used as a measure of the conservation of free, or available energy in carrying out a task.

An examination of the task of heating a house provides an illustration of the difference between first law and second law efficiencies. In an example provided by Ehrlich et al. (1977) a standard furnace is able to deliver 1 unit of energy for heating a house for every 1.5 units of energy extracted from its fuel. The first law efficiency is

$$\frac{1 \text{ unit of heat}}{1.5 \text{ units supplied}} = 67 \%. \quad (83)$$

By using the most efficient Carnot heat pump where the COP is solely dependent on the temperature difference inside and outside the house the minimum amount of available work required to deliver 1 unit of heat is 0.07 units. The available work in a chemical fuel is approximately equal to its heat of combustion or enthalpy. The available work used by the furnace remains at 1.5 units. The second law efficiency is

$$\frac{0.07 \text{ units minimum available work}}{1.5 \text{ units available work of furnace}} = 4.7 \%. \quad (84)$$

The second law efficiency is based on comparing actual processes with idealistic processes that do not necessarily include a realistic time frame. There is a trade-off between efficiency and power. An infinitesimally slow reversible process may be carried out with maximum efficiency but with a penalty of a power output approaching zero. A very rapid process, on the other hand, approaches a maximum power input but at zero efficiency and zero power output. Life forms and the activities of humankind require energy processes to be carried out at an intermediate range of rates that fall well short of the maximum second law efficiency. Odum and Pinkerton (1955) propose that natural systems tend to operate at an efficiency that produces a maximum power output but Peet and Baines (1986) caution that although the maximum power principle represents deduction from a wide range of empirical observations, its universality has yet to be proved or generally accepted.

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