



FUNDAMENTALS OF ANALYSES OF PROCESSES

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Abstract—A number of popular restrictions on the range of validity of thermodynamics are reviewed and found to be invalid, and the separation into first law and second law analyses of a process is discussed and shown to be unjustifiable and misleading. As a result of these reviews and discussions, we conclude that: (i) we should stop claiming that we can perform first and second law analyses separately; (ii) in every process, we should use at least both the energy and entropy balances simultaneously; and (iii) we should recognize the dynamic character of thermodynamics and the need to include in our analyses states that are not thermodynamic equilibrium. © 1997 Elsevier Science Ltd.

Entropy generation Finite time processes First law and second law analyses Heat Nonstatistical
thermodynamics States that are not stable

1. INTRODUCTION

Most textbooks claim that thermodynamics is a theory which is restricted to being statistical and macroscopic, applicable only to stable or thermodynamic equilibrium states, and reversible only for infinite time intervals; and that one can perform a first law analysis of a process, and then perhaps, but not necessarily, follow up with a second law evaluation. Upon close examination of these claims from the standpoint of the foundations of the science of thermodynamics, we find that the restrictions are not valid, and the separation into first law and second law analyses is both unjustifiable and misleading.

The restrictions are not valid because the laws of thermodynamics are not statistical, and without modification apply equally well to all systems (large and small, or macroscopic and microscopic) and to all states (stable equilibrium and not stable equilibrium), and phenomena can be reversible over all time intervals (infinite and finite).

The separation into first law and second law analyses is unjustifiable because, in the so-called first-law analyses, the energy balance is erroneously considered a statement of the first law and, in second-law analyses, the entropy balance is erroneously considered a statement of the second law despite the fact that both balances require all the laws.

The separation is misleading, because it results in misconceptions that distort the meaning of thermodynamics, and foreclose opportunities for novel contributions at the frontier of natural science. Some of these misconceptions are: (i) the causal association of entropy generation exclusively with temperature, pressure, and total potential differences, though such generation is always due to the spontaneous evolution of a non-stable state towards a stable equilibrium state, and temperature, pressure, and total potential differences are the results and not the causes of entropy generation or irreversibility; (ii) the presumptions that temperature, heat, pressure, and either total or chemical potentials can be completely understood without reference to the second law though such understanding is impossible; and (iii) the assertion that the first law or more precisely energy can be defined in terms of heat only, as it can in terms of mechanical effects only, though such a definition is ambiguous and incomplete.

The purpose of this paper is to elaborate on the issues just cited by briefly reviewing the laws and some theorems of thermodynamics, and some theoretical considerations and experimental results that contradict the misconceptions. As a result of this review, we conclude that: (i) we should stop claiming that we can perform first law and second law analyses separately; this is analogous to what is done in mechanics where processes are studied without explicit reference to any particular law; (ii) in the analysis of every process, we should use at least both the energy and entropy balances

concurrently; and (iii) we should recognize the dynamic character of thermodynamics and stop trying to describe every problem in terms of stable or thermodynamic equilibrium states, that is, we should recognize the need to include in our analyses states that are not thermodynamic equilibrium, and to develop the theory for treating such states.

The paper is organized as follows. The invalidity of the restrictions is discussed in Section 2, the unjustifiable separation into first law and second law analyses in Section 3, some misleading consequences of the separation in Section 4, and conclusions in Section 5. To avoid misunderstandings, a brief summary of the laws and major theorems of thermodynamics is given in the Appendix.

2. INVALID RESTRICTIONS

2.1. *Is thermodynamics a statistical and macroscopic theory?*

The answer to this question is no. Nothing in the statements of either the laws of thermodynamics, or in the derivations of theorems from these laws, requires the consideration of statistical probabilities, that is, probabilities which reflect our ignorance about the exact state of the system and the initial conditions, or our inability to perform complicated and elaborate calculations, or our lack of the enormous time necessary to carry out such calculations, or any combination of these difficulties. In addition, no aspect of the laws and their theorems imposes a limitation on either the size or the number of degrees of freedom of the system (the number of coordinates necessary to describe the configuration of the constituents of the system in space).

The reason, of course, is the reproducible, accurate and unambiguous experimental evidence which is regularized by the laws and their theorems. Experiments illustrative of the nonstatistical character are provided by electricity storage batteries, the Peltier effect, and the mixing of hot and cold water. For example, given a large number of simultaneously charged batteries of the same class, any person can extract the same amount of energy from each of these batteries. In sharp contrast, given a large number of the same batteries, but internally discharged while wrapped in perfect insulation, no one has ever been able to extract even a small fraction of the energy from any such batteries. Again, no one has ever observed a junction of two dissimilar metals act as a cooler if the flow of current through the junction is in the direction opposite to that required by the cooling mode of the Peltier effect, and vice versa for a Peltier heater. The experiments are extremely accurate, and the switch from the cooling to the heating mode occurs at precisely zero value of the current. Again, no one has ever experienced lukewarm water separating spontaneously into hot and cold water, though tens of billions of times daily people experience hot and cold water mixing and becoming lukewarm water.

Experiments illustrative of the validity of thermodynamics for small systems are provided by dilute spin systems and the electromagnetic field. For example, the negative temperatures of dilute spin systems are observed on single spins. Again, because photons do not interact with each other, the black body spectrum is obtained by summing over individual photons, each of which is in a stable equilibrium state [1].

Other definite experiments are suggested by the complete equation of motion discovered by Beretta *et al.* [2, 3]. Incidentally, Beretta's equation has been proven to be the only equation of motion which satisfies all the known requirements that must be satisfied by any equation purporting to represent the complete equation of motion of all physical phenomena [4, 5].

2.2. *Is thermodynamics restricted to equilibrium states only?*

The answer to this question is an unqualified no. Though not widely appreciated, this negative answer is inherent in two universally accepted and very practical results of the theory, the principle of energy conservation and the principle of entropy nondecrease. These two principles would be meaningless and useless unless they refer to time evolution, unless comparisons are made of time-varying or nonequilibrium energies and entropies at different instants in time, keeping always in mind that later results are compared to earlier results and not vice versa.

We reach the same negative answer even from a more general point of view. We recall that nothing in the statements of the first and second laws of thermodynamics restricts any of the two

laws to any particular class of states. Accordingly, neither the laws nor the general theorems derived from these laws are restricted to any particular class of states except for theorems that are derived under specified state restrictions, such as the theorems derived exclusively for stable equilibrium states.

2.3. Does finite-time thermodynamics make sense?

The answer to this question is another unqualified no. Because the complete thermodynamic equation of motion is not yet widely understood, all current applications are based primarily on the energy, mass, and entropy balances plus, if appropriate, the mechanical momentum balance. Without any modification whatsoever, each of these balances is valid equally well either for a short time interval or for a long time interval between end states and, therefore, no time-length distinction is warranted by the laws of thermodynamics.

Of course, the same conclusion would be valid even if the complete equation of motion were used, because then the balances would be inherent in this equation, and the equation would be equally valid not only for all time intervals, but also for both reversible and irreversible processes.

Over the past two decades, a school of thought has been evolving which promotes the idea of finite time or irreversible thermodynamics. The basic arguments of this school are as follows. Reversible processes require an infinite interval in time and, therefore, are the subject of infinite time thermodynamics. On the other hand, irreversible and, according to the school, practical processes require a finite interval in time and, therefore, the special techniques of finite time thermodynamics [6–8]. As already stated, these arguments are contrary to the theoretical results. Moreover, they are not consistent with the overwhelming experimental evidence.

One experiment is provided by two identical electricity storage batteries with an internal-discharge-time-constant of 100 days. We can discharge one battery very slowly, say over 10^4 days, and the other very fast, say over one day, and ask “Which discharge process is closer to reversible?” [9]. As is very well-known from billions of experiments, the fast process is very close to reversible, whereas the slow process is totally irreversible because in the fast process practically all the stored adiabatic availability is transferred out, whereas in the slow process practically no adiabatic availability is transferred; it is all dissipated in the battery.

Another experiment involves two spark-ignition internal combustion engines, one with only one spark plug, and the other with 1000 spark plugs. It is well-known that the combustion process in the first engine is about 1000 times slower than in the second engine, and so we can ask “Which of the two combustion processes is closer to reversible?” Of course, the answer is that both processes are equally irreversible because the spontaneous generation of entropy is determined by the end states, which in the two experiments under consideration are identical, and not by the rate of combustion.

A third experiment is provided by a so-called endoreversible engine which is assumed to represent any power plant, and which has an optimum thermal efficiency of $1 - (T_L/T_H)^{1/2}$, where T_L and T_H are the low and high temperatures between which the endoreversible engine operates. As evidence of the validity of their analyses, the proponents of finite time thermodynamics use the thermal efficiencies of a large number of relatively old power plants and find that these efficiencies correlate very well with $1 - (T_L/T_H)^{1/2}$.

The good correlation between the thermal efficiencies of the old power plants and $1 - (T_L/T_H)^{1/2}$ must be a numerical accident for at least two reasons. First, the plants that are considered in the comparisons were not designed to achieve the optimum thermal efficiency of finite-time thermodynamics and, therefore, it would be a miracle if each self-optimized itself to the point of best performance. Second, and perhaps more importantly, last year General Electric announced the great achievement of a gas-turbine, combined-cycle power plant with a thermal efficiency of 60%. If this efficiency correlated with the results of finite-time thermodynamics, it would imply a ratio $T_L/T_H = 0.16$ and, therefore, an available energy or exergy of the products of combustion of the gas of about 84% of the exergy of natural gas! As a result, we would be compelled to conclude that the loss of exergy of the fuel upon combustion is only 16% though every calculation and every measurement yield a loss of about 30%!

3. THE UNJUSTIFIABLE SEPARATION

3.1. *Is the separation into first and second law analyses warranted?*

The answer to this question is no. Usually, what is meant by first law analysis is the application of the energy balance, and by second law analysis either the application of the energy and entropy balances, or the energy and a linear combination of the energy and entropy balances, that is, the exergy (available energy) balance. First, as is clear from the discussions in the Appendix, neither the energy balance represents the first law nor the entropy or exergy balance the second law. These balances require all the laws.

To make the last point clear, we recall that practical considerations compel us to apply the balances primarily: (i) to stable equilibrium end states so that we can minimize the number of independent state variables; and (ii) to specific types of interactions, such as work, heat, bulk flow, and diffusion, so that we can specify unambiguously the flows of energy, mass, and entropy at the system boundary. Both the specification of the minimum number of independent state variables, such as temperature and pressure, and the clear definitions of flows at the system boundary require all the laws. Accordingly, the separation into first law and second law analyses is unjustifiable. All the laws are used and must be used concurrently.

4. MISLEADING CONSEQUENCES

4.1. *Are thermodynamic potential differences the causes of entropy generation?*

The answer to this question is no. In the interest of brevity, we can discuss the question only in terms of temperature differences because pressure and total or chemical potential differences admit a similar explanation.

By definition, in a heat interaction between a system A , initially in a stable equilibrium state A_1 at temperature T_1 , and a reservoir at temperature $T > T_1$, heat Q^- and entropy Q^-/T cross the boundary of A and change its state from A_1 to A_2 (Fig. 1). In general, state A_2 is not a stable equilibrium state.

Depending on the nature of A , state A_2 can, but need not, proceed spontaneously either rapidly or slowly toward the stable equilibrium state A_2 at temperature T_2 , where the value of T_2 is solely determined by A_1 and the value of Q^- . Assuming that the spontaneous change of A_2 ends in state

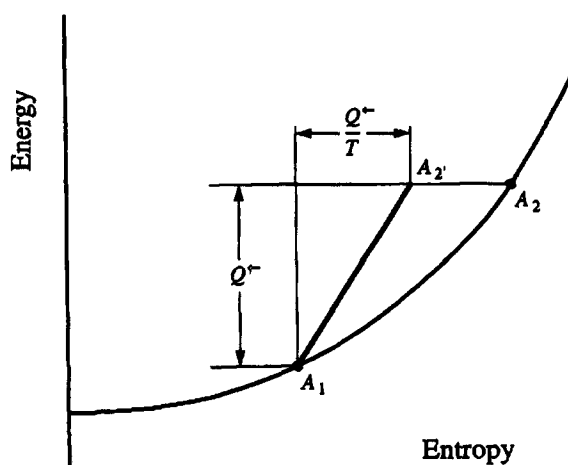


Fig. 1. Representation of a heat interaction on the projection of the property hyperspace on the energy vs entropy plane for given values of amounts of constituents and parameters (such as volume).

A_2 , we can write the entropy balance in the form

$$S_2 - S_1 = \frac{Q^-}{T} + S_{\text{irr}} \quad (1)$$

where S_{irr} is the entropy generated spontaneously because of the natural tendency of systems to proceed from a state that is not stable equilibrium to a stable equilibrium state.

The value of S_{irr} depends on Q^- and Q^-/T and not on $T_2 - T_1$. For a given Q^- , the temperature difference $T_2 - T_1$ is determined solely by Q^- , whereas the value of S_{irr} is dictated primarily by T , that is, S_{irr} is large if T is large, and zero if $T = Q^-/(S_2 - S_1)$ (Fig. 1).

Analogous conclusions are reached for interactions that result in either a pressure difference, a total potential difference, a chemical potential difference or any combination of thermodynamic potential differences.

So the explanations that entropy generation in system A is due to temperature differences just outside the container of a system, or along the thickness of the wall of the container, or just inside the container, or pressure differences, or total potential differences are not consistent with the foundations of thermodynamics. For a consistent explanation, we need to develop a better understanding of the time-dependent spontaneous evolution of a state that is not stable toward a stable equilibrium state.

4.2. Can T , p , μ_i 's and heat be defined without using all the laws?

The answer to all parts of the question is no. As shown in the Appendix, temperature T , pressure p , and either total potential or chemical potential μ_i of the i th constituent of a system are defined via the fundamental relation $S(E, n, \beta)$ which in turn is fully determined as a consequence of all three laws of thermodynamics. So the casual introduction of these important intensive properties of stable equilibrium states in the introductory remarks of most expositions of thermodynamics without any reference to the three laws is misleading.

Of course, one could give definitions of T , p and μ_i different from those described in the Appendix, and valid even for states that are not stable equilibrium. There is no doubt that such a possibility exists. However, we should immediately recognize that such definitions would not be relevant to the conditions for mutual stable equilibrium between systems and, more importantly, that the new T would not be measurable by a thermometer, and the new p by a pressure gauge. The reasons are that both the conditions for mutual stable equilibrium, and the measurements of T and p are solely related to the definitions of T and p given in the Appendix. Incidentally, measurements of T and p are necessary also for the measurement of μ_i .

Regarding heat, most expositions of thermodynamics introduce the concept as part of the statement of what they call the first law, that is, $dU = \delta Q^- - \delta W^-$. Disregarding the fact that the last relation is a special energy balance and not the first law, we must recognize that the distinguishing feature between Q^- and W^- is the entropy that accompanies Q^- , and the zero entropy associated with W^- , and that the relation is proposed for stable equilibrium states only. It can be shown [10] that, in order to define the concept of heat, we must know the concepts of entropy, fundamental relation, and temperature, that is, we must use all the laws of thermodynamics.

4.3. Can the first law be defined only in terms of heat?

The answer to this question is also no. As a result of an unambiguous definition of the term work in terms of a weight process, we conclude that the first law implies the existence of a property, state function, called energy, and specifies the energy change $E_2 - E_1$ of system A from any state A_1 to any other state A_2 by means of the relation

$$E_2 - E_1 = -W_{12}^- \quad (2)$$

where W_{12}^- is the work done by the system as it changes from any state A_1 to any other state A_2 .

In some expositions of thermodynamics, equation (2) is presented as the first law and not an

implication of the first law, and then it is argued that this law can be formulated equivalently in terms of heat so that

$$E_2 - E_1 = Q_{12}^- \quad (3)$$

where Q_{12}^- is the heat received by the system as it changes from state A_1 to state A_2 , and the arbitrary restriction that A_1 and A_2 are both stable equilibrium states.

In contrast to equation (2), however, this apparently innocuous analogy between work and heat in equations (2) and (3) is misleading. As discussed earlier and in the Appendix, a heat interaction involves both an energy flow of Q_{12}^- and an entropy flow Q_{12}^-/T at the boundary of the system, and a given Q_{12}^- can be associated with an infinite number of entropy flows Q_{12}^-/T , depending on the value of T . Moreover, state A_2 need not be stable equilibrium even if A_1 is such a state. In contrast to equation (2), equation (3) is incomplete and restrictive. Moreover, it cannot be completed unless all three laws of thermodynamics are used.

5. CONCLUSIONS

Consideration of all the points made earlier suggest the following general remarks:

(i) We should stop claiming that we can perform first law and second law analyses separately, and that one approach is better than the other. We should analyze every process by using all the laws concurrently both because this is conceptually appropriate and because it gives a correct and broader picture of the scope of thermodynamics. Besides, the recommended new approach is analogous to what is practiced in mechanics, both classical and quantum. In these two sciences, after the corresponding laws are introduced, all processes are studied without explicit reference to the particular laws that are used.

(ii) In every process, we should use at least both the energy balance and the entropy balance concurrently. If appropriate, we can replace one of these two balances by a linear combination of them and thus introduce an exergy balance or available energy balance. In this manner, exergetic analyses will lose their aura of mystery and will be viewed just as a convenient algebraic operation.

(iii) We should recognize the dynamic character of thermodynamics and, wherever possible and practical, introduce states that are not stable equilibrium. Said differently, we should make a conscious effort not to approximate every process only by stable equilibrium end states. As a result of this effort, the need for the discovery of the complete equation of motion of thermodynamics will become more appreciated by a larger number of scientists and engineers, and the problem will be solved.

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APPENDIX

This Appendix is a very brief summary of some key concepts from Ref. [11]. It is included to specify the meaning of some terms used in the paper.

The first law

The *first law* asserts that any two states of a system may always be the initial and final states of a weight process, that is, a process that involves no net effects external to the system except the change in elevation between z_1 and z_2 of an inertial

mass or, simply, mass M —a mechanical effect. Moreover, for a given mass, the value of the expression $Mg(z_1 - z_2)$ is fixed only by the end states of the system, where g is the gravitational acceleration.

Energy and energy balance

A main consequence of the first law is that every system A in any state A_1 has a property called *energy*, with a value denoted by E_1 . The energy E_1 can be evaluated by a weight process that connects A_1 and a reference state A_0 to which is assigned an arbitrary reference value E_0 so that

$$E_1 = E_0 - Mg(z_1 - z_2). \quad (\text{A1})$$

We can prove that energy is an additive property. Moreover, we can prove that energy has the same value at the final time as at the initial time if the system experiences a zero-net-effect weight process, and that it remains invariant in time if the process is spontaneous—occurs in an isolated system. In either of the last two processes, $z_2 = z_1$ and $E(t_2) = E(t_1)$ at time $t_2 > t_1$, that is, *energy is conserved*. It is noteworthy that energy conservation is independent of the magnitude of the interval $t_2 - t_1$, and that it is established without knowledge of the complete equation of motion of thermodynamics.

Energy can be exchanged between systems as a result of interactions. Denoting by E^{+-} the amount of energy that crosses the boundary between system A and its environment in a process that changes the state of A from A_1 to A_2 , we can use energy additivity and energy conservation to prove the *energy balance*

$$(E_2 - E_1)_{\text{system } A} = E^{+-} \quad (\text{A2})$$

where E^{+-} is positive if energy flows into A , and negative if it flows out of A .

Though we derive the energy balance by using only the first law, all applications of this balance require all three laws, first, second and third, because both the dependence of E on other independent properties or variables, and the complete specification of E^{+-} are based on all three laws.

Mass balance

In principle, inertial mass or, simply, mass is neither additive nor conserved. Yet to an excellent approximation, for most applications we can disregard these limitations and write the *mass balance* as

$$(m_1 - m_2)_{\text{system}} = m^{+-} \quad (\text{A3})$$

where m^{+-} is the mass that crosses the boundary of system A as the system changes from state A_1 to state A_2 . The quantity m^{+-} is either positive if mass flows from the environment to system A , or negative if mass flows from A to the environment.

The second law

Starting either from a nonequilibrium state or from an equilibrium state that is not stable, energy can flow out of the system and affect a mechanical effect without leaving any other net changes in the environment. In contrast, experience shows that, starting from a stable equilibrium state, a system cannot affect the mechanical effect just cited. This impossibility is one of the most striking consequences of all the laws of thermodynamics.

The existence of stable equilibrium states is not self-evident. It is the essence of the second law. The *second law* (simplified version) asserts that among all the states of a system with a given value of energy, and given values of the amounts of constituents and the parameters, there exists one and only one stable equilibrium state.

Generalized available energy

As one of the many consequences of the first and second laws, we can prove the existence of a limit on the optimum (either largest or smallest) amount of energy that can be exchanged between a weight and a composite of a system and an auxiliary reservoir. We call this optimum *generalized available energy*, denote it by Ω^R , and can prove that it is additive. It is a generalization of the concept of motive power of fire first introduced by Carnot.

For an adiabatic process of system A only, in the course of which the state of A changes from A_1 to A_2 , we can prove that the energy change $E_1 - E_2$ of A , and the generalized available energy change $\Omega_1^R - \Omega_2^R$ of the composite of A and an auxiliary reservoir R satisfy the relations. If the adiabatic process of A is reversible:

$$E_1 - E_2 = \Omega_1^R - \Omega_2^R. \quad (\text{A4})$$

If the adiabatic process of A is irreversible:

$$E_1 - E_2 < \Omega_1^R - \Omega_2^R. \quad (\text{A5})$$

Entropy and entropy balance

Energy E and generalized available energy Ω^R define a property of system A called *entropy*, and denoted by the symbol S . For A in any state A_1 , the value of entropy S_1 is found by means of the auxiliary reservoir R , a reference state A_0 with energy E_0 and generalized available energy Ω_0^R , to which is assigned a reference value S_0 , and the expression

$$S_1 = S_0 + \frac{1}{c_R} [(E_1 - E_0) - (\Omega_1^R - \Omega_0^R)] \quad (\text{A6})$$

where c_R is a well-defined positive constant that depends on R only. We can prove that S is independent of R , that is, S is a property of system A only, and that it can be assigned values that are nonnegative and that vanish for all states encountered in mechanics.

Because of equations (A4) and (A5), we can prove that S remains invariant in time in any reversible adiabatic process of A , and increases in time in any irreversible adiabatic process of A . These conclusions are valid also for spontaneous processes and for zero-net-effect processes of A . The latter features are known as the *principle of nondecrease of entropy*. It is noteworthy that this principle is independent of the magnitude of the time interval over which the process occurs, and that it is established without knowledge of the complete equation of motion of thermodynamics.

The entropy increase in time in the course of an irreversible spontaneous process as time assumes larger values is called *entropy generated by irreversibility*. It is the result of the natural tendency of any system in a state that is not stable to proceed spontaneously toward a stable equilibrium state. Because both energy and generalized available energy are additive properties, definition (A6) implies that entropy is also additive.

Like energy, entropy can be transferred between systems as a result of interactions. Denoting by S^{4-} the amount of entropy exchanged between A and the environment as the state of A changes from A_1 to A_2 , and using the principle of nondecrease of entropy, we can derive the entropy balance

$$(S_2 - S_1)_{\text{system}} = S^{4-} + S_{\text{irr}} \quad (\text{A7})$$

where S^{4-} is positive if entropy flows from the environment to the system, and negative if the flow is from the system to the environment, and S_{irr} is nonnegative and represents the entropy generated spontaneously in system A in the time interval from t_1 to t_2 required to affect the change from state A_1 to state A_2 . Like the energy balance, the entropy balance is valid for all values of the time interval $t_2 - t_1$.

Stable equilibrium states

In general, a system consists of r constituents and has s parameters. The values of the amounts of the constituents are $\mathbf{n} = \{n_1, n_2, \dots, n_r\}$, and the values of the parameters are $\boldsymbol{\beta} = \{\beta_1, \beta_2, \dots, \beta_s\}$. We can prove that among the many states of the system that have given values of the energy E , the amounts of constituents \mathbf{n} , and the parameters $\boldsymbol{\beta}$, the entropy of the unique stable equilibrium state that corresponds to these values is larger than that of any other state with the same E , \mathbf{n} , $\boldsymbol{\beta}$, and can be expressed as a function

$$S = S(E, \mathbf{n}, \boldsymbol{\beta}) \quad (\text{A8})$$

Equation (A8) is called the *fundamental relation*. It is concave with respect to energy.

We can use the fundamental relation to define other properties of stable equilibrium states, such as temperature T

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{\mathbf{n}, \boldsymbol{\beta}} \quad (\text{A9})$$

total potentials μ_i of the i th constituent

$$\mu_i = -T \left(\frac{\partial S}{\partial n_i} \right)_{E, \mathbf{n}, \boldsymbol{\beta}} \quad \text{for } i = 1, 2, \dots, r \quad (\text{A10})$$

and pressure p

$$p = T \left(\frac{\partial S}{\partial V} \right)_{E, \mathbf{n}, \boldsymbol{\beta}} \quad \text{for } \beta_1 = V = \text{volume.} \quad (\text{A11})$$

It is noteworthy that T , μ_i , and p all require energy, entropy and the fundamental relation for their definitions, that is, the first and second laws, and third law of thermodynamics discussed next. The third law fixes the range of values of T .

Third law

The *third law* of thermodynamics or the *Nernst principle* asserts that for each given set of values of the amounts of constituents and the parameters of a system, there exists one stable equilibrium state with zero temperature. For systems that admit both positive and negative temperatures, there exist two different stable equilibrium states with zero temperature.

General comment

The laws of thermodynamics are not statistical, and are not restricted to any particular classes of systems, states, and time intervals. Accordingly, unless explicitly qualified, theorems derived from these laws are not statistical, and are not restricted to any particular classes of systems, states, and time intervals.

Equation of motion and interactions

If the complete equation of motion of thermodynamics were widely recognized, we would analyze each process by specifying the initial state of the system and the interaction forces with its environment, and by solving the equation of motion to find the final state. In such an analysis, we would not need to apply the laws of thermodynamics explicitly because they would be built into the equation of motion. For example, in mechanics we do not have to apply separately the principle of energy conservation because this principle is a consequence of Hamilton's equations. Similarly, in thermodynamics we would not have to apply separately the principle of nondecrease of entropy because this principle would be a consequence of the complete equation of motion.

Because the complete equation is not yet fully understood, thermodynamics has an ingenious method for the approximate analysis of a special class of practical problems. The method consists of the following steps: (i) the end-states of the process are prespecified to be stable equilibrium; thus, the number of independent state variables of the system is reduced to a minimum; (ii) the effects of interactions of the process are described in terms of flows or exchanges of energy, entropy, and constituents at the boundary of the system; and (iii) by using the balance equations, we can relate changes in properties of the system, changes in the independent state variables, to the exchanges at the boundary of the system and thus complete the analysis of the process.

Four interactions, work, heat, bulk flow and diffusion, and the corresponding flows or exchanges at the boundary of a system are listed in Table A1. They can be used individually, sequentially, or concurrently because energy, entropy and amount of a constituent are additive.

Table A1. Exchanges in four different interactions

Exchange	Interaction			
	Work	Heat	Bulk flow ^a	Diffusion
Energy	W^-	Q^-	$(h + \frac{\xi^2}{2} + gz)n^-$	E^-
Entropy	0	$\frac{Q^-}{T_0}$	sn^-	$\frac{E^- - \mu_0 n^-}{T_0}$
Constituent	0	0	n^-	n^-

^aThe specific enthalpy h and specific entropy s refer to the stable equilibrium state part of the bulk flow state. The speed ξ , and elevation z in the gravity field g refer to the mechanical features of the bulk flow state. Flow of the constituent is into the system if n^- is positive.