UMR-MEC Conference on Energy / UMR-DNR Conference on Energy

12 Oct 1978

On the Thermodynamics of Direct Energy Conversions

A. A. Rahman

ON THE THERMODYNAMICS OF DIRECT ENERGY CONVERSIONS

A. A. RAHMAN
School of Engineering, Oakland University
Rochester, Michigan 48063

Abstract

In this work, a generalized thermodynamic analysis was developed for direct energy converters that operate as heat engines. Examples for various converters as thermoelectric, MHD and Nernst generators were solved. The possibilites of utilizing these concepts on designing generators to convert heat or solar energy directly into electricity were also discussed.

1. INTRODUCTION

Attainment of a combination of certain thermal, electrical and magnetic properties of some solids or gaseous mixtures was always a desirable property for power or other industrial applications using direct energy conversion devices. The basic problem in a thermoelectric or thermomagnetic system is that "given a system consisting of one or several physico-chemical phases, what will be the output electro-chemical potential at any point in the system or the immediate surroundings if one or more of the intensive parameters was (were) changed."

The thermodynamic analysis gives the relation between various transport properties regardless of the structural or atomic properties of the system. Usually such analysis not only gives the relation between the transport properties but also the minimum number of such parameters that needed to be determined if experimental investigation is required to determine the characteristics of a system.

The thermodynamic theory of the thermoelectric phenomena in isotropic media was first investigated by Callen (1) using the linearization methods proposed by Onsager and Casimir and treated extensively by DeGroot (2).

Osterle (3) classified any kind of energy converters into two classes depending upon whether it is the input force or the input flux that induce the output force. If the output force is induced by the input force the device is called an even type converter. On the otherhand, if the output force is induced by the input flux, the device is called an odd type converter. A quantitative study of a system using this approach is very difficult without a priori knowledge of the system. The analysis becomes very complicated if more than one input forces or fluxes were encountered. Domenicali (4) paper should be noted for its analysis of the effect anisotropy or the limitations imposed by crystal symmetry.

2. ANALYTICAL FORMULATION

In the kinetic theory approach of microscopic thermodynamics, it is customary to describe the mass diffusion, the heat conduction and the flow of electricity in terms of a "velocity". The "velocity" can be a flow of matters "atoms, electrons, and/or holes" as in mass diffusion or electricity or a flow of energy as in heat conduction.

A driving force (that causes the flow) is a quantity that indicates the extent to which a system is displaced from equilibrium. For example in mass diffusion the driving force "X" is the gradient of the concentration.

Onsager (5) assumed that if the deviation from the thermodynamic equilibrium is not large, a linear set of equations called the thermodynamic equations of motion can be formulated by assuming that the flows are linearly dependent upon the driving forces. The general form of the equations is

$$J_i = \sum_j L_{ij} X_j \tag{2.1}$$

Where L_{ij} are phenomenological coefficients that satisfy some reciprocity theorem as will be discussed later.

The general procedure to formulate the thermodynamic equations of motion is as follows,

(1) If two or more flows are present, coupling may be present.
(2) Linear equations can be assumed for each flow relating the flow to the primary force and the coupling forces.
(3) The unknown coefficient can be found if a number of experimental relations equal to the number of the unknown coefficients were performed.

Some restrictions on Onsager method have been formalized in statements known as Curie's theorem which states that "quantities whose tensorial characters differ by an odd integer cannot interact in an isotropic system." For example a change in the flow velocity (the divergence of the velocity) which is a scalar cannot induce heat transfer which is a vector. On the other hand a temperature gradient (a vector)can induce a mass flow (a vector). This is known as Soret-effect.

The thermodynamic equations of motion can be further simplified by considering the reciprocity of the coefficients L_{ij}, i.e., $L_{ij}=L_{ji}$ (magnetic free case)(2.2)

and $L_{ij}(H) = L_{ji}(-H)$ (magnetic field case) (2.3)

Mazur and Prigogine (6) have shown that the algebra is greatly simplified if the dynamical equations were inverted in such a way that the electric currents and the temperature gradients,which are the experimentally controlled variables,to appear in the right side.

The general thermodynamics equations of motion can be written in a matrix form as

$$\begin{bmatrix} \nabla V \\ q \end{bmatrix} = \begin{bmatrix} \alpha & \beta \\ \gamma & \delta \end{bmatrix} \begin{bmatrix} J \\ \nabla T \end{bmatrix} \tag{2.4}$$

The column vector $\nabla V = \left[\frac{\partial V}{\partial x} \; \frac{\partial V}{\partial y} \; \frac{\partial V}{\partial z}\right]^T$ is the gradient of the electrical potential. Superscript (T) denotes the transpose of the matrix. In a similar manner, the heat flux $q = \left[q_x \; q_y \; q_z\right]^T$ is simply a column vector with components in the x, y and z directions respectively. The vector $J = \left[J_x \; J_y \; J_z\right]^T$ is the electric current flux vector and $\nabla T = \left[\frac{\partial T}{\partial x} \; \frac{\partial T}{\partial y} \; \frac{\partial T}{\partial z}\right]^T$ is the temperature gradient. The matrices α, β, γ and δ are 3 x 3 coefficient matrices. Assuming a general magnetic field $H = [H_x \; H_y \; H_z]^T$ with positive components in the positive directions of the axes, the coefficient matrices can be determined using the same procedure used by Callen (7), to get (Fig.1)

$$\alpha = \begin{bmatrix} \sigma^{-1} & H_z R & H_y R \\ -H_z R & \sigma^{-1} & -H_x R \\ -H_y R & H_x R & \sigma^{-1} \end{bmatrix}, \beta = \begin{bmatrix} -\varepsilon & -H_z \eta & -H_y \eta \\ H_z \eta & -\varepsilon & H_x \eta \\ H_y \eta & -H_x & -\varepsilon \end{bmatrix} \tag{2.5}$$

$$\gamma = \begin{bmatrix} -T\varepsilon & -TH_z \eta & -TH_y \eta \\ TH_z \eta & -T\varepsilon & TH_x \eta \\ TH_y \eta & -TH_x \eta & -T\varepsilon \end{bmatrix} \text{and } \delta = \begin{bmatrix} -K & -H_z K\Lambda & -H_y K \\ H_z K & -K & H_x K\Lambda \\ H_y K\Lambda & -H_x K\Lambda & -K \end{bmatrix}$$

Where σ is the electrical conductivity (mho·cm), R is the isothermal Hall coefficient $\left(R \equiv \frac{\partial V/\partial x_i}{H_j J_k}\right)$, K is the coefficient of thermal conductivity of the medium, ε is the seebeck coefficient $\left(\frac{\partial V}{\partial T}\right)$, η is the isothermal Nernst coefficient $\left(\eta \equiv \frac{\partial V/\partial x_i}{H_j \frac{\partial T}{\partial x_k}}\right)$ and Λ is called the Leduc-Righi coefficient $\left(\Lambda \equiv \frac{\partial T/\partial x_i}{H_j \frac{\partial T}{\partial x_k}}\right)$.

The energy output of a device can be written as

$$E = \int_V -\nabla V \cdot J \, dV = \int_V -(\alpha J + \beta \; \Delta T) \cdot J \, dV \tag{2.6}$$

Where the dot· product denotes the inner products of the two vectors and v is the device volume.

Similarly, the input energy to a device can be taken as

$$Q = [\gamma J + \delta \; \Delta T] \cdot A \tag{2.7}$$

Here the vector $A = [A_x \; A_y \; A_z]^T$ is the device external area subjected to the input flows.

The thermal efficiency of the device η_t is

$$\eta_t = \frac{E}{Q} \tag{2.8}$$

It should be mentioned that the above analysis is only valid for heat engine devices.

The following examples demonstrate how the above analysis can be used for some direct energy conversion devices.

2.1 THERMOELECTRIC GENERATOR

Consider a generator as that shown in Fig.2

Here $J_y = J_z = \frac{\partial T}{\partial y} = \frac{\partial T}{\partial z} = H_x = H_y = H_z = 0$

The voltage gradient (**From equation 2.4&2.5**) is,

$$\frac{\partial V}{\partial x} = \varepsilon \frac{\partial T}{\partial x} - \sigma^{-1} J_x \qquad (2.1.1)$$

For a homogeneous system $\frac{\partial V}{\partial x} \simeq \frac{V_x}{\ell}$

Where V_x is the potential difference across the generator. The value of $\frac{\partial T}{\partial x}$ may be determined by solving Fourier equation with the corresponding boundary conditions

$$K \frac{\partial^2 T}{\partial x^2} + \sigma^{-1} J_x^{\,2} = 0 \qquad (2.1.2)$$

and $T = T_H$ @ $x = 0$

$T = T_C$ @ $x = \ell$

Thus the gradient

$$\frac{dT}{dx} = \left(\frac{T_H - T_C}{\ell}\right) - \frac{1}{2} J_x^{\,2} \frac{\sigma^{-1}}{K} \qquad (2.1.3)$$

And the potential difference across the device is given by

$$V_x = \varepsilon\, \Delta T - \frac{1}{2} J_x^{\,2} \left(\frac{\varepsilon\sigma^{-1}}{K}\right) \ell - \sigma^{-1} \ell\, J_x \qquad (2.1.4)$$

The first term is Seebeck voltage, the second term is an induced voltage drop and the third term is the voltage drop due to the internal resistance.

The input energy can be found as (**From equation 2.5**)

$$Q = A\, q_x = KA \frac{\Delta T}{\ell} + T\varepsilon I - \frac{1}{2} R \frac{I^2}{A} \qquad (2.1.5)$$

Where $R = \sigma^{-1} \ell$

Thus the thermal efficiency will be

$$\eta_t = \frac{VAJ_x}{Q} = \frac{\varepsilon I \Delta T - \frac{R}{A} I^2 - \frac{1}{2} \frac{I^3}{A^2}\left(\varepsilon \frac{R}{K}\right)}{KA \frac{\Delta T}{\ell} + T\varepsilon I - \frac{1}{2} R \frac{I^2}{A}} \qquad (2.1.6)$$

Setting VI_x equal to $I^2 R_o$, where R_o is the external load resistance, the above equation is the same as that proved elsewhere [8,9].

For a combination of an n-type and p-type materials as shown in Fig.3, the input energy for the joint can be written as

$$Q = K_{eq} \cdot \Delta T + \varepsilon_{eq} \cdot T \cdot I - \frac{1}{2} I^2 \cdot R_{eq}$$

where $K_{eq} = \frac{K_n A_n}{\ell_n} + \frac{K_p A_p}{\ell_p}$

$$\varepsilon_{eq} = |\varepsilon_p| + |\varepsilon_n|$$

and $R_{eq} = \frac{R_p}{A_p} + \frac{R_n}{A_n}$

Here the subscript "eq" denotes equivalent, p and n denotes the properties for p-type and n-type material respectively.

2.2 NERNST GENERATOR

Consider a generator as shown in Fig.4, in this case

$$\frac{\partial T}{\partial y} = \frac{\partial T}{\partial z} = H_x = H_y = 0$$

Thus $\frac{\partial V}{\partial y} = -H_z \eta \frac{\partial T}{\partial x} - \sigma^{-1} J_y$

The potential difference will be (For homogeneous gen.)

$$V = \eta\, H_z \left(\frac{\Delta T}{a}\right) \cdot \ell - RJ_y - \frac{1}{2} J_y^{\,2} \left(\frac{R}{k}\right) \qquad (2.2\cdot1)$$

which is similar in form to that for thermoelectric generator.

The input energy can be expressed as

$$Q = \left(K \frac{\Delta T}{a} - TH_z \eta \frac{I}{A_{xz}}\right) A_{yz} - \frac{1}{2} RI^2 \qquad (2.2\cdot2)$$

And the thermal efficiency is then

$$\eta_t = \frac{I^2 R_o}{\left(K \frac{\Delta T}{a} - TH_z \eta \frac{I}{A_{xz}}\right) A_{yz} - \frac{1}{2} RI^2} \qquad (2.2\cdot3)$$

It should be mentioned that the generalized thermodynamic equations can be used for any media solid, liquid or gases though some modifications are required to take into consideration the hydrodynamic mass flows, the pressure and the viscosity of the fluid. For example consider the following case.

2.3 MAGNETOHYDRODYNAMIC GENERATOR

In a MHD generator, if the average flow velocity in the generator is u in the axial direction (Fig.5)the charge carriers (mainly electrons) move with a different velocity u_n called the drift velocity. This drift velocity depends upon the electron concentration and the applied magnetic field. For a continuous electrode, the local current components are given by [8]

$$J_{nx} = \frac{\sigma\, \beta_n (E_y - u H)}{1 + \beta_n^{\,2}} \quad \text{and} \quad J_{ny} = \frac{\sigma (E_y - uH)}{1 + \beta_n^{\,2}} \qquad (2.3.1)$$

Here β_n is called the Hall parameter. This is equal to

$$\beta_n = \mu_n H$$

μ_n is the electron mobility.

The power output δp_o per unit length of the generator is;

$$\delta p_o = E_y J_y \cdot A\, \delta x \qquad (2.3.2)$$

A here is the cross sectional area of the generator.

Substituting for $E_y = (\frac{\partial V}{\partial y})$ from equations (2.4) and (2.5) one gets

$$\delta p_o = \{(H_z\ R\ J_x - \sigma^{-1}\ J_y) + H_z \eta\ \frac{\partial T}{\partial y}\Big|_{y=0}\} J_y \cdot (b_{av} \cdot \ell) \quad (2.3.3)$$

Now the input power is dependent upon the methods of heating the gas and the seeding materials. In general if there is a temperature gradient in the core fluid, i.e., $\frac{\partial T}{\partial x} \neq 0$ and a temperature gradient between the boundary and the fluid i.e., $\frac{\partial T}{\partial y} \neq 0$ and assume the heating of the fluid was accomplished by heating the boundaries, then the energy input to the control boundaries is

$$Q_T = q_x \cdot A_{yz} + q_y A_{xz}$$

$$= (-TH_z \eta J_y - K\frac{\partial T}{\partial z} - KH_z \Lambda \frac{\partial T}{\partial y}) A_{yz} + \{(TH_z \eta J_x) + H_z K \Lambda \frac{\partial T}{\partial z} - K \frac{\partial T}{\partial y} A_{xz}\} \quad (2.3.4)$$

A_{yz} and A_{xz} are the areas in the y-z plane and x-z plane respectively.

The terms $- TH_z \eta J_y$ and $TH_z \eta J_x$ denotes the cooling and the heating in the fluid due to the magnetic field and the electrons flow respectively. Sometimes it is customary to substitute for $K \frac{\partial T}{\partial y}$ by $h\ \Delta T$ where h is the surface coefficient of heat transfer and ΔT is the temperature difference between the boundary and the interior of the fluid.

3. Concluding Remarks

From the above thermodynamical analysis using the generalized dynamical equations one can conclude that

a) The equations not only gives a unified treatment of several known devices but can also predict the performance if other input forces or magnetic fluxes were considered.

b) It helps in minimizing the number of parameters that has to be determined experimentally for a material

c) The analysis simplified the design procedures since it gives the output and input potentials, currents or energy simultaneously.

It should be mentioned that the mentioned direct energy devices can be utilized for either thermal or solar power generation. Thermoelectric and Nernst generators performance is temperature dependence due to the sensitivity of the semiconductors to be used on the temperatures of the hot and the cold junctions. Customary a parameter called the figure of merit $(\frac{\varepsilon^2}{\sigma^{-1} K})$ is used to indicate the optimum working conditions for thermoelectric type generators. A similar figure of merit is also used for Nernst generators. Utilization of a magnetic field may reduce the overall output of the generators due to the losses in the magnet. When possible, superconducting magnets at very low temperatures can be used. In MHD or thermionic generators, the higher the temperature of the medium, the better will be the performance of the generator. The strength of the materials to be used and the magnetic losses are of considerable importance here.

4. References

1) H. B. Callen, Phys. Rev. 73, 1349 (1948)

2) S. R. DeGroot, Thermodynamics of Irreversible processes, North Holland Publishing Co, 1951.

3) J. F. Osterle, Applied Scientific Research, Section A, 12 pp. 425-434 (1964).

4) Charles A. Domenicali, Reviews of modern physics V.26, N. 2, April (1954).

5) L. Onsager, Physics Rev. 37 (1931).

6) P. Mazur and I. Prigogine, J. Phys. radium 12, 616 (1951).

7) H. B. Callen, Thermodynamics, J. Wiley and Sons 1960.

8) Stanely W. Angrist, Direct energy conversion, Allyn and Bacon (1977).

9) D. A. Wright, Thermoelectric generation, ed. by K. H. Spring, Academic Press (1965).

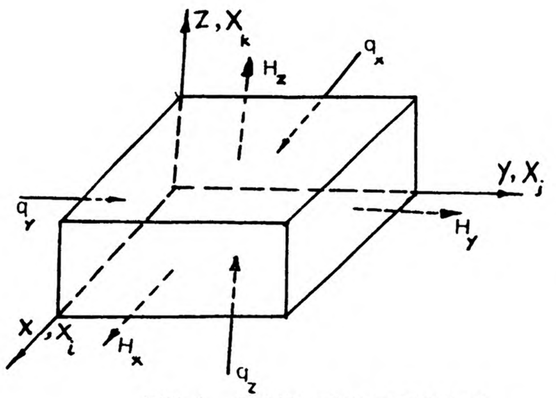

FIG.1- SYSTEM CONFIGURATION

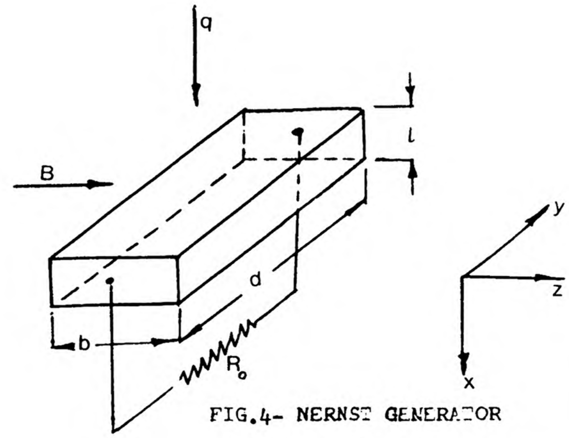

FIG.4- NERNST GENERATOR

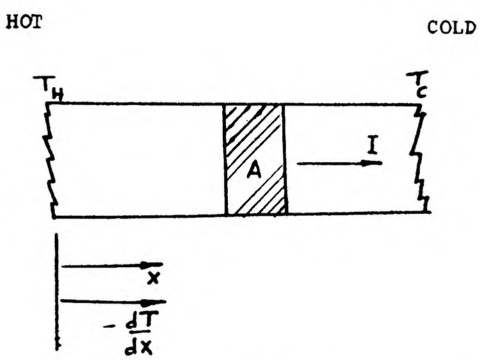

FIG.2- SIMPLE THERMOELECTRIC GEN.

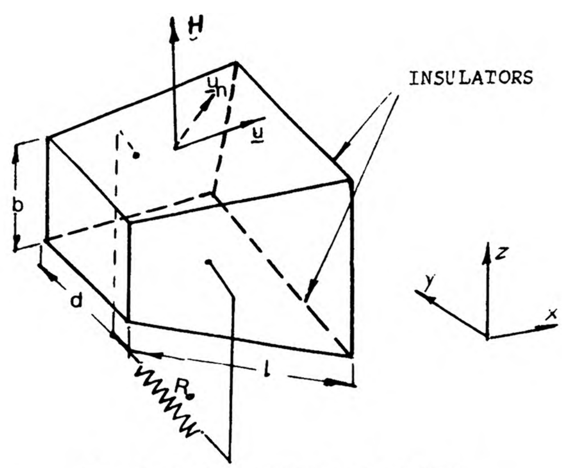

FIG.5- CONTINIOUS MHD GENERATOR

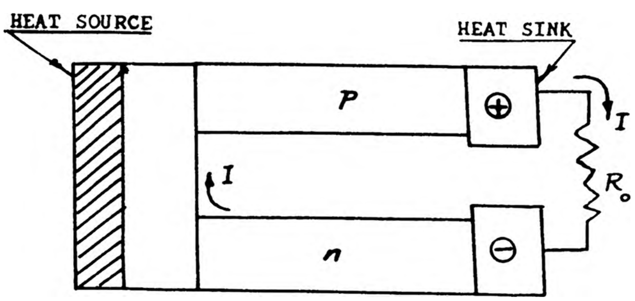

FIG.3- A COMPOUND THERMOELECTRIC GEN.