Available Work in Geothermal Energy

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PREFACE

This report contains a draft of material on basic thermodynamics as it applies to the operation of geothermal installations for the production of electricity. Two years of research, discussion and exchange of information within the group of Centers for the Analysis of Thermal/Mechanical Energy Conversion sponsored by the Division of Geothermal Energy of the Department of Energy have modified our earlier views and convinced the present writer of the desirability of a shift in emphasis away from the traditional use of thermal efficiency and in the direction of basing the analysis on the concept of available work.

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1. Introduction

The purpose of this report is to assemble and to present to the reader the most important thermodynamic considerations which are needed for a clear understanding of the operation of geothermal installations used for the production of electricity. The need for this report arises from the fact that the commonly used method of thermodynamic cycle analysis (so-called First-Law analysis) is less suitable for our purpose than the method of available work (so-called Second-Law approach) favored here. It will be pointed out later that in the case of heat engines operating on fossil fuels the two methods are nearly equally useful though even in this case the method of available work leads to a superior level of understanding. In our case it also lends itself to a more purposeful classification of geothermal wells from the point of view of their thermodynamic potential for the production of work. It is particularly apt in cases when the chemical constitution of the working fluid changes as it traverses the installation.

It is recognized that a designer working for a potential investor must ultimately justify his recommendations on the basis of a realistic calculation of the expected cost of production per kilowatt-hour of electricity at the terminal. It is further recognized that the economic optimum in given circumstances is not coincident with the thermodynamic optimum that we seek to establish in this report. However, past experience shows that the latter contains valuable indications for the former and constitutes an indispensable first step. Furthermore, the thermodynamic optimum depends on objective circumstances and the laws of nature whereas the economic optimum takes into account political, fiscal and legal aspects which govern investment, as well as one's perception of the future course of inflation. These factors are in a continuous flux. For this reason the process of discovering the economic

optimum is never definitive. By contrast, the establishment of the thermodynamic optimum can be made into a clear-cut, well-defined scientific problem.

We begin our discussion with a brief description of the nature of a geothermal reservoir and proceed to describe the characteristics of the most practical systems for the conversion of geothermal energy into work. This enables us to recognize the essential features of a convenient open system on which to construct the analysis. We then derive the appropriate specialized forms of the First and Second Laws of thermodynamics and introduce the related concepts of optimum available work, w_o^o , available work, w^o , entropy production, θ , dissipated energy, w_d , and utilization factor, η_u . To persuade the reader of the utility of these concepts, we discuss the shortcomings of the method of cycle analysis when applied to geothermal plants.

Special attention is devoted to a detailed discussion of the most important general indicators that follow for the designer from a thermodynamic analysis. These include the recognition of the important role of the condenser temperature as it affects work and its sensitivity to changes in the condenser temperature as well as to the diurnal and annual fluctuations in the temperature of the natural heat sink. Similarly, the overall influence of dissolved salts and evolving inert gases is analyzed.

Section 16 describes in detail various methods of graphically interpreting the concept of available work, and Section 17 discusses the importance of easily accessible, reliable formulations of the thermophysical properties of the pure substances, solutions and mixtures that the designer needs for success. Existing data are incomplete and contain in them inconsistencies that may present the designer with a seriously confused picture.

2. The geothermal reservoir

The term "geothermal energy" used in the title of this report relates to the production of electricity, that is, of work in the thermodynamic sense, from hot fluids under pressure naturally found at a reasonable depth (1-2 km) in the earth's crust. Disregarding the complex geological details of the formation of such natural reservoirs of hot fluids, it is possible to schematize them in the manner shown in Figs. 1 and 2. The high temperature of the fluid of order $250 - 300^{\circ}\text{C}$ maximum is caused by the natural convection of high-pressure water through a matrix of permeable rock. The convective cell transfers heat from a hot magmatic intrusion to a more accessible layer whence it may be extracted through an artificially drilled well, with or without the aid of a "downhole" pump. These convective cells operate on a large spatial scale and may extend over as much as 30 km horizontally. Similarly, the characteristic time of the transfer of heat from the magma is geological in order of magnitude ($10^5 - 10^6$ yr). At the present time it is not possible to determine the lifetime of a geothermal reservoir, to assess whether the existing natural circulation can make up for the loss of hot fluid for exploitation or whether by reinjection of the spent fluid it might be possible to establish continuous recirculation thus rendering the resource "renewable". Accumulated experience, however, shows that individual geothermal wells (as distinct from geothermal reservoirs) lose their usefulness after something like 10 yr and must be treated as exhaustible.

As the liquid circulates through the permeable strata it dissolves smaller or larger quantities of minerals, such as sodium chloride (NaCl), potassium chloride (KCl), calcium chloride (CaCl_2), or silica (SiO_2), etc., and often also gases, most frequently carbon dioxide (CO_2) and nitrogen (N_2). In the geopressured reservoirs of the Gulf of Mexico it is common to encounter

Fig. 1. Schematic diagram of the convective cells in a geothermal reservoir showing the temperature distribution, after Facca (1973)

Fig. 2. Schematic diagram of a characteristic geothermal reservoir in a permeable rock showing possible heat transfer and fluid circulation, after White (1973)

dissolved, combustible methane (CH_4). Typical compositions of naturally existing geothermal brines together with their thermodynamic characteristics can be found in Williams et al. (1977) and R. DiPippo (1978 a, b, c, d, e).

The type of geothermal resource considered here is described by the term *hydrothermal*. The possibility of creating an artificially maintained forced circulation through fissures in hot dry rocks is not discussed because it is still in an early stage of development. We also refrain from discussing geopressured resources, resources that rely on radiogenic heating or the methods of exploiting normal gradients and the tapping of heat in the magma.

The geothermal resource, then, is most probably an exhaustible reservoir of a high-pressure, high-temperature aqueous solution of salts and gases in varying proportions. As this substance is made to flow through the well upwards into the regions of lower static pressure, it may flash into steam if at some point the static pressure falls below the saturation pressure for the prevailing temperature. The latter is close to, but not exactly equal to, the vapor pressure of pure water due to the influence of the dissolved substances on the boiling point. Accordingly, the designer may have at his disposal wells which supply him with

- (a) wet steam ("vapor-dominated");
- (b) slightly superheated or saturated steam ("vapor-dominated");
- (c) a liquid solution whose pressure is higher than that at saturation for the given temperature ("liquid-dominated");
- (d) a low-quality, liquid-vapor mixture ("liquid-dominated").

It is clear that the first requirement placed on the design is to adapt the elements of the plant to the physical nature of the available fluid.

3. Thermodynamic state at inlet and exit

The fluid available at the wellhead is utilized, directly or indirectly, to drive a turbine. Proposals to employ alternative types of expanders, particularly in the form of a total-flow machine, have not reached the stage of economic exploitation. When steam is available ("vapor-dominated" reservoir), it is used directly with or without prior separation of its moisture, depending on conditions. Liquid brine ("liquid-dominated" reservoir) can be used to produce superheated or supercritical vapor of a suitable working fluid (freon, isobutane, etc.) which operates a specially designed turbine, the transfer of heat occurring, in most proposals, in a surface heat exchanger. This is the binary type of plant. Alternatively, the brine can be subjected to a single-stage or multiple-stage process of throttling as a result of which a fraction of it flashes into steam or into steam mixed with an inert gas. This is then used to drive a steam turbine. All such systems share the common characteristic that the brine, brought to the surface at a pressure and temperature exceeding in magnitude the pressure, P_0 , of the surrounding atmosphere and its temperature, T_0 , is expanded and cooled, supplying work at the same time. Thus, the fundamental process of extracting work from the resource does not rely on a cycle, but on the transformation of the working fluid from its initial state 1 (P_1, T_1) to some final state 2. The final state 2 is related to the pressure and temperature in the surrounding atmosphere and to the degree of perfection with which we can design the elements of the plant. The basic question that we seek to answer is how to secure the largest work rate attainable per unit mass rate of flow of a given brine.

In our quest for the thermodynamic optimum we shall assume that the initial state 1 is that prevailing at the wellhead. The change in thermodynamic state which occurs between the reservoir and wellhead, and which involves a

loss in specific work, cannot be ignored by the designer; it must be taken into account when the design and operation of the well itself is fitted into the general scheme.

We recognize here that the designer of a geothermal plant is in a different situation from that of the designer of a fossil-fuel plant or, even, a nuclear plant in that his freedom to choose the inlet conditions of to optimize with respect to them is much more limited. Nevertheless, he can exert some influence on the state at the wellhead under some conditions by his decision to employ or to omit a downhole pump. For example, if conditions are suitable, flashing in the well can be prevented by a downhole pump. Whether the use of such a pump is or is not justified in a particular field is not discussed in this report.

The pressure P_0 and temperature T_0 of the surrounding atmosphere are also beyond the designer's control. The pressure P_0 changes little but the temperature T_0 is subject to quasiperiodic fluctuations on two widely differing time-scales: Diurnal and annual. These quasiperiodic fluctuations exert a profound effect on the design of a geothermal plant. In order to understand this influence it is convenient first to analyze the thermodynamic processes that occur here on the assumption of a constant value of T_0 (as well as P_0). The effect of varying T_0 must be studied separately, and the variation of P_0 constitutes no more than a trivial perturbation of the main analysis. The rate of variation of T_0 is always slow enough to permit us to regard the time-dependent regime as quasisteady.

The final state 2 is one that the design analysis will determine. The most desirable, and, as must be expected, unattainable optimum will correspond to the highest value, w_0^0 , of work per unit mass of fluid flowing through the installation. Here, the principles of thermodynamics supply a clear general rule: The largest amount of work will become available under the hypothetical

conditions when the process of expansion from state 1 to state 2 and the process of discharge into the surrounding atmosphere occur without entropy production, that is, reversibly. In other words, the non-zero change in the entropy of the brine from state 1 to state 2 must be compensated by an equal and opposite change in the entropy of the surrounding atmosphere. For each departure from ideal conditions, a different final state 2 results.

4. Typical installations

Before we proceed to define the systems in terms of which the thermodynamic analysis is best conducted, it is useful to become familiar with several of the most practical arrangements currently employed or contemplated in the geothermal industry. Schematics of these are contained in Figs. 3-8.

Figure 3 represents the system used to exploit a direct, dry-steam resource. Steam at state 1 (P_1, T_1) and rate $\dot{m}$ from the production well operates a condensing steam turbine which drives the generator and supplies work at a rate $\dot{W}$ to the surroundings. The condensed liquid, after transferring heat at a rate $\dot{Q}_0$ to the surroundings, is returned to the reinjection wells at state 2 (P_2, T_2). In general, the chemical composition of the working fluid will also change between states 1 and 2. For the sake of simplicity, it is assumed here that the steam contains no noncondensable gases. The thermodynamic system inside the control surface shown in broken lines is an open one; it communicates with the well at 1, and with the atmosphere around the remainder of its boundary. The work rate $\dot{W}$ is the net quantity measured at the bus bar, with that required to drive the pumps, fans and other auxiliaries subtracted.

The cooling tower shown in the sketch discharges large quantities of vapor into the atmosphere. This is symbolized by a discharge of fluids at a rate $\dot{m}_3$ and at state 2₃. The condensed fluid at state 2₂ and rate $\dot{m}_1$ is discharged

Fig. 3. Schematic diagram of a direct dry-system plant

through the injection wells. By continuity we must have

$$\dot{m} = \dot{m}_1 + \dot{m}_3 \quad (1)$$

Since up to 80% of the flow passing through the turbine may be lost through evaporation, a careful water budget must be established for each plant. In an alternative analysis, the operation of the cooling tower may be accounted for separately and the control surface may be drawn through the supply and discharge line of the condenser.

Figure 4 contains a schematic diagram of a hydrothermal-steam turbine unit in which the two-phase mixture at 1 is first separated into a stream of vapor and liquid. The thermodynamic open system defined by the broken lines is the same in its essentials as that shown in Fig. 3, except that now the installation rejects liquid water through two channels: the separated condensate at state 2_1 and rate $\dot{m}_1$ and the spent condensate at state 2_2 and rate $\dot{m}_2$, with

$$\dot{m} = \dot{m}_1 + \dot{m}_2 + \dot{m}_3 \quad (1a)$$

The schematic diagram in Fig. 5 illustrates the operation of a single-flash system which admits a high-pressure, high-temperature liquid aqueous solution of state 1 (P_1, T_1) from the wells, throttles it in the flasher to produce a stream of liquid rejected at a rate $\dot{m}_1$ and a stream of steam which it directs to the turbogenerator. Ultimately, this is rejected as condensate at state 2_2 and rate $\dot{m}_2$ after passing through the condenser and cooling tower. The latter loses fluid at rate $\dot{m}_3$ and state 2_3 as before.

The diagram in Fig. 6 depicts a so-called double-flash system which operates with a two-phase fluid issuing from the wellhead. The brine is usually found in liquid form in the reservoir but flashes at a relatively

Fig. 4. Schematic diagram of a plant which utilizes a two-phase mixture

Fig. 5. Schematic diagram of a single-flash system

Fig. 6. Schematic diagram of double-flash system

high pressure into a mixture in the well. Steam is separated from the mixture in the separator, and the remaining high-pressure liquid is throttled once more in the flasher. In this manner the turbine is presented with two streams of steam, each dry but at a different pressure, and must be designed either as a two-cylinder unit or as a single-cylinder unit with two inlet points.

It would seem advantageous from a thermodynamic point of view to increase the number of flashes in such an installation because an increase in the number of throttling stages improves the utilization factor, but the increased complexity of the plant reduces the attractiveness of such an arrangement.

The schematic of Fig. 7 represents a binary energy conversion system. Here the hot brine yields its energy in a counterflow heat exchanger to a suitably chosen working fluid characterized by a low boiling point. This may be a fluorocarbon, a hydrocarbon such as isobutane or pentane, or a mixture of similar substances. The brine transforms its state from 1 to 2 without much change in composition and it should be noted that it does not transfer its heat at a constant temperature but over a range of temperatures from T_1 to T_2 . The installation is equivalent to an open system which produces net work at a rate $\dot{W}$, rejects heat at a rate $\dot{Q}_0$, admits brine at a rate $\dot{m}$ at state 1 and rejects it at states 2_1 and 2_3 at the same total rate. The system contains an internal loop consisting of the working-fluid side of the heat exchanger, of the turbine and the condenser. The working fluid circulating through this internal loop performs a closed Rankine cycle.

In the final example represented by Fig. 8 it is assumed that the entering brine at state 1 contains in it a dissolved inert gas, such as CO_2 or N_2 . Since the solubility of a gas at the inlet conditions is relatively high, the inlet flow will occur, in most cases, in a single phase. Similarly, as

Fig. 7. Schematic diagram of binary unit

Fig. 8. Schematic diagram of a single-flash plant in which the fluid carries a substantial proportion of an inert gas

shown here, the mixture of steam and inert gas is homogeneous. This mixture is made to flow through a turbine in which the shaft work is now produced by the joint expansion of vapor and inert gas. Along the path of expansion the steam will partly condense, and the condenser will evolve two phases: the liquid phase in which the dissolved gas constitutes a negligible quantity, and an equilibrium mixture of water vapor and gas. This gas, after initial compression and partial cooling in coil c accompanied by further condensation, must be compressed again before it can be rejected to the atmosphere. Compression can occur by means of an ejector, which is intrinsically inefficient, or through a rotary compressor. In any case a substantial amount of work must be expended, and this reduces the net work rate $\dot{W}$ compared with an installation with no inert gas. The difference in operation, compared with the previous examples, can be reduced to the observation that the open system has now acquired a channel through which gas at a rate $\dot{m}_3$ is rejected to the atmosphere at state 2₃. The control volume shown in the sketch is so drawn as to place the compressor inside it.

5. The thermodynamic system

The examples of different installations presented in Section 4 convince us that we can choose for the analysis of geothermal installations the general open system depicted in Fig. 9. The system receives a steady stream at mass-flow rate $\dot{m}$ of a fluid at state 1. The state of the entering fluid is described by its temperature T_1 , its pressure P_1 (or its quality x_1), the set of mol or mass fractions, ξ_1 , of the noncondensable gases dissolved in it and of the mol or mass fractions, ζ_1 , of the dissolved solids. The system rejects against a pressure P_0 n streams at respective rates $\dot{m}_1, \dots, \dot{m}_i, \dots, \dot{m}_n$, each state being described by a similar set of parameters: P_{2i}, T_{2i} (or x_{2i}), ξ_{2i} and ζ_{2i} . If the exit pressures are higher than P_0 , it is possible to gain

Fig. 9. Open system chosen for the analysis

extra work by allowing each stream to expand from P_{2i} to P_0 . In the opposite case, compressors are needed. The system is assumed to communicate with an ideal heat reservoir of constant temperature T_0 with which it exchanges heat at a rate $\dot{Q}_0$ (positive if into the system, and negative if out of the system). Once started, the system is assumed to operate "spontaneously" producing net work at a rate $\dot{W}$.

We conduct the analysis in terms of open systems operating in steady state. This is justified for two reasons. First, geothermal installations are intrinsically intended for base-load operation involving very long periods of functioning under fixed conditions. Secondly, as already mentioned in connection with temperature variations, the effect of variable conditions is best studied as a quasisteady perturbation of the steady state.

6. The atmosphere

In the preceding choice of system, the atmosphere has been idealized into a work reservoir of constant back-pressure P_0 and a heat reservoir of constant temperature T_0 . In accordance with the accepted methodology of thermodynamics we assume that the *atmosphere*, as distinct from the system, is always in equilibrium which is equivalent to saying that it can perform only reversible processes. Thus the work performed by the atmosphere when it is displaced at a volumetric rate $\dot{V}$ is

$$\dot{W}_a = P_0 \dot{V}, \quad (2)$$

its energy changes at a rate

$$\dot{U}_a = -\dot{Q}_0, \quad (3)$$

and its entropy changes at a rate

$$\dot{S}_a = -\dot{Q}_0/T_0. \quad (4)$$

Even though the system performs work against the atmosphere or has work performed on it at the rate $\dot{W}_a$, the assumption of "infinite size" for the work reservoir allows us to neglect this term in the computation of $\dot{U}_a$, but not in the energy balance of the system proper.

It should be emphasized at this point that the preceding framework for the analysis has been built around the two entities which exist naturally: the brine and the atmosphere. In particular, it recognizes the fact that the atmosphere constitutes the single heat sink which need not be sustained artificially.

7. The Second Law and entropy production

The so-called second part of the Second Law of thermodynamics (Kestin 1966, 1968, Kestin and Dorfman 1971) is usually formulated as the assertion that the entropy of an *isolated* system at the end of an irreversible process exceeds that at its beginning. The restriction to an isolated system is not really necessary, it being sufficient to consider an *adiabatic* system. Thus we can assert that the entropy of an adiabatic system which exchanges only work with the surroundings must increase from its value S_α^{ad} at the initial equilibrium state to its value S_β^{ad} at the final equilibrium state, having performed an irreversible process $\alpha \rightarrow \beta$. It is now convenient to introduce here a concept which has proved very fruitful in the study of irreversible processes in continuous systems--that of entropy production θ . In the present application, the difference

$$S_\beta^{ad} - S_\alpha^{ad} = \theta, \quad \theta > 0, \quad (5)$$

is *defined* as the entropy produced by the irreversible process $\alpha \rightarrow \beta$. Taking into account eq. (5), we can state the second part of the Second Law by simply asserting that the entropy production must be positive. We may, if we wish,

add that in the unattainable case of reversible operation the entropy production vanishes ($\theta = 0$).

8. The governing equations

8.1 First Law

In order to write down the two laws of thermodynamics for the open system shown in Fig. 9, it is convenient to create a closed adiabatic system by observing the installation during an interval of time dt and by including in it

the geothermal plant--the open system of Fig. 9

the atmosphere

$\dot{m}dt$ units of brine about to enter the plant (this part

"vanishes" from the adiabatic system after time dt)

and by excluding

n elements of volume $\dot{m}_i v_{2i} dt$ about to be filled by the effluents

(these parts "appear" in the adiabatic system after time dt).

The adiabatic system is shown sketched in Fig. 10 which emphasizes that work must now be performed at the rates

$$-\dot{m}P_1 v_1 \text{ plus } n \text{ terms } + \dot{m}_i P_{2i} v_{2i}$$

on its boundary in addition to the rate $\dot{W}$. Here v denotes the specific volume, and the generic term $\dot{m}Pv$ represents the rate at which an atmosphere performs work on a fluid being displaced by or against its pressure, as stated in eq. (2). The energy of the heat reservoir, included in the closed system, changes at a rate $\dot{U}_a = -\dot{Q}_o$, as indicated in eq. (3).

In an adiabatic system of this kind, the rate of change of energy

$$\dot{U}_a - \dot{m}u_1 + \sum_{i=1}^n \dot{m}_i u_{2i} = -\dot{Q}_o - \dot{m}u_1 + \sum_{i=1}^n \dot{m}_i u_{2i}, \quad (6a)$$

Fig. 10. Adiabatic system

must be balanced by the rate at which work is done by the system

$$\dot{W} = \dot{m}P_1 v_1 + \sum_{i=1}^n \dot{m}_i P_{2i} v_{2i} \quad (6b)$$

Collecting all terms, and introducing the enthalpy $h = u + Pv$, we obtain the following, simple rate equation:

$$\dot{Q}_O - \dot{W} = \sum_{i=1}^n \dot{m}_i h_{2i} - \dot{m} h_1, \quad (7)$$

with

$$\sum_{i=1}^n \dot{m}_i = \dot{m} \quad (7a)$$

In cases where the specific potential energy, gL , with L denoting vertical location with respect to an arbitrary level, and the specific kinetic energy of the entering and leaving streams, $\frac{1}{2} v^2$, with v denoting the velocity, are significant, the energy u must be replaced by

$$u + gL + \frac{1}{2} v^2, \quad (8)$$

and eq. (7) acquires the more general form

$$\dot{Q}_O - \dot{W} = \sum_{i=1}^n \dot{m}_i \left(h_{2i} + gL_{2i} + \frac{1}{2} v_{2i}^2 \right) - \dot{m} \left(h_1 + gL_1 + \frac{1}{2} v_1^2 \right) \quad (9)$$

In what follows, we shall make use of the form of eq. (7) for simplicity, relying on the fact that the user can add the kinetic and potential energy terms to the enthalpy when circumstances justify it.

8.2 Second Law

In an analogous way, we can write the entropy balance equation (5) for the closed system. First, we transform eq. (5) into the very simple rate equation

$$\dot{S}^{ad} = \dot{O}, \quad (10)$$

and note that the rate $\dot{S}^{ad}$ must include that for the open system as well as for the heat reservoir in accordance with eq. (4). The former is

$$-\dot{m}s_1 + \sum_{i=1}^n \dot{m}_i s_{2i} ,$$

and we obtain

$$-\dot{Q}_0/T_0 - \dot{m}s_1 + \sum_{i=1}^n \dot{m}_i s_{2i} = \dot{\Theta} \quad (11)$$

By the elimination of the heat rate $\dot{Q}_0$ among eqs. (7) and (11), we obtain the following expression which relates the work rate $\dot{W}$ to the change in state between inlet and outlets and the rate of entropy production caused by the intrinsically irreversible character of real processes:

$$\dot{W} = \left\{ \dot{m}h_1 - \sum_{i=1}^n \dot{m}_i h_{2i} \right\} - T_0 \left\{ \dot{m}s_1 - \sum_{i=1}^n \dot{m}_i s_{2i} \right\} - T_0 \dot{\Theta} . \quad (12)$$

It is useful to introduce the concept of specific work

$$w = \dot{W}/\dot{m} \quad (13)$$

per unit mass of brine into eq. (8). The entropy production per unit mass of brine is denoted by θ , so that

$$\theta = \dot{\Theta}/\dot{m} . \quad (13a)$$

We then obtain the equivalent form

$$w = \left\{ h_1 - \sum_{i=1}^n \mu_i h_{2i} \right\} - T_0 \left\{ s_1 - \sum_{i=1}^n \mu_i s_{2i} \right\} - T_0 \theta , \quad (14)$$

where

$$\mu_i = \dot{m}_i/\dot{m} . \quad (15)$$

This, and the equivalent eq. (12), are the most important expressions in this analysis. In the next section we shall proceed to interpret these equations

and to adapt them to different circumstances.

As already stated, the two equivalent eqs. (12) and (14) relate the specific work (or the work rate) to the change in state described by the properties h and s (plus L and V if necessary) which has occurred between inlet and outlet. Hence, implicitly at this stage, it is supposed that state 1 as well as all states 2_i are known. The entropy production, θ , which is a measure of irreversibility cannot be calculated other than by following all internal processes in detail. The only assumption of importance made during the derivation is that the open, steady-state system exchanges heat with a single thermal reservoir of constant temperature T_o .

The importance of eqs. (10) and (14) stems from the fact that they are valid for any working fluid without restriction, that they include in one formula the effects of the pressure and temperature of the working fluid, the temperature and pressure of the surroundings, the change in composition and phase of the working fluid and, if necessary, the change in elevation and flow velocity.

The quantity of work

$$w^o = \left\{ h_1 - \sum_i \mu_i h_{2i} \right\} - T_o \left\{ s_1 - \sum_i \mu_i s_{2i} \right\} \quad (16)$$

obtainable during reversible operation (i.e. at $\theta = 0$) occupies an important place in our considerations. There is no general agreement as to the terminology for it. Terms such as *maximum work*,[#] *available work* or *exergy* have been advocated. In the next section we shall discover the need for two new terms. For this reason we shall adopt the designation *available work* for the quantity w^o from eq. (16) which represents the work that a system is capable

[#]The quantity w^o is not really a maximum of w with respect to θ , because the derivative of w does not vanish at $\theta = 0$; it is a so-called supremum (largest value over an interval).

of furnishing during an arbitrary reversible process between a *prescribed* initial state 1 and a *prescribed* final state 2. In the present study state 2 consists of n state specifications for the effluents. The largest possible value, w_o° , of w° for given inlet conditions will be defined as the exergy of state 1.

Some authors also introduce the *availability function*

$$b = h - T_o s, \quad (17)$$

in terms of which eq. (16) can be written

$$w^\circ = b_1 - \sum_{i=1}^n \mu_i b_{2i}. \quad (18)$$

We shall not use the availability function in this report.

It is worth adding here parenthetically that for $w^\circ < 0$ we have

$$|w^\circ| = \left\{ \sum_{i=1}^n \mu_i h_{2i} - h_1 \right\} - T_o \left\{ \sum_{i=1}^n \mu_i s_{2i} - s_1 \right\}, \quad (19)$$

which constitutes the smallest[#] absolute value of work done on the system.

9. Capacity to perform work

We now proceed to use the form of eq. (14) to deduce an expression for the largest amount of work that can be derived from a unit mass of brine in its thermodynamic state at the wellhead, state 1, given a set of conditions in the atmosphere.^{##} We regard this best value, w_o° of w , as the brine's "capacity to perform work." In a conventional exposition which favors the cycle method, this role is ascribed to the "heat content," that is to the difference

[#]In modern mathematical terminology this is described as an *infimum* (smallest value over an interval).

^{##}If our goal were to assess the potential represented by a geothermal reservoir, we would choose state one in the reservoir itself at shut-off conditions.

between the energy or enthalpy of the brine at state 1 and the effluents at the temperature T_0 . We shall motivate our preference in Section 14.

Since the entropy production, θ , in eq. (14) must always be positive, the vanishing of θ is a necessary condition for w to be largest. This, however, is not sufficient, because the process of discharge, as well as all processes external to the adiabatic system of Fig. 10 must be reversible. To achieve reversibility outside the boundaries of the open system, it is further necessary to ensure that all effluents reach pressure P_0 and temperature T_0 , otherwise the mixing of fluids in the atmosphere at different temperatures or pressures would cause further entropy production. Following J. H. Keenan (1932, 1941), we shall describe states 2_1 characterized by P_0 , T_0 as the *dead state*. However, even this is not sufficient, because the chemical nature of the effluents is different from that of the atmosphere, and entropy production due to the mixing of *different fluids* at constant pressure and temperature will occur. In order to avoid the latter it would be necessary to exhaust the effluents through semipermeable membranes or at a state in which the chemical potential of each species is equal to that which it possesses in the atmospheric air. Such an additional process would increase the amount of work performed. A moment's reflection convinces us that this last possibility is unrealistic and that its adoption would be misleading because it would set for the designer a goal that he could not hope to approach by a sizeable, finite margin. For this reason, we adopt as our measure of the brine's capacity to perform work that quantity which results when operation incurs no internal entropy production

$$\theta = 0, \quad (20)$$

and when brine at state 1 is transformed into n effluent streams, each discharge occurring at P_0 , T_0 but at a composition $\underline{x}_2$, $\underline{x}_2$ dictated by the

operation of the actual plant. For example, in Fig. 8 we assume that the condensate leaving the plant is pure water or an aqueous salt solution, and that the inert gas leaves it at P_o , T_o (with a very small addition of water vapor) rather than at a state of reduced chemical potential to match that prevailing in the atmosphere.

Bearing in mind the preceding limitations, we now distinguish between two expressions for available work: (a) The available work w^o which can be obtained by reversible operation for the actual states 2_i prevailing at the exit, and (b) the available work w_o^o which characterizes fictitious reversible operation to the dead state. We choose the latter as a measure of the brine's capacity to perform work. Thus, we record the following equations:

(a) Actual conditions:

$$w = \left\{ h_1 - \sum_i^n \mu_i h_{2i} \right\} - T_o \left\{ s_1 - \sum_i^n \mu_i s_{2i} \right\} - T_o \theta ; \quad (21a, b)$$

$$w^o = \left\{ h_1 - \sum_i^n \mu_i h_{2i} \right\} - T_o \left\{ s_1 - \sum_i^n \mu_i s_{2i} \right\} ;$$

state at exit: $P_{2i}, T_{2i}, E_{2i}, L_{2i}$.

(b) Dead state reached at exit:

$$w_o^o = \left\{ h_1 - \sum_i^n \mu_i h_{oi} \right\} - T_o \left\{ s_1 - \sum_i^n \mu_i s_{oi} \right\} ; \quad (22)$$

state at exit: P_o, T_o, E_{2i}, L_{2i} .

In order to distinguish between the available work, w^o , which characterizes two arbitrary states 1 and 2, and its highest value, w_o^o , for a given state 1 with respect to a prescribed atmosphere of pressure P_o and temperature

T_o , we shall introduce the term *exergy* and the symbol e for the latter.[#]

Hence eq. (22) is equivalent to

$$e_1 \equiv w_o^o = \left\{ h_1 - \sum_{i=1}^n \mu_i h_{oi} \right\} - T_o \left\{ s_1 - \sum_{i=1}^n \mu_i s_{oi} \right\} . \quad (23)$$

The exergy, e_1 , of state 1 acquires the character of a thermodynamic potential as soon as P_o and T_o are laid down. It is easy to see that

$$w^o = e_1 - e_2 \quad (24)$$

with

$$e_2 = \sum_{i=1}^n \mu_i e_{2i} \quad (25)$$

and

$$w = e_1 - e_2 - T_o \theta . \quad (26)$$

10. Energy dissipation and utilization factor

The difference between the available work w^o and the actual work delivered, w , for *identical inlet and exhaust conditions* is a measure of the shortcomings of the geothermal installation; it represents the *work* (or what is now fashionably, but inconsistently, called energy) *dissipated* or lost,

$$w_d = w^o - w = T_o \theta . \quad (27)$$

The difference

$$w_{do} = w_o^o - w = (w_o^o - w^o) + (w^o - w) \quad (28)$$

is a measure of two effects: of the dissipation

$$w_d^a = w_o^o - w^o = T_o \theta^a = w_{do} - w_d = e_2 \quad (29)$$

[#]Exergy, e , and availability, b , become identical if the enthalpy and entropy of the dead state are both normalized to zero, $h_o = s_o = 0$.

resulting from our inability to reach the dead state at exit, and the dissipation

$$w_d = w^o - w = T_o \theta \quad (30)$$

which generates entropy θ in the plant and is transferred to the atmosphere.

The entropy production θ , or the real work w , can be calculated for an existing installation by carefully assessing all imperfections in the design. This is done by analyzing the thermodynamic processes undergone by the working fluid and by identifying all sources of irreversible behavior in the plant. Such a calculation will also lead us to the determination of all states 2_1 , and hence of w_d^a and w_{do} . In a preliminary design analysis it is customary to introduce an empirical factor η_u , called the utilization factor, whose value is taken from earlier experience with similar installations or simply guessed. The utilization factor *for the whole plant* is defined as

$$\eta_u = w/w_o^o = 1 - T_o(\theta^a + \theta)/w_o^o \quad (31)$$

that is as the ratio of the work actually delivered to the maximum possible with the given thermodynamic state at the inlet and the characteristics of the atmosphere. Typical values of η_u for a variety of completed installations and based on the exergy $e_1 = w_o^o$ of the fluid at the well-head can be found in R. DiPippo (1978b).

The quantities $\theta^a + \theta$, w_{do} and η_u are related to each other through the equations

$$w_{do} = \frac{1-\eta_u}{\eta_u} w = w_o^o(1 - \eta_u) \quad (32)$$

and

$$\theta^a + \theta = \frac{1-\eta_u}{\eta_u} \frac{w}{T_o} = \frac{w_o^o(1-\eta_u)}{T_o} \quad (33)$$

The concept of a utilization factor can also be applied to a work-producing component of the plant, such as, for example, the turbine itself. In this case the utilization factor η'_u of the component is defined as

$$\eta'_u = w/w^o = 1 - T_o \theta / w^o \quad (31a)$$

The relations corresponding to eqs. (32) and (33) are

$$w_d = \frac{1 - \eta'_u}{\eta'_u} w = w^o (1 - \eta'_u) \quad (32a)$$

and

$$\theta = \frac{1 - \eta'_u}{\eta'_u} \frac{w}{T_o} = \frac{w^o (1 - \eta'_u)}{T_o} \quad (33a)$$

11. Rate of heat rejection to atmosphere

Equation (7) combined with eq. (12) allows us to calculate the rate at which heat is rejected to the atmosphere. Calculating

$$q_o = \dot{Q}_o / \dot{m} \quad (34)$$

that is the rate of heat rejection per unit mass of brine, we obtain

$$-q_o = T_o \left\{ s_1 - \sum_{i=1}^n \mu_i s_{2i} + \theta \right\} \quad (35)$$

This equation shows that the actual amount of heat rejected exceeds that which would be rejected under ideal operating conditions by the product of the absolute temperature of the atmosphere and the entropy generated by irreversible operation, that is by the dissipated work. By the use of eq. (31) it is possible to replace the latter by a combination of a work term and utilization factor.

The ratio

$$r = (-q_o)/w = (-q_o^o + T_o \theta)/(w^o - T_o \theta) \quad (36)$$

of the heat rejection to the work, and its ideal value

$$r_o^o = (-q_o^o)/w_o^o, \quad (37)$$

is a measure which gives an initial idea of the size of the heat rejection system.

We revert to this point in Section 12.

12. Numerical examples

In order to benefit from the equations of Sections 9-11 to the full extent it is necessary to have access to reliable tables of thermodynamic properties of brines of prescribed compositions and of solutions of inert gases in them. These are quite scarce at present, and the matter will be discussed again in Sec. 17. For this reason most contemporary calculations rely on the use of simplified models for the properties of brines. Clearly the simplest model is afforded by pure water substance whose thermodynamic properties have been carefully tabulated and sanctioned by a series of international agreements [C. A. Meyer et al., 1967]. However, the effect of dissolved solids must not be underestimated. The diagram in Fig. 11 depicts graphically the variation of the available work, $w_o^o = e_1$, of pure water at a pressure of $P_1 = 8.59$ MPa (saturation pressure for 300°C) as a function of temperature for $T_o = 25^\circ\text{C}$. The diagram also contains curves for solutions of sodium chloride under the same condition and for varying mass fractions ζ . At $\zeta = 1$ molal (corresponding roughly to 5.5% of NaCl by weight), the loss in available work due to the presence of the solute ranges from 6.6% at 150°C to 7.0% at 300°C. The properties of the salt solution were taken from Silvester and Pitzer (1976).

Fig. 11. Available work, w_o^o of pure water at a pressure $P_1 = 8.59$ MPa (saturation pressure for 300°C) as a function of temperature T_1 for $T_o = 25^\circ\text{C}$ and for various solutions of common salt at saturation pressure

Similarly important is the admixture of an inert gas. The diagram in Fig. 12 represents the variation of the exergy for a vapor-dominated well as a function of temperature with the mass fraction, $\xi = \dot{m}_{\text{CO}_2} / \dot{m}_{\text{total}}$, of carbon dioxide as a parameter. The case $\xi_1 = 0.15$ roughly corresponds to the conditions encountered in some wells at Larderello in Italy. The calculations have been performed on the assumption that the heat of mixing is negligible. The properties of steam were taken from Keenan et al. (1969) and those of carbon dioxide from Din (1956). The atmospheric temperature has been assumed at $T_0 = 25^\circ\text{C}$.

The preceding two diagrams confirm the utility of employing available work to rank geothermal wells. Identical quantities of water and brine at the same temperature possess different capacities to perform work. For example, at $T_1 = 150^\circ\text{C}$, $w_0^\circ = 88.0 \text{ kJ/kg}$ for $\xi_1 = 0$ and $w_0^\circ = 71.6 \text{ kJ/kg}$ for $\xi_1 = 4 \text{ molal}$. Similarly, the same value $w_0^\circ = 200 \text{ kJ/kg}$ occurs at $T_1 = 220^\circ\text{C}$ for $\xi_1 = 0$, and at $T_1 = 242^\circ\text{C}$ for $\xi_1 = 4 \text{ molal}$. Analogous remarks apply to the mixture of saturated steam and carbon dioxide. One kilogram of mixture with $\xi = 0.15$ has a lower capacity to perform work than pure saturated steam (by approximately 17% at $T_1 = 250^\circ\text{C}$), both mixtures being at the same temperature but at different pressures, even though in the case of the mixture the *partial* pressure of steam is equal to its saturation pressure, the addition of carbon dioxide serving to increase the *total* pressure.

It is interesting to note that the available work of vapor-dominated wells, with or without an inert gas dissolved in the steam, passes through a maximum at a temperature slightly larger than 300°C .[#]

[#]The broken lines in Fig. 12 indicate that the properties of the working fluid have been computed assuming ideal mixing.

Fig. 12. Available work, w_o^o for a vapor-dominated well as a function of temperature T_1 and a mass fraction of carbon dioxide, $\xi = \dot{m}_{\text{total}}$. The case $\xi_1 = 0.15$ roughly corresponds to the conditions encountered at Larderello in Italy

The diagram in Fig. 13 plots in one graph the ideal available work w_o° as well as the ideal rejected heat, $-q_o^\circ$, for a vapor-dominated well for pure steam when $\theta = 0$. The quantities are given as functions of the inlet temperature T_1 with $T_o = 25^\circ\text{C}$. The diagram of Fig. 14 contains a cross-plot and represents the ideal ratio

$$r_o^\circ = (-q_o^\circ)/w_o^\circ . \quad (38)$$

This ratio decreases from the very large value $r_o^\circ = 4.3$ at $T_1 = 100^\circ\text{C}$ to $r_o^\circ = 1.6$ at $T_1 = 300^\circ\text{C}$. The diagram illustrates clearly the fact that the heat rejection rate per unit power produced tends to be very large in geothermal turbines and eq. (36) shows that irreversible operation increases the quantity quite considerably by increasing the numerator and decreasing the denominator by the dissipated work $w_d = T_o \theta$.

For purposes of comparison we have plotted in Fig. 15 the ratio r_o° for near-critical and supercritical steam turbines operating at $T_1 = 540^\circ\text{C}$ and different pressures. In nuclear installations which employ a boiling-water reactor, the steam is dry saturated at turbine inlet. The practical range of temperature $230\text{--}350^\circ\text{C}$ is marked in Figs. 13 and 14. The three diagrams underline the fact that the relative heat rejection rate for a geothermal turbine tends to be higher than for its competitors, necessitating a larger (and more expensive) condenser per unit output. It must, however, be realized that the heat-rejection rate

$$-\dot{Q}_o = -q_o \dot{m} \quad (39)$$

is not identical with the rating of the condenser, because the latter handles only the fraction $\mu_{\text{H}_2\text{O}}$ of condensed water which leaves the installation through it. For example, the separated liquid in a flash-type plant bypasses the condenser, but the heat rejected by it to the atmosphere is included in

Fig. 13. The ideal available work, w_o^0 , and the corresponding rejected heat $-q_o^0$ for vapor-dominated wells with $T_o = 25^{\circ}\text{C}$. The thick lines correspond to the practical range encountered in nuclear power plants

Fig. 14. Cross-plot from Fig. 13 showing the ideal heat-rejection ratio $r_o^o = (-q_o^o)/w_o^o$. The thick line corresponds to the practical range encountered in nuclear power plants

Fig. 15. The ideal heat-rejection ratio r_o^0 for fossil turbines operating at $T_1 = 540^\circ\text{C}$ and different pressures

$(-q_o^\circ)$. A detailed assessment of the proper condenser load presents no difficulty in individual cases.

It should not be automatically assumed that q_o or q_o° are necessarily negative, even if they turn out to be so in geothermal energy conversion. We shall show in Section 13 that for combustion processes $-q_o^\circ$ is negative ($q_o^\circ > 0$) signifying that the process, like a heat pump, extracts heat from the surroundings. In such cases the available work may become larger than the total change in enthalpy $h_1 - \sum_{i=1}^n \mu_i h_{2i}$ per unit mass of working fluid. The only quantity with a definite sign is that of entropy production, θ , which must always be positive.

The very high heat rejection ratio which occurs at lower temperatures T_1 , illustrated in Fig. 14, suggests that the operation of a geothermal plant must be sensitive to the heat rejection temperature of the working fluid. Here it is necessary to distinguish two effects: (a) an increase in the brine rejection temperature T_2 ; (b) an increase in the temperature of the environment, T_o . For pure water, in the former case

$$w_o^\circ = h_1 - h_2 - T_o(s_1 - s_2) \quad \text{and} \quad -q_o^\circ = T_o(s_1 - s_2) \quad (22b,c)$$

are analyzed as functions of T_2 with $T_o = \text{const}$. In the second case, the expressions

$$w_o^\circ = h_1 - h_o - T_o(s_1 - s_o) \quad \text{and} \quad -q_o^\circ = T_o(s_1 - s_o) \quad (23b,c)$$

are analyzed as functions of T_o on the supposition that $T_2 = T_o$.

Case (a) implies that the brine is cooled to temperature $T_2 > T_o$, but that heat is rejected in the condenser at the ideal temperature T_o . This case is illustrated in Figs. 16 and 17 which plot the available work $w^\circ = e_1 - e_2$ and the heat rejection ratio $r^\circ = (-q^\circ)/w^\circ$ for pure water operating in an environment of $T_o = 25^\circ\text{C}$ with $T_2 = 25, 40$ and 55°C . The sensitivity to

Fig. 16. The effect of the exit temperature T_2 on the available work w° .
 Brine modelled as pure water. Atmosphere at $T_o = 25^\circ\text{C}$

Fig. 17. Effect of the exit temperature T_2 on the heat-rejection ratio $r^0 = (-q^0)/w^0$. Atmosphere at $T_0 = 25^\circ\text{C}$. Brine modelled as pure water

changes in T_2 is of a few percent (approximately 2% on changing T_2 from 25°C to 55°C at 250°C).

Case (b) implies that the brine is always cooled to T_o equal to the rejection temperature which, itself, is made to assume the values $T_o = 25, 40$ and 55°C . This case is illustrated in Figs. 18 and 19, and, as expected, the effect turns out to be considerably larger than previously, reaching a drop of 43% in w_o° on changing T_o from 25°C to 55°C with $T_1 = 150^\circ\text{C}$ as well as an increase of 42% in r_o° under the same conditions.

It is seen from the preceding equations that a change in T_o in case (b) to $T'_o = T_2$ of case (a) reduces the available work by

$$(T'_o - T_o) (s_1 - s_2) .$$

The graphs show that the operation of a geothermal plant is very sensitive to the heat-rejection temperature, particularly, as might be expected, at the lower end of the inlet-temperature range. Comparison with Fig. 18 shows that at $w_o^\circ = 200 \text{ kJ/kg}$ an increase of 15°C or 30°C in the heat-rejection temperature $T_2 = T_o$ is equivalent to a loss of 19°C and 34°C, respectively, in the brine inlet temperature.

Similar diagrams could be prepared for operation with saturated steam, but we shall not present them here for the sake of brevity. The matter will be illustrated graphically with the aid of T,s diagrams in Section 16.

13. Fossil fuel

The ideal available work w_o° in a fossil fuel is governed by the same general expression as that valid for geothermal energy, eq. (23b) in Section 12. The fossil fuel is usually fed to the burner at atmospheric pressure and temperature, and the optimum end condition for the combustion gases is the dead state. Furthermore, the air used for combustion is also aspirated at the dead state. Consequently, it is easy to see that the enthalpy

Fig. 18. Effect of heat-rejection temperature, T_o , on the ideal available work, w_o^o . Brine modelled as pure water

Fig. 19. Effect of heat rejection temperature T_0 , on the ideal heat-rejection ratio $r_0^o = (-q_0^o)/w_0^o$. Brine modelled as pure water

and entropy differences in the above equation can be interpreted as the enthalpy of combustion, ΔH° , and the entropy of combustion, ΔS° , both taken at the standard state P_0 , T_0 . In actual fact the *negative* of these quantities must be taken because the usual convention in chemical tables is to use the symbol Δ in ΔH° and ΔS° to mean the difference between products (state 2) and reactants (state 1). Consequently,

$$w_0^\circ = - \left\{ \Delta H^\circ - T_0 \Delta S^\circ \right\} = - \Delta G^\circ \quad (40)$$

where ΔG° denotes the Gibbs free energy of the reaction taken at standard conditions.

For example, from standard tables (Kestin, 1968) we can find for the complete combustion of carbon, $\Delta H^\circ = - 32805$ kJ/kg and $\Delta G^\circ = - 32877$ kJ/kg so that heat $T_0 \Delta S^\circ = 72$ kJ/kg could be added to a reversible reactor. Similarly, for the complete combustion of methane, $\Delta H^\circ = - 50181$ kJ/kg; $\Delta G^\circ = - 50084$ kJ/kg; $T_0 \Delta S^\circ = - 97$ kJ/kg. These two examples demonstrate that the exergy of a fossil fuel differs very little from the enthalpy which can be derived from it upon complete combustion and cooling down to ambient temperature. The circumstance that $T_0 \Delta S^\circ > 0$ for carbon, indicating that q_0° is positive, that is that heat is absorbed from the atmosphere when such a reaction is performed *reversibly*, as implied by the equation, is secondary for our purposes. We merely add parenthetically that the ideal work of a reversible fuel cell would exceed the enthalpy made available by the same amount of fuel burned irreversibly.

14. Energy and cycle efficiency as a measure of capacity to perform work

The conventional method of ranking thermal power plants and of crudely assessing their economy is to indicate their thermal efficiency. The simplest

Carnot cycle assumes the existence of an energy reservoir which is capable of transferring heat at a rate $\dot{Q} = -\dot{U}$ without changing its temperature to an engine operating cyclically.[#] The adiabatic system which can be used to analyze the performance of such an engine is shown in Fig. 20. The First Law gives

$$-\dot{U} - \dot{U}_a + \dot{W} = 0 \quad \text{or} \quad \dot{W} = \dot{Q} + \dot{Q}_o, \quad (41a)$$

where $\dot{Q}$ and $\dot{Q}_o$ are reckoned positive when transferred to the Carnot engine. To conform with accepted conventions, we assign a positive value Q_o when it is rejected to the atmosphere at T_o and obtain the well-known expression

$$\dot{W} = \dot{Q} - \dot{Q}_o. \quad (41b)$$

With the same convention, the Second Law equation becomes

$$-\dot{Q}/T_1 + \dot{Q}_o/T_o = \dot{\theta}. \quad (42)$$

Referring to a unit mass of working fluid circulating at rate $\dot{m}$ through the Carnot engine, we can easily derive that

$$w = q (1 - T_o/T_1) - T_o \theta \quad (43)$$

and

$$w^o = q (1 - T_o/T_1). \quad (44)$$

The preceding argument shows that the standard formula implied in the Carnot efficiency

[#]In this section we refer to any cyclic engine which operates between two reservoirs of constant temperatures as a Carnot *engine* and make an explicit distinction between a reversible and an irreversible Carnot *engine*, as distinct from a reversible Carnot *cycle*.

Fig. 20. Carnot engine

$$\eta^o = \frac{w^o}{q} = 1 - T_o/T_1 \quad (45)$$

is contained as a special case in the method of available work. The plant efficiency, taking into account the production of entropy, is

$$\eta = \frac{w}{q} = 1 - \frac{T_o}{T_1} - \frac{T_o \theta}{q} \quad (46)$$

It is normally argued that an engine operating with two heat reservoirs is superior if the entropy production, θ , is reduced to a minimum, and if T_1 is as large as possible. This implies that the reference quantity, the heat per unit mass supplied, q , can serve as an acceptable measure of the operating cost. In a fossil-fuel plant the heat supplied, q , is usually set equal to the negative of the standard enthalpy of combustion $-\Delta H^o$, so that

$$\eta = \frac{w}{(-\Delta H^o)} = 1 - \frac{T_o}{T_1} - \frac{T_o \theta}{(-\Delta H^o)} \quad (47)$$

can be accepted as a first measure of economy. It was shown in Sec. 13 that the exergy of a fossil fuel is nearly equal to its Standard heat of reaction and it follows that the utilization factor

$$\eta_u = \frac{w}{w^o} \quad (48)$$

is practically identical with the plant efficiency, eq. (46), in the circumstances. Hence either η or its equivalent, η_u , can be adopted as a crude economic measure, because $-\Delta H^o$ or w^o are proportional to the economic value of the fuel. A fossil fuel can be burned in a furnace at a temperature far exceeding the maximum admissible for existing turbine-blade materials, and T_1 can, therefore, be interpreted as the contemporary metallurgical limit.

In the geothermal application the circumstances are different. First, the maximum temperature of a brine is far below the metallurgical limit. Consequently, the process of cooling the brine from T_1 to T_o cannot be modelled by a heat reservoir of constant temperature T_1 . Instead, the work per unit mass of brine is now

$$w = h_1 - h_2 - T_o (s_1 - s_2) - T_o \theta, \quad (49)$$

if we simply assume (as in a binary system) that the brine is used to heat a working fluid which performs a Rankine cycle. In a plant of this kind

$$\begin{aligned} \eta_u = \frac{w}{w^o} &= \frac{h_1 - h_2 - T_o (s_1 - s_2) - T_o \theta}{h_1 - h_2 - T_o (s_1 - s_2)} = \\ &= 1 - \frac{T_o \theta}{h_1 - h_2 - T_o (s_1 - s_2)}, \end{aligned} \quad (50)$$

whereas the thermal efficiency would become

$$\eta = \frac{w}{h_1 - h_2} = 1 - \frac{T_o (s_1 - s_2)}{h_1 - h_2} - \frac{T_o \theta}{h_1 - h_2}. \quad (51)$$

Now, the utilization factor and the thermal efficiency are not, even approximately, equal, because $T_o (s_1 - s_2)$ and $h_1 - h_2$ are of comparable orders of magnitude.

The diagram in Fig. 18 represents the available work w_o^o for pure water at saturation pressure as a function of temperature T_1 for three rejection temperatures $T_o = 25^\circ\text{C}$, 40°C and 55°C . The corresponding ideal cycle efficiency is seen plotted in Fig. 21. If we wanted to judge the percentage improvement achieved by a well operating at $T_1 = 300^\circ\text{C}$ compared with one at $T_1 = 150^\circ\text{C}$ with heat rejection at 40°C , we would compare $w_o^o = 338 \text{ kJ/kg}$ with

Fig. 21. Ideal thermal cycle efficiency, η , from eq. (51) with $\theta = 0$ as a function of temperature T_1 for three values of T_0 .

$w_0^o = 67$ kJ/kg from Fig. 18 and conclude that the improvement is one by a factor of 5. Indeed, the first installation would, other things being equal, deliver more than five times as much power as the first one. On the basis of plant thermal efficiency we would compare $\eta = 0.285$ with $\eta = 0.145$ and conclude that the improvement was merely by a factor of 2. The difference stems from the fact that comparison on the basis of two different enthalpy differences, $h_1 - h_2 = 465$ kJ/kg in the first case and $h_1 - h_2 = 1177$ kJ/kg in the second case, though consistent with the method of cycles, does not provide us here with an appropriate criterion.

Taking into account the preceding argument, we can motivate our preference for the use of the ideal available work, w_0^o or w^o , as a first measure of a reservoir's "capacity to perform work" because it more nearly represents a thermodynamically defined objective function subject to optimization than does the "heat content" or the efficiency. It is the former quantity rather than the latter two (or the temperature T_1) which truly ranks brines from the point of view of their utility for the production of electricity.

The utility of this concept is enhanced by the fact that it embraces in one short formula the influence of the pressure, temperature, composition and depth of location of the brine and the effect of the pressure and temperature of the surroundings as already mentioned in Section 8.2. Furthermore, it applies to all types of geothermal resources, including geopressured, as well as to competing plants: fossil and nuclear. Finally, it provides us with a statement of the thermodynamic ideal for every element of the plant which the designer will attempt to approach more and more closely knowing that he will never reach it. Thus it can serve as a very useful framework for a detailed pre-design analysis.

15. Historical digression

The concept of available work, w^o , with respect to an idealized atmosphere which has proved so useful as a basis for an initial thermodynamic analysis of geothermal resources is far from being new. Even though there is no universal agreement as to its utility, it seems to belong to the category of concepts which are discovered and re-discovered quite independently from time to time, and many have claimed, or been assigned, priority of discovery. The concept occurs quite explicitly in J. W. Gibbs's famous treatise (1928 or 1961) written in 1878 and in a paper written by M. Gouy in 1889. Its characteristics for chemical reactions seem to have been known to M. E. Jouguet (1917), and the famous author of the first standard treatise on steam and gas turbine design, A. Stodola (1927) makes good use of it; the first, German edition of his work appeared before the First World War! The idea is also mentioned in M. Roy's once popular French treatise on continuum mechanics (1947), its use has been advocated by Z. Rant (1953, 1956) in Germany and introduced into academic teaching by F. Bosnjakovic (1935) and H. D. Baehr (1966). In this country, J. H. Keenan advocated its use as early as 1932 (see also Keenan et al. 1973), quoting G. Darrieus (1930) as his predecessor. A recent Russian textbook (available in English translation of 1976) by V. A. Kirillin, V. V. Sychev and A. E. Sheindlin devotes much space to it. Last, we may mention J. Kestin's (1966) general treatise which introduces the concepts of lost and maximum work to the reader.

16. Graphical representation of available work

When the working fluid is a pure substance or when it passes through the installation without change in its chemical composition, the available work can be represented geometrically by areas or distances on thermodynamic diagrams. These diagrams are also useful when, as a first approximation, the geothermal fluid is modelled by pure water substance. Graphical methods and illustrations can be extended to include mixtures. However, the details of these developments have not been worked out so far.

16.1 General T,s diagram

The diagrams in Figs. 22a,b contain a geometrical interpretation of the available work with respect to the dead state, or exergy, in a general T,s diagram. In Fig. 22a $(s_1 - s_0) > 0$, whereas in Fig. 22b $(s_1 - s_0) < 0$. To understand the diagram it should be remembered that the area under an isobar between two points on it is equal to the enthalpy difference. For the process $1 \rightarrow 0$ under consideration, with 0 denoting the dead state, the enthalpy difference is equal to area 10'ca, point 0' being the projection on isobar P_1 of point 0 along the curve $h = h_0$. The rectangle d0ba represents the quantity $-T_0 (s_1 - s_0)$. The exergy e_1 is equal to the area 10'cb0d enclosed by the heavy line. (The reader will observe that the preceding description applies to both versions of the diagram.)

16.2 T,s diagram for steam

In the case of water and steam, the dead state with $P_0 \sim 1 \text{ atm}$ and $T_0 \sim 25^\circ\text{C}$ lies very close to the vapor-pressure curve. Moreover, the isobars for liquid water for pressures considerably below the critical merge with the vapor-pressure line for all practical purposes. These details may sometimes cause difficulties of interpretation. The diagram in Fig. 23 gives a

Fig. 22a. Representation of exergy as an area on a T,s diagram.

$$(s_1 - s_0) < 0$$

Fig. 22b. Representation of exergy as an area on a T,s diagram.

$$(s_1-s_0) > 0$$

representation of exergy for saturated liquid water substance, point 1, modelling a brine being cooled to the dead state 0. The distances between the vapor-pressure curve and the lines of constant pressure in the liquid region have been exaggerated for emphasis. The accompanying diagram of Fig. 24 is the more familiar version in which the distinction between the vapor-pressure curve and the isobars has been suppressed. The enthalpy difference $h_1 - h_0$ is represented by area 10'ca, and the term $T_0 (s_1 - s_0)$, area 0dab, is subtracted from it. The condenser pressure P' has the saturation value for T_0 and is lower than the atmospheric pressure P_0 . State e corresponds to the exit from the condenser, and the pumping work, equal to $h_0 - h_e$, has been automatically subtracted from the area which represents the exergy. In many calculations this work is neglected, because it is quite small, as seen from the coalescence of state e and 0 in Fig. 24. The available work, $w_0^o = e_1$, is the work that would be recovered in an ideal total-flow machine.

16.3 Loss due to free exhaust

The diagram in Fig. 25 interprets the ideal work, $w_0^o = e_1$, of saturated steam upon expansion to the dead state, area 1def. If the same steam were expanded to the atmospheric back-pressure P_0 , the available work would be reduced to area 1d'e'f, and the diagram illustrates the large amount of additional available work, e_2 , equal to area e'd'de, attributable to the employment of a condenser. The available work, w^o , of a turbine operating with atmospheric exhaust, area 1d'e'f, is equal to the difference

$$w^o = e_1 - e_2 \quad (52)$$

of the exergy e_1 at state 1 and the exergy e_2 at state d'.

Fig. 24. Exergy for pure water (distance of dead state 0. from vapor-pressure line to scale)

Fig. 25. Gain in available work due to the use of a condenser

To obtain a clearer understanding of the important reason for investing in a condenser, we have prepared the diagram of Fig. 26 which plots the available work carried by saturated steam ranging in temperature from 150°C to 350°C (pressure from 0.48 MPa to 16.5 MPa) and working against a condenser at 25°C (3.2 kPa). The reduction in work in operation with free exhaust is quite large ranging from 66% at $T_1 = 150^\circ\text{C}$ to 37% at 300°C. The reader will recognize that the present diagram constitutes an analog of Fig. 18 drawn for saturated steam and corresponds to $T_0 = 100^\circ\text{C}$ (atmospheric back-pressure).

It should be clear that the available work in the last example is identical with the ideal work in a reversible Rankine cycle. This is due to the fact that in such circumstances the process of heating in the boiler from state 0 to state 1 is simply the reverse of isobaric cooling from 1 to 0.

16.4 Change in exit temperature and in heat-rejection temperature

To conclude our study of T,s diagrams, we return to Section 12 and illustrate the difference between allowing the brine to leave at a temperature $T_2 > T_0$ and changing T_0 itself. This is done in Figs. 27a and b. Recalling the diagram of Fig. 24, we see that the loss due to cooling the brine to $T_2 > T_0$ is represented by area 2edf which is equal to $e_1 - e_2$. In Fig. 27b, the dead state shifts to 0' and coincides with previous state 2. Now the loss is equal to area 00'ed which is larger than the earlier loss by the rectangle $(T'_0 - T_0)(s_1 - s_2)$ as stated in Section 12.

16.5 The general Mollier diagram

The available work can be represented by a length instead of an area if a Mollier (h,s) diagram is employed. The sketch in Fig. 28 contains

Fig. 26. Loss of available work with atmospheric exhaust

Fig. 27a. Effect of leaving temperature on available work; changing T_2

Fig. 27b. Effect of leaving temperature on available work; changing T_0

Fig. 28. Mollier diagram for substance whose dead state 0 is far

removed from the two-phase region

$$(\alpha = \tan^{-1} T_0)$$

such a diagram for a substance for which the dead state 0 lies far away from the two-phase region. The projection 0' of the dead state 0 on the vertical through state 1 marks the difference $h_1 - h_0$. Recalling that

$$(\partial h / \partial s)_P = T, \quad (53)$$

we conclude that the tangent 00" to P_0 at 0 has a slope equal to T_0 , so that line 00" forms an angle

$$\alpha = \tan^{-1} T_0, \quad (54)$$

with the axis of abscissae. This line is called the *line of the surroundings*; it intersects line 10' at 0" and marks a distance 0'0" whose measure is

$$T_0 (s_0 - s_1).$$

It follows that the distance 10" represents

$$w_0^o = e_1 = h_1 - h_0 - T_0 (s_1 - s_0). \quad (55)$$

We note for future reference that the line of the surroundings drawn through the dead state intersects the line $s_1 = \text{const}$ at a point whose distance from point 1 is the exergy e_1 .

We verify that the equation of the straight line 00" is

$$\frac{h - h_0}{s - s_0} = T_0 \quad \text{or} \quad h = h_0 + T_0 (s - s_0).$$

This line is the locus of all points for which $e = 0$. Similarly, any line drawn at an angle α is a line of constant exergy, as shown. In particular, the line through point 1 drawn parallel to $e = 0$ is the locus of all points $e_1 = \text{const}$; this line is different from the tangent to P_1 at 1, shown dotted,

whose slope is T_1 . For completeness we record that the equation of a line of constant exergy e in a Mollier diagram is

$$h = h_0 + T_0 (s - s_0) + e \quad (56)$$

16.6 Mollier diagram for steam: adiabatic expansion

Circumstances are somewhat more complex for water substance because the region of the Mollier diagram near the dead state is characterized by lines intersecting at inconvenient acute angles and is usually omitted from the chart. The geometric relationships can be illustrated with the aid of Fig. 29 which analyzes the adiabatic but non-isentropic expansion $1 \rightarrow 2$ of saturated steam in a turbine, assuming expansion to a condenser in which the saturation pressure $P_2 < P_0$ prevails, the corresponding temperature T_2 exceeding T_0 . The line of the surroundings $e = 0$ is the line P' whose slope T_0 is less than either T_1 or T_2 .

The work of the adiabatically operating turbine must satisfy eqs. (24) and (28) from which it follows that

$$w = h_1 - h_2 \quad (57)$$

and

$$\theta = (s_2 - s_1)/T_0 \quad (58)$$

The available work

$$w^0 = e_1 - e_2 = h_1 - h_2 + T_0 (s_2 - s_1) > w \quad (59)$$

could be obtained if the process $1 \rightarrow 2$ were conducted fully reversibly, but exchanging heat with the surroundings at the single temperature T_0 . Evidently such a process would not be adiabatic or isentropic.

Fig. 29. Adiabatic expansion in turbine

The real work, w , is represented by segment 12', whereas the available work, w^o , corresponds to segment 12'', the distance 2'2'' being equal to the work

$$w_d = w^o - w = T_o (s_2 - s_1) \quad (60)$$

dissipated in the turbine. The distance 2''2_o is the work dissipated in the atmosphere, eq. (29), or

$$w_d^a = w_o^o - w^o = T_o \theta^a .$$

The diagram of Fig. 29 can be used to illustrate the difference between the conventional definition of turbine efficiency, η_t , and the component utilization factor, η_u' . In the former, the real work w is compared with that of a fictitious process 1 → 2''' which continues to be adiabatic, is reversible, and occurs against the prescribed condenser pressure P_2 . At the end of this fictitious process the steam leaves the turbine at the fictitious state 2''' and produces work

$$w_s = h_1 - h_{2'''} \quad (61)$$

The (isentropic) turbine efficiency is

$$\eta_t = \frac{w}{w_s} = \frac{h_1 - h_2}{h_1 - h_{2''}} \quad (62)$$

The method of available work avoids the introduction of the fictitious state 2''' and compares the work of the turbine with that which would be obtained reversibly between the same end states, that is with w^o . Hence the component utilization factor is defined as the ratio

$$\eta_u' = \frac{w}{w^o} = \frac{h_1 - h_2}{e_1 - e_2} = \frac{h_1 - h_2}{h_1 - h_{2''}} \quad (63)$$

Evidently

$$\eta'_u > \eta_t, \quad (63a)$$

because

$$w^o < w_s. \quad (64)$$

The advantage of applying the method of available work becomes clear in cases when the turbine is considered as a part of a larger installation, or if process $1 \rightarrow 2$ in Fig. 29 is interpreted as that which occurs in a single stage. This is a consequence of the fact that state 2 and not state $2''$ prevails at the inlet of the next stage or element of the installation.

In cases when the state 2 at stage or turbine exit lies in the wet region of the diagram, it is possible to derive a simple relation between the efficiency, η_t , and the component utilization factor, η'_u . This is done by noting that

$$w_s = h_1 - h_2 - T_2 (s_1 - s_2),$$

because segment $2'2''$ in Fig. 29 equals $T_2 (s_2 - s_1)$. Since

$$\eta_t = \frac{h_1 - h_2}{h_1 - h_2 + T_2 (s_2 - s_1)} \quad \text{and} \quad \eta'_u = \frac{h_1 - h_2}{h_1 - h_2 + T_o (s_2 - s_1)},$$

we conclude that

$$\frac{(1/\eta_t) - 1}{(1/\eta'_u) - 1} = \frac{T_2}{T_o} \quad (65)$$

16.7 Adiabatic expansion in T,s diagram

The process $1 \rightarrow 2$ of irreversible adiabatic expansion from Fig. 29 has been cross-plotted into the T,s diagram of Fig. 30. In this diagram

Fig. 30. Adiabatic turbine expansion in T, s diagram

$w_o^o = e_1$ is represented by area $0\delta 12_0$

e_2 is represented by area $0\alpha 22'_0$, or area $0\beta 2''2_0$

w^o is equal to area $\beta\delta 12''$ or area $\alpha\delta 12'''$ minus

$$\text{area } 2'''22'_0 2_0 \quad [= (T_2 - T_o) (s_2 - s_1)]$$

$w_d = T_o \theta$ is equal to area $2_0 2'_0 ed$

w_s is equal to area $\alpha\delta 12'''$.

16.8 Exergy-entropy diagram

To conclude this Section, we reproduce an (e,s) exergy-entropy diagram for steam after Z. Rant (1960), Fig. 31. The structure of the diagram should now be completely clear to the reader.

17. A note on thermophysical properties

The considerations of the preceding sections demonstrate that even in the initial stages of a design study, particularly when extensive calculations are to be made with a view to optimizing variously selected objective functions, it is necessary to be in possession of an extensive collection of data on the thermophysical properties of a number of substances. In order to calculate available work we must know the thermodynamic properties of substances. For the calculation of entropy production (or, equivalently, work dissipated), it is also necessary to know such transport properties as viscosity, thermal conductivity, and diffusion coefficients which determine the Reynolds, Prandtl and Schmidt numbers. In contemporary practice, the thermodynamic properties are usually embodied in a computer code based on an analytic formulation of a fundamental equation.[#]

[#]A fundamental equation is one from which all equilibrium properties of a substance can be obtained without having recourse to integration. Thus a fundamental equation contains in it complete information regarding the equilibrium properties. The functions $u = u(s, v, \underline{\xi}, \underline{\zeta})$, $h = h(s, P, \underline{\xi}, \underline{\zeta})$, the Helmholtz free energy $f = f(T, v, \underline{\xi}, \underline{\zeta})$, etc. are examples of suitable forms.

Fig. 31. Exergy-entropy diagram after Rant (1960)

In the case of a pure substance the sufficient minimum information consists of a formulation of the P, v, T equations augmented by the spectroscopic data of the ideal-gas state. A peculiar difficulty is presented by the near-critical region which should, rigorously speaking, be described by the use of so-called scaling laws (Sengers and Levelt Sengers, 1978).

The list of substances is large: it includes brines, i.e., aqueous solutions of a wide variety of salts with or without gases dissolved in them and about a dozen potentially useful fluorocarbons and hydrocarbons for binary-system applications.

In assessing the situation it is necessary to emphasize that the present-day state of affairs still leaves much to be desired. The most important need is to develop verified correlation methods for the handling of the thermophysical properties of mixtures when the corresponding properties of the pure components are known. Fortunately, the thermodynamic properties of brines are not radically different from those of pure water. Consequently, in general studies, modelling with the aid of pure water reveals the essential trends and influence functions in sensitivity studies. However, a fully reliable and scientifically justified procedure for design analysis would require more extensive formulations for brines and mixtures.

Without attempting to exhaust the subject we proceed to impart to the reader the most essential items of information on thermophysical properties.

17.1 Water substance

After 50 years of international cooperation, the properties of water substance have been measured, correlated and approved internationally over a wide range of pressures and temperatures and to an extent which makes it the best documented substance in existence. As far as geothermal applications are concerned, it is possible to regard this information as complete.

The fundamental equation for water substance exists in four versions: (a) The 1967 IFC[#] Formulation for Industrial Use (Meyer et al. 1967, Schmidt 1969); (b) The 1968 IFC Formulation for Scientific and General Use (Rivkin et al. 1978); (c) The set of steam tables published by J. H. Keenan, F. G. Keyes et al. (1969); (d) The fundamental equation formulated by Pollak (1976). As far as geothermal applications are concerned, all these forms are equivalent. There exists a series of national steam tables published in a number of countries (Schmidt 1969, Rivkin et al. 1978, etc.) which derive from (a) or (b). Evidently, these should also be considered equivalent. In view of the degree of perfection achieved through the international effort, all earlier formulations, and all proposals which are not expressly compatible with the above, should be ignored.^{##} The rigorous, and thermodynamically compatible formulation of the properties in the near-critical region is described in Sengers et al. (1978).

All tabulations of viscosity and thermal conductivity based on the 1964 international agreement are now obsolete, even though they form integral parts of most sets of valid tables. The new, internationally agreed, and much more reliable, values are covered by two recent Releases disseminated by the International Association for the Properties of Steam (Anon. 1976, Kestin 1978).

17.2 Aqueous solutions

The International Association for the Properties of Steam has embarked on a program of correlation paralleling that for pure water, but so far no agreements in this field have been reached. Solutions of sodium chloride

[#]International Formulating Committee of the International Association for the Properties of Steam.

^{##}With the possible exception of very accurate data intended for calibration and similar purposes.

have been reasonably well explored and are sometimes used for the modelling of geothermal brines when pure-water models are thought to be inadequate. There exist two comprehensive tabulations (Haas 1976, Silvester and Pitzer 1976), and it is interesting to test them for mutual consistency. This has been done by computing the available work, w_o^o , of saturated liquid as a function of temperature for different values of ζ_1 ($= 2, 4, 6$ molal) against a dead state of $P_o = 0.1$ MPa and $T_o = 25^\circ\text{C}$. The resulting graphs are shown in Fig. 32 which is an elaboration of Fig. 11. Here the full lines were obtained with the aid of Silvester and Pitzer's data (1976) and the border line with reference to Haas's data (1976). The diagrams demonstrate an absence of mutual consistency in that the two results differ by as much as 9.8% at $\zeta_1 = 6$ molal and $T_1 = 250^\circ\text{C}$. The lower value $\zeta_1 = 4$ molal is typical of the KAGRA at Niland in California, but even in this case the percentage discrepancy ranges from 1.8% at 150°C to 6.5% at $T_1 = 250^\circ\text{C}$.

A comprehensive representation of the viscosity of sodium chloride solutions (up to 150°C) is contained in a set of tables prepared by J. Kestin et al. (1977). No data on thermal conductivity seem to exist.

17.3 Hydrocarbons: Isobutane

A complete survey of the thermophysical data of hydrocarbons (as well as fluorocarbons) is beyond the scope of this report. It is, however, worth mentioning that for isobutane, which seems to possess optimum thermodynamic properties for binary installations - there exist four different formulations of the fundamental equation:

- (1) Starling, equation 1 (1973);
- (2) Starling, equation 2 (1977);
- (3) Eubank (Das et al. 1973);
- (4) Milora and Combs (1977); see also Milora and Tester (1976).

Fig. 32. The ideal available work $w_0^e = e_1$, for saturated solutions of sodium chloride (NaCl) against a dead state of $P_0 = 0.1$ MPa and $T_0 = 50^\circ\text{C}$, for $\zeta_1 = 0, 2, 4, 6$ molal

———— data from [Silvester and Pitzer]

----- data from [Haas]

See also Fig. 11

A direct comparison between the four formulations is tedious (and is reserved for another detailed report) because the nature of the discrepancies very much depends on the domain of pressure and temperature considered. For this reason it is more interesting to follow through the results of a simple design analysis. We have chosen for this purpose a counterflow heat exchanger operating between pure water and supercritical isobutane.

In all cases, the inlet temperature of the water is $T_1 = 200^\circ\text{C}$ and the exit temperature is $T'_0 = 50^\circ\text{C}$, the environment being at $T_0 = 35^\circ\text{C}$. For this set of conditions we prescribe an identical inlet temperature $T'_1 = 35^\circ\text{C}$ for the isobutane, and a pinch-point temperature difference $\Delta T_p = 5^\circ\text{C}$. The following design data have been calculated:

- (1) The exit temperature, T''_1 , of the isobutane;
- (2) The mass-flow ratio of isobutane to water, $\dot{m}_{ib}/\dot{m}_w$;
- (3) The specific heating surface $A/\dot{m}_w$ per unit mass of water flowing;
- (4) The specific heating surface $A/\dot{m}_{ib}$ per unit mass of isobutane flowing;
- (5) The ideal available work (exergy, $w^\circ_0 = e''_1$, in the isobutane at turbine entry;
- (6) The ideal available work in the isobutane at turbine entry, $\dot{m}_{ib} w^\circ_0/\dot{m}_w$, per unit mass of brine flowing.

The numerical results are seen summarized in Table 1. They clearly bring into relief the absence of mutual consistency in the data and the wide discrepancies in design recommendations which hinge merely on the choice of the correlating fundamental equation. For example, the maximum difference in the heating surface (and hence cost) of the heat exchanger per unit mass flow of water reaches 18% and 25% per unit mass flow of isobutane, items (3) and (4). The largest difference in the available work in a unit mass of

isobutane at turbine inlet reaches 75%, item (5). Finally, the ratio $\dot{m}_{ib} w_o / \dot{m}_w$ in column (6), which is a measure of the ideal work obtainable at the expense of a unit mass of brine reaches 31%.

The situation with regard to some fluorocarbons is somewhat better, but that concerning some others, or the less popular hydrocarbons, is worse.

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The earlier versions of this Report have been discussed and criticized by my co-workers on this project, Professors DiPippo, Khalifa and Ryley. I profited from their interest and feel that several points were clarified in the process.

Mr. E. Michaelides, a Graduate Student at Brown University, patiently helped with the tedious work of proofreading and supervising the preparation of the diagrams for which he also supplied the calculations.

My Secretary, Mrs. L. Giacin, efficiently typed the several versions of this report.

Table 1.

Characteristic design parameters for simple water-isobutane heat exchanger.

Environment at $T_o = 35^\circ\text{C}$; water temperature at inlet $T_1 = 200^\circ\text{C}$; at exit $T'_o = 50^\circ\text{C}$; isobutane inlet temperature $T'_1 = 35^\circ\text{C}$; pinch-point temperature $\Delta T_p = 5^\circ\text{C}$.

Data calculated with the aid of four different formulations of the properties of isobutane: (a) Starling (1) (1973); (b) Starling 2 [Kumar et al. (1977)]; (c) Eubank (Das et al. (1973); (d) Milora and Combs (1977).

Formulation	[1]	[2]	[3]	[4]	[5]	[6]
(1)	153	1.30	539	415	90	117
(2)	153	1.30	500	385	90	117
(3)	140	1.56	540	473	100	115
(4)	162	1.14	588	377	57	89

[1] Isobutane exit temperature, T''_1 , $^\circ\text{C}$

[2] Ratio of flow rates $\mu = \dot{m}_{ib}/\dot{m}_w$ of isobutane to water

[3] Specific heating surface $A/\dot{m}_w$ per unit flow of water, $\text{m}^2\text{s/kg}$

[4] Specific heating surface $A/\dot{m}_{ib}$ per unit flow of isobutane, $\text{m}^2\text{s/kg}$

[5] Ideal available work (exergy) in isobutane at turbine entry, w_o° , kJ/kg

[6] Ideal available work (exergy) in isobutane at turbine entry, $m_{ib} w_o^\circ/\dot{m}_w$, per unit mass of brine, kJ/kg .

LIST OF SYMBOLS

Latin

b	availability function
e	exergy
e_1	exergy recoverable upon expansion to dead state
e_2	exergy of fluid coming out of turbine at atmospheric exhaust
F	Helmholtz's free energy
g	gravitational acceleration
H	enthalpy
L	elevation
$\dot{m}$	mass flow rate
$\dot{m}_1, \dot{m}_2, \dot{m}_3$	mass flow rates of various streams in a geothermal plant
P	pressure
Q	rate of heat flow
r	heat rejection ratio
S	entropy
T	temperature
U	internal energy
V	volume
V	velocity
W	work

The corresponding low case letters of the extensive properties refer to the specific property, i.e., the property per unit mass.

Greek

α	angle
Δ (operator)	difference between products and reactants in a chemical reaction
$\underline{\xi}$	set of mass or mole fractions of solids
ζ_i	mass or mole fraction of ith component
η	efficiency
η_u	utilization factor
η_t	turbine efficiency
θ	entropy production
μ_i	mass fraction of ith steam
$\underline{\xi}$	set of mass or mole fractions of inert gas
ξ_i	mass or mole fraction of ith inert gas

Superscripts:

o	refers to operation at zero entropy production
.	denotes time rate
ad	refers to adiabatic process

Subscripts

o	refers to ambient conditions
i	refers to properties of the ith stream of the geothermal fluid
n	refers to the n streams of geothermal fluid
a	refers to the atmosphere
s	refers to isentropic
d	denotes dissipated
α, β	refers to states α and β

Subscripts

- 1 refers to initial state
- 2 refers to final state.

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Captions to Figures

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Fig. 29. Adiabatic expansion in turbine

Fig. 30. Adiabatic turbine expansion in T,s diagram

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———— data from [Silvester and Pitzer]

----- data from [Haas]

See also Fig. 11