PART I

THE APPLICATION OF SOME THERMODYNAMIC PRINCIPLES TO ESTIMATE THE LIKELIHOOD OF LIFE IN THE SOLAR SYSTEM

James Paul Wesley

University of Missouri, Rolla, Missouri

Final report on work done under the National Aeronautics and Space Administration grant: NGR 26 004 014 over the period from February 1965 to February 1966.

Abstract

27929

The present monograph constitutes Part I of the material which will be eventually written. If living objects are defined to be open thermodynamic systems which create and maintain internal states of low entropy by dissipating energy, then only certain environments are favorable to life. One measure of the ability of an environment to support life is its entropy production. A finer measure of the ability of an environment to support life is the efficiency with which the available solar energy can be converted to useful mechanical work. The maximum efficiency with which thermal energy can be converted to useful mechanical power is considered for two idealized heat engines. An upper bound is postulated for the power efficiency of any actual heat engine which is less than the Carnot efficiency. The likelihood of life having entered the solar system from without is considered. It is indicated that sophisticated life forms might be found close to the sun.

Part II will examine the potentials of the various planets, asteroids, and sun for sustaining life, utilizing some of the general theory derived in the present monograph.

CONTENTS

INTRODUCTION

There has been considerable speculation about the possible existence of life on the various planets in the solar system (eg., Jackson and Moore, 1962; Oparin and Fesenkov, 1961; and Tocquet, 1962). This speculation has been largely limited to estimating the static characteristics of a planet's surface. The temperature, pressure, chemical composition of the atmosphere of the planets have been considered to get some idea of the type of chemical compounds that might exist on the planet. It is generally assumed that life must be based upon carbon chemistry and that the environment must be capable of supporting complex organic compounds such as found on the earth. Because life on the earth tends to favor the production of compounds that show optical rotary activity while inorganic synthesis does not, it has been proposed that life might be detected on the surface of a planet by measuring the optical activity of the compounds found on the surface.(Stryer, 1966).

While the use of chemical techniques to evaluate the possibility of life existing on the various planets should be capable of estimating the likelihood of earth-like life being present, it cannot yield a proper estimate of the likelihood of extremely alien life forms existing. A novel and more fundamental approach to the problem is proposed here. Rather than identifying life by its chemical structure and its static characteristics, it is proposed that life may be better identified by its thermodynamic behavior. For example, life consumes high utility energy in order to maintain an internal state of low entropy; so that the consumption of energy may be chosen as one thermodynamic behavioral characteristic which serves to distinguish the living from the nonliving. It is the dynamic, rather than the static, characteristics of the surface of a planet which can, thus, yield more pertinent information with respect to the problem of the likelihood of life existing. For example, an environment favorable to life must supply high utility energy at a constant rate in order to support the energy requirements of life.

PROPOSED DEFINITION OF LIFE

Before it is possible to estimate the likelihood of life occurring somewhere in the solar system, it is necessary to establish some means of identifying _life_. As is now generally recognized, there is no absolute way to distinguish living objects from nonliving objects (Pirie, 1937). In everyday usage the word _life_ is primarily anthropomorphic; the more characteristics an object has which are similar to those of man, the more the object is imbued with _life-like_ properties.

While the anthropomorphic connotations of the word _life_ may be deplored as being egocentric, unscientific, and nonobjective, they do serve to indicate the real reason and motivation for the search for _life_ in the solar system. The search is for man-like objects. The likelihood of finding anything elsewhere in the solar system even remotely similar to man with all of his multitudinous attributes is, of course, extremely unlikely. Never-the-less, certain properties of objects are of more interest than other properties depending upon how man-like these properties are. The problem of estimating the likelihood of finding _life_ in the solar system may now be placed in its proper perspective: It is the search for objects with man-like properties. There is no need to claim that the search is for objects with some strange, peculiar, unique, or mysterious properties which distinguish them absolutely as living. It is now possible to list the properties of interest quite naively and without regard for any absolute or mystical definition of life.

The man-like properties of greatest interest should not, of course, be trivial properties. For example, even the most anthropomorphic view does not attribute life to a statue merely because the geometrical conformation of the statue agrees approximately with the gross external static geometrical conformation of a man. The greatest concern here will be with objects which are man-like in the most fundamental thermodynamic sense. In particular, the objects or life whose existence is sought are taken to have the following characteristics:

1) Objects that are open thermodynamic systems exchanging energy, compounds, and radiation with their environment.

2) Objects that maintain elements in internal states of entropy which are lower than the entropy of the same elements as normally found in the environment.

3) Objects that create or maintain thermodynamic order (low entropy) by dissipating high utility energy to low utility energy.

These three attributes may be too few to distinguish what is ordinarily regarded as life; yet, these characteristics are so overwhelmingly important that further delineations would merely serve to detract from the utility of this generalized thermodynamic concept of life.

A refrigerator satisfies these three criteria: A refrigerator is an open system consuming electrical energy and eliminating thermal energy. It maintains an internal state of lower entropy (by maintaining an internal state of lower temperature). And the internal state of higher thermodynamic order (lower entropy) is achieved by the dissipation of high utility electrical energy to low utility thermal energy. At first glance it appears absurd to call a refrigerator a living object; and according to the usual multitudinous criteria used to define living objects it is absurd. Yet if we recognize the fact that a refrigerator is at least man-like in the essential three thermodynamic characteristics mentioned, then we can view the refrigerator as a most unusual object, one which in the present context might be worthy of being called living.

If a refrigerator-like object were discovered on Mars, it would be a discovery equivalent in importance to finding grass-like objects or objects similar to other common earth-like life. Not only is the refrigerator an unusual object by itself, it also implies the simultaneous existence of other life forms. The refrigerator plays only one small role in the ecological thermodynamics of the earth's surface. If found on Mars the refrigerator (or refrigerator-like object) would also presumably function as only part of the ecological thermodynamics of the surface of Mars. The refrigerator would presumably be found in conjunction with other life forms.

Automobiles and other devices powered by heat engines also satisfy the three general thermodynamic characteristics that are man-like, assuming the work produced by these devices is used to create or maintain thermodynamic order (low entropy). These are objects which would also be of extreme interest if found elsewhere in the solar system. Devices operated by heat engines are playing an ever increasing role in the ecological thermodynamics of the earth's surface. It is very useful to include machines within the category of living things in order to get an undistorted thermodynamic picture of the biosphere. As an indirect indication of the importance of such devices, it has been estimated that over the last 50 years the burning of fossil fuels (about 30 percent being consumed by heat engines) has increased the CO_2 content of the atmosphere by 13 percent (Bray, 1959).

Objects even farther removed from what we ordinarily regard as living can also satisfy these three thermodynamic criterion. For example, consider a salt crystal growing in a shallow ocean bay where the water is continually evaporated by sunlight thereby keeping the salt solution always saturated. The salt crystal under these circumstances is an open system which consumes sodium and chlorine ions and dissipates thermal energy. The crystal maintains an internal state of low entropy, the entropy of the sodium and chlorine ions being much greater in solution than in the crystal. The saturated (or slightly supersaturated) salt solution provides the high utility energy necessary for crystal growth. The low utility energy becomes dissipated as heat.

While one might shrink from labling crystals in a state of exchange with their environment as living, a number of pertinent observations can be made: Basically the structure of life, as it is now being revealed by good electron micrographs of the smallest organelle membranes, is crystaline, i.e., is highly ordered arrays of molecules. (The protoplasmic soup of 30 years ago has vanished with modern knowledge.) Since the most basic structure of life is the crystal, the life-like properties of the growing salt crystal should not be discounted.

Crystal growth can play an important role in the thermodynamics of the earth's surface (e.g., the growth of ice crystals). The process of crystalization frequently envolves a reduction of entropy by concentrating one compound which may have been originally extremely dilute in the environment.

The process of crystal growth yields ore deposits which can be utilized by man as well as other life forms. Crystals may thus be likened to homotrophic organisms which provide food for heterotrophic organisms.

The process of growth and the ability to reproduce by growing on seed crystals are certainly life-like properties. If one is to conjecture about the evolution of complicated life forms from inanimate beginnings, one is forced to consider the crystal as a most likely forebearer. The existence of certain chemicals in the environment such as amino acids is the first step; but the next step is necessarily the structural arrangement of these chemicals in ordered arrays. The competitive crystalization (and or polymerization) of these ordered arrays from the primordial soup may then be envisioned as favoring the more complicated structures which have evolved into present-day life.

The environmental conditions which permit a crystal to grow are the conditions which permit the system to decrease in entropy. Environments which provide the opportunity for entropy reduction are rare. Since ordinary life forms can only exist in entropy reducing environments, a growing salt crystal arises from precisely the same basic thermodynamic conditions as support ordinary life forms. It may therefore be expected that crystal growth may compete both for high utility energy and certain chemicals with ordinary life forms.

All of these important similarities between a growing crystal and ordinary life forms, besides the conformity with the general thermodynamic definition of living objects, indicate the usefulness of including the growing crystal among living objects.

If the surface of Mars possesses growing crystals, this is thermodynamically equivalent to Mars possessing any form of life.

The usual approach to the search for <u>life</u> in the solar system is based upon a static definition or concept of <u>life</u>. It is usually assumed that carbon compounds are a necessary ingredient of <u>life</u>. According to this definition <u>life</u> will only exist where the appropriate carbon chemistry can exist. Unfortunately this criterion or definition of life does not tell one either the thermodynamic role that a <u>living</u> object is likely to play in the environment or how the <u>living</u> object is likely to behave. It is easy to conceive of an object that could be manufactured to look and act like a man, but would, in fact, be composed of metals and would be powered by electric motors or internal combustion engines. The fact that such a robot or mechanical android is conceivable indicates that the gross external behavior of an object need have little to do with its internal chemical composition. The general dynamic definition adopted here immediately singles out those objects that are of interest by virtue of their unique behavior; it is independent of any particular internal structure. When attempting to cope with a living object by trying to ward off its hostile attacks, by trying to communicate with it, by trying to kill it, or by having any time dependent interaction with it, it is the dynamic behavior of the object which is of overriding importance. Its internal chemistry is largely a matter of indifference. A fresh cadaver being comprized of exactly the same compounds as the living man still lacks the dynamic features which would be necessary to say that it is alive.

It is frequently claimed that carbon chemistry is requisite for <u>life</u>, because only carbon chemistry can provide the requisite complexity. But ordinary life forms, in agreement with the general thermodynamic definition of <u>life</u> adopted here, are comprized of compounds of low entropy which were derived from compounds of higher entropy in the environment. This means that ~~life~~ produces simpler ~~systems~~ rather than more complex systems. Thermodynamically the microstate of a system is specified when the position and momenta of all of the atoms comprizing the system are specified. The greater the thermodynamic order, the lower the entropy, and the fewer statememts are needed to specify the microstate of the system. For example, the microstate of a pure crystal may be specified by the lattice spacings, the crystal orientation, and position of the crystal, the position (neglecting small oscillations) of each of the atoms being thereby specified. If the same atoms were in a gaseous state the position and momenta of each atom would have to be specified independantly to specify the microstate of the system. Thus, microscopically or thermodynamically a crystal is a simpler system (it requires fewer statements for its microscopic specification) than the same atoms in the gaseous phase. In general a lower entropic state is thermodynamically simpler. The assumption that life requires a complex chemistry is contrary to the direction of behavior of living systems. It is conceivable that an alien life form having no carbon atoms and being quite simple in structure could replace and eliminate man if such alien life were capable of preempting the available supply of high utility energy. The argument for complexity being merely specious, there is no need to assume carbon chemistry for life.

It may also be noted that complex carbon chemistry can occur in nature without the apparent intermediation of life (at least, in so far as it is known on the earth). Carbonaceous meteorites have been found to possess extremely complicated aromatic hydrocarbons which could not have arisen as products of life chemistry as it is known on the earth (Studier, et al, 1965).

The stipulation that life be composed of carbon compounds or any other particular compounds is a micromorphological specification which is quite comparable to ascribing life to a statue merely because it has the macromorphological approximation of a man. The most basic characteristics to differentiate life should be based upon the thermodynamic behavior of an object. The thermodynamic behavior of an object indicates the potential dynamic relationship that man may have with the object. Objects which utilize high utility energy sources to maintain internal states of low entropy are potential threats to man's survival in the same environment. Such objects might be able to compete with man for the energy supply available. Such objects,on the other hand,may be useful sources of high utility energy. In either case man's survival in an alien environment will depend upon the life (as defined here) which is already in the environment.

Another characteristic which is frequently proposed as a defining property to distinguish living objects from nonlinving objects is the specification that living objects self replicate. This criterion is broad enough to include some crystals that need a seed, nuclei, germ, or information from a parent crystal in order to reproduce. For example, in World War I the Americans were initially unable to synthesize trinitrotoluene (TNT) in crystalline form; it remained in a liquid phase. It was only after crystalline TNT from a dud German shell was imported into the United States that it was possible to manufacture crystalline TNT. Today there are enough nuclei in the air at all times to produce crystaline TNT with ease.

This definition fails, however,to include virus, since virus do not self replicate. A virus particle carries information into a host cell. The host cell then acts as a factory which manufactures the new virus particles. The definition also fails to include such thermodynamically interesting objects as automobiles or refrigerators. While automobiles and refrigerators do not carry the information for their own reproduction as do crystals, virus, and other life forms, they are reproduced. Automobiles and refrigerators are reproduced in factories where the information for their manufacture is permanently stored.

Even if the self replicating property were a good criterion for differentiating _living_ objects from nonliving objects (which it is not), the triviality of the property seriously detracts from its usefulness. If we again conceive of a robot that is constructed of metal and electric motors and that behaves like a man, the question of whether or not this object self replicates or is reproduced in a factory becomes purely academic. One will be usually concerned with how the object behaves. How it was manufactured or brought into being in the first place is of quite secondary importance. The detailed nature of the reproduction of life should not be chosen as an important feature to delineate _living_ objects from nonliving objects.

While the general thermodynamic definition of _life_ adopted here appears to neglect many of the secondary features that we associate with _life_, many of these secondary characteristics can be shown to follow from the definition. For example, in the process of creating compounds of lower entropy there is a process of growth or an increase of biomass. The decrease in the entropy of the earth's surface with geologic time is in part effected by life tending toward an increased biomass. In general it may be expected that the growth of a single object will be limited due to the exhaustion of appropriate compounds in the immediate neighborhood of the object together with limited transport of compounds to the object or will be limited due to a variety of circumstances. The tendency for an increase in biomass must in general be reflected in the growth of a number of identical objects. The death or decay of the objects will then give rise to new objects. The process of replacement and growth, which can be called reproduction, should therefore be a characteristic of all forms of life. Man, virus, automobiles, and salt crystals are all reproduced (even though they are not reproduced by the same mechanism).

Motility is another secondary characteristic of life which may be deduced from the general thermodynamic definition adopted here. Since the living process involves a process of increasing thermodynamic order, randomly arrayed atoms must be selected from a large volume of the environment and converted into internal ordered arrays in a small volume. This means that atoms must be moved from the random sites to the sites where they are organized into ordered arrays. There must be material transport in order for compounds to be converted from states of high entropy to compounds in states of low entropy. Since mass transport is requisite for growth, and therefore life, it may be expected that life forms will evolve which will enhance mass transport. The occurrence of cilia which move fluids at a faster rate than provided by natural diffusion is an example of such specialization. Thermodynamically the organism moving the fluid is equivalent to the organism moving itself through the fluid. Therefore, motility is expected to be a frequent evolutionary specialization as implied by the general thermodynamic definition of life. Living objects need not, however, be motile; they can depend upon natural transport processes such as provided by the wind or diffusion of salts in solution.

It should be noted that the general thermodynamic definition of life adopted here, being a dynamic concept, is not dichotomous. The definition implies a continuous gradation from a state of greater life (or faster living) to a state of lesser life (or slower living) to a state of no life (or zero rate of living). For example, a salt crystal growing at a fast rate is more alive than a salt crystal growing at a slow rate. If the salt crystal is not growing at all, then it is in a state of no life. It is similarly possible to define various states of death or dying depending upon how fast the salt crystal is dissolved away. According to the present thermodynamic definition an amoeba while frozen in ice for thousands of years is not alive, since it is not an open thermodynamic system and it does not dissipate high utility energy to low utility energy. If such an amoeba (as may actually be found in the Antarctic ice pack) is thawed out it will again carry on its usual life processes. It proceeds from a state of zero life to a state of active life. Those who use a chemical or micromorphological definition of life might prefer to say the frozen amoeba was alive. Here, however, the frozen amoeba merely possesses the potential for life and cannot be said to be alive.

Systems or objects which possess the potential for life while in a state of zero life are, quite obviously, of great interest.

SOME THERMODYNAMIC BACKGROUND

One of the more significant characteristics of ordinary living organisms as known on the earth is their ability to create and maintain an internal state of entropy lower that the entropy of the same elements in the usual environment (Schroedinger, 1956; Asimov, 1962; and Pardee and Ingraham, 1960). Since most physical systems in nature when left to themselves proceed with time toward a state of thermodynamic disorder or high entropy, only very special environmental conditions are compatible with the thermodynamic ordering behavior of living systems. It is evidently by virtue of the continual dissipation of energy that living organisms can create and maintain internal states of low entropy. They take energy of high utility (a large fraction of such energy may, in principle, be converted to mechnical work) and convert it to energy of low utility (only a small fraction of such energy may, in principle, be converted to mechanical work). For example, green plants dissipate the high utility energy of sunlight by converting it into low utility thermal energy (neglecting the small fraction which becomes stored as chemical energy). In this way green plants convert gaseous CO_2 and liquid H_2O, which have high entropy, into solid cellulose which has low entropy. They also reduce the entropy of the atmosphere when the 0.033 percent of CO_2 is separated from the remaining constituents of the atmosphere (the entropy of mixing).

Second law of thermodynamics

The second law of thermodynamics (Sears, 1953a) states that the net change of the entropy of the universe for a given process never decreases,

$$dS(\text{universe}) \geq 0 \quad , \tag{1}$$

where S is the entropy and the equality holds for reversible processes only. In order for living organisms to decrease the entropy of the materials taken from the environment and included within their bodies, the remainder of the universe mustsuffer a correspondingly larger increase in entropy; from Eq.(1) this means

$$- dS(\text{internal to organism}) < dS(\text{universe external to organism}) \quad . \tag{2}$$

An important conclusion may be drawn from Eq.(2): the larger the right side, the larger the left side can be potentially. Thus, the larger the increase in the entropy external to the organism, the greater the potential the organism has for creating thermodynamic order internally. It may be concluded that ordering processes, including life, will arise only in environments that are increasing the entropy of the universe. The environment that produces the greater time rate of increase in the entropy of the universe (the <u>entropy production</u>) will provide the greater potential for ordering processes such as life to occur.

<u>Entropy production of planets</u>

A closed system cannot increase the entropy of the universe indefinitely, so that a closed system will not be able to support life indefinitely. The surface of a planet is an open system supplied with high utility solar energy which is reradiated as low utility thermal energy. The surface of a planet increases the entropy of the universe at a steady rate. Radiant energy, dQ, that leaves the surface of the sun decreases the entropy of the sun by the amount $-dQ/T_1$ where T_1 is the effective surface temperature of the sun. This radiant energy leaving the sun carries away an equivalent amount of entropy (Epstein, 1937), in order for the second law of thermodynamics to be satisfied for the reversible radiative process (Eq.(1) with the equality). If this radiant energy is absorbed by a planet an equivalent amount of energy is reradiated in order for the planet to maintain thermal equilibrium. The energy reradiated will be at the temperature T_2 of the planet's surface. The energy passes into deep space carrying an entropy dQ/T_2. The planet, thus, converts radiant energy from the sun carrying entropy of the amount dQ/T_1 to radiant energy passing into deep space carrying entropy of the amount dQ/T_2. The net entropy production (net increase in the entropy of the universe per unit time) by the planet is then

$$\frac{dS}{dt}(\text{universe produced by planet}) = \frac{dQ}{dt}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad . \tag{3}$$

Since the surface of a planet increases the entropy of the universe with time, according to Eq.(3), the surface of a planet has the potential of becoming more ordered with time. In particular, writing the second law, Eq.(1), in the form

$$-\frac{dS}{dt}(\text{internal to planet}) < \frac{dS}{dt}(\text{universe external to planet}) \quad , \tag{4}$$

where the increase in the entropy of the universe external to the planet may be taken as Eq.(3), it becomes apparent that the entropy of the planet has the potential of decreasing with time.

Examining the earth about us there are many indications that the earth is becoming more ordered with geologic time (Gutenberg, 1951). There was a vast decrease in entropy when the earth condensed out of the primordial gas cloud. The separation of the compounds forming the crust, mantle, and core represent another vast decrease in entropy. The lithosphere appears to be separated into highly differentiated deposits of compounds compared with the relatively homogeneous underlying basalt. The separate deposits of limestone, salt, iron oxide, coal, etc. represent a decrease in entropy. These deposits appear to have arisen from both organic and inorganic processes.

Energy dissipation and entropy

The present investigation,being concerned with dynamic (time dependent) processes, is faced with the problems of irreversible thermodynamics (Onsager, 1931; Prigogine, 1955; and de Groot and Mazur, 1962) as opposed to ordinary thermodynamics (or thermostatics) where time is not treated explicitly. The relationship between the internal entropy of a nonisolated system and the rate of dissipation of energy is an important relationship for living systems (Bertalanffy, 1950). Not only does the internal state of low entropy that each organism enjoys depend upon upon the rate at which it can dissipate energy but the low entropy of the entire biosphere depends upon the rate at which the biosphere dissipates energy.

The essential characteristics of a system that maintains an internal state of low entropy by dissipating energy is provided by the example of an ideal gas conducting heat between two plane boundary surfaces a distance b apart, one surface being maintained at temperature $T_o + \Delta T$ and the other at a temperature $T_o - \Delta T$. When the gas is at a uniform temperature T_o the entropy, S_o, per unit area of the boundary surfaces, as given by the ideal gas formula (Sears, 1953b), is

$$S_o = C_v \ln T_o \quad , \tag{5}$$

to within an additive constant where C_v is the heat capacity at constant volume per unit boundary area.

Letting the distance normal to the boundary surfaces be designated by x, the left-hand boundary at $-b/2$ is maintained at the temperature $T_o + \Delta T$, and the right-hand boundary at $+b/2$ is maintained at the temperature $T_o - \Delta T$. The entropy per unit distance (and area) may be written as

$$dS/dx = (C_v/b) \ln T(x) \quad , \tag{6}$$

where in general T may also be a function of the time t. Assuming the thermal conductivity of the gas does not change with temperature (the total range of temperature being maintained small enough) the steady-state equilibrium temperature will be a linear function of the distance between the boundary surfaces; in particular,

$$T = T_o - 2\Delta T\, x/b \quad . \tag{7}$$

Substituting Eq.(7) into (6) yields the steady-state value for the entropy per unit distance (per unit area)

$$(dS/dx)_s = (C_v/b)\ln(T_o - 2\Delta T\, x/b) \quad . \tag{8}$$

Integrating Eq.(8) yields the total steady-state entropy per unit area,

$$\begin{aligned} S_s &= C_v \ln T_o - C_v\left\{1 + (1/2y)\ln\left[(1-y)/(1+y)\right] - \tfrac{1}{2}\ln(1-y^2)\right\} \\ &= C_v \ln T_o - C_v\left\{\frac{y^2}{2\cdot 3} + \frac{y^4}{4\cdot 5} + \frac{y^6}{6\cdot 7} + \cdots\right\}, \end{aligned} \tag{9}$$

where $y = \Delta T/T_o$. Comparing Eqs.(5) and (9), it is clear that the entropy of the gas is less than it would be if no heat were flowing.

A number of interesting observations may now be made concerning the steady-state equilibrium of this simple system. The greater the temperature difference maintained, the lower the entropy of the gas. The rate that the system dissipates energy per unit area is given by

$$dQ/dt = 2\sigma\Delta T/b \quad , \tag{10}$$

where σ is the thermal conductivity of the gas. From Eqs.(10) and (9) it may be concluded that the greater the dissipation of thermal energy, the lower the internal entropy that can be maintained.

The entropy production may be computed by noting that the heat source on the left experiences a decrease in entropy per unit time (per unit area) of the amount $-(T_o + \Delta T)^{-1}dQ/dt$, while the heat sink on the right experiences an increase in entropy per unit time of the amount $+(T_o - \Delta T)^{-1} dQ/dt$, the net increase in the entropy of the universe per unit time (per unit area) being

$$\left(\frac{dS}{dt}\right)_s = \frac{2\Delta T}{T_o^2 - (\Delta T)^2}\frac{dQ}{dt} = \frac{4\sigma}{b}\frac{(\Delta T)^2}{T_o^2 - (\Delta T)^2} . \qquad (11)$$

Solving Eq.(11) for $y = \Delta T/T_o$ in terms of $(dS/dt)_s$ and substituting into Eq.(9), it may be seen that the greater the entropy production, the lower the entropy that can be maintained internally. In particular, for small y Eq.(9) yields

$$S_s \approx C_v \ln T_o - (C_v b/24\sigma)(dS/dt)_s . \qquad (12)$$

This simple example illustrates many of the essential thermodynamic characteristics of both a single living organism and the environment in which it lives.

Internal entropy changing with time

Since the surface of the earth is evolving with geologic time, it is not quite in steady-state equilibrium. Similarly, a growing organism is not quite in steady-state equilibrium. These systems involve a slowly varying transient change in internal entropy.

An extremely simple example of such a non-isolated system undergoing a transient change in internal entropy is provided by the above example of an ideal gas conducting heat between two plane boundaries before the gas has had time to attain steady-state equilibrium. To find the temperature of the gas between the infinite plane boundaries as a function of position and time the appropriate equation (assuming a small total range of temperatures) is the diffusion equation,

$$\partial T/\partial t - k\,\partial^2 T/\partial x^2 = 0 \;, \tag{13}$$

where the diffusivity, k, (Joos, 1934) is defined by $k = \sigma/\rho c$ where ρ is the density and c is the specific heat at constant volume per unit mass.

Assuming an initial state of steady-state equilibrium, the temperature being specified by Eq.(7), it is of interest to inquire into the change in the internal entropy with time when the boundaries are suddenly changed and maintained at new temperatures, $T_o + \Delta T_2$ on the left and $T_o - \Delta T_2$ on the right. The differential equation (13) is to be solved subject to the intial temperature distribution given by

$$T = T_o - 2\Delta T\, x/b + (\Delta T_2 - \Delta T)\left[1 - u(x + b/2) - u(x - b/2)\right] \;, \tag{14}$$

where u(x) is the unit step function , 1 for $x \geq 0$ and 0 for $x < 0$.
The solution of Eq.(13) subject to the initial condition, Eq.(14) may be taken as the final steady-state solution (Eq.(7) with ΔT_2 replacing ΔT) plus an appropriate transient solution that vanishes as $t \rightarrow \infty$. Assuming that T may be written as the product of a time function and a space function and expanding the space function into an odd Fourier series (Morse and Feshbach, 1953), the solution is found to be

$$\begin{aligned} T = T_o - 2\Delta T_2\, x/b + \frac{2}{\pi}\sum_{n=1}^{\infty}\Big\{2(-1)^n\Delta T + (\Delta T_2 - \Delta T)\Big[(-1)^n \\ - \cos(n\pi/2)\Big]\Big\}\, n^{-1}\sin(n\pi x/b)\,\exp\left[-k(n\pi/b)^2 t\right] \;. \end{aligned} \tag{15}$$

The important characteristic of the transient part of this solution, Eq.(15), is the exponential time decay. Whether the new ΔT_2 is greater than or less than the original ΔT, the solution proceeds monotonically to its final steady-state temperature distribution. If the temperature difference is increased the entropy of the gas decreases. If the temperature difference is decreased the entropy of the gas increases. The monotonic character of the time variation of the internal entropy (neglecting microscopic fluctuations) in this example may be assumed to be valid in general for any non-isolated system proceeding toward steady-state equilibrium, since it may be shown that the steady-state equilibrium is a state of stable equilibrium (Prigogine, 1955). This means that if the entropy of the surface of the earth is decreasing with time (as appears to be the case), then it has been decreasing for geologic times in the past and will continue to decrease far into the future until a final steady-state equilibrium is attained.

Utility of energy

Since energy must be conserved according to the first law of thermodynamics, dissipation of energy merely means the conversion of energy from a state of high utility to a state of low utility. The concept of the utility of energy, thus, becomes very important. It is the measure of the value of a unit of energy and would presumably determine the economic price of a unit of energy. Here the utility of energy will be precisely defined as the ratio of the amount of energy that in principle could be converted to mechanical work to the total amount of energy available. Since the total amount of energy that can be converted to useful mechanical work is always less than or equal to the amount of energy available, the utility of energy, η, will lie between zero and unity. According to this definition, the utility of mechanical work is unity and is therefore valued the most.

The energy stored in many mechanical systems has a utility of unity, since it may all be recovered as useful work. Such sources of maximum utility include the kinetic energy of a moving macroscopic body, gravitational potential energy, electrostatic potential energy, the potential energy of deformation of a spring (neglecting internal friction), etc.

For statistical processes the amount of energy that can be converted to useful mechanical work is necessarily less than than the total amount of energy available (Sears, 1953a). For example, the utility of thermal energy at a temperature T (in degrees Kelvin) may be taken as the efficiency of a Carnot engine (Epstein, 1937b) operating between this temperature, T, and some infinite heat sink at a temperature T_o; thus,

$$\eta_c = 1 - T_o/T \quad . \tag{16}$$

From this expression it is clear that the higher the temperature T, the higher the utility of the source of thermal energy. The temperature T_o may be chosen as any convenient reference temperature (eg., 20°C).

In an isothermal process the work done by a system equals the decrease in the Helmholtz free energy, $dW = - dA$ (where $A = E - TS$ where E is the internal energy, and S is the entropy). In an isobaric process the heat evolved (heat of reaction) equals the increase in the enthalpy, $dQ = dH$ (where $H = E + pV$). The utility of the energy released by a chemical reaction performed at constant pressure, p, and temperature, T, becomes

$$\eta = dW/dQ = - (dA/dH)_{T,p} \quad , \tag{17}$$

(Rossini, 1955).

It is important to note that the <u>utility of energy</u> only has meaning within the context of the prescribed conditions for conversion of the energy to useful mechanical work. The above examples, Eqs.(16) and (17) are the utility of the energy for processes carried out infinitely slowly. These examples are valid only within the thermostatic context. In general for processes carried out at a finite rate the utilities will be smaller.

Maximum efficiency of conversion of heat to work at a finite rate

Investigations into time rate processes or irreversible thermodynamics (or simply thermodynamics) have been largely limited to the investigation of simultaneous diffusion processes. For example, the diffusion of electric charge through a conductor together with the simultaneous diffusion of heat. Little progress has been made beyond Onsager's original paper (1931). Since many of the irreversible processes of interest here do not explicitly involve diffusion processes, the work of Onsager is not particularly applicable. A problem of great interest in irreversible thermodynamics, and of particular interest here, is the problem of finding a realistic upper limit (or upper bound) for the efficiency of conversion of heat to work at a finite rate (eg., Green, 1963; Osterle, 1964; and Kayan, 1964).

A Carnot heat engine is a theoretical device whose efficiency, Eq.(16), is attained only under the assumption that all processes are carried out infinitely slowly, i.e., thermostatically or reversibly. Because of this requirement, a Carnot engine of finite size delivers infinitesimal or zero mechanical power. The efficiency of the Carnot engine, therefore, does not represent a realistic estimate of an upper bound for the efficiency of conversion of heat to work at a finite rate. The efficiency of the Carnot engine, while useful for establishing the second law of thermostatics and for deducing possible internal thermostatic states of systems, has little direct bearing upon the problem here of finding a realistic upper bound for the power efficiency of actual heat engines which operate at a finite rate.

From the second law of thermostatics it is deduced that it is impossible for any heat engine (operating either infinitely slowly or at a finite rate) to exceed the efficiency of a Carnot engine. The efficiency of the Carnot engine, therefore, does in fact provide an upper bound for the power efficiency of actual heat engines. Unfortunately, this upper bound is much too high to be of any real significance. As will be shown, the maximum power efficiency (the time rate of delivery of mechanical work to the time rate of consumption of thermal energy) that can be attained is far less than the thermostatic efficiency of the Carnot engine.

Ideal heat engine operating at a finite rate - To obtain a smaller and more realistic upper bound for the power efficiency of actual heat engines an idealized device may be considered which when operated at a finite rate will yield the greatest efficiency conceivable. Such a device must have the fewest possible irreversible losses, in order for the power efficiency obtained to be an upper bound for all actual heat engines.

The idealized device must also be sufficiently simple so that the efficiency obtained will be a function of the nature of the source and sink without reference to internal design parameters. In this way the ideal power efficiency obtained will remain an upper bound for all actual heat engines independent of the particular internal design of the actual heat engine.

These requirements lead to the particular idealized device represented within the dashed lines in Figure 1. This ideal heat engine consists of a reversible heat engine (Carnot engine)operated in competition with a parallel irreversible heat loss for the thermal energy provided at a finite rate. In particular, this ideal heat engine is assumed to be operated under the following conditions:

1) Heat is supplied at a fixed finite rate, $\dot{Q}$.

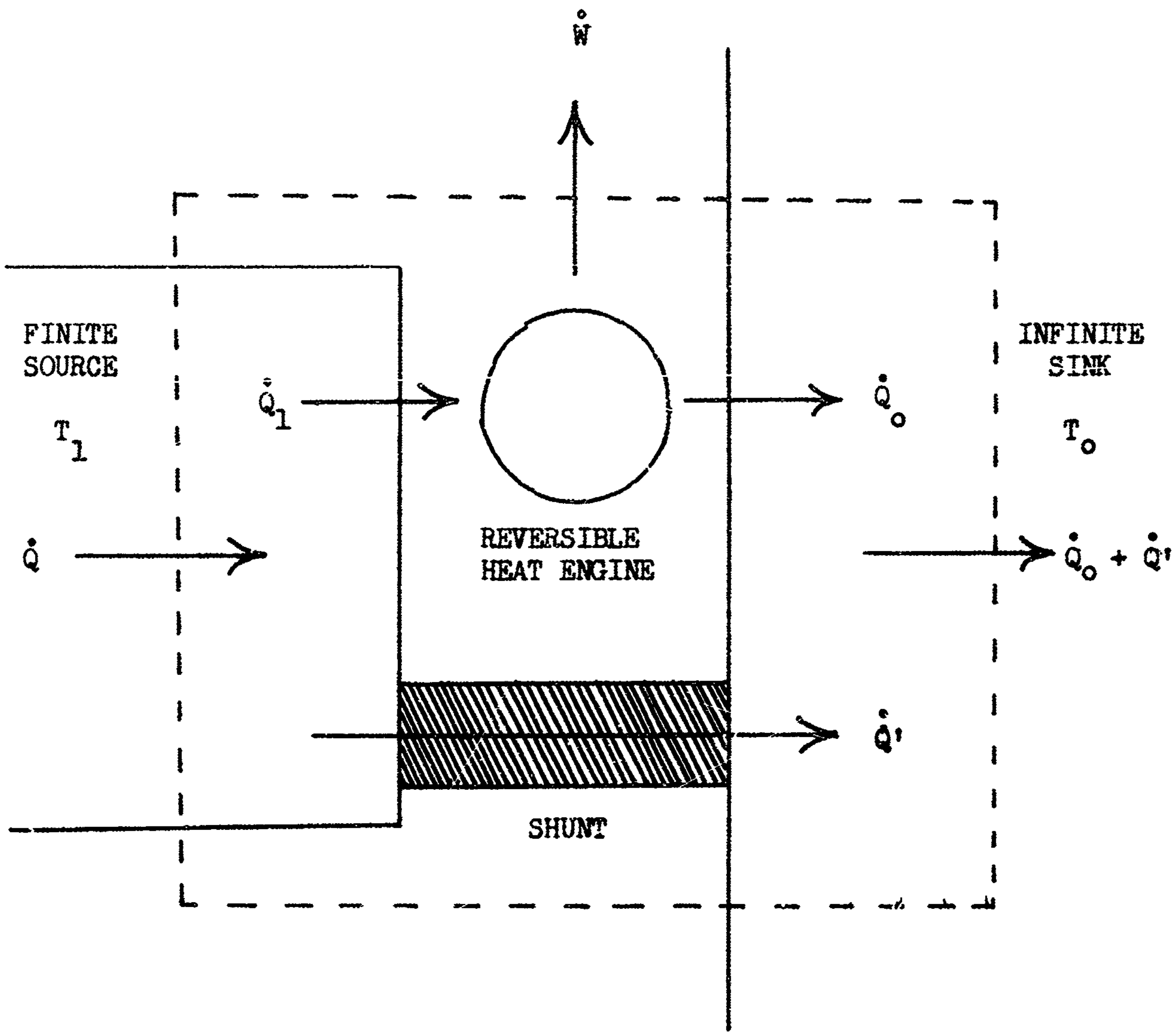

Figure 1. Ideal device (contained within the dashed lines) operating at a finite rate between a finite source and an infinite sink which consists of a reversible heat engine together with an irreversible heat loss through a shunt (shaded area). Symbols are defined in the text.

2) The temperature of the source, T_1, is not prescribed initially.

3) Heat is lost at a finite rate, $\dot{Q}'$, directly to an infinite sink (maintained at the temperature T_o) through a loss mechanism that bypasses the reversible heat engine.

4) The reversible heat engine (the circle in Figure 1) is assumed to operate reversibly at all finite rates; so that $\dot{Q}_1/\dot{Q}_o = T_1/T_o$, where $\dot{Q}_1$ is the rate heat is delivered to the reversible engine and $\dot{Q}_o$ is the rate that heat is rejected by the reversible heat engine.

5) The rate that heat is lost directly to the sink, $\dot{Q}'$, through the loss mechanism is assumed to be a linear function of the temperature difference between source and sink, $\dot{Q}' = K(T_1 - T_o)$.

Power efficiency of the ideal heat engine - If $\dot{Q}_1$ is the rate that heat flows to the reversible heat engine and $\dot{Q}_o$ is the rate that heat is rejected to the infinite sink, then the rate that mechanical work is performed is given by

$$\dot{W} = \dot{Q}_1(1 - T_o/T_1) \quad , \tag{18}$$

according to Eq.(16) and assumption 4) above. From the conservation of energy the heat delivered at the finite fixed rate $\dot{Q}$ must equal the sum of the heat delivered to the reversible engine plus the heat lost directly to the sink,

$$\dot{Q} = \dot{Q}_1 + \dot{Q}' \ . \tag{19}$$

From assumption 5) above the irreversible thermal loss directly to the sink is proportional to the temperature difference,

$$\dot{Q}' = K(T_1 - T_o) \ . \tag{20}$$

The efficiency of the device for any temperature of the source T_1 may be found from Eqs.(18), (19), and (20) by eliminating $\dot{Q}_1$ and $\dot{Q}'$; thus,

$$\eta = \dot{W}/\dot{Q} = \left[1 - (K/\dot{Q})(T_1 - T_o)\right](1 - T_o/T_1) \quad . \tag{21}$$

To obtain the maximum power efficiency Eq.(21) may be differentiated with respect to T_1 and set equal to zero to yield the optimum operating temperature, $T_1 = T_m$ where

$$T_m = \left[T_o(T_o + \dot{Q}/K)\right]^{\frac{1}{2}} \quad . \tag{22}$$

Solving Eq. (22) for $K/\dot{Q}$ and substituting into Eq.(21) yields the desired maximum efficiency in terms of the optimum temperature T_m,

$$\eta_m = (T_m - T_o)/(T_m + T_o) \quad . \tag{23}$$

The remarkable feature of this result is that it does not depend upon the detailed nature of the idealized device. The maximum efficiency depends explicitly only upon the nature of the source and sink as indicated by the two parameters T_m and T_o. It is, of course, implicitly assumed that a parallel irreversible thermal loss varying linearly with the difference in temperature between the source and sink does exist.

Comparing this result, Eq.(23) with the efficiency of a Carnot engine, η_c, Eq.(16) operating between the same two temperatures, it is apparent that the efficiency of the ideal device operating at a finite rate is much less; thus,

$$\eta_m = \eta_c/(2 - \eta_c) < \eta_c \tag{24}$$

For high temperature sources where $\eta_c \rightarrow 1$ the maximum efficiency for the ideal heat engine operating at a finite rate approaches that of the Carnot heat engine. For low temperature sources where $\eta_c \rightarrow 0$ the maximum efficiency for the finite time rate of conversion of heat to work becomes just one half of the Carnot efficiency.

It may be noted that for the idealized device considered here that the source temperature rises to a peak value T_p when the reversible heat engine is disconnected. Ordinarily the peak temperature cannot be obtained in fact; since mechanisms, not considered here, usually come into play to limit the peak temperature that can be obtained. It may be noted that this parameter T_p from Eqs.(20) and (22) becomes

$$T_p = \dot{Q}/K + T_o = T_m^2/T_o \quad . \tag{25}$$

Plausibility arguments indicating that no actual heat engine can exceed the power efficiency specified by Eq.(23) - The idealized device diagrammed in Figure 1 would be of little interest except for the essential point that it suggests that no actual heat engine can have a power efficiency that is greater. To indicate that Eq.(23) probably is an upper bound for all actual heat engines the five assumptions presented above concerning the operation of the device will now be considered in some detail:

Assumption 1) that thermal energy is supplied at a finite rate is a requirement that is valid for all actual conditions as they exist in the real world for actual heat engines. Even if energy is extracted from a large or almost infinite source (such as the warm surface waters of the ocean) the actual device that can convert this energy into mechanical power can only be of a finite size, so that the time rate that heat can be delivered to any actual device necessarily remains finite. (The choice of a fixed rate, as opposed to a variable rate, is merely to properly normalize the conditions for computing the maximum power efficiency.)

Assumption 2) that the source temperature T_1 is variable and assumption 3) that there are thermal losses directly to the sink is in accord with the observed facts that all actual heat sources remain at finite temperatures less than some theoretical maximum and all actual heat engines will have irreversible heat losses which do not contribute to the production of mechanical work. If no loss mechanism allowing heat to be lost directly to the sink were provided, then a finite time-rate of delivery of thermal energy as required by assumption 1) would result in a steady rise in the temperature of the source when the reversible engine was disconnected. Then this idealized heat engine without the thermal shunt could have a source temperature indefinitely high and 100 percent of the energy could be converted to work. Assumptions 2) and 3) are, thus, necessary if the source temperature is to remain finite and assumption 1) is to remain valid.

Assumption 4) states that apart from the heat energy lost directly to the sink, bypassing the reversible heat engine, there are no irreversible losses assumed. The impossibility of operating a reversible heat engine at a finite rate does not concern us here, since only an upper bound is sought and irreversible processes are considered apart from the reversible heat engine. Assumption 4) means that, apart from the shunt representing irreversible thermal losses directly to the sink, the ideal device may be specified without specifying detailed internal design parameters. This ideal model of a heat engine operating at a finite rate, therefore, yields a power efficiency that depends only upon the nature of the source, sink, and the shunt. Assumption 4) indicates that the efficiency of this ideal device serves as an upper bound for all actual heat engines operating at a finite rate independent of the internal design parameters of the actual heat engines.

Assumption 5) that heat is lost directly to the sink as a linear function of the temperature difference between source and sink is the simplest functional relation that can be assumed. Most actual thermal losses are, in fact, linear functions of the temperature difference between source and sink to an excellent first approximation. Since actual thermal dissipation occurs more rapidly than provided for by a linear relation (see Figure 2), the linear assumption provides for the least possible irreversible dissipation of heat, making the present model device more efficient than any actual heat engine operating at a finite rate.

When heat is lost by ordinary conduction through solids, liquids, or gases, the linear relationship is reasonably good. When heat is lost by convection the linear relationship also applies reasonably well. When heat is lost by radiative transfer the rate of loss is proportional to the difference in the fourth power of the source temperature and the sink temperature; thus,

$$\dot{Q}' \propto T_1^4 - T_o^4 = (T_1^2 + T_o^2)(T_1 + T_o)(T_1 - T_o) \quad , \tag{26}$$

where it is seen that the radiative heat losses may also be regarded as a linear function of the temperature difference, the conductivity increasing as the third power of the temperature.

To show that the linear relationship provides a smaller loss than would be found in any actual heat engine the temperature variation of thermal conductivities may be considered. An increase in the thermal conductivity with temperature leads to a higher thermal loss than would occur for a constant thermal conductivity as assumed here for the ideal device. A decrease in the thermal conductivity with an increase in temperature would appear to lead to lower thermal losses; but materials whose conductivity decreases with temperature are those with very large thermal conductivities at low temperatures (Zemansky, 1943); and such materials would produce losses far greater than need be assumed for the ideal device. Similarly it is found

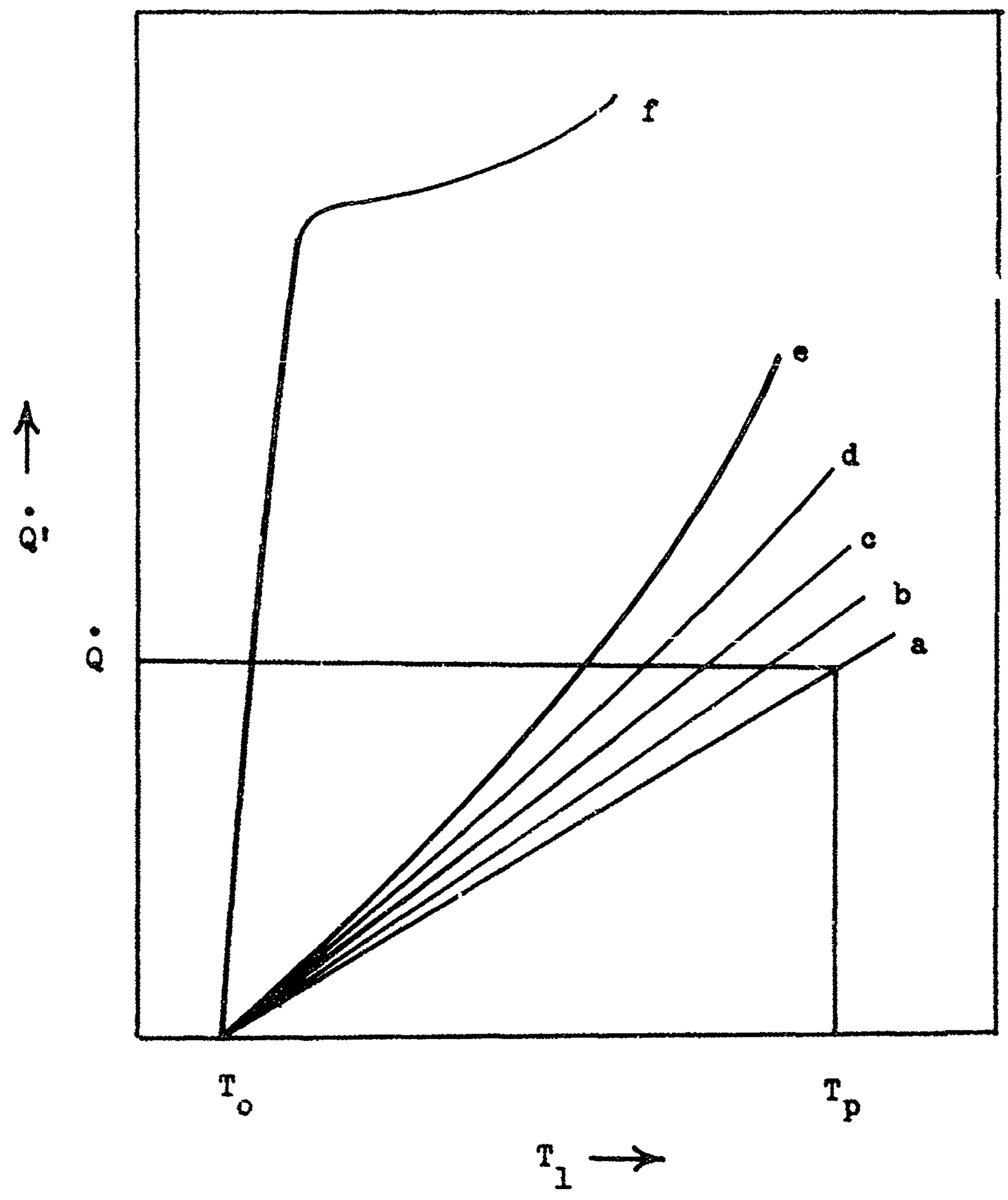

Figure 2. A qualitative sketch showing that the linear idealized curve a) falls to the right of all actual curves of thermal loss for a given rate of energy loss. Curve b) represents loss through an insulator; c) through a gas; d) by convection; e) by radiative transfer; and f) by metalic conduction. The actual curves, falling to the left of a), means that all actual heat engines will operate at a lower optimum temperature T_m and will have a lower efficiency than the idealized device considered here.

that losses due to convection increase faster than the first power of the temperature difference. Figure 2 is a qualitative sketch indicating that the linear assumption leads to a thermal loss less than would be experienced by any actual heat engine, provided only that a sufficiently small value of the thermal conductivity is assumed (or a sufficiently large temperature T_m, Eq.(22), is chosen). While this indicates that the correct functional relationship between source and sink has been chosen for the ideal device, it does not indicate the value of T_m that should be used.

Ideal combustion engine operating at a finite rate - To further indicate the generality of the upperbound efficiency given by Eq.(23) an ideal combustion engine may also be considered. Figure 3. represents such an ideal combustion engine operating continuosly at a finite rate. A combustible mixture of gases at the sink temperature T_o is fed at a constant rate,

$$\dot{m} = \rho v A \ , \tag{27}$$

where ρ is the density of the gases, v is the velocity, and A the cross-sectional area of the intake pipe, into a heat exchanger where it is preheated by the exhaust gases to the temperature T_a. The gases are then burned isobarically in the combustion chamber at the higher temperature T_1. The combustion represents a finite rate of heating,

$$\dot{Q} = \dot{m} h \ , \tag{28}$$

where h is the mass specific heat of reaction or change in enthalpy. Heat is simultaneously extracted from the hot gases at the same temperature T_1 at the rate $\dot{Q}_1$ by a reversible heat engine (which is again assumed to be able to

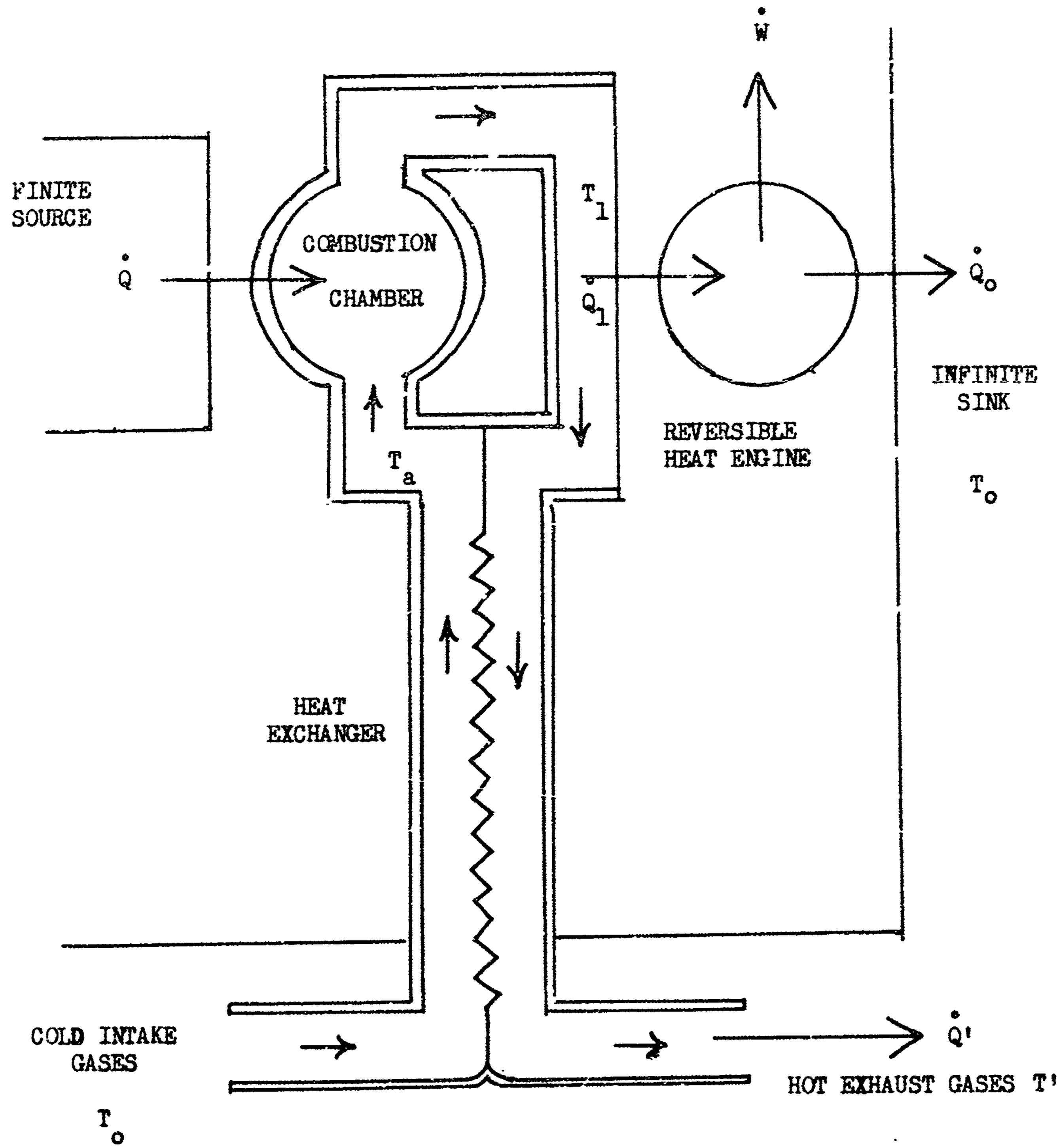

Figure 3. An ideal combustion engine operating continuously at a finite rate which consists of a reversible heat engine together with a combustion chamber and heat exchanger. Irreversible heat losses occur in the heat lost in the hot exhaust gases. Symbols are defined in the text.

operate reversibly at a nonzero rate). The exhaust gases are than passed through the heat exchanger and are finally rejected at the lower temperature T'.

An infinitely long heat exchanger would allow the exhaust gases to be the same temperature as the intake gases, $T' = T_o$, and T_a would equal T_1. In this case the exhaust gases could not provide energy for further work, the exit pressure being the same as the pressure throughout and presumably equal to the atmospheric pressure. In this case all of the energy provided by combustion, $\dot{Q}$, passes to the reversible heat engine, and the efficiency becomes just the Carnot efficiency. It is assumed that there is no kinetic energy of flow in the gases of the system.

Similarly, if the flow is assumed to proceed infinitely slowly so that thermal equilibrium could be established across each portion of the heat exchanger, then the exhaust temperature would again be T_o and the efficiency would again be the Carnot efficiency, Eq.(16). In this case of infinitely slowly flowing gases, $v = 0$, the rate at which heat can be added, $\dot{Q}$, Eqs.(28) and (27), to a finite engine must go to zero and the power output $\dot{W}$ goes to zero, even though the work efficiency goes to a maximum.

For a fixed nonzero rate of adding heat $\dot{Q}$ and a finite real heat exchanger the rate that heat $\dot{Q}'$ is rejected by the hot exhaust gases will remain greater than zero. To estimate $\dot{Q}'$ it may be noted that the net energy added to the gases between the intake into the combustion chamber and the exhaust into the heat exchanger is

$$\dot{Q} - \dot{Q}_1 = \dot{m}(c_{p1}T_1 - c_{pa}T_a) , \tag{29}$$

assuming the gases to be ideal, and where c_{p1} is the mass specific heat capacity at constant pressure for the exhaust gases and c_{pa} is the mass specific heat capacity at constant pressure for the intake gases. Due to conservation of mass $\dot{m}$ will be a constant at all points. To simplyfy the analysis it will be assumed that the ideal engine runs on gases such that

$$c_{p1} = c_{pa} = c_p \; . \tag{30}$$

From the fact that the total energy in $\dot{Q}$ goes into the reversible heat engine, $\dot{Q}_1$, and into the exhaust, $\dot{Q}'$, it is found that

$$\dot{Q} = \dot{Q}_1 + \dot{Q}' \; . \tag{31}$$

Combining Eqs.(31), (30) and (29) then gives

$$\dot{Q}' = \dot{m}\, c_p(T_1 - T_a) \; . \tag{32}$$

Comparing the exhaust gases with the intake gases, the net heat lost in the exhaust gases is given by

$$\dot{Q}' = \dot{m}\, c_p(T' - T_o) \; . \tag{33}$$

Assuming that the temperature difference accross the heat exchanger is made constant throughout its length, the rate of flow of heat across the heat exchanger becomes

$$\dot{Q}_a = B(T_1 - T_a) = B(T' - T_o) = \dot{m}\, c_p(T_a - T_o) = \dot{m}\, c_p(T_1 - T') \; , \tag{34}$$

where the last two expressions are obtained from the increase in energy of the intake gases and the decrease in energy of the exhaust gases as they pass through the heat exchanger, and where B is a constant indicating the total thermal conductivity in the heat exchanger (assuming a linear relation).

Eliminating T_a between Eqs.(32) and (34) or T' between Eqs.(33) and (34) the rate that energy is lost in the exhaust gases may be written in the form

$$\dot{Q}' = K(T_1 - T_o) \; , \tag{35}$$

where the constant K has the value

$$K = (\dot{m}\ c_p)^2/(\dot{m}\ c_p + B) \quad . \tag{36}$$

Comparing the present Eqs.(31) and (35) with Eqs.(19) and (20) for the previous ideal heat engine operating at a finite rate, it is clear that the conditions are mathematically identical. The optimum operating temperature is again given by Eq.(22) and the maximum power efficiency by Eq.(23). The optimum operating temperature is again obtained by adjusting the power consumed by the reversible heat engine. The fact that this particular device can in principle run infinitely slowly at the maximum work efficiency, i.e., at the Carnot efficiency, Eq.(16), (with zero power output) and also run at a finite rate at the maximum power efficiency, Eq.(23), (with a finite power output) indicates the theoretical versatility of this idealized device.

It might appear that when the reversible heat engine is disconnected that the temperature T_1 could be driven up indefinitely by making the heat exchanger longer and longer (similarly to the previous example). Eventually, however, the chemical processes become endothermic (the gases absorbing energy upon dissociation) and no energy will be obtained at sufficiently high temperatures. The mass specific enthalpy change, Eq.(28) will go to zero at sufficiently high temperatures. It might seem that isovolumic heating would allow for higher final temperatures (since $c_p > c_v$, the mass specific heat at constant volume). This however is not the case, since the isobaric heating (or combustion) takes place with greater preheating of the intake gases. The peak temperature that can be obtained, disconnecting the reversible heat engine, will depend solely upon the chemical equilibrium conditions.

It remains to be shown that the rate of irreversible dissipation of energy, Eqs.(35) and (36) is less for the present theoretical device than for any actual heat engine operating at an optimal rate. For a fixed rate of input of thermal energy, $\dot{Q}$, Eq.(28), the coefficient K may be written as

$$K = (\dot{Q}\, c_p)^2 / h(\dot{Q}\, c_p + Bh) \quad . \tag{37}$$

The mass specific enthalpy is a decreasing function of the temperature, while c_p and B are increasing functions of the temperature. While it is not obvious that the ideal value for K can always be chosen less than actual values, it appears reasonable. Moreover, all actual heat engines will dissipate kinetic energy of flow, $\frac{1}{2}\rho v^2 A = \frac{1}{2}\dot{m}\, v$; and they will not burn the gases to completion, resulting in a loss in chemical energy in the exhuast gases, $\dot{Q}(h_o/h - 1)$, where h_o is the enthalpy change for the process going to completion and h is the observed enthalpy change in an actual heat engine. It appears safe to assume in the present example that no actual combustion engine operating at a finite rate will be able to exceed the maximum power efficiency given by Eq.(23).

Comparison with actual heat engines - It is of interest to compare the efficiencies of actual heat engines with the maximum power efficiency, η_m, predicted by Eq.(23). Figure 4. shows this efficiency plotted as a function of T_o/T_m. Also plotted in Figure 4. is the efficiency of a Carnot engine, η_c, Eq.(16), operating between the same two temperatures T_m and T_o. This Carnot efficiency is an upper bound on the efficiency of any actual heat engine operating at a finite rate, since even operating at the optimal temperature T_m involves irreversible losses. The maximum power efficiency, η_m, provides a smaller and more realistic upper bound for actual heat engines (see Eq.(24)).

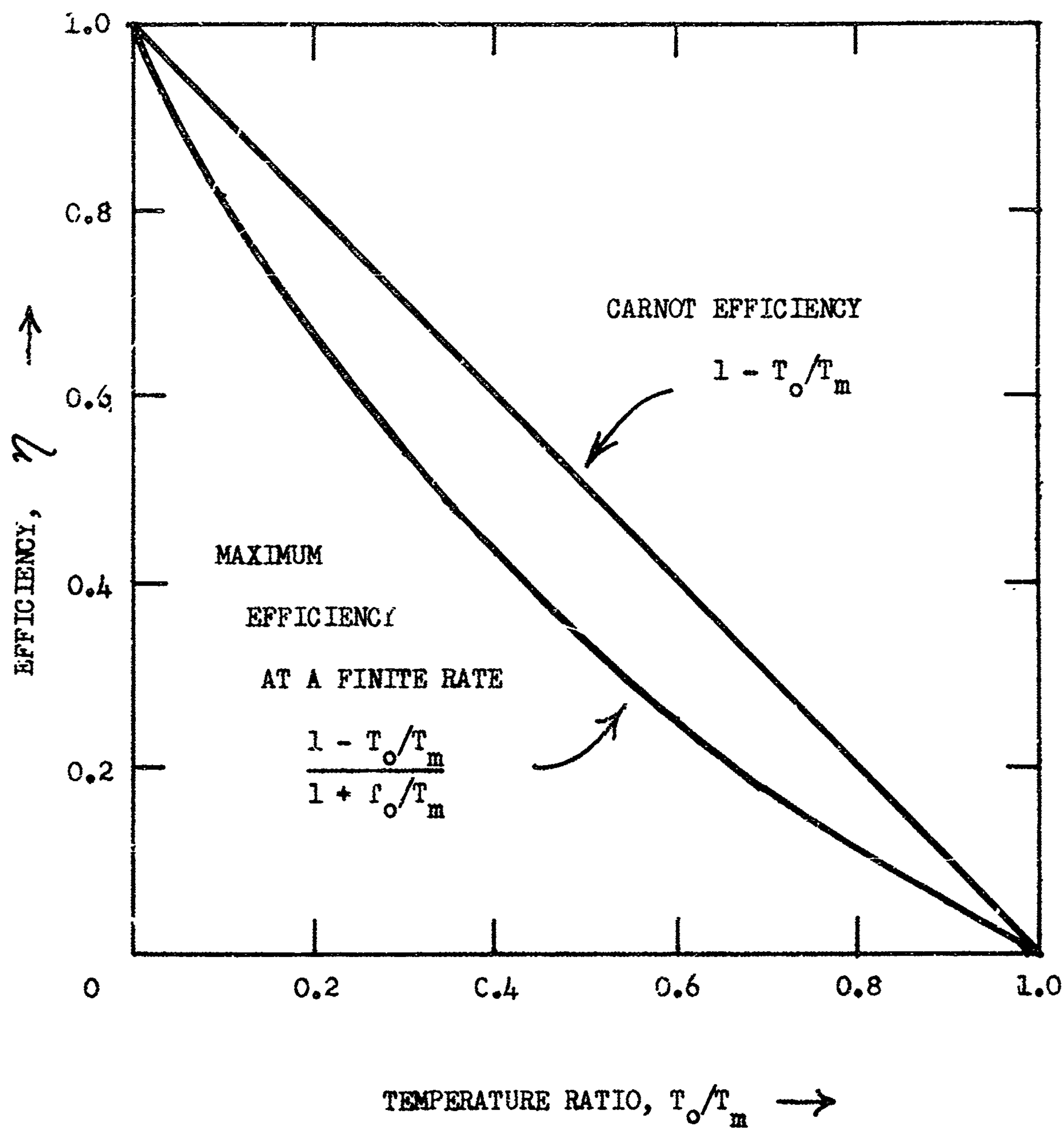

Figure 4. A plot of the maximum efficiency of a heat engine operating at a finite rate as a function of the ratio of the sink temperature to the optimum temperature, T_o/T_m, Eq.(23). The efficiency of a Carnot engine operating between these same two temperatures, T_m and T_o, is also shown for comparison.

Actual heat engines are designed in such a way that even with ideal operation of the engines infinitely slowly (with zero power output) the efficiency could not approach the Carnot efficiency. For example, if a steam engine is represented by an idealized Rankine cycle operating between the boiler temperature of 205 °C and a condenser temperature of 39°C, it will have an efficiency of 30.6%, while a Carnot engine between the same two temperatures would be 34.7%. Comparing the mechanical power output to the chemical energy input a steam engine operating at a finite rate between these temperatures might be expected to have an actual efficiency of at most about 12%. This may be compared with the maximum power efficiency, η_m, Eq.(23), for any heat engine operating at a finite rate between these temperatures of 21.0%. A heat engine operating between the temperatures of 565°C and 27°C, values appropriate for a Diesel engine or steam turbine, the Carnot efficiency would be 64% while the maximum power efficiency according to Eq.(23) is only 47%. Diesel engines and steam turbines can operate around 30% efficiency with some estimates as high as 39%. Gasoline engines operate at efficiencies around 25% at best.

From this analysis it appears that the maximum power efficiency, η_m, Eq.(23), provides a more accurate upper bound for the actual power efficiencies of actual heat engines. It may also be concluded that the primary reason for the difference in efficiency between the Carnot efficiency and the actual efficiency is the need to run the heat engine at a finite rate in competition with irreversible heat losses.

<u>A general theory in support of η_m, Eq.(23), being an upper bound</u> - If the irreversible rate of energy loss is given by $\dot{Q}'$ [illegible] any heat engine operating at a finite rate with a constant input $\dot{Q}$, the power efficiency becomes

$$\eta = \dot{W}/\dot{Q} = (\dot{W}/\dot{Q}_1)(\dot{Q}_1/\dot{Q}) = \eta_c(1 - \dot{Q}'/\dot{Q}) , \tag{38}$$

where $\dot{Q}_1$ is the heat energy used reversibly, Eq.(19) or (31), for example, and η_c is the reversible or Carnot efficiency Eq.(16). This result Eq.(38) is precisely correct, since it may be used to define what is meant by the irreversible heat loss $\dot{Q}'$.

For an infinite sink at the temperature T_o and all parameters held fixed except T_1 the temperature of the source (which may be altered by changing $\dot{Q}_1$), the irreversible heat loss $\dot{Q}'$ becomes a function of T_1. This function may be expanded as a power series about the sink temperature T_o; thus,

$$\dot{Q}' = \sum_{n=0}^{\infty} K_n(T_1 - T_o)^n \quad . \tag{39}$$

Since the irreversible heat dissipation must go to zero as $T_1 \rightarrow T_o$, the zeroth term in Eq.(39) must vanish, the series starting with the first power in $T_1 - T_o$.

Now if

$$\dot{Q}'(\text{ideal}) = K\,(T_1 - T_o) < K(T_1 - T_o) + \sum_{n=2}^{\infty} K_n(T_1 - T_o)^n , \tag{40}$$

then the irreversible heat losses in the ideal heat engine will be less than in an actual heat engine and the maximum power efficiency, η_m, Eq.(23) will in fact be an upper bound. It seems extremely plausible to assume that the irreversible heat losses will increase more rapidly than just the linear power in $T_1 - T_o$. It will, thus, be postulated or assumed that Eq.(40) will be true for all heat engines and therefore that η_m does represent an upper bound for the power efficiency of any actual heat engine.

Maximum power efficiency of a solar engine

A problem of considerable interest to the problem of life in the solar system is the problem of the maximum utilization of solar energy. It is conceivable (no matter how unlikely) that sophisticated life forms other than man may also be able to construct heat engines for the maximum conversion of solar energy to mechanical power. The maximum rate of conversion to mechanical work also gives a direct estimate of the maximum rate that sunlight can be utilized for any ordering process.

The ideal device considered here is diagramed in Figure 5. This device is assumed to exist in space in orbit about the sun. Sunlight is focused by a parabolic mirror upon the surface A'. Heat from this surface is delivered to a reversible or Carnot engine (which is assumed here to remain reversible even while running at a finite rate) which rejects heat to a sphere of radius a which radiates the thermal energy into deep space. It will be assumed that the radius of the parabolic mirror is also equal to a, so that no sunlight impinges upon the cold radiating sphere which faces away from the sun as shown. It will be assumed that the radiating sphere is sufficiently distant from the parabolic mirror and the reversible heat engine so that the thermal energy may be assumed to radiate over 4π stereradians into deep space. It will be further assumed that the parabolic mirror is ideal and reflects 100% of the light incident upon it.

From geometrical opticical consideration (ray tracing) or from the second law of thermodynamics no focusing device can yield an illumination brighter than the surface brightness of the original diffuse surface radiating light. This means that the surface upon which the sun's rays are focused can never exceed the brightness of the sun's surface or can never exceed the temperature of the sun's surface (assumed here to be 5800°K). If the surface upon which the sun's rays are focused A' is assumed to be a black body it will reradiate energy (back toward the sun, assuming A' small compared with area intercepted by parabolic mirror), so that the net rate that energy will be absorbed is

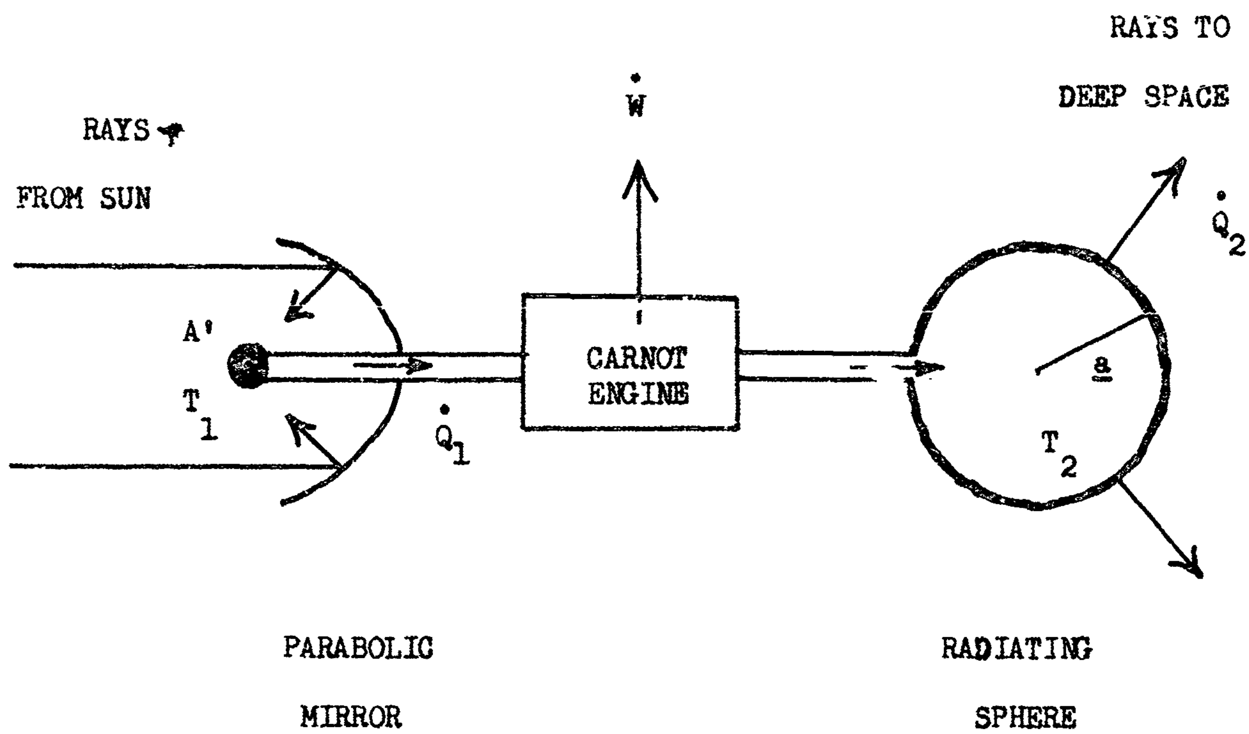

Figure 5. Diagram of an idealized solar engine consisting of an idealized parabolic mirror of radius a which concentrates the sun's rays onto the surface A' at the temperature T_1 and a Carnot engine operating between the source at T_1 and a heat sink consisting of an ideal radiating sphere (also of radius a) at the temperature T_2.

given by

$$\dot{Q}_1 = A'\sigma(T_s^4 - T_1^4) , \tag{41}$$

where the incident flux is taken to be equivalent to radiation from a portion of the sun's surface of area A' and σ is the Stefan-Boltzman constant appropriate for the fourth power law for thermal radiation emitted by a black body, and where T_s is the effective temperature of the sun's surface ($T_s \approx 5800^{\circ}K$) and T_1 is the temperature of the surface A'

The rate that solar energy impinges upon the parabolic mirror, $\dot{Q}$, is given by the rate at which it leaves the sun per unit area, decreased by the inverse square of the distance times the area intercepted by the mirror; thus,

$$\dot{Q} = \pi \underline{a}^2 (r_s/r)^2 \sigma T_s^4 , \tag{42}$$

where r_s is the radius of the sun and r is the distance of the device from the center of the sun. Since the rate that energy impinges upon the surface A' is taken to be the same as the flux from the sun's surface, the value of A' appropriate for the present idealized circumstances is

$$A' = \pi \underline{a}^2 r_s^2 / r^2 . \tag{43}$$

The cold sink (the sphere on the right in Figure 5 which is shielded from the direct rays of the sun) is assumed to radiate into deep space as a black body. Taking the temperature of deep space to be T_o (where $T_o = 3.5^{\circ}K$) and the temperature of the radiating sphere to be T_2, the rate that energy is radiated off into deep space is given by

$$\dot{Q}_2 = 4\pi \underline{a}^2 \sigma (T_2^4 - T_o^4) . \tag{44}$$

It is assumed that the reversible heat engine connected between the hot source at temperature T_1 and the sink at temperature T_2 does work at the rate

$\dot{W}$ such that all of the work is utilized internally to the device and such that all of the energy is eventually converted back into thermal energy by friction, etc., at the temperature T_2 and if it is assumed that there is no net accumulation of stored energy such as internal chemical energy, then the rate that the surface A' absorbs energy must equal the rate that the cold sphere reradiates energy. Thus to maintain thermal equilibrium for the system and neglecting any time rates of accumulation of stored energy, the heat fluxes in Eqs.(41) and (44) may be equated, yielding the temperature T_2 as a function of T_1,

$$T_2 = \left[T_o^4 + (r_s/2r)^2(T_s^4 - T_1^4)\right]^{\frac{1}{4}}, \tag{45}$$

where A' has been replaced by Eq.(43).

From Eq.(41) for the power delivered to the Carnot engine and from Eq.(16) for the efficiency of a Carnot engine, the rate that work may be delivered by the device becomes

$$\dot{W} = A\,\sigma(T_s^4 - T_1^4)\left[1 - T_2(T_1)/T_1\right], \tag{46}$$

where T_2 as a function of T_1 is specified by Eq.(45). The temperature T_1 may be adjusted by changing the rate of doing work $\dot{W}$, thus the maximum rate of doing work under the present circumstances is given by differentiating Eq.(46) with respect to T_1 and setting the result equal to zero, using Eq.(45). Letting

$$x = T_1/T_s, \quad x_o = T_o/T_s, \quad b^2 = r_s/2r, \tag{47}$$

the maximizing condition may be shown to yield the expression

$$-4x^5\left[b^4(1 - x^4) + x_o^4\right]^{3/4} + 4x^4\left[b^4(1 - x^4) + x_o^4\right] + (1 - x^4)(b^4 + x_o^4) = 0. \tag{48}$$

Since the root of this expression is always a sizeable fraction less than unity (i.e., the optimum temperature will be a sizeable fraction less than the surface temperature of the sun) and since for all values of r in the solar system

$$b^2 = r_s/2r > 5\times10^{-5} \gg x_o^2 = (T_o/T_s)^2 = (3.5/5800)^2 \quad , \tag{49}$$

x_o^4 may be neglected in Eq.(48), yielding upon getting rid of the fractional exponent

$$-4^4x^{20} + (1 - x^4)(4x^4 + 1)^4b^4 = 0 \quad . \tag{50}$$

Letting

$$z = 4x^4 \quad , \tag{51}$$

Eq.(50) may be written in the form

$$-z^5 + b^4(4 - z)(1 + z)^4 = 0 \quad . \tag{52}$$

Expanding out in powers of z and introducing the constant

$$c^5 = 4b^4/(1 + b^4) \quad , \tag{53}$$

Eq.(52) may be written in the form

$$-4z^5 + c^5(4 + 15z + 20z^2 + 10z^3) = 0 \quad . \tag{54}$$

Since c is generally much less than unity (Eqs.(53) and (47)), the root of Eq.(54) may be found as a power series in c, the first three terms being readily found as

$$z_m = c + 3c^2/4 + 7c^3/16 + \cdots \quad . \tag{55}$$

For the case $r \gg r_s$, b^4 may be neglected compared with unity and from Eq.(53)

$$c \approx (4b^4)^{1/5} = (r_s/r)^{2/5} \quad . \tag{56}$$

From Eqs.(47), (51) and (55) the optimum temperature becomes approximately

$$T_m = T_s(r_s/r)^{1/10}/4^{\frac{1}{4}} \quad . \tag{57}$$

Substituting this result into Eq.(46) divided by the incident solar flux, $A'\sigma T_s^4$, using Eq.(45), neglecting T_o as being negligibly small, the maximum efficiency for this solar engine operating at a finite rate becomes

$$\eta_m = 1 - (5/4)(r_s/r)^{2/5} \quad , \tag{58}$$

to within the smallest power of r_s/r. This result is less than the Carnot efficiency between the temperatures 3.5°K and 5800°K, Eq.(16), η_c = 99.940%. The efficiency however is sufficiently large to be essentially 100% even at the distance from the sun of the earth's radius, η_m(at earth orbit) = 99.533%.

In outer space not on the surface of a planet it is possible to achieve very large efficiencies (in principle) for the conversion of solar energy to useful work. Here however the problem is to maximize the rate at which work is obtained, and this varies according to the distance from the sun. Thus, for a solar engine with the present design which is fixed in size the quantity to maximize is obtained by multiplying the efficiency η_m, Eq.(58), by the energy flux from the sun incident upon the parabolic mirror,

$$\dot{W} = \pi a^2 \sigma T_s^4 (r_s/r)^2 \left[1 - (5/4)(r_s/r)^{2/5}\right] . \tag{59}$$

Differentiating Eq.(59) with respect to r (or equivalently with respect to (r_s/r)) and setting the result equal to zero, the distance from the sun at which maximum useful power may be obtained is found to be

$$r_m = (3/2)^{5/2} r_s \doteq 2.75\, r_s \, . \tag{60}$$

To indicate the significance of this result it may be noted that the ratio of the optimum power available at the distance of the earth from the sun to the maximum power available (as obtained by substituting Eq.(60) into (59)) at any radius is given by

$$\mathring{W}(\text{earth})/\mathring{W}(\text{maximum}) = 8.47\text{x}10^{-4} \approx 10^{-3} \, . \tag{61}$$

A heat engine of a fixed size will deliver much more power closer to the sun than the distance of the earth from the sun.

To see how practical the optimum distance for operating the present solar heat engine is it may be noted that the equilibrium temperature at $2.75r_s$, assuming reradiation over 4π steradians is 2500°K and over 2π steradians is 3500°K. These temperatures are marginal for the operation of solid devices. Actually at the distance of $2.75r_s$ the sun subtends a sufficiently large solid angle to hamper the reradiation into space of thermal energy over a solid angle of 4π steradians. The optimum distance from the sun for the operation of this particular heat engine will be somewhat greater than $2.75r_s$.

While it is extremely tempting to postulate that the idealized solar heat engine considered here yields the maximum possible time rate of conversion of solar energy to useful work, it is not clear that quantum processes involving heat traps cannot improve upon the present device. Irreversible or time rate processes do not permit the easy assumptions of thermostatics. Whether or not the present idealized device can be improved upon, it is undoubtedly true that the efficiency indicated by Eq.(58) yields a more realistic estimate of the upper limit for the efficiency of actual solar engines operating at a finite r te.than is provided by the Carnot efficiency between the sun's surface temperature, $5800^{\circ}K$, and the temperature of deep space, $3.5^{\circ}K$.

It may be noted that the maximum efficiency defined by Eq.(23) is not applicable to the present circumstances, since it assumes an infinite heat sink. The solar engine operating with a finite heat sink will, of course, have an efficciency less than η_m given by Eq.(23), where T_m is specified by Eq.(57) and T_o is the temperature of deep space, $3.5^{\circ}K$.

LIKELIHOOD OF LIFE FROM BEYOND THE SOLAR SYSTEM

The problem of estimating the likelihood of life existing in the solar system (presumably apart from the earth) involves not only the problem of estimating the likelihood of life evolving 'spontaneously' within the solar system but also the problem of estimating the likelihood of life having entered and established itself in the solar system having evolved originally in another stellar system.

Primitive life from beyond the solar system

It is conceiveable that very primitive life from beyond the solar system could have become established in a particularly favorable environment within the solar system. Once an initial 'seed' or 'germ' became established evolution could have then produced the advanced life forms that might be expected to be found today (such as actually found on the earth). This case is of little interest, however, since the process of evolution, evolving life forms dictated by the environment, is the primary instrument for the life forms as finally observed. It makes little difference whether the initial 'seed' is assumed to have had an origin from beyond the solar system or whether the initial 'seed' is assumed to have been generated 'spontaneously' within the solar system; the end results are the same.

Advanced life forms from beyond the solar system

If instead of assuming that primitive life from beyond the solar system became established in the solar system, it is assumed that some highly evolved life forms immigrated to the solar system, it then becomes of some interest to ask what part of the solar system provides the optimal environment for such advanced life forms and, consequently, where might they be found in the solar system.

It might be argued that such life forms would seek out the environments similar to those from which they originally evolved. Advanced life from beyond the solar system could, therefore, have established itself almost anywhere in the solar system that can support life at all. Under these assumptions the environment in which such life forms are to be found will be quite similar to the environments in which they originally evolved; consequently, such life forms could conceivably also evolve locally (i.e., within the solar system) to fit the environment. The likelihood of such life forms evolving locally becomes the same as the likelihood of such life forms evolving in similar environments beyond the solar system, the conditions being comparable. It does not appear that the time scale beyond the solar sytem could be largely different, since the universe is estimated to be only about 7 billion years old and it has taken about 2 billion years to evolve the life on the earth. This means that it is unlikely that highly evolved life forms from beyond the solar system would settle in a favorable environment within the solar system in which the local fauna have not as yet evolved to as high a degree. The region of the universe within any reasonable radius of the solar system may be assumed to have roughly the same age as the solar system; and therefore it seems unlikely that life forms suitable for a particular environment could have evolved more rapidly elsewhere and then could have immigrated to the solar system. It is apparently sufficient to treat the problem of the likelihood of life arising spontaneously within the solar system environment; the question of whether or not the life forms found came from beyond the solar system being largely a matter of indifference.

Sophisticated life forms from beyond the solar system

If it is assumed that sophisticated life forms, which are not restricted to any particular narrow range of environments, have immigrated to the solar system, then it may be assumed that such life forms would choose the optimal environment within the solar system from among all of those available. For example, man together with his machines, space ships, and elaborate technology represents such a sophisticated form of life capable of 'living' in a very wide range of environments (at least potentially if not currently). Since sophisticated life is the only life which could conceivably transport itself accross interstellar distances, it is only sophisticated life from beyond the solar system which apparently needs concern us. Sophisticated life can have an accelerated evolutionary rate (eg., man and machines); so that sophisticated life from beyond the solar system could conceivably be more advanced than the life forms which have evolved within the solar system.

If the sophisticated life obtained its high utility energy from contained nuclear reactions (such as fission or fusion energy), it seems unlikely that such life would enter the solar system (except possibly to obtain matter).

If, however, such contained reactions tended to poison their environment with radioactive wastes, it might be that such life would seek a natural nuclear reactor such as the sun. The sun obtains its energy at a low temperature as compared with the temperature needed in thermonuclear devices for the direct conversion of deuterium to helium. The low temperature of the sun, in addition to its very cool envelope of only $5800^{\circ}K$, provides a very safe source of energy which need not radioactively poison the environment. Since it is assumed that life is essentially in a solid phase, the need to avoid extraneous disruption of atoms from their proper sites might be a sufficient motivation for sophisticated life to enter the solar system from without.

Assuming that sophisticated life does choose to utilize solar energy, where is the optimum environment in the solar system and where should one, therefore, search for such sophisticated life? The optimal environment appears to be in free space revolving around the sun in free fall. The surface of a planet presents a number of awkward features which seriously detracts from its desirability. A planet which rotates has periods of light and dark. During the dark periods no energy is available, so that living processes must either cease during the night or else energy must be stored during the day to be utilized at night. In either case living processes are seriously handicapped. At the very best the high utility energy available is halved in rate.

On the surface of a planet with an atmosphere the sink temperature for the dissipation of low utility energy is much higher than the temperature of deep space. For example, if it is assumed that Venus has a surface temperature of $600^{\circ}K$, the maximum efficiency for the time rate conversion of solar energy to useful work, according to Eq.(23), letting T_m be the temperature of the surface of the sun as an outside limit, becomes

$$\eta_m = (5800 - 600)/(5800 + 600) = 81\% ,$$

whereas assuming the temperature of 5800°K is available in outer space with an infinite cold source at 3.5°K, the efficiency becomes

$$\eta_m = (5800 - 3.5)/(5800 + 3.5) = 99.9\% .$$

Actually the energy available on the surface of Venus, or on any planet with a dense atmosphere is extremely small due to the absorption of the sunlight in the atmosphere; and only a minute percent of the solar energy is available for useful work.

In empty space the transport of matter necessary for the ordering processes associated with life can take place along a geodesic without the expenditure of energy. Man, for example, comsumes a large fraction of the energy he expends in the transport of men and materials accross the surface of the earth. In outer space there would be no need to overcome frictional energy, and there would be no necessity for the large expenditure of energy for the lateral transport of materials.

The transport processes on the surface of a planet being restricted to the surface of the planet is essentially two dimensional; whereas, in outer space it would, in principle, be possible to order substances within a true three dimensional array. The ordering of materials in a three dimensional array could occur at a much faster rate and more economically than is possible for a two dimensional ordering process.

The time rate at which materials may be transported in a vacuum can be very large; the frictional drag of an atmosphere would not interfere with the time rate of transport of materials.

The absence of an atmosphere permits a fantastic control over the possible temperatures that may be readily obtained. By shielding a body from the direct rays of the sun it is possible to obtain cryogenic temperatures down to about $3.5^{\circ}K$. On the other hand, using a mirror to focus the sun's rays it is possible to obtain temperatures approaching the temperature of the sun's surface of $5800^{\circ}K$. With little effort and no energy expenditure it is possible to obtain a wide range of temperatures in outer space; while on the surface of a planet with an atmosphere extremely elaborate and costly systems must be constructed to achieve the same results.

In outer space buildings and structures need not have the strength to overcome the effects of gravity. The only limitations in outer space on the strength of structures is prescribed by the impulses imparted to the structure by the users of the structure. Structures need not be so severely limited in size as is presently the case on the earth, for example.

A vacuum being readily available in outer space permits a wide variety of technologies presently impossible on the surface of a planet with an atmosphere.

Direct line-of-sight communications which is impossible on the surface of a planet is readily available in outer space.

There are a few apparent disadvantages to living in outer space. An environment requiring volitile liquids and gases under pressure needs a containing envelope of some strength. No such envelopes are needed on the surface of a planet which contains an atmosphere already at the required pressure. Matter required must be taken from a body in the solar system with a great deal of effort and a large expenditure of energy. However, once the matter has been placed in the appropriate orbit about the sun. it will be available for ever after without any additional expenditure of energy. The matter needed may, thus, be accumulated slowly and indefinitely over a period of time; and no large drain upon the reserves of the sophisticated life forms need be assumed. Cosmic rays, as well as soft X rays from the sun, might produce disordering effects upon the sophisticated life forms. However, magnetic fields established over a large volume of space would effectively shield life from energetic charged particles; and low density gas in a large region would effectively stop soft X rays. The magnetic field could be maintained without energy expenditure by using currents in superconductors which may be readily maintained in a superconducting state by virtue of the cryogenic environment always available in outer space. The gases at low densities could be maintained in large balloons. None of the disadvantages to living in outer space appear to be insurmountable to sophisticated life. The advantages to living in outer space as opposed to living on the surface of a planet appear to far outweigh the disadvantages.

It being concluded that sophisticated life forms will not choose to live on the surface of a planet, the question still remains as to where such life might be found if it were in the solar system. Assuming that the sophisticated life will utilize solar energy, it may then be assumed that such life will be found where it can utilize solar energy optimally. In the previous Section for the particular idealized solar engine considered there the optimum distance from the sun was given by Eq.(60) or at 2.75 times the sun's radius. At this distance 141 watts/cm^2 of useful mechanical power may be obtained at an efficiency of 17%. At farther distances from the sun the efficiency will increase (but the maximum power for a fixed parabolic mirror will decrease). Assuming the parabolic mirror is made of real materials and reradiates the solar energy it absorbs over a 4π solid angle it will attain an equilibrium temperature, $T_s(r_s/2r_m)^{\frac{1}{2}} \simeq 2500^{\circ}K$. If this high temperature is inconvenient for the parabolic mirror, then the sophisticated life forms might be expected at some distance farther from the sun. It seems reasonable to expect that such sophisticated life forms would choose some radius from the sun lying between the orbit of Mercury at 83.4 times the sun's radius and the sun's surface.

If such life forms had entered the solar system millions of years ago, and had been successful in maintaining themselves close to the sun, it is perhaps reasonable to expect that by this time they might be utilizing a measurable fraction of the energy radiated by the sun. There appears to be no evidence that this is the case; solar energy appears to reach the earth unimpeded by any large size or large number of objects close to the sun. If sophisticated life has entered the solar sytem and if it has entered to utilize solar energy, then it must have entered recently (perhaps within the last 100,000 years).

The present analysis is,perhaps,more useful in indicating where man will eventually choose to settle and attain his highest utilization of energy, rather than indicating where sophisticate life from beyond the solar system has already chosen to settle.

REFERENCES

ASIMOV, I. (1962). "Life and Energy". Doubleday and Company, Garden City, New York. p. 302.

BERTALANFFY, L. V. (1950). Science 111, 23-29.

BRAY, J. R. (1959). Tellus 11, 220-230.

DE GROOT, S.R. AND P. MAZUR (1962). "Non-Equilibrium Thermodynamics". North-Hollan Publishing Company, Amsterdam.

EPSTEIN, P. S. (1937). "Textbook of Thermodynamics". John Wiley and Sons, New York. pp. 330-334.

______ (1937b). Loc. cit., p. 55.

GREEN, H. S. (1963). Int. J. Engng. Sci. 1, 5-21.

GUTENBERG, B. (1951). editor of "Internal Constitution of the Earth" 2nd ed. Dover Publications, New York.

JACKSON, F. L. and P. A. MOORE (1962). "Life in the Universe". W. W. Norton Company, New York.

JOOS, G. (1934). "Theoretical Physics". G.E. Stechert and Company, New York. pp. 459-463.

KAYAN, C. F. (1964). Int. J. Heat Mass Transfer. 7, 75-85.

MORSE, P. M. and H. FESHBACH (1953). "Methods of Theoretical Physics" Vol.II. McGraw-Hill Book Company, New York. pp. 1584-1586.

ONSAGER, L. (1931). Phys. Rev. 37, 405-426.

OPARIN, A. I. and FESENKOV, V. G. (1961). "Life in the Universe". Twayne Publishers, New York.

OSTERLE, J. F. (1964). Appli. Sci. Res. A 12, 425-434.

PARDEE, A. B. and L. L. INGRAHAM (1960). in "Metabolic Pathways" Vol.1. edited by D. M. Greenberg, Academic Press, New York. pp. 24-39.

PIRIE, N. W. (1937) in "Perspectives in Biology" edited by J. Needham and D. E. Green. Cambridge University Press, Cambridge.

PRIGOGINE, I. (1955). "Introduction to the Thermodynamics of Irreversible Processes". Charles C. Thomas Publishers, Springfield, Illinois.

ROSSINI, F. D. (1955). "Thermodynamics and Physics of Matter". Princeton University Press, Princeton, New Jersey. Section A, p. 44.

SCHROEDINGER, E. (1956). "What is Life and Other Scientific Essays". Doubleday and Company, Garden City, New York. pp. 67-84.

SEARS, F. W. (1953a). "An Introduction to Thermodynamics, the Kinetic Theory of Gases and Statistical Mechanics". Addison-Wesley Publishing Company, Cambridge, Massachusetts. pp. 127-146.

______ (1953b). Loc. cit., p. 152.

STRYER, L. (1966). in "Biology and the Exploration of Mars" edited by C. S. Pittendrigh, W. Vishniac, and J. P. T. Pearman, Publication 1296, National Academy of Sciences National Research Council, Washington, D. C. pp. 141-146.

STUDIER, M. H., R. HAYATSU, and E. ANDERS (1965). Science 149, 1455-1459; and (1966). Science 152, 102-107.

TOCQUET, R. (1962). "Life on the Planets". Grove Press, New York.

ZEMANSKY, M. W. (1943). "Heat and Thermodynamics" 2nd ed. McGraw-Hill Book Company, New York. p. 78.