

UNIT IIIB

ENTROPY, EQUILIBRIUM DISTRIBUTIONS, AND THE SECOND LAW OF THERMODYNAMICS

The concept of equilibrium provides a basis for the definition of a new property, *entropy*. The second law of thermodynamics is formulated in terms of entropy. The distribution of the most probable (an equilibrium) macrostate is developed without recourse to trial and error. This development leads to a relationship among macroscopic properties, the Gibbs equation, which is a foundation of the analysis of property changes. It is found that three terms contribute to the entropy change of a system. One is a reversible heat effect. The other two are the thermal and mechanical sources of irreversible entropy generation. In the light of these contributions a general thermodynamic design principle is advanced. The optimum design to accomplish a given objective is the one that minimizes the increase of the entropy of the universe.

Objectives

The objectives of this unit are divided into two categories. The objectives of Sections I and IV pertain to entropy, its macroscopic application and the second law. These objectives are required of all students.

1. State and use the definition of entropy in terms of W .
2. State and draw conclusions from the second law principle as applied to the universe.
3. Write the Gibbs equation for a specified simple or complex media.
4. Describe conditions that cause mechanical and thermal irreversible entropy production.
5. Evaluate the magnitude of the reversible, and irreversible thermal or mechanical contributions to entropy change.
6. Write and draw conclusions from the Clausius inequality.
7. For given conditions, if possible, specify the direction of change of the entropy of a system.

The objectives of Sections II and III of the unit are required only of students who intend to continue in Units III. These objectives are:

8. Write, and discuss the meaning of, the equilibrium distribution function for Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics.
9. Find the appropriate expression for the equilibrium entropy of Boltzons, Bosons and Fermions.
10. Apply the equilibrium distribution for Boltzons to the calculation of entropy.
11. Distinguish between reversible work and heat or irreversible work on a microscopic basis.

CONTENTS

I. ENTROPY DEFINED	1
II. EQUILIBRIUM DISTRIBUTION FUNCTIONS	4
A. The Distribution Function for Boltzons	5
B. Distribution Functions for Bosons and Fermions	11
III. ENTROPY IN MACROSCOPIC TERMS, THE GIBBS EQUATION	11
IV. DETERMINING ENTROPY PRODUCTION	15
A. Mechanical Entropy Production	17
B. Thermal Entropy Production	19
SUMMARY QUESTIONS	23
APPENDIX IIB-A, DIFFERENTIATION OF S^{MB}	25
APPENDIX IIB-B, EQUILIBRIUM IN FERMIONS AND BOSONS	26

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Unit IIIA initiated our study of macroscopic systems from the viewpoint that the behavior of real systems results from the collective microscopic behaviors of the particles of the system. By studying successively larger systems we surmised that real systems have unimaginably enormous numbers of microstates and enormous numbers of macrostates. With no reason to expect the (isolated) system to prefer any specific microstate, it was assumed that all microstates of an isolated system are equally probable. With this single assumption, it was shown that a relatively small percentage of the macrostates possesses a vast majority of the system's microstates, that the properties of the macrostates in this group are virtually identical, and that whenever a system is in a macrostate not belonging to this group, collisions drive the system overwhelmingly toward distributions (and consequent properties) of these probable, equilibrium group macrostates. This characteristic behavior of isolated systems of particles is the Second Law of Thermodynamics.¹ To express these concepts quantitatively this unit defines the property, *entropy*, and uses it to formulate the second law. This formulation is used to develop tools for the calculation of macroscopic properties in terms of entropy and to evolve statements of the second law for nonisolated systems.

I. ENTROPY DEFINED

The microscopic property that determines if a macrostate (i) is a member of the equilibrium group is the relative magnitude of its number of microstates, W_i . Therefore, W_i is a property that can be used to describe the approach to equilibrium, $W_i \rightarrow W_{eq}$, where eq represents equilibrium or a member of the most probable group. Since W_i is proportional to the number of particles in the system it is an extensive property. We also know that W_i is proportional to the probability of macrostate i. The probability of occurrence of two independent events is the product of probability of each. So if the particles of a system were partitioned into parts A and B, then W_i would equal $W_{A,i} \cdot W_{B,i}$, where $W_{A,i}$ and $W_{B,i}$ are the number of microstates in macrostate space for portions A and B. This multiplicative nature of W_i is inconvenient; no other extensive property we have encountered behaves this way (other extensive properties are additive). To eliminate this difficulty we define a new property that increases as W_i increases (i.e., when the isolated system ap-

¹The second law can be stated as "all microstates of an isolated system are equally probable" since this is the single assumption of the statistical approach.

proaches equilibrium), yet is additive over the subdivisions of a system. This property, called entropy (S) is defined for any macrostate (i) as²

$$S_i = k \ln W_i \quad (\text{IIIB-1})$$

where k is the Boltzmann constant defined in Unit IA.³ Thus, as a system approaches equilibrium, $W_i \rightarrow W_{eq}$, and the entropy of the system increases monotonically, $S_i \rightarrow S_{eq}$. Furthermore, if two systems are combined,

$$S_i = k \ln W_i = k \ln (W_{A,i} \cdot W_{B,i}) = k \ln W_{A,i} + k \ln W_{B,i} = S_{A,i} + S_{B,i}$$

Entropy like all other properties has an ensemble average value, as defined by eqn. IIIA-11

$$\hat{S} = \sum_{i=1}^{I^*} p_i S_i = \sum_{i=1}^{I^*} p_i k \ln W_i \quad (\text{IIIB-2})$$

Using the perception developed in Unit IIIA, for real systems

$$S_{eq} \rightarrow \hat{S} = k \ln W_{eq}$$

In Unit IIIA, we used trial-and-error procedures to determine the distributions, $n_{j,i}$. (W_i is analytically determinable once the $n_{j,i}$ are known.) The recognition that trial-and-error techniques are operationally impossible for real systems makes the development of the concept of equilibrium an extremely significant result of Unit IIIA. Since equilibrium macrostates have properties that are indistinguishable from the ensemble average, we need only determine the properties of this group to obtain average system properties. Furthermore, the properties of any member of this group are virtually the same so we can choose the one most amenable to analysis. This is the *most probable macrostate* characterized by W_{mp} . Its distribution and properties can be determined without trial and error using analytical procedures developed below. With this choice the equilibrium condition in terms of the property, entropy, is

$$\hat{S} = S_{eq} = S_{mp} = k \ln W_{mp} \quad (\text{IIIB-3})$$

This is Boltzmann's equation.

With the knowledge that entropy of an isolated system is maximized in equilibrium, we can write the *Second Law of Thermodynamics* as

$$dS_{isol} \geq 0 \quad (\text{IIIB-4})$$

If the system was in equilibrium when isolated the equality holds, otherwise the entropy of the system increases until equilibrium is attained.

²Reference 1, pg. 147, establishes this form with an argument of functional analysis.

³The rationale for the introduction of Boltzmann's constant is explained later.

Example 1. Table IIIA-8 summarized the results of the 30-particle example. Use this table to determine the entropy of the most, 10th most, 20th most, and least probable macrostates. Also determine the relative change in entropy as the system goes from the 10th, 20th, and least probable macrostates to the most probable.

From Table IIIA-7 we find $W = 2.648 \cdot 10^{29}$ and that $p_{mp} = 0.0639$; $p_{10} = 0.0271$, $p_{20} = 0.0162$; $P_{lp} = 1.13 \cdot 10^{-22}$. This allows us to determine W_i for each of these macrostates.

$$W_{mp} = p_{mp} W = 1.69 \cdot 10^{28}, \quad W_{10} = 0.718 \cdot 10^{28}, \quad W_{20} = 0.429 \cdot 10^{28}, \quad W_{lp} = 0.299 \cdot 10^8.$$

The entropies are

$$S_{mp} = k \ln W_{mp} = 1.38 \cdot 10^{-23} \text{ J/K} \cdot \ln (1.69 \cdot 10^{28}) = 8.97 \cdot 10^{-22} \text{ J/K}$$

$$S_{10} = 8.85 \cdot 10^{-22} \text{ J/K}, \quad S_{20} = 8.78 \cdot 10^{-22} \text{ J/K}, \quad S_{lp} = 2.37 \cdot 10^{-22} \text{ J/K}$$

The percent changes between these and the most probable macrostate are

$$\frac{S_{mp} - S_{10}}{S_{mp}} = \frac{(8.97 - 8.85) \cdot 10^{-22}}{8.97 \cdot 10^{-22}} = 1.45\%, \quad \frac{S_{mp} - S_{20}}{S_{mp}} = 2.12\%, \quad \frac{S_{mp} - S_{lp}}{S_{mp}} = 73.6\%$$

This illustration reaffirms our hypothesis; the changes in entropy among the probable macrostates are small. But the change from the least to the most significant macrostate is quite pronounced.

Exercise 1. Examine the definition of the entropy, eqn. IIIB-1, and determine the lowest possible value of entropy. Using the perspective of this answer, reflect on the idea of increasing entropy being synonymous with increasing disorder. How ordered is the state that corresponds to the lowest possible entropy?

The formulation of the second law as $dS_{isol} \geq 0$ (eqn. IIIB-4) appears limited since it applies only to isolated systems (closed systems without work or heat interaction). However, the equation can be immediately generalized by recognizing that the universe is an isolated system.⁴ For application we divide the universe into a system (the subject of attention) and its surroundings. Thus

⁴The specification of the entire universe (as opposed to immediate surroundings) as an isolated system has interesting philosophical implications. From this perspective, all processes tend to maximize the entropy of the universe, i.e., to drive it toward equilibrium. Any approach to equilibrium in turn, decreases the driving potential that causes the process to occur. The driving potential for our planet is the energy of the sun which sustains all life, either directly or indirectly. However, the sun is continually approaching equilibrium with the other bodies in the solar system; it is burning out. Therefore, the sun's energy is being distributed uniformly within the solar system. Similarly, a universe, considered as an isolated system, is eventually destined to an "entropy death" (though the time required for this to happen is virtually beyond our conception).

One can relate our concepts of these processes to a perspective of a supreme being through a number of questions. How was the universe arranged in its original nonequilibrium condition? Is the universe isolated, such that it obeys eqn. IIIB-4? Or is there an interaction with something outside the universe, which could periodically or continuously restore the universe to, or toward, its original low-entropy nonequilibrium condition?

$$dS_{\text{univ}} = dS_{\text{sys}} + dS_{\text{surr}} \geq 0 \quad \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0 \quad (\text{IIIB-5})$$

Eqn. IIIB-5 is so far only symbolic since W_i , and hence S_i and S , are to this point calculable only by trial and error. In Section II below, we develop the equilibrium distribution on an analytic, closed form basis that allows the macroscopic equilibrium thermodynamic properties, including entropy, to be determined from microscopic models. This procedure is used in application in Units IIIC, D, and E. And in Section III the equilibrium distribution provides the basis for the relation of entropy to other macroscopic properties.

Note to the Student. The following is a rationale of the objectives for this unit.

1. The material of Sections I and IV is important to all students for both conceptual and practical applications of the second law. Therefore, all students will be examined on its form, meaning, and application (Objectives 1-7).
2. Students who do not proceed to additional Units III will not be examined on Sections II and III. However, since Sections II and III develop the macroscopic relations of Section IV, at least a cursory reading of these sections is recommended.
3. The development in Sections II and III is the foundation for the remainder of Units III. Students who continue in this sequence will be examined on the objectives of this portion (Objectives 8 to 11), in addition to those of Sections I and IV.

II. EQUILIBRIUM DISTRIBUTION FUNCTIONS

The equilibrium properties of a real system are those of its equilibrium group macrostates. One of the equilibrium macrostates is the most probable. If we can find its distribution and its properties we will have found those of the system in equilibrium. It is advantageous to consider the most probable macrostate because its entropy is the greatest and therefore its distribution can be determined by means of the extremum principle. Specifically we wish to find the distribution, $n_{j,i}$, whose entropy is a maximum subject to the constraints imposed on the system by its energy, U , volume, V , and number of articles, N .⁵ This problem is expressed in the mathematical form

$$dS = k d[\ln W_i(n_{j,i})] = 0 \quad (\text{IIIB-6a})$$

$$dN = d\left(\sum_j n_{j,i}\right) = \sum_j \delta n_{j,i} = 0; \quad dU = d\left[\sum_j n_{j,i} \epsilon_j(V)\right] = \sum_j \epsilon_j(V) \delta n_{j,i} \quad (\text{IIIB-6b,c})^{6,7}$$

⁵Recall that the development of Unit IIIA was, implicitly, for a simple compressible system, $\bar{X}_k = V$. The set (U, V, N) is an extensive set of 3 variables consistent with the State Postulate, Unit IB.

⁶The derivative of $n_{j,i}$ is written as $\delta n_{j,i}$ instead of $dn_{j,i}$ as a reminder that $n_{j,i}$ is a discrete variable (i.e., $n_{j,i} = 0, \pm 1, \pm 2, \dots$).

⁷The derivative of $\epsilon_j(V)$ is zero since the volume is fixed.

The solution of the equation with constraints is $n_{j,mp}$. Unit IIIA presented expressions for W_i for the independent particle systems for the three statistics. However, before substitution of W_i explicitly we can perform some operations symbolically.

There are two procedures to solve the extremum problem prescribed by eqns. IIIB-6.⁸ These are the method of Lagrange Multipliers and the method of Steepest Descent. We will use the method of *Lagrange Multipliers*. To use this method we multiply eqns. IIIB-6b and c by unknown parameters α and β , respectively, then subtract them from eqn. IIIB-6a.⁹

$$d\left(\frac{S}{k} - \alpha N - \beta U\right) = d[\ln W(n_{j,i})] - \alpha \sum_j \delta n_{j,i} - \beta \sum_j \epsilon_j(V) \delta n_{j,i} = 0 \quad (\text{IIIB-7})$$

Eqn. IIIB-7 can be solved to obtain the most probable distribution as a function of the unknown multipliers, $n_{j,mp}(\alpha, \beta)$. Then the solution can be completed by identifying the physical meaning of α and β by further consideration of the physical conditions on U , N , and S . To proceed we need an explicit expression for W_i . These expressions were presented in Unit IIIA for the three statistics. We will first treat Boltzons.

Note to the Student. The results developed below are important though algebraically tedious. The logic for some of the algebraic steps and approximations lies in knowing the forms of results desired. Do not let the algebraic detail obscure its intent or results. Study or reproduce the algebra (most of which is presented in the appendices) only so far as you personally require to believe and understand the results.

A. The Distribution Function for Boltzons

In Unit IIIA the number of microstates (W_i) of a macrostate (i) of a Maxwell-Boltzmann system was shown to be calculable using eqn. IIIA-7a, $W_i^{MB} = N! \prod_j (g_j^{n_{j,i}} / n_{j,i}!)$. The derivative of $\ln W_i^{MB}$ is derived in Appendix IIIB-A. The result is

$$d(\ln W_i^{MB}) = \sum_j \ln \left(\frac{g_j}{n_{j,i}} \right) \delta n_{j,i}$$

Substituting this into eqn. IIIB-7 we obtain

$$\sum_j \left[\ln \left(\frac{g_j}{n_{j,i}} \right) - \alpha - \beta \epsilon_j(V) \right] \delta n_{j,i} = 0$$

⁸The term extremum refers to maximum and minimum, as does the condition $dS = 0$. The second derivative of S will show that our results pertain to the maximum.

⁹Lagrange's method is explained in Ref. 3, Appendix A.

Ans. 1. No occupied macrostate can have less than one microstate, $W_i \geq 1$. Since $\ln 1 = 0$, the lowest possible entropy is zero, $S_{\min} = 0$. Such a state would be completely certain, i.e., totally ordered. This answer supports the disorder analogy.

Since the $n_{j,i}$ are linearly independent, the satisfaction of eqn. IIIB-7 requires that the bracketed term be zero for each j .¹⁰ Thus, the macrostate that satisfies eqns. IIIB-6, the most probable ($i = mp$), is determined.

$$\ln \left(\frac{g_j}{n_{j,mp}} \right) = \alpha + \beta \epsilon_j(V) \quad n_{j,mp}^{MB} = \frac{g_j}{e^{\alpha + \beta \epsilon_j(V)}} \quad (\text{IIIB-8})$$

This result is not yet useful since α and β are unknown. For Maxwell-Boltzmann statistics α can be readily determined as a function of N , β , g_j and $\epsilon_j(V)$. Substitution of the expression for $n_{j,mp}^{MB}$ into eqn. IIIB-6b $N = \left(\sum_j n_{j,i} \right)$ yields¹¹

$$\alpha = \ln \left(\frac{Z}{N} \right) \quad \text{or} \quad e^{-\alpha} = \frac{N}{Z}$$

The function Z is called the *partition function*.

$$Z(V, \beta) \equiv \sum_j g_j e^{-\beta \epsilon_j(V)}$$

The partition function is a sum that appears frequently in calculations of thermodynamic properties. Its definition saves considerable writing.

To determine β we first write entropy as a function of β, U , the partition function, $Z(\beta, V)$, and N . For a Maxwell-Boltzmann system the expression for entropy of a macrostate (as shown in Appendix IIIB-A) is

$$S_i^{MB} = k \ln W_i^{MB} = k \left\{ \left[\sum_j n_{j,i}^{MB} \ln \left(\frac{g_j}{n_{j,i}^{MB}} \right) \right] + N \ln N \right\} \quad (\text{IIIB-A3})$$

To find the equilibrium entropy we substitute the equilibrium distribution into the above equation as follows

$$n_{j,mp}^{MB} = \frac{N g_j e^{-\beta \epsilon_j(V)}}{Z} \quad \text{and} \quad \ln \left(\frac{g_j}{n_{j,mp}^{MB}} \right) = \ln Z - \ln N + \beta \epsilon_j(V)$$

Therefore

$$\begin{aligned} S_{eq}^{MB} &= k \left\{ \left[\sum_j n_{j,i} (\ln Z - \ln N + \beta \epsilon_j) \right] + N \ln N \right\} \\ &= k \left(\ln Z \sum_j n_{j,i} - \ln N \sum_j n_{j,i} + \beta \sum_j n_{j,i} \epsilon_j + N \ln N \right) \end{aligned}$$

¹⁰This statement is an oversimplification as there is some interdependence through the constraints. A more rigorous treatment yields the same conclusions.

¹¹The steps are

$$N = \sum_j n_{j,i}^{MB} = \frac{\sum_j g_j e^{-\beta \epsilon_j(V)}}{e^{\alpha}}$$

But since $\sum_j n_{j,i} = N$ and $\sum_j n_{j,i} \epsilon_j = U$, the equilibrium entropy can be written as

$$S_{eq}^{MB}(\beta, U, N, V) = k\beta U + Nk \ln [Z(\beta, V)] \quad (\text{IIIB-9})$$

Now we turn our attention to the task of relating the remaining unknown multiplier, β , to a macroscopic property. This is accomplished by considering the process of thermal equilibration of an isolated system. The second law for such a process is $dS_{isol} \geq 0$. Consider a system composed of Boltzons and subdivided into regions A and B, Fig. IIIB-1. The wall that

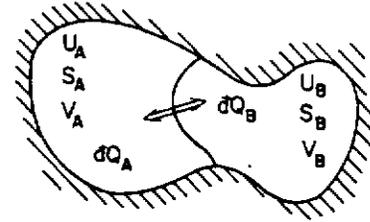


Fig. IIIB-1 Thermal Equilibration in an Isolated System

separates A from B is rigid and impermeable (there is no work or particle transfer; N_A , N_B , V_A and V_B are fixed). The wall allows energy transport as heat. Thus if the two regions are not initially in thermal equilibrium, a heat interaction, $dQ_A = -dQ_B$, will occur until equilibrium is achieved. As a result of this process the energy of each region will change subject to the isolation condition (viz., $dU = dU_A + dU_B = 0$ or $dU_A = -dU_B$). We wish to study the effect of this process on the system entropy. This can be done by determining the entropy change of regions A and B, since $S = S_A + S_B$. The determination of dS_A and dS_B is facilitated if we specialize our system so that each separate region remains in an extensive equilibrium state. Since our intent is the study of the effect of an equilibration process on the overall system, this limitation does not defeat our purpose. With this restriction, eqn. IIIB-9 is applicable; it allows us to relate the entropy change of each region to the equilibration causing energy transport. The coefficient that relates these parameters is the partial derivative of the entropy with respect to the energy.¹²

$$dS_A = \left(\frac{\partial S_A}{\partial U_A} \right)_{V_A, N_A} dU_A \quad \text{and} \quad dS_B = \left(\frac{\partial S_B}{\partial U_B} \right)_{V_B, N_B} dU_B$$

This coefficient is developed for Boltzons in the following example.

Example 2. Use eqn. IIIB-9 for Boltzons to derive the expression $(\partial S / \partial U)_{N, V} = k\beta$.

The equilibrium entropy of a Boltzon system is $S_{eq}^{MB} = k\beta U(\beta, V, N) + Nk \ln [Z(\beta, V)]$. Therefore

$$\left(\frac{\partial S_{eq}^{MB}}{\partial U} \right)_{N, V} = \frac{\partial}{\partial U} [k\beta U(\beta, V, N) + Nk \ln Z(\beta, V)]_{N, V}$$

¹²Unit S2 presents the definition of a partial derivative and illustrates example determinations.

$$\left(\frac{\partial S_{eq}^{MB}}{\partial U}\right)_{N,V} = k\beta + kU \left(\frac{\partial \beta}{\partial U}\right)_{V,N} + Nk \frac{\partial}{\partial \beta} [\ln Z(\beta, V)]_V \left(\frac{\partial \beta}{\partial U}\right)_{V,N}$$

The last term is simplified as

$$\frac{\partial}{\partial \beta} [\ln Z(\beta, V)]_V = \frac{1}{Z} \left(\frac{\partial Z}{\partial \beta}\right)_V = \frac{1}{Z} \sum_j g_j \frac{\partial}{\partial \beta} \left(e^{-\beta \epsilon_j(V)} \right)_V = -\frac{1}{Z} \sum_j \epsilon_j g_j e^{-\beta \epsilon_j(V)}$$

Multiplying by N/N and introducing $n_{j,mp}^{MB} = \frac{N}{Z} g_j e^{-\beta \epsilon_j(V)}$, gives

$$\frac{\partial}{\partial \beta} [\ln Z(\beta, V)]_V = -\frac{1}{N} \sum_j n_{j,mp}^{MB} \epsilon_j(V) = -\frac{U}{N}$$

So we have

$$\left(\frac{\partial S_{eq}^{MB}}{\partial U}\right)_{N,V} = k\beta + kU \left(\frac{\partial \beta}{\partial U}\right)_{V,N} - Nk \frac{U}{N} \left(\frac{\partial \beta}{\partial U}\right)_{V,N} = k\beta, \quad \text{QED.}$$

The preceding example established that the entropy changes of regions A and B are given as, $dS_A = k\beta_A dU_A$ and $dS_B = k\beta_B dU_B$. A first law analysis of these regions shows $(dU_A = dQ_A + dW_A) = - (dU_B = dQ_B + dW_B)$. Thus the entropy change of the system can be written

$$dS|_{isol} = dS_A + dS_B = kdQ_A(\beta_A - \beta_B) \geq 0$$

Examine the dimensions of this relationship. Both entropy and heat are extensive. Therefore, β must be a fundamentally intensive property. As equilibrium is achieved, the entropy reaches a maximum ($dS|_{isol} = 0$) and $\beta_A \rightarrow \beta_B = \beta_{eq}$. β is a fundamentally intensive property that is uniform when a system is in thermal equilibrium. This is the same characteristic that is displayed by temperature. We conclude that $\beta = \beta(T)$. To determine the form of the relationship consider the expression developed above for the isolated system, $dS|_{isol}$. If heat enters system A, $dQ_A > 0$, then the second law, $dS|_{isol} > 0$, requires that $\beta_A > \beta_B$. So heat flows from regions of low β toward regions of high β . This is opposite to the relationship of heat flow and temperature. The relationship between β and T is reciprocal, $\beta \propto 1/T$. We choose as our explicit relationship the simplest form that satisfies our objectives

$$\beta \equiv \frac{1}{kT} \quad \text{(IIIB-10)}$$

Boltzmann's constant, k , is required to ensure the same numerical values for temperature as our previous scales (Unit IA).

The equilibrium distribution for Boltzons can now be written in terms of measurable parameters.

$$n_j^{MB} = \frac{N g_j e^{-\epsilon_j(V)/kT}}{Z(T,V)} \quad \text{where} \quad Z(T,V) = \sum_j g_j e^{-\epsilon_j(V)/kT} \quad (\text{IIIB-11,12})$$

In eqn. IIIB-11, and in the rest of the unit, the subscript, mp, is omitted. It is implied in the expression for the distribution function. Similarly, we will omit the subscript, eq, in the expression for entropy.

$$S^{MB} = \frac{U}{T} + Nk \ln Z(T,V) \quad (\text{IIIB-13})$$

The use of the distribution function can be illustrated by example. Although most physical systems have an infinite number of states and levels (e.g., the particle in a box, Table IIIA-1), it is simpler to consider a system with only a few levels. A physical example that serves this purpose is a laser. The lasing states are a few levels in an infinite array of available excitation levels, one of which has a long time constant for decay to equilibrium relative to the others. For processes performed in times small in comparison to the decay time, this metastable state and the ground state can be considered isolated.

Example 3. The operation of a ruby laser can be analyzed as an isolated system of electrons existing in two levels—the ground level, $4A_2$, and the metastable level, $2E$. Operating at liquid nitrogen temperatures, 77 K, a particular ruby crystal has the following characteristics:¹³

$$\epsilon_1 = 0, \quad g_1 = 6.40 \cdot 10^{22}, \quad \epsilon_2 = 2.88 \cdot 10^{-20} \text{ J/particle}, \quad g_2 = 3.20 \cdot 10^{21}$$

The total number of electrons trapped in this isolated subsystem is 10^{18} .

(a) Determine the number of electrons in each level of the subsystem when it is in equilibrium with the rest of the crystal (77 K). Determine the total energy of the subsystem under these conditions. (b) A power source is used to add energy to the lasing system (i.e., to pump it) until the number of electrons in the upper level is $n_2 = 5.00 \cdot 10^{16}$. Find the amount of energy added.

(a) We first compute the partition function.

$$\begin{aligned} Z &= \sum_j g_j e^{-\epsilon_j/kT} = g_1 e^{-\epsilon_1/kT} + g_2 e^{-\epsilon_2/kT} \\ &= 6.40 \cdot 10^{22} + 3.20 \cdot 10^{21} \cdot \exp\left(\frac{-2.88 \cdot 10^{-20} \text{ J/part}}{1.38 \cdot 10^{-23} \text{ J/(part K)} \cdot 77 \text{ K}}\right) \\ &= 6.40 \cdot 10^{22} + 3.20 \cdot 10^{21} \cdot \exp(-27.1) = 6.40 \cdot 10^{22} \end{aligned}$$

¹³The energy change, $\Delta\epsilon = \epsilon_2 - \epsilon_1$, is correct for the lasing states of a ruby crystal. But ϵ_1 , g_1 and g_2 were selected arbitrarily for simplicity.

$$\text{Thus, } n_2 = \frac{Ng_2 e^{-\epsilon_2/kT}}{Z} = \frac{10^{18} \cdot 3.2 \cdot 10^{21} \cdot \exp(-27.1)}{6.4 \cdot 10^{22}} = 8.5 \cdot 10^4 \text{ particles}$$

$$n_1 = N - n_2 \approx 10^{18} \text{ particles } U = n_1 \epsilon_1 + n_2 \epsilon_2 = 10^{18} \cdot 0 + 8.50 \cdot 10^4 \text{ part} \cdot 2.88 \cdot 10^{-20} \text{ J/part} = 2.45 \cdot 10^{-15} \text{ J.}$$

(b) After pumping, $n_2 = 5.00 \cdot 10^{16}$, and $n_1 = N - n_2 = 95.0 \cdot 10^{16}$. We solve for the new temperature from

$$\frac{n_2}{n_1} = \frac{g_2 e^{-\epsilon_2/kT}}{g_1 e^{-\epsilon_1/kT}} = \frac{g_2}{g_1} e^{-(\epsilon_2 - \epsilon_1)/kT}$$

Or,

$$T = \frac{-(\epsilon_2 - \epsilon_1)}{k \ln \left(\frac{n_2/g_2}{n_1/g_1} \right)} = \frac{-2.88 \cdot 10^{-20} \text{ J/part}}{1.38 \cdot 10^{-23} \text{ J/part} \cdot \ln \left(\frac{5 \cdot 10^{16} \cdot 6.4 \cdot 10^{22}}{95 \cdot 10^{16} \cdot 3.2 \cdot 10^{21}} \right)} = -4.07 \cdot 10^4 \text{ K}$$

A negative temperature? Yes, systems with a limited number of allowed (bounded) states can and do achieve negative temperatures. The positive temperatures of our experience are defined on the basis of equilibrium distributions. As seen from the expression for T above, the nonequilibrium condition necessary for laser operation, $(n_2/g_2) > (n_1/g_1)$, is responsible for its negative temperature. But, negative temperatures are high, not low, temperatures, as can be seen from this example—the conditions that led to a negative temperature resulted from energy addition to the system.¹⁴ The new energy is

$$U = \sum_j n_j \epsilon_j = 0 + 5.00 \cdot 10^{16} \text{ part} \cdot 2.88 \cdot 10^{-20} \text{ J/part} = 1.44 \cdot 10^{-3} \text{ J}$$

Once the system has been pumped as described, a discharge is triggered with a signal at the proper frequency. As the electrons drop back into lower energy states energy is released in the form of coherent emission of photons from different positions in the crystal. This accumulated effect causes the emission of a very high intensity monochromatic beam whose wavelength is given by

$$\lambda = \frac{hc}{\epsilon_2 - \epsilon_1} = \frac{6.626 \cdot 10^{-34} \text{ J} \cdot \text{s/part} \cdot 2.998 \cdot 10^8 \text{ m/s}}{2.88 \cdot 10^{-20} \text{ J/part}} = 6897 \text{ \AA}. \text{ A vivid red light.}$$

Exercise 2. An isolated Maxwell-Boltzmann system has three energy levels ($\epsilon_1 = 0, g_1 = 10^4$; $\epsilon_2 = 2.76 \cdot 10^{-21} \text{ J/part}, g_2 = 3.00 \cdot 10^4$; $\epsilon_3 = 4.14 \cdot 10^{-21} \text{ J/part}, g_3 = 3.00 \cdot 10^4$). The system is found in a macrostate with $n_1 = 6430, n_2 = 2610, n_3 = 960$. (a) What are the overall constraints on this system, N and U ? (b) Determine whether the specified (continued)

¹⁴ Many students may find it discomforting that negative temperatures are "hotter" than normal positive temperatures. That is, that temperature is not a monotonically increasing function. (There is a discontinuity as the scale goes from $+\infty$ to the next higher temperature, $-\infty$. The highest temperature is -0 .) This characteristic can be altered by defining temperature as minus θ , viz., $\theta \equiv -\beta$. A correspondence between the two scales T and θ in the order of increasing "hotness" is ($T = +0, \theta = -\infty$; $T = +\infty, \theta = -0$; $T = -\infty, \theta = +0$; $T = -0, \theta = +\infty$).

(Exercise 2, continued) macrostate is an equilibrium macrostate, that is, is it consistent with eqn. IIIB-11? If it is an equilibrium macrostate, what is the system's equilibrium temperature? (c) A second macrostate has $n_2 = 3000$. Is this an equilibrium macrostate?

B. Distribution Functions for Bosons and Fermions

The procedures to derive the distribution functions for Bosons and Fermions are analogous to that used above for Boltzons. One starts with eqn. IIIB-7 which is applicable to all statistics. Specificity is introduced by the substitution of the appropriate expression for W_1 , eqns. IIIA-7b or c. The development, including the identification of β as $1/kT$ by the differentiation of the entropy, is presented in Appendix IIIB-B. These results will be employed extensively in Units IIIC and D. Students who continue with these units may wish to examine this derivation. The results for Fermions are

$$n_j^{FD} = \frac{g_j}{e^{\alpha + \epsilon_j/kT} + 1} \quad (\text{IIIB-14})$$

$$S^{FD} = \frac{U}{T} + Nk\alpha + k \sum_j g_j \ln \left[1 + e^{-\alpha - \epsilon_j(V)/kT} \right] \quad (\text{IIIB-15})$$

And for Bosons, the results are

$$n_j^{BE} = \frac{g_j}{e^{\alpha + \epsilon_j/kT} - 1} \quad (\text{IIIB-16})$$

$$S^{BE} = \frac{U}{T} + Nk\alpha - k \sum_j g_j \ln \left[1 - e^{-\alpha - \epsilon_j(V)/kT} \right] \quad (\text{IIIB-17})$$

The identification of the parameter α for these statistics is not easy to accomplish in general. This step is deferred to Units IIIC and IIID, where it is needed for application.

At this point we have evaluated the equilibrium distribution functions for all three types of independent particles. These will enable us to evaluate the properties of substances based on microscopic models. The development was done in terms of isolated systems (fixed U , V , and N). But the conclusions are valid for any system in equilibrium. The results are simply applied to the nonisolated system in terms of its *instantaneous* values of U , V , and N .

III. ENTROPY IN MACROSCOPIC TERMS, THE GIBBS EQUATION

We have formulated the second law in terms of the entropy, eqn. IIIB-5. Our original definition of entropy was in microscopic form, eqn. IIIB-1. In the preceding section we were able to formulate the equilibrium entropy as an analytic function, eqn. IIIB-13, 15 or 17. But the formulation still contains microscopic parameters $\{\epsilon_j(V)$ and $g_j\}$.

Totally macroscopic application of the second law requires that we be able to determine entropy change on a purely macroscopic basis. We obtain this by combining the energy conservation principle with the equilibrium distribution function developed above.

On a microscopic basis the internal energy of a system is $U = \sum_j n_{j,i} \epsilon_j(V)$. Our previous development concerned isolated systems. The principal means by which closed system states are altered are through heat and/or work interactions. The relationship between internal energy, heat, and work is the intrinsic first law. Since our development is in terms of simple compressible media [$\epsilon_j = \epsilon_j(V)$], we employ eqn. IB-16c.

$$dU = \sum_j \epsilon_j(V) \delta n_{j,i} + \sum_j \left(n_{j,i} \frac{d\epsilon_j(V)}{dV} \right) dV = (dQ + dW_{irr}^i) - p dV$$

Processes that occur at constant volume must satisfy the condition

$$dQ + dW_{irr}^i = \sum_j \epsilon_j(V) \delta n_{j,i} \quad (\text{IIIB-18})$$

Such energy addition processes do not affect the magnitude of the levels, [$d\epsilon_j(V) = 0$], rather they shift particles from lower into higher energy levels. The volume change is independent of eqn. IIIB-18; therefore, the terms in dV are also separately equal.¹⁵

$$dW_{rev,c}^i = -p dV = \sum_j \left(n_{j,i} \frac{d\epsilon_j(V)}{dV} \right) dV = \sum_j n_{j,i} d\epsilon_j(V) \quad (\text{IIIB-19})$$

This relationship developed for simple compressible media is valid for other simple and complex media as well

$$dW_{rev}^i = \sum_j n_{j,i} d\epsilon_j(V) \quad (\text{IIIB-19})$$

Thus, if a reversible work interaction occurs to a system in equilibrium ($n_{j,i} = n_{j,eq}$) the system remains in equilibrium during the process ($\delta n_{j,i} = 0$). The energy is altered exclusively by the change in the level magnitudes. If heat or irreversible work interaction occurs the system must re-equilibrate to new equilibrium states after each energy addition. Thus rapid heat and/or irreversible work processes tend to leave the system in nonequilibrium states.

Example 4. The 10^4 distinguishable particles of a fictitious, but illustrative, system are distributed among two levels ($\epsilon_1 = 0$, $g_1 = 5 \cdot 10^2$; $\epsilon_2 = 6.90 \cdot 10^{-21}$ J/part, $g_2 = 10^3$). The system is in equilibrium and its total energy is $U = 2.07 \cdot 10^{-17}$ J. (a) Determine the temperature and entropy of the system in this equilibrium state. (b) Reversible (cont'd)

¹⁵This relationship also gives us the true microscopic meaning of pressure, as opposed to the "pseudopressure" of Unit IIIA,

$$p_{j,i} = - n_{j,i} \frac{d\epsilon_j(V)}{dV}; \quad p_i = \sum_j n_{j,i} \frac{d\epsilon_j(V)}{dV}; \quad p_{eq} = \sum_j n_{j,eq} \frac{d\epsilon_j(V)}{dV}$$

(Example 4, continued) adiabatic work is performed on the system causing the energy levels to change to ($\epsilon_1 = 2.30 \cdot 10^{-26}$ J/part, $\epsilon_2 = 11.5 \cdot 10^{-21}$ J/part; g_1 and g_2 are unchanged). Determine the work done on the system and the new temperature.

The energy of the system uniquely determines the distribution since there are only two states

$$U = n_1 \epsilon_1 + n_2 \epsilon_2 = 0 + n_2 \epsilon_2; \quad n_2 = \frac{U}{\epsilon_2} = \frac{2.07 \cdot 10^{-17} \text{ J}}{6.90 \cdot 10^{-21} \text{ J/part}} = 3 \cdot 10^3 \text{ part}$$

This gives $n_1 = N - n_2 = (10^4 - 3) \cdot 10^3 = 7 \cdot 10^3$ part. Since the particles are distinguishable they are Boltzons. In equilibrium

$$n_1 = \frac{Ng_1 \exp(-\epsilon_1/kT)}{Z} \quad \text{or} \quad Z = \frac{10^4 \text{ part} \cdot 5 \cdot 10^2 e^{-0}}{7 \cdot 10^3 \text{ part}} = 714$$

Then using

$$n_2 = \frac{Ng_2 \exp(-\epsilon_2/kT)}{Z}; \quad -\frac{\epsilon_2}{kT} = \ln \left(\frac{n_2 Z}{Ng_2} \right)$$

or

$$T = \frac{-\epsilon_2}{k \ln \left(\frac{n_2 Z}{Ng_2} \right)} = \frac{-6.90 \cdot 10^{-21} \text{ J/part}}{1.38 \cdot 10^{-23} \text{ J/(part K)} \cdot \ln \left(\frac{3 \cdot 10^3 \text{ part} \cdot 714}{10^4 \text{ part} \cdot 10^3} \right)} = 324 \text{ K}$$

Ans. 2. (a) $N = \sum_j n_{j,i} = 6430 + 2610 + 960 = 10^4$,

$$U = \sum_j n_{j,i} \epsilon_j = 0 + 2610 \text{ part} \cdot 2.76 \cdot 10^{-21} \text{ J/part} + 960 \text{ part} \cdot 4.14 \cdot 10^{-21} \text{ J/part} = 1.12 \cdot 10^{-17} \text{ J}$$

(b) If the system is in equilibrium, then

$$n_{j,i} = \frac{Ng_j \exp(-\epsilon_j/kT)}{Z}; \quad \text{or} \quad 6430 = \frac{10^4 \cdot 10^4 e^{-0}}{Z};$$

and

$$2610 = \frac{10^4 \cdot 3.00 \cdot 10^4}{Z} \exp \left[\frac{-2.76 \cdot 10^{-21} \text{ J/part}}{1.38 \cdot 10^{-23} \text{ J/(part K)} T} \right] = \frac{3 \cdot 10^8}{Z} \exp \left(\frac{-200 \text{ K}}{T} \right)$$

$$960 = \frac{10^4 \cdot 3.00 \cdot 10^4}{Z} \exp \left[\frac{-4.14 \cdot 10^{-21} \text{ J/part}}{1.38 \cdot 10^{-23} \text{ J/(part K)} T} \right] = \frac{3 \cdot 10^8}{Z} \exp \left(\frac{-300 \text{ K}}{T} \right)$$

These are 3 equations in two unknowns (Z and T). We can solve for Z with the n_1 condition; $Z = 1.56 \cdot 10^4$. Then solve for T with the n_2 condition; $T = 100 \text{ K}$. Then test to see if these answers are consistent with the n_3 condition; they are. The macrostate is an equilibrium macrostate. If $n_2 = 3000$, then

$U = \sum_j n_{j,i} \epsilon_j = 1.12 \cdot 10^{-17} \text{ J} = 0 + 3000 \cdot 2.76 \cdot 10^{-21} \text{ J} + n_3 \cdot 4.14 \cdot 10^{-21} \text{ J/part}$ gives $n_3 = 700$ and $n_1 = 10^4 - 3700 = 6300$. This is not an equilibrium state. It does not obey eqn. IIIB-11. Other equilibrium states for this system are

$$(n_{1,\text{eq}} = 6429, n_{2,\text{eq}} = 2613, n_{3,\text{eq}} = 958) \text{ and } (n_1 = 6431, n_2 = 2607, n_3 = 962).$$

These still satisfy eqn. IIIB-11 with $T = T_{\text{eq}} = 100 \text{ K}$, to three-place accuracy.

Then

$$S = \frac{U}{T} + Nk \ln Z = \frac{2.07 \cdot 10^{-17} \text{ J}}{323 \text{ K}} + 10^4 \text{ part} \cdot 1.38 \cdot 10^{-23} \text{ J/(part K)} \cdot \ln 714 = 97.0 \cdot 10^{-20} \text{ J/K}$$

(b) the work interaction is adiabatic reversible, $dW_{\text{rev}} = \sum n_j d\epsilon_j$. The distribution is unchanged $n_{j,b} = n_{j,a}$. Thus

$$U_b = n_1 \epsilon_{1,b} + n_2 \epsilon_{2,b} = 7 \cdot 10^3 \text{ part} \cdot 2.30 \cdot 10^{-21} \text{ J/part} + 3 \cdot 10^3 \text{ part} \cdot 11.5 \cdot 10^{-21} \text{ J/part} \\ = 5.06 \cdot 10^{-17} \text{ J}$$

The work can be determined from the first law

$$U_b - U_a = \cancel{Q} + \cancel{W}_{\text{irr}} + W_{\text{rev}}^i = (5.06 - 2.07) \cdot 10^{-17} = 2.99 \cdot 10^{-17} \text{ J}$$

The new temperature can be determined directly by writing the ratio

$$\frac{n_1}{n_2} = \left(\frac{Ng_1 \exp(-\epsilon_{1,b}/kT_b)}{Z} \right) \left(\frac{Z}{Ng_2 \exp(-\epsilon_{2,b}/kT_b)} \right)$$

or

$$T_b = \frac{\epsilon_{2,b} - \epsilon_{1,b}}{k \ln \left(\frac{n_1 g_2}{n_2 g_1} \right)} = \frac{(11.5 - 2.3) \cdot 10^{-21} \text{ J/part}}{1.38 \cdot 10^{-23} \text{ J/(part K)} \cdot \ln \left(\frac{7 \cdot 10^3 \text{ part} \cdot 10^3}{3 \cdot 10^3 \text{ part} \cdot 5 \cdot 10^2} \right)} = 433 \text{ K}$$

Exercise 3. Exmp. 3 considered work addition to "pump" a ruby laser into a lasing condition, viz., to achieve a negative temperature. Reexamine this problem and decide whether it was reversible or irreversible work that was added.

The solutions of the preceding problems depended on insight gained by making a microscopic distinction between a reversible work interaction, $dW_{\text{rev}}^i = \sum n_{j,i} d\epsilon_j$, and that of irreversible work and/or heat, $dQ + dW_{\text{irr}}^i = \sum_j \epsilon_j \delta n_{j,i}$. That this distinction also allows us to establish entropy change on a totally macroscopic basis is evident if one differentiates the microscopic expression for the equilibrium entropy for any of the three statistics, eqn. IIIB-13, 15 or 17. Among the resulting terms will be an expression for reversible work, eqn. IIIB-19. Identification of this term gives the desired connection between entropy change and other macroscopic variables, the *Gibbs Equation*.

$$dS = \frac{dU - dW_{\text{rev}}^i}{T} \quad (\text{IIIB-20a})$$

The derivation of the Gibbs Equation is completed for Boltzons in the following example. As a further example the same technique is employed in Appendix IIIB-B to complete the derivation for Fermions and, as an exercise, for Bosons. The result is the same for all three particle types. The Gibbs equation, which is our principal bridge between properties, is not restricted to a particular type of particle.

Example 5. Differentiate the equilibrium entropy for a closed system of Boltzons and substitute eqn. IIIB-19 to derive the Gibbs equation.

The equilibrium entropy of a system of Boltzons is given by eqn. IIIB-13. Its differential in a closed system ($N = \text{const}$) is

$$d(S^{\text{MB}})|_N = d\left(\frac{U}{T} + Nk \ln Z(T,V)\right)|_N = \frac{dU}{T} - \frac{UdT}{T^2} + \frac{Nk}{Z} \left[\left(\frac{\partial Z(T,V)}{\partial T}\right)_V dT + \left(\frac{\partial Z(T,V)}{\partial V}\right)_T dV \right]$$

Now by the definition of Z , eqn. IIIB-12

$$\frac{Nk}{Z} \left(\frac{\partial Z(T,V)}{\partial T}\right)_V = \frac{Nk}{Z} \left[\frac{\partial}{\partial T} \left(\sum_j g_j e^{-\epsilon_j(V)/kT} \right) \right]_V = \frac{Nk}{ZkT^2} \left(\sum_j \epsilon_j g_j e^{-\epsilon_j(V)/kT} \right)$$

Substituting the distribution function $n_j^{\text{MB}} = [Ng_j \exp(-\epsilon_j(V)/kT)]/Z$, we obtain

$$\frac{Nk}{Z} \left(\frac{\partial Z}{\partial T}\right)_V = \frac{-1}{T} \sum_j n_j^{\text{MB}} \epsilon_j = -\frac{U}{T^2}$$

Similarly

$$\frac{Nk}{Z} \left(\frac{\partial Z(T,V)}{\partial V}\right)_T = \frac{Nk}{Z} \left[\frac{\partial}{\partial V} \left(\sum_j g_j e^{-\epsilon_j(V)/kT} \right) \right]_T = -\frac{Nk}{ZkT} \sum_j \frac{d\epsilon_j(V)}{dV} g_j e^{-\epsilon_j(V)/kT}$$

and again substituting n_j^{MB} , we have

$$\frac{Nk}{Z} \left(\frac{\partial Z}{\partial V}\right)_T = -\frac{1}{T} \sum_j n_j^{\text{MB}} \frac{d\epsilon_j(V)}{dV}$$

Thus the differential entropy is

$$d(S^{\text{MB}})|_N = \frac{dU}{T} - \frac{UdT}{T^2} + \frac{U}{T^2} dT - \frac{1}{T} \sum_j n_j^{\text{MB}} \frac{d\epsilon_j(V)}{dV} dV = \frac{dU}{T} - \frac{dW_{\text{rev}}^i}{T} \quad \text{QED.}$$

IV. DETERMINING ENTROPY PRODUCTION

Eqn. IIIB-5 is the most general form of the second law. But its use requires the determination of entropy change. The Gibbs equation is the origin of all macroscopic determinations of entropy change. For general complex, simple, and simple compressible media it is, respectively

$$dS = \frac{dU - dW_{\text{rev}}^i}{T} = \frac{dU - \sum_{k=1}^K \bar{F}_k \cdot d\bar{X}_k}{T} \quad \text{(IIIB-20a)}$$

$$dS = \frac{dU - \bar{F} \cdot d\bar{X}}{T}; \quad dS = \frac{dU + p dV}{T} \quad \text{(IIIB-20b,c)}$$

The Gibbs equation is valid for any process between equilibrium states; it is independent of the path.

Exercise 4. Write the Gibbs equation for: (a) A simple magnetic substance, (b) A simple electric substance, (c) A complex substance with appreciable compressible and surface work modes.

Exercise 5. When the Gibbs equation is applied to an isolated system ($dU=dV=dN=0$), it predicts $dS=0$. But the second law for an isolated system, eqn. IIB-4, is $dS \geq 0$. Are these two statements in conflict? How can their difference be explained?

Although the Gibbs equation is our principal means to evaluate entropy change, it has no direct second law significance.¹⁶ Second law significance is obtained when the entropy change for the system and the surroundings are substituted into eqn. IIB-5 to determine ΔS_{univ} . This quantity, which is a measure of the irreversibility of a process, is called its *entropy "production"* (or just *production*).

It is helpful in the development of engineering judgement to recognize how production originates. If we substitute the intrinsic form of the first law, $dU=dQ+dW_{\text{irr}}^i+dW_{\text{rev}}^i$, into the Gibbs equation we obtain

$$dS = \frac{dQ + dW_{\text{irr}}^i}{T} \quad (\text{IIB-21})$$

We have established the fact that irreversible work is positive semidefinite, $dW_{\text{irr}}^i \geq 0$ (Unit IB, Section III). Therefore, eqn. IIB-21 can be expressed in the form

$$dS \geq \frac{dQ}{T} \quad (\text{IIB-22})$$

This expression, called the *Clausius inequality*, indicates a second law limitation imposed upon the system alone. When Clausius inequality is applied to a closed system undergoing an adiabatic process, we see that its entropy can only increase.

$$dS|_{\text{ad}} \geq 0 \quad (\text{IIB-23})$$

Though this expression has the same form as eqn. IIB-4, it is not restricted to isolated systems; work interactions are allowed.

Eqn. IIB-23 is not a complete statement of the second law. It only describes the second law consequences for an adiabatic process. Each of our second law statements, eqns. IIB-4, 5, 22, and 23 expresses a tendency for the entropy to increase. The student must remember that it is the entropy of the universe, not that of an interacting system that cannot decrease.

¹⁶The Gibbs equation also provides a general link between measurable and unmeasurable properties. It is the basis for the development of the Maxwell Relations, Unit IVD.

Ans. 3. Initially the entire crystal was in equilibrium. The "pumping" process added energy to the lasing states causing a nonequilibrium condition in the crystal. As discussed above this requires irreversible work (or heat). Further evidence that this is the case is provided by the fact that the energy levels of the lasing states are not altered.

Exercise 6. The following facts are known about five separate processes that occur to a closed system. Specify, as best you can, the entropy change that occurs to the *system*. Answer increases, decreases, or can't tell. Process (a) $Q = 2$ J; (b) $Q = -2$ J; (c) $Q = -2$ J and $W = 3$ J; (d) $Q = -2$ J and $W_{irr}^i = 1$ J; (e) $Q = -2$ J and $W_{irr}^i = 3$ J.

Exercise 7. A closed system undergoes a process with an entropy change of -2 J/K. What conclusions can be drawn about (a) the entropy change of the surroundings? (b) the direction of heat flow?

Exercise 8. A system is made to undergo, in turn, two processes between the same initial and final equilibrium states. One of the two processes is reversible, the other irreversible. Which process will result in a greater entropy change of: (a) the system? (b) the universe? What is the entropy change of the universe for the reversible process?

The production that occurs within a system can be explicitly determined by carefully examining the terms of eqn. IIIB-21. We define them as the thermal and mechanical entropy change, respectively.

$$dS = \frac{dQ + dW_{irr}^i}{T_{eq}} = dS_{th} + dS_m \quad (\text{IIIB-21})$$

where

$$dS_{th} \equiv \frac{dQ}{T_{eq}} \quad dS_m \equiv \frac{dW_{irr}^i}{T_{eq}} \quad (\text{IIIB-24a,b})$$

We have explicitly identified the temperature as its equilibrium value, T_{eq} . This specificity is necessary since we will deal with systems that are not in thermal equilibrium, i.e., those with nonuniform temperature. The equilibrium temperature corresponding to a nonequilibrium state is the temperature that would be achieved were the system isolated and allowed to relax to equilibrium.

Note to the Student. In the following sections we identify the sources of entropy production. We reinforce these principles with numerical illustrations requiring separate consideration of the magnitude of force and temperature differentials within the system. Use of these calculation procedures is not an objective of the unit. (Calculation of the net effect of thermal and mechanical irreversibility are objectives of Units IVA and IVC.) Study these problems insofar as they help you to recognize the sources of mechanical and thermal irreversibility.

A. Mechanical Entropy Production

Since irreversible work is positive semidefinite, $dW_{irr}^i \geq 0$, the mechanical entropy term is pure production.

$$dS_m = \frac{dW_{irr}^i}{T_{eq}} \geq 0 \quad (\text{IIIB-24b})$$

Mechanical irreversibility can originate in any intrinsic work mode. As specific illustrations, we cite the three mechanical irreversibilities considered in Section III of Unit IB.

The Sticky Spring. We use the sticky spring to model real spring behavior by accounting for a friction component $F_s = K(X_s - X_{s,0}) \pm \delta F_s$. The irreversible work is found to be $dW_{irr}^i = |\delta F_s dX_s|$. Thus the mechanical production is

$$dS_m = \frac{|\delta F_s dX_s|}{T_{eq}} \geq 0$$

Viscous Fluid Flow. The motion of a viscous fluid during compression work produces pressure drop and irreversible work

$$dS_m = \frac{|(p_B - p_{eq}) dV|}{T_{eq}} \geq 0$$

Electric Resistance. Entropy is generated at a rate that is proportional to the current squared.

$$\frac{dS_m}{dt} = \frac{I^2 R}{T_{eq}} \geq 0$$

The sources of mechanical entropy production arise due to friction within a specific intrinsic work mode. The following example shows, more specifically, the effect of production on a practical system.

Example 6. A large ship requires a propulsive force of 8000 lb_f to realize a speed of 20 knots (approx. 23 mph). This energy is dissipated into the ocean, primarily in wave making (but with some surface friction) as the ship moves. Calculate the rate of increase of the entropy of the ocean as a result of the ship's passing. (The local ocean temperature is 520 R.)

For purposes of analysis, choose the ocean as the system. Using the intrinsic form of the first law on a rate basis, we have

$$\frac{dU}{dt} = \frac{dQ}{dt} + \frac{dW_{irr}^i}{dt} + \frac{dW_{rev}^i}{dt}$$

The water is a simple compressible substance and its volume does not change; so the intrinsic reversible work is zero. The transfer mechanism of the propulsive energy from the ship to the water is force acting through a resistance; hence, it is irreversible work, not heat. We have

$$\frac{dU}{dt} = \frac{dW_{irr}^i}{dt} = 8000 \text{ lb}_f \cdot 23 \text{ mil/hr} \cdot 5280 \text{ ft/mil} = 9.7 \cdot 10^8 \text{ ft lb}_f/\text{hr}$$

The rate of increase of the entropy of the ocean (and the universe, since the ship is in steady state $(ds/dt)_{\text{ship}} = 0$), can be determined from eqn. IIIS-7.

Ans. 4. (a) $ds = \frac{du - \mu_0 v \bar{H} \cdot d\bar{M}}{T}$	(b) $ds = \frac{du - v \bar{E} \cdot d\bar{P}}{T}$	(c) $ds = \frac{du + pdv - \sigma da}{T}$
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Ans. 5. The Gibbs equation is applicable between equilibrium states. The entropy of an isolated system increases until it reaches equilibrium. After that $dS|_{\text{isol}} = 0$. There is no inconsistency in the statements.

$$\frac{dS}{dt} = \frac{1}{T_{eq}} \left(\frac{dQ}{dt} + \frac{dW_{irr}^i}{dt} \right) = \frac{dS}{dt} \Big|_m = \frac{9.7 \cdot 10^8 \text{ ft lb}_f/\text{hr}}{520 \text{ R} \cdot 778 \text{ ft lb}_f/\text{BTU}} = 2.4 \cdot 10^3 \text{ BTU}/(\text{hr R})$$

The part of the ship's power that was used to overcome hull-water friction resulted in immediate entropy production. That part of the power that went into wave making was initially reversibly converted to kinetic and potential energy in the bow and stern wave. But this energy is subsequently dissipated as the wave action is damped.

B. Thermal Entropy Production

Since heat can enter or leave a system, dS_{th} , unlike dS_m , is not pure production. Indeed thermal entropy change contains both a reversible and irreversible component. Since our purpose is to identify production sources, it is desirable that we separate the two components. We begin by observing that heat interactions require a differential between the boundary, T_B , and system, T_{eq} , temperatures. We define

$$\delta T_{neq} \equiv T_B - T_{eq} \tag{IIIB-25}$$

If this definition is substituted into eqn. IIIB-22a, we obtain

$$dS_{th} = \frac{dQ}{T_B} + \frac{dQ}{T_{eq}} \frac{\delta T_{neq}}{T_B} \tag{IIIB-26}$$

Exercise 9. Substitute eqn. IIIB-25 into eqn. IIIB-24a to derive eqn. IIIB-26.

Now consider the sign of the second term. If heat is to leave the system, $dQ < 0$, the interior must be hotter than the boundary, $\delta T_{neq} < 0$. The term is positive. Conversely, if heat enters the system both $dQ > 0$ and $\delta T_{neq} > 0$; the term remains positive. This is a positive semidefinite component. It is the thermal entropy production.

$$dS_{th,irr} = \frac{dQ}{T_{eq}} \frac{\delta T_{neq}}{T_B} \geq 0 \tag{IIIB-27}$$

<p><u>Ans. 6.</u> Refer to eqn. IIIB-21, or 22. (a) When Q is positive system entropy must increase. (b) When Q is negative entropy could decrease; it depends on the magnitude of W_{irr}^i. Can't tell. (c) Still can't tell, since W_{irr}^i is still unknown. (d) Q is negative and larger than W_{irr}^i; decreases. (e) Q is negative but less than W_{irr}^i; increases.</p>
<p><u>Ans. 7.</u> (a) $\Delta S_{univ} \geq 0$. So for this process $\Delta S_{surr} \geq 2 \text{ J/K}$. (b) a decrease in entropy in a closed system can only occur due to heat rejection.</p>
<p><u>Ans. 8.</u> (a) Entropy is a property. The change in all properties between two specified equilibrium states is the same for all paths. (b) The entropy of the universe cannot decrease. For the reversible process $\Delta S_{univ} = 0$. For the irreversible process $\Delta S_{univ} > 0$.</p>

Thus necessary and sufficient conditions for a reversible heat effect are that it occur without a temperature differential.

The first term in eqn. IIIB-26 changes its sign but not its magnitude, if the direction of heat flow is reversed. It can be thought of as a reversible transfer of entropy between the system and its surroundings.

$$dS_{th,rev} = \frac{dQ}{T_B} \quad (\text{IIIB-28})$$

When this expression is solved for dQ an analogy with intrinsic work is recognized

$$dQ = T_B dS_{th,rev} \quad dW_k^i = \bar{F}_{B,k} \cdot d\bar{X}_k$$

In this analogy boundary temperature, T_B , plays the role of boundary force, $\bar{F}_{B,k}$, and the reversible thermal entropy change, $dS_{th,rev}$, plays the role of displacement, $d\bar{X}_k$.¹⁷ The analogy can be extended to recognize the reversible and irreversible components of a heat interaction. This is accomplished by substituting eqn. IIIB-25 for the boundary temperature.

$$\begin{aligned} dQ &= T_{eq} dS_{th,rev} + \delta T_{neq} dS_{th,rev} \\ dQ_{rev} &= T_{eq} dS_{th,rev} \quad dQ_{irr} = \delta T_{neq} dS_{th,rev} \end{aligned} \quad (\text{IIIB-29a,b})$$

If this analogy is to be complete we require that $dQ_{irr} \geq 0$. We leave this verification to the following exercise.

Exercise 10. Verify that dQ_{irr} is positive semidefinite. Use a physical argument based on the relationship between the signs of δT_{neq} and $dS_{th,rev}$.

Discussion of the analogy is continued by examination of the relationship between thermal entropy production and irreversible heat.

Example 7. Show that thermal production is analogous to mechanical production by demonstrating that $dS_{th,irr} = dQ_{irr}/T_{eq}$ just as $dS_m = dW_{irr}/T_{eq}$.

The proof can be completed with eqn. IIIB-27 by substitution of $dS_{th,irr} = (dQ_{irr} \delta T_{neq}) / (T_B T_{eq})$ and the introduction of eqn. IIIB-28, $dS_{th,irr} = dS_{th,rev} (\delta T_{neq} / T_{eq})$. Finally the substitution of eqn. IIIB-29b gives

$$dS_{th,irr} = \frac{dQ_{irr}}{T_{eq}}$$

We have now codified the mechanisms of entropy change within a closed system into three components

¹⁷There is an apparent discrepancy in this analogy in that $dS_{rev,th}$ is only part of the entropy change, whereas $d\bar{X}$ is all of the mechanical displacement. The rationale is that only that part of the entropy that is conserved can be considered to cross the boundary. All of the displacement is conserved.

$$dS = dS_{th,rev} + dS_{th,irr} + dS_m = \frac{dQ}{T_B} + \frac{dQ}{T_{eq}} \frac{\delta T_{neq}}{T_B} + \frac{dw_{irr}^i}{T_{eq}} \quad (IIIB-30)$$

Only the irreversible terms contribute to production. The reversible term has no effect on the entropy of the universe.

Example 8. Show that $dS_{th,rev}$ does not contribute to the increase of the entropy of the universe.

To demonstrate this result we apply eqn. IIIB-30 to both the system and the surroundings and substitute into the second law, eqn. IIIB-5.

$$dS_{univ} = dS_{sys} + dS_{surr} = \left(\frac{dQ}{T_B} + \frac{dQ}{T_{eq}} \frac{\delta T_{neq}}{T_B} + \frac{dw_{irr}^i}{T_{eq}} \right)_{sys} + \left(\frac{dQ}{T_B} + \frac{dQ}{T_{eq}} \frac{\delta T_{neq}}{T_B} + \frac{dw_{irr}^i}{T_{eq}} \right)_{surr} \geq 0$$

Heat that enters the system leaves the surroundings, $dQ_{sys} = -dQ_{surr}$, and by definition, the boundary temperatures are the same in both terms, $T_{B,sys} = T_{B,surr}$. We see that

$$dS_{th,rev} \Big|_{sys} + dS_{th,rev} \Big|_{surr} = \frac{dQ}{T_B} \Big|_{sys} + \frac{dQ}{T_B} \Big|_{surr} = 0$$

and

$$dS_{univ} = (dS_{th,irr} + dS_m)_{sys} + (dS_{th,irr} + dS_m)_{surr}$$

$$dS_{univ} = \left(\frac{dQ}{T_{eq}} \frac{\delta T_{neq}}{T_B} + \frac{dw_{irr}^i}{T_{eq}} \right)_{sys} + \left(\frac{dQ}{T_{eq}} \frac{\delta T_{neq}}{T_B} + \frac{dw_{irr}^i}{T_{eq}} \right)_{surr}$$

The preceding example demonstrates that production originates in both the system and the surroundings due to thermal and mechanical irreversibility. If there is no production within the system the process is said to be "internally reversible." A reversible process is one in which there is no production in either the system or the surroundings, that is, $\Delta S_{univ} = 0$.

Like mechanical irreversibility, thermal irreversibility deteriorates performance. We have suggested a thermodynamic design principle—*an optimum design is one that accomplishes given objectives and results in the minimum increase (or rate of increase) in the entropy of the universe.* The validity of this premise, as it relates to thermal irreversibilities, will be expanded by the consideration of thermal engines, Unit IVB, and heat exchangers, Unit IVC.

Example 9. A styrofoam ice chest has an inside and outside wall temperature of 32°F and 80°F, respectively. The insulatory value and thickness of wall are such that heat enters the cooler at a rate of 10 BTU/hr per square foot of surface area. Taking a square foot of the wall as the system, determine its rate of reversible and irreversible (continued)

Ans. 9.
$$dS_{th} = \frac{dQ}{T_{eq}} = \frac{dQ}{T_B} \frac{T_B}{T_{eq}} = \frac{dQ}{T_{eq} T_B} (T_{eq} + \delta T_{neq})$$

(Example 9, continued) entropy change. What is the net rate of entropy change of the styrofoam? What is the rate of increase of the entropy of the universe as a result of this process?

The styrofoam acquires reversible entropy at its outside boundary and loses it at its inside boundary. The net result is

$$\frac{1}{A} \frac{dS}{dt} \Big|_{th,rev} = \frac{\dot{Q}}{A} \left(\frac{1}{T_o} - \frac{1}{T_i} \right) = 10 \text{ BTU}/(\text{hr ft}^2) \cdot \left(\frac{1}{540 \text{ R}} - \frac{1}{492 \text{ R}} \right) = -0.0018 \text{ BTU}/(\text{hr ft}^2\text{R})$$

Notice that this term represents a decreasing system entropy. To find the thermal production, we must determine T_{eq} . In this system we expect a linear temperature distribution. Thus

$$T_{eq} = \frac{T_o + T_i}{2} = \frac{(32 + 80)^\circ\text{F}}{2} = 56^\circ\text{F} = 516 \text{ R}$$

Heat crosses the boundary on both surfaces so there are also two components to the thermal entropy production.

$$\begin{aligned} \frac{1}{A} \frac{dS}{dt} \Big|_{th,irr} &= \frac{\dot{Q}_o}{A} \frac{(T_o - T_{eq})}{T_o T_{eq}} + \frac{\dot{Q}_i}{A} \frac{(T_i - T_{eq})}{T_i T_{eq}} \\ &= \frac{10 \text{ BTU}/(\text{hr ft}^2) \cdot (24 \text{ R})}{540 \text{ R} \cdot 516 \text{ R}} + \frac{-10 \text{ BTU}/(\text{hr ft}^2) \cdot (-24 \text{ R})}{492 \text{ R} \cdot 516 \text{ R}} = 0.0018 \text{ BTU}/(\text{hr ft}^2\text{R}) \end{aligned}$$

Notice the cancellation of the reversible and irreversible components

$$\frac{1}{A} \frac{dS}{dt} \Big|_{th} = \frac{1}{A} \frac{dS}{dt} \Big|_{th,rev} + \frac{1}{A} \frac{dS}{dt} \Big|_{th,irr} = 0$$

The system is in steady state. All properties are time invariant. The production occurs in the surroundings. (We assume they are uniform in temperature and are thermally reversible.)

$$\frac{1}{A} \frac{dS}{dt} \Big|_{surr} = \frac{1}{A} \frac{dS}{dt} \Big|_{o,surr} + \frac{1}{A} \frac{dS}{dt} \Big|_{i,surr} = \frac{\dot{Q}}{A} \left(-\frac{1}{T_o} + \frac{1}{T_i} \right) = 0.0018 \text{ BTU}/(\text{hr ft}^2\text{R})$$

and the net production for this process is

$$\frac{1}{A} \frac{dS}{dt} \Big|_{univ} = \frac{1}{A} \left(\frac{dS}{dt} \Big|_{syst} + \frac{dS}{dt} \Big|_{surr} \right) = 0.0018 \text{ BTU}/(\text{hr ft}^2\text{R})$$

The entropy of the universe is growing—the process is irreversible. If the production could be reduced would the design be better? Yes, thicker or better insulation would reduce \dot{Q}/A and, therefore, reduce production. A final redesign decision would of course include consideration of cost and profit.

The preceding example illustrates for a system dependent primarily on heat effects what we saw earlier for work dominated systems, that minimization of production is a useful design concept. The examples that we have used to illustrate this principle have been too obvious to illustrate its full significance. But when two quite different design

Ans. 10. For heat out, $\delta T_{neq} < 0$ (see eqn. IIIB-25), and $dS_{th,rev} < 0$ (see eqn. IIIB-29b). Thus $dO_{irr} > 0$. For heat in both δT_{neq} and $dS_{th,rev}$ are positive.

concepts or two different design modifications are under consideration, it may not be obvious which is better. In these cases a determination of production or the reduction in production for both alternatives can be an important criterion.

Exercise 11. A transmission cable in steady state carries a full load current of $3 \cdot 10^3$ A and has a resistance per length of $1.2 \cdot 10^3 \Omega/\text{m}$. The joulean heating within the wire results in a mean temperature (an equilibrium value) that is 1.5°C above the surface temperature, 50°C . Calculate the magnitude of the thermally reversible and irreversible, as well as the irreversible mechanical contribution to the rate of entropy change of the wire (in W/m K). What is the rate of change of the entropy of the wire? What is the rate of increase of the entropy of the universe if the surroundings are reversible?

The problems of this section have specified a temperature distribution to enable the determination of thermal entropy production. The procedures by which such temperature distributions are deduced are treated in heat transfer courses. Thus the detailed consideration of thermal and mechanical production within the system by an explicit determination of δT_{neq} or $\delta \bar{F}_{\text{neq}}$ is beyond our scope in this course.¹⁸ In subsequent units we will determine only the net production, ΔS_{univ} . The student should continue to recognize the contributions to such irreversibilities as to their thermal or mechanical origin.

SUMMARY QUESTIONS

The following questions are designed to aid you to verify your understanding of the important concepts of this unit before beginning application of the second law.

1. What condition does the second law impose on the entropy of the universe?
2. State a sufficient condition to assure that the entropy of a closed system increases.
3. What are the necessary and sufficient conditions to assure that the entropy of a closed system will decrease during a differential process?
4. What restrictions are placed on the application of the Gibbs equation, $ds = (du + p dv)/T$?
5. What property is constant during an adiabatic reversible process?
6. What is the difference between an internally reversible process and a reversible process?
7. State a sufficient condition to assure that thermal entropy production is not present within a system.
8. To combat the "energy crisis" we are bombarded with the slogan "conserve energy." From a thermodynamicist's perspective this request is vacuous! What is wrong with it and how would you rephrase it?

¹⁸The determination of mechanical irreversibility is a topic of such courses as fluid and solid mechanics, electric circuits and electromagnetic fields.

ANSWERS TO SUMMARY QUESTIONS

1. The entropy of the universe cannot decrease, $\Delta S_{\text{univ}} \geq 0$.
2. From Clausius inequality, $dS \geq dQ/T$, we conclude that if heat enters a closed system its entropy must increase.
3. From the preceding we see that a necessary condition is heat rejection, $dQ < 0$. Sufficiency is added when $|dQ| > |dW_{\text{irr}}^i|$. (See eqn. IIIB-21.)
4. The Gibbs equation is a relationship between properties. It is applicable to any process, reversible or irreversible, that begins and ends in an equilibrium state. The form shown is restricted to simple compressible media but the equation can be reformulated for any substance.
5. The entropy.
6. An internally reversible process precludes entropy production within the system. (Production can occur in the surroundings, often at the interface between the system and the surroundings.) In a reversible process there is no production in either the system or the surroundings, $\Delta S_{\text{univ}} = 0$.
7. The temperature in the system is uniform.
8. The first law demands that energy be conserved. "It can't be destroyed." "Minimize entropy production" is a suitable new phrase, but we have a serious communication gap. Perhaps conserve "available energy" (see Unit IVA) would be more meaningful to the public at large.

Ans. 11. The cable is steady state. $\frac{dQ}{dt} = \frac{dQ}{dt} + \frac{dW_{\text{irr}}^i}{dt} + \frac{dW_{\text{rev}}}{dt}$

$$\therefore -\frac{dQ}{dt} = \frac{dW_{\text{irr}}^i}{dt} = I^2 R = 1.08 \cdot 10^4 \text{ W/m} \quad \frac{dS_{\text{m}}}{dt} = \frac{1}{T_{\text{eq}}} \frac{dW_{\text{irr}}^i}{dt} = 33.28 \text{ W/(m K)}$$

$$\frac{dS_{\text{rev,th}}}{dt} = \frac{1}{T_{\text{B}}} \frac{dQ}{dt} = -33.43 \text{ W/(m K)} \quad \frac{dS_{\text{irr,th}}}{dt} = \frac{\delta T_{\text{neq}}}{T_{\text{eq}} T_{\text{B}}} \frac{dQ}{dt} = 0.15 \text{ W/(m K)}$$

$$\frac{dS}{dt} = \frac{dS_{\text{rev,th}}}{dt} + \frac{dS_{\text{irr,th}}}{dt} + \frac{dS_{\text{m}}}{dt} = 0, \text{ the wire is in steady state.}$$

$$\frac{dS_{\text{univ}}}{dt} = \frac{dS_{\text{sys}}}{dt} + \frac{dS_{\text{surr}}}{dt} = -\frac{1}{T_{\text{B}}} \frac{dQ_{\text{sys}}}{dt} = 33.43 \text{ W/(m K)}$$

APPENDIX IIIB-A
DIFFERENTIATION OF S_i^{MB}

The entropy of a macrostate is defined by eqn. IIIB-1. It is specialized for Boltzons by substitution of the expression for the number of microstates in a Boltzon macrostate, eqn. IIIA-7a.

$$S_i^{MR} = k \ln W_i^{MB}; \quad \text{where } W_i^{MB} = N! \prod_j \frac{g_j^{n_{j,i}}}{n_{j,i}!} \quad (\text{IIIB-1, IIIA-7a})$$

To derive the equilibrium distribution function, $n_{j,mp}^{MB}$, it is necessary to differentiate S_i^{MB} with respect to $n_{j,i}$ and simplify.

$$d(S_i^{MB}) = kd \left(\ln W_i^{MB} \right) = kd \left[\ln \left(N! \prod_j \frac{g_j^{n_{j,i}}}{n_{j,i}!} \right) \right]$$

Differentiation is simplified by expressing the logarithm of a product as the sum of the logarithms, viz.

$$\ln \left(\prod_{j=1} x_j \right) = \ln(x_1 \cdot x_2 \cdot x_3 \dots) = \ln x_1 + \ln x_2 + \ln x_3 + \dots = \sum_j \ln x_j$$

Applied to $\ln W_i^{MB}$, this yields

$$\ln \left(N! \prod_j \frac{g_j^{n_{j,i}}}{n_{j,i}!} \right) = \ln(N!) + \sum_j [n_{j,i} \ln g_j - \ln(n_{j,i}!)]$$

This result can be further simplified by representing the factorials using *Stirling's approximation*

$$x! \approx (2\pi x)^{\frac{1}{2}} x^x e^{-x} \quad (\text{IIIB-A1})$$

Stirling's formula is accurate for arguments $x \geq 10$ (see Table IIIB-A1). But we need the logarithm of the factorial. The logarithm of eqn. IIIB-A1, viz., $\ln(x!) \approx [\ln(2\pi x)/2 + x \ln x - x]$ provides the required result. But the first of these terms is small in comparison to the last two and can be omitted when $x \geq 10^2$.

$$\ln(x!) \approx x \ln x - x \quad (\text{IIIB-A2})$$

The accuracy of this approximation is illustrated in Table IIIB-A1.

TABLE IIIB-A1: THE ACCURACY OF STIRLING'S APPROXIMATION, eqns. IIIB-A1 and A2

x	x!	$\frac{(x! - SA)}{x!} \%$	$\ln(x!)$	$\frac{ \ln(x!) - \ln SA }{\ln(x!)}$
10^1	$3.628 \cdot 10^9$	0.76	$1.510 \cdot 10^4$	13.8
10^2	$9.333 \cdot 10^{160}$	0.082	$3.637 \cdot 10^5$	0.887
10^3	$4.024 \cdot 10^{2570}$	0.0083	$5.914 \cdot 10^{16}$	0.105

Substituting eqn. IIIB-A2 into $\ln W_i^{MB}$, we obtain¹⁹

$$\ln W_i^{MB} = N \ln N - N + \sum_j (n_{j,i} \ln g_j - n_{j,i} \ln n_{j,i} + n_{j,i}); \text{ then since } N = \sum_j n_{j,i}$$

$$S_i^{MB} = kN \ln N + k \sum_j [n_{j,i} \ln g_j - n_{j,i} \ln n_{j,i}] \quad (\text{IIIB-A3})$$

The differential we require is obtained (N and g_j are constant) so,

$$d(S_i^{MB}) = kd(\ln W_i^{MB}) = \sum_j \left(\ln g_j - \frac{n_{j,i}}{n_{j,i}} - \ln n_{j,i} \right) \delta n_{j,i}$$

and using the fact that $\sum_j \delta n_{j,i} = 0$, we have

$$d(S_i^{MB}) = k \sum_j n_{j,i} \frac{g_j}{n_{j,i}} \delta n_{j,i} \quad (\text{IIIB-A4})$$

APPENDIX IIIB-B

EQUILIBRIUM CHARACTERISTICS OF FERMIONS AND BOSONS

The text of the Unit uses systems of Boltzons as its illustration in the development of equilibrium characteristics in microscopic terms. This appendix presents similar developments for Fermions and Bosons.

I. THE DISTRIBUTION FUNCTION FOR FERMIONS AND BOSONS

In this section we develop the distribution function for a System of Fermions and set up an exercise to determine the distribution function for Bosons. The distribution function for any system of independent particles is determined by solving eqn. IIIB-7.

$$d\left(\frac{S}{K} - \beta U - \alpha N\right) = d(\ln W_i) - \beta \sum_j \epsilon_j(V) \delta n_{j,i} - \alpha \sum_j \delta n_{j,i} = 0 \quad (\text{IIIB-7})$$

The variation in the solution stems from the substitution of W_i for the different statistics described by eqns. IIIA-7. For Bosons and Fermions these are

$$W_i^{BE} = \prod_j \frac{(g_j + n_{j,i} - 1)!}{(g_j - 1)! n_{j,i}!}; \quad W_i^{FD} = \prod_j \frac{g_j!}{(g_j - n_{j,i})! n_{j,i}!} \quad (\text{IIIA-7b,c})$$

¹⁹The use of eqn. IIIB-A2 for $\ln(n_{j,i}!)$ does not imply that no single $n_{j,i}$ is less than 10^2 ; but rather that the sum over j remains accurate since many $n_{j,i}$ are much greater than 10^2 .

Example B1. Substitute eqn. IIIA-7c into eqn. IIIB-1 and simplify using Stirling's approximation for the logarithm of a factorial (eqn. IIIB-A2) to develop S_i^{FD} as a sum of two terms in $n_{j,i}$ and g_j .

The logarithm of eqn. IIIA-7c can be expressed as a sum by using the rule for the logarithm of a product (see Appendix IIIB-A).

$$\ln W_i^{FD} = \sum_j [\ln (g_j!) - \ln [(g_j - n_{j,i})!] - \ln (n_{j,i}!)]$$

Then when $\ln x! = x \ln x - x$ (eqn. IIIB-A2) is used to approximate the logarithms, we obtain

$$\ln W_i^{FD} = \sum_j [g_j \ln g_j - g_j - (g_j - n_{j,i}) \ln (g_j - n_{j,i}) + (g_j - n_{j,i}) - n_{j,i} \ln n_{j,i} + n_{j,i}]$$

Cancelling and collecting terms we obtain the entropy, eqn. IIIB-B1 shown below.

The expression for the entropy of a Fermion macrostate was simplified in the preceding example. It is

$$S_i^{FD} = k \ln (W_i^{FD}) = k \sum_j \left[g_j \ln \left(\frac{g_j}{g_j - n_{j,i}} \right) + n_{j,i} \ln \left(\frac{g_j - n_{j,i}}{n_{j,i}} \right) \right] \quad (\text{IIIB-B1})$$

In the following example this expression is differentiated to derive the distribution function for a Fermi-Dirac system in equilibrium.

Example B2. Differentiate eqn. IIIB-B1 (at fixed N and V). Then use eqn. IIIB-7 to obtain the most probable distribution, $n_{j,mp}^{FD}$, in terms of α and β .

It is somewhat easier to differentiate the logarithms when they are written separately, see the last equation in Exmp. B1. Its differential is²⁰

$$d \left(\frac{S_i^{FD}}{k} \right) = d (\ln W_i^{FD}) = \sum_j \left[+ \ln (g_j - n_{j,i}) - \ln (n_{j,i}) + \frac{(g_j - n_{j,i})}{(g_j - n_{j,i})} - \frac{n_{j,i}}{n_{j,i}} \right] \delta n_{j,i} = \sum_j \left[\ln \left(\frac{g_j - n_{j,i}}{n_{j,i}} \right) \right] \delta n_{j,i}$$

Then substituting into eqn. IIIB-7, we obtain

$$\sum_j \left[\ln \left(\frac{g_j - n_{j,i}}{n_{j,i}} \right) - \alpha - \beta \epsilon_j(V) \right] \delta n_{j,i} = 0$$

But since $\delta n_{j,i}$ are linearly independent, each coefficient separately satisfies

$$\ln \left(\frac{g_{j,mp}}{n_{j,mp}} \right) = \alpha + \beta \epsilon_j(V)$$

And taking the antilogarithm we obtain eqn. IIIB-B2, see below.

The equilibrium distribution for Fermions is

$$n_{j,mp}^{FD} = \frac{g_j}{e^{\alpha + \beta \epsilon_j(V)} + 1} \quad (\text{IIIB-B2})$$

²⁰ g_j is a constant.

The interested student can repeat the same steps for Bosons, Exers. IIIB-B1 and B2, below. In this case the appropriate expression for W_i is eqn. IIIB-7b. When this expression is substituted into eqn. IIIB-1 and simplified we obtain

$$S_i^{BE} = k \ln W_i^{BE} = k \sum_j \left[g_j \ln \left(\frac{g_j + n_{j,i}}{g_j} \right) + n_{j,i} \ln \left(\frac{g_j + n_{j,i}}{n_{j,i}} \right) \right] \quad (\text{IIIB-B3})$$

Then one differentiates this result and solves eqn. IIIB-7 to obtain

$$n_{j,mp}^{BE} = \frac{g_j}{e^{\alpha + \beta \epsilon_j(V)} - 1} \quad (\text{IIIB-B4})$$

Exercise B1. Take the logarithm of eqn. IIIA-7b and use Stirling's approximation for the logarithm of a factorial, eqn. IIIB-A2 as well as the assumption that $g_j \gg 1$ to derive eqn. IIIB-B3.

Exercise B2. Differentiate eqn. IIIB-B3 at fixed N and V . Then use Lagrange multipliers in the form of eqn. IIIB-7 to derive eqn. IIIB-B4.

The parameter β can be identified for both Fermions and Bosons using the same procedure as employed in the text for Boltzons. It requires the differentiation of the equilibrium entropy with respect to the energy holding the volume and number of particles constant, i.e., determine $(\partial S_{eq} / \partial U)_{N,V}$. We illustrate below for Fermions.

Example B3. Obtain a simplified expression for S_{eq}^{FD} by substitution of eqn. IIIB-B2 and elimination of $n_{j,mp}^{FD}$ from eqn. IIIB-B1.

We begin by writing eqn. IIIB-B1 in a more compact form.

$$S_{eq}^{FD} = k \ln W_{mp}^{FD} = k \sum_j g_j \ln \left(\frac{g_j}{g_j - n_{j,mp}^{FD}} \right) + k \sum_j n_{j,mp}^{FD} \ln \left(\frac{g_j}{n_{j,mp}^{FD}} - 1 \right)$$

Then arranging eqn. IIIB-B2 in forms suitable for substitution

$$\ln \left(\frac{g_j}{n_{j,mp}^{FD}} - 1 \right) = \alpha + \beta \epsilon_j(V) \quad \text{and} \quad \frac{g_j}{g_j - n_{j,mp}^{FD}} = \frac{1}{1 - \frac{1}{\exp[\alpha + \beta \epsilon_j(V)] + 1}} = 1 + \exp[-\alpha - \beta \epsilon_j(V)]$$

This gives

$$S_{eq}^{FD} = k \sum_j n_{j,mp}^{FD} [\alpha + \beta \epsilon_j(V)] + k \sum_j g_j \ln \{ 1 + \exp[-\alpha - \beta \epsilon_j(V)] \}$$

Since $N = \sum_j n_{j,mp}^{FD}$ and $U = \sum_j n_{j,mp}^{FD} \epsilon_j(V)$, we obtain the relationship

²¹Recall that g_j is a constant.

$$S_{eq}^{FD} = k\beta U + Nk\alpha + k \sum_j g_j \ln \left[1 + e^{-\alpha - \beta \epsilon_j(V)} \right]$$

Example B4. Use the form of S_{eq}^{FD} developed in Exmp. B1 to show that $(\partial S_{eq}^{FD} / \partial U)_{N,V} = k\beta$.

The terms in the partial derivative are²¹

$$\begin{aligned} \left(\frac{\partial S_{eq}^{FD}}{\partial U} \right)_{N,V} &= k\beta + kU \left(\frac{\partial \beta}{\partial U} \right)_{N,V} + Nk \left(\frac{\partial \alpha}{\partial U} \right)_{N,V} + \sum_j \frac{-\epsilon_j g_j e^{-\alpha - \beta \epsilon_j(V)}}{1 + e^{-\alpha - \beta \epsilon_j(V)}} \cdot \left(\frac{\partial \beta}{\partial U} \right)_{N,V} \\ &\quad + k \sum_j \frac{-g_j e^{-\alpha - \beta \epsilon_j(V)}}{1 + e^{-\alpha - \beta \epsilon_j(V)}} \cdot \left(\frac{\partial \alpha}{\partial U} \right)_{N,V} \end{aligned}$$

Then recognize that

$$n_{j,mp}^{FD} = \frac{g_j}{[e^{\alpha + \beta \epsilon_j(V)} + 1]} = \frac{g_j e^{-\alpha - \beta \epsilon_j(V)}}{[1 + e^{-\alpha - \beta \epsilon_j(V)}]}$$

And substitute to obtain

$$\left(\frac{\partial S_{eq}^{FD}}{\partial U} \right)_{N,V} = k\beta + k \left(\frac{\partial \beta}{\partial U} \right)_{N,V} \left[U - \sum_j n_{j,mp}^{FD} \epsilon_j(V) \right] + k \left(\frac{\partial \alpha}{\partial U} \right)_{N,V} \left(N - \sum_j n_{j,mp}^{FD} \right) = k\beta$$

A review of the identification of β in Section II will reveal that $(\partial S_{eq} / \partial U)_{N,V} = k\beta$ is sufficient to obtain the result. Thus $\beta = 1/kT$ is valid for Fermions. The following exercises obtain analogous results for Bosons. We thus obtain the equilibrium distribution functions and entropies of Fermions and Bosons as

$$n_{j,mp}^{FD} = \frac{g_j}{e^{\alpha + \beta \epsilon_j(V)/kT} + 1} \qquad n_j^{BE} = \frac{g_j}{e^{\alpha + \beta \epsilon_j(V)/kT} - 1} \qquad \text{(IIIB-B2, -B4)}$$

$$S_{eq}^{FD} = \frac{U}{T} + Nk\alpha + k \sum_j g_j \ln \left[1 + e^{-\alpha - \beta \epsilon_j(V)/kT} \right] \qquad \text{(IIIB-5)}$$

$$S_{eq}^{BE} = \frac{U}{T} + Nk\alpha - k \sum_j g_j \ln \left[1 - e^{-\alpha - \beta \epsilon_j(V)/kT} \right] \qquad \text{(IIIB-6)}$$

Ans. B1. The logarithm of eqn. IIIA-7b by the product rule is

$$\ln W_i^{BE} = \sum_j \{ \ln [(g_j + n_{j,i} - 1)!] - \ln [(g_j - 1)!] - \ln (n_{j,i}!) \}$$

Then, since $g_j \gg 1$ and by $\ln x! = x \ln x - x$, we have

$$\ln W_i^{BE} = \sum_j [(g_j + n_{j,i}) \ln (g_j + n_{j,i}) - (g_j + n_{j,i}) - g_j \ln g_j + g_j - n_{j,i} \ln (n_{j,i}) + n_{j,i}]$$

Collecting terms with common coefficients, we have

$$\ln W_i^{BE} = \sum_j g_j \ln \left(\frac{g_j + n_{j,i}}{g_j} \right) + n_{j,i} \ln \left(\frac{g_j + n_{j,i}}{n_{j,i}} \right)$$

This gives eqn. IIIB-B3 when multiplied by k , i.e., $S_i^{BE} = k \ln W_i^{BE}$.

Exercise B3. Derive S_{eq}^{BE} , eqn. IIIB-6, in terms of β by substituting eqn. IIIB-B4 into eqn. IIIB-B3 and simplifying.

Exercise B4. Partially differentiate eqn. III-6 to show that $(\partial S_{eq}^{BE} / \partial U)_{N,V} = \frac{1}{T} = k\beta$.

II. THE GIBBS EQUATION FOR FERMIONS AND BOSONS

The Gibbs equation was derived in Section III of the text by differentiating the entropy and recognizing the microscopic expression for reversible work, $dW_{rev}^i = \sum_j n_{j,i} d\epsilon_j(V)$. This same procedure can be followed for both Fermions and Bosons. We demonstrate the procedure for Fermions in Exmp. B5 and ask that you complete the same derivation for Bosons, Exer. B5.

Example B5. Differentiate eqn. IIIB-B5 at fixed N and simplify to obtain the Gibbs equation.

The development is very similar to Exmp. B4. We differentiate term by term

$$dS^{FD} \Big|_N = \frac{dU}{T} - \frac{UdT}{T^2} + Nk d\alpha + k \sum_j \left[\frac{g_j}{e^{\alpha + \epsilon_j(V)/kT} + 1} \right] \left(-d\alpha \frac{-1}{kT} \frac{d\epsilon_j(V)dV}{dV} + \frac{\epsilon_j(V)dT}{kT^2} \right)$$

Then recognizing $n_{j,mp}^{FD}$, we have

$$dS^{FD} \Big|_N = \frac{dU}{T} - \left(\frac{U}{T^2} + \frac{k \sum_j n_{j,mp}^{FD} \epsilon_j(V)}{kT^2} \right) dT + \left(Nk - k \sum_j n_{j,mp}^{FD} \right) d\alpha - \frac{1}{T} \sum_j n_{j,mp}^{FD} d\epsilon_j(V)$$

or

Ans. B2. Differentiate the terms of eqn. IIIB-B3, to obtain

$$d \left(\frac{S_i^{BE}}{k} \right) = \sum_j \left[\frac{g_j}{g_j + n_{j,i}} + \ln \left(\frac{g_j + n_{j,i}}{n_{j,i}} \right) + \left(\frac{n_{j,i}}{g_j + n_{j,i}} - \frac{n_{j,i}}{n_{j,i}} \right) \delta n_{j,i} \right] \delta n_{j,i} = \sum_j \ln \left(\frac{g_j + n_{j,i}}{n_{j,i}} \right) \delta n_{j,i}$$

Substitute into eqn. IIIB-7 for

$$\sum_j \ln \left[\left(\frac{g_j + n_{j,i}}{n_{j,i}} \right) - \alpha - \beta \epsilon_j(V) \right] \delta n_{j,i} = 0 \quad \text{or} \quad \ln \left(\frac{g_j + n_{j,i}}{n_{j,i}} \right) = \alpha + \beta \epsilon_j(V)$$

whose antilog is eqn. IIIB-B4

$$dS = \frac{dU - dW_{\text{rev}}^i}{T}$$

Exercise B5. Differentiate eqn. IIIB-B6 at fixed N and simplify to obtain the Gibbs equation. (This development is sufficiently similar to Exmp. B5 and it can be used as a guide and no solution is given.)

Ans. B3. In preparation for substitution we rearrange eqn. III-B4

$$\frac{n_{j,mp}^{BE}}{g_j} = \frac{1}{e^{\alpha + \beta \epsilon_j(V)} - 1}; \quad 1 + \frac{n_{j,mp}^{BE}}{g_j} = \frac{e^{\alpha + \beta \epsilon_j(V)}}{e^{\alpha + \beta \epsilon_j(V)} - 1} = \frac{1}{1 - e^{-\alpha - \beta \epsilon_j(V)}}$$

So

$$\ln \left(\frac{g_j + n_{j,mp}^{BE}}{g_j} \right) = \ln \left[1 - e^{-\alpha - \beta \epsilon_j(V)} \right]$$

Then

$$\frac{g_j}{n_{j,mp}^{BE}} = e^{\alpha + \beta \epsilon_j(V)} - 1 \quad \text{so} \quad \ln \left(\frac{g_j + n_{j,mp}^{BE}}{n_{j,mp}^{BE}} \right) = \alpha + \beta \epsilon_j(V)$$

Since

$$S_{\text{eq}}^{BE} = -k \sum_j g_j \ln \left[1 - e^{-\alpha - \beta \epsilon_j(V)} \right] + k \sum_j n_{j,mp}^{BE} [\alpha + \beta \epsilon_j(V)]$$

This is recognized as eqn. IIIB-B6 with $\beta = 1/kT$ and $\sum_j n_{j,mp}^{BE} = N$, $\sum_j n_{j,mp}^{BE} \epsilon_j(V) = U$.

Ans. B4.

$$\begin{aligned} \left(\frac{\partial S_{\text{eq}}^{BE}}{\partial U} \right)_{N,V} &= \frac{1}{T} - \frac{U}{T^2} \left(\frac{\partial T}{\partial U} \right)_{N,V} + Nk \left(\frac{\partial \alpha}{\partial U} \right)_{N,V} - k \sum_j \frac{g_j e^{-\alpha - \beta \epsilon_j(V)}}{[1 - e^{-\alpha - \beta \epsilon_j(V)/kT}]^2} + \left(\frac{\partial \alpha}{\partial U} \right)_{N,V} - \frac{\epsilon_j(V)}{kT^2} \left(\frac{\partial T}{\partial U} \right)_{N,V} \\ &= \frac{1}{T} - \left(\frac{U}{T^2} - \frac{\sum_j n_{j,mp}^{BE} \epsilon_j(V)}{T^2} \right) \left(\frac{\partial T}{\partial U} \right)_{N,V} + \left(Nk - k \sum_j n_{j,mp}^{BE} \right) \left(\frac{\partial \alpha}{\partial U} \right)_{N,V} \end{aligned}$$