Statistical Thermodynamics

The first law of thermodynamics is written
$dQ = dE + dW$ **……(1)**

where *dE* is the change in internal energy of the system ,*dQ* the heat absorbed by the system from its surroundings and *dW* the work done by the system on its surroundings.

The second law of thermodynamics implies that
$dQ = T\,dS$ **……..(2*)***
where *T* is the thermodynamic temperature, and *dS* the change in entropy of the system.

the work done on the environment is
$dW = p\,dV$ **,,,, where *p* is the pressure, and *dV* the change in volume.**

Ideal Gas Equation of State

Let us commence our discussion of classical thermodynamics by considering the simplest possible macroscopic system, which is an ideal gas. All of the thermodynamic properties of an ideal gas are summed up in its equation of state, which specifies the relationship between its pressure, volume, and temperature. Unfortunately, classical thermodynamics is unable determine this equation of state from first principles. In fact, classical thermodynamics cannot determine anything from first principles. We always need to provide some initial information before classical thermodynamics can generate new results. This initial information may come from statistical physics

that the number of accessible states of a monotonic ideal gas varies like

$$\Omega \propto V^N X(E) \quad \text{……(3)}$$

where *N* is the number of atoms, and $\chi(E)$ depends only on the energy of the gas (and is, therefore, independent of the volume).
Because the energy of an ideal gas is independent of the atomic coordinates (given that there are no interatomic forces in an ideal gas), the integrals over these coordinates just reduced to *N* simultaneous volume integrals, giving the *V N* factor in the previous expression.
Consider the following statistical result

$$X_\alpha = \frac{1}{\beta}\frac{\partial\, In\, \Omega}{\partial X_\alpha} \quad \text{……(4)}$$

Where X_α is the mean force conjugate to the external parameter X_α (i.e., $dW = \sum_\alpha X_\alpha \, dX_\alpha$), and $\beta = 1/(k\,T)$. For an ideal gas, the only external parameter is the volume, and its conjugate force is the pressure (because $dW = p\,dV$). So, we can write

$$X_\alpha = \frac{1}{\beta}\frac{\partial\, In\, \Omega}{\partial V} \qquad \text{.....(5)}$$

It immediately follows from Equation (3) that

$$p = \frac{NkT}{V} \qquad \text{.....(6)}$$

However, $N = \nu\, N_A$, where ν is the number of moles, and N_A is Avagadro's number. Also, $k\ N_A = R$, where R is the molar ideal gas constant.
This allows us to write the equation of state in its standard form

$$\mathbf{P\,V = \nu\,RT} \qquad \text{.....(7)}$$

Incidentally, the fact that $\Omega = \Omega(V, E)$ **in Equation (A), suggests that the macroscopic state of an ideal gas can be uniquely specified by giving the values of two independent parameters (e.g., the energy and the volume, the pressure and the volume, the temperature and the volume, et cetera).**

There is one other conclusion that we can draw from Equation (3). The statistical definition of temperature

$$\frac{1}{kT} = \frac{\partial\ \ln \Omega}{\partial\, E} \qquad \text{.....(8)}$$

It follows that

$$\frac{1}{kT} = \frac{\partial\ \ln X}{\partial\, E} \qquad \text{.....(9)}$$

We can see that, because χ is a function of the energy, but not of the volume, the temperature must also be a function of the energy, but not the volume.
This implies that

$$E = E(T) \qquad \text{.....(10)}$$

In other words, the internal energy of an ideal gas depends only on the temperature of the gas, and is independent of the volume. This is a fairly obvious result, because if there are no intermolecular forces then increasing the volume, which effectively increases the mean separation between molecules, is not going to affect the molecular energies. Hence, the energy of the whole gas is unaffected.

The volume independence of the internal energy can also be derived directly from the ideal gas equation of state. The internal energy of a gas can be considered to be a general function of the temperature and volume, so that

$E = E(T, V)$ ……..(11)

It follows from mathematics that

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \quad \text{……(12)}$$

where the subscript *V* reminds us that the first partial derivative is taken at constant volume, andthe subscript *T* reminds us that the second partial derivative is taken at constant temperature. The first and second laws of thermodynamics imply that for a quasi-static change of parameters,

$$T\,dS = dE + p\,dV \text{ ……(13)}$$

[See Equation (7)].The ideal gas equation of state, ($pV = \nu RT$), can be used to express the pressure in
term of the volume and the temperature in the previous expression:

$$dS = \frac{I}{T} dE + \frac{\nu R}{V} dV \quad \text{……(14)}$$

Using Equation (12), this becomes

$$dS = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \left\{\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V}\right\} dV \quad \text{…….(15)}$$

However, *dS* is the exact differential of a well-defined state function, *S* . This means that we can consider the entropy to be a function of the temperature and volume. Thus, *S* = *S* (*T*, *V*), and mathematics immediately yields

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad \text{……..(16)}$$

The previous expression is valid for all small values of *dT* and *dV*, so a comparison with equation (15) gives

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V \quad \text{…….(17)}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V} \quad \text{…….(18)}$$

A well-known property of partial differentials is the equality of second derivatives, irrespective of the order of differentiation, so

$$\frac{\partial^2 S}{\partial V\,\partial T} = \frac{\partial^2 S}{\partial T\,\partial V} \quad \text{……(19)}$$

This implies that

$$\left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial S}{\partial V}\right)_T \text{.....(20)}$$

The previous expression can be combined with Equations (17) and (18) to give

$$\left(\frac{1}{T}\frac{\partial^2 E}{\partial V\,\partial T}\right) = \left[-\frac{1}{T^2}\left(\frac{\partial E}{\partial V}\right)_T + \frac{1}{T}\,\frac{\partial^2 E}{\partial T\,\partial V}\right] \quad \text{.....(21)}$$

Because second derivatives are equivalent, irrespective of the order of differentiation, the previous relation reduces to

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \quad \text{.....(22)}$$

which implies that the internal energy is independent of the volume for any gas obeying the ideal equation of state. This result was confirmed experimentally by James Joule in the middle of the nineteenth century.

Specific Heat

Suppose that a body absorbs an amount of heat ΔQ, and its temperature consequently rises by ΔT. The usual definition of the heat capacity, or *specific heat,* of the body is

$$C = \frac{\Delta Q}{\Delta T} \qquad \text{……(23)}$$

If the body consists of ν moles of some substance then the *molar specific heat* (i.e., the specific heat of one mole of this substance) is defined

$$C = \frac{1}{\nu}\frac{\Delta Q}{\Delta T} \qquad \text{…….(24)}$$

In writing the previous expressions, we have tacitly assumed that the specific heat of a body is independent of its temperature. In general, this is not true. We can overcome this problem by only allowing the body in question to absorb a very small amount of heat, so that its temperature only rises slightly, and its specific heat remains approximately constant. In the limit that the amount of absorbed heat becomes infinitesimal, we obtain

$$C = \frac{1}{\nu}\frac{\mathrm{d}Q}{\mathrm{d}T} \quad \text{……..(25)}$$

In classical thermodynamics, it is usual to define two molar specific heats. Firstly, the molar specific heat at constant volume, denoted

$$C_V = \frac{1}{\nu}\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_V \text{…….(26)}$$

and, secondly, the molar specific heat at constant pressure, denoted

$$C_P = \frac{1}{\nu}\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_P \text{…….(27)}$$

Consider the molar specific heat at constant volume of an ideal gas. Because $dV = 0$, no work is done by the gas on its surroundings, and the first law of thermodynamics reduces to

$$\mathrm{dQ} = \mathrm{dE} \text{ ……..(28)}$$

It follows from Equation (26) that

$$C_V = \frac{1}{\nu}\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_V \quad \text{……..(29)}$$

Now, for an ideal gas, the internal energy is volume independent. [See Equation (22).] Thus, the previous expression implies that the specific heat at constant volume is also volume independent. Because *E* is a function of *T* only, we can write

$$dE = \left(\frac{dE}{dT}\right)_V dT \qquad \text{……..(30)}$$

The previous two expressions can be combined to give

$$dE = \nu\, C_V dT \qquad \text{……..(31)}$$

for an ideal gas.

Let us now consider the molar specific heat at constant pressure of an ideal gas. In general, if the pressure is kept constant then the volume changes, and so the gas does work on its environment.
According to the first law of thermodynamics,

$$dQ = dE + pdV = \nu\, C_V dT + pdV \qquad \text{……..(32)}$$

where use has been made of Equation (31). The equation of state of an ideal gas, (7), implies that if the volume changes by *dV*, the temperature changes by *dT*, and the pressure remains constant, then

$$p\,dV = \nu\, R\, dT \qquad \text{……(33)}$$

The previous two equations can be combined to give

$$dQ = \nu\, C_V dT + \nu\, R\, dT \qquad \text{……(34)}$$

Now, by definition

$$C_P = \frac{1}{\nu}\left(\frac{dQ}{dT}\right)_P \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (35)$$

so we obtain

$$C_P = C_V + R \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (36)$$

for an ideal gas. Note that, at constant volume, all of the heat absorbed by the gas goes into increasing its internal energy, and, hence, its temperature, whereas, at constant pressure, some of the absorbed heat is used to do work on the environment as the volume increases.

This means that, in the latter case, less heat is available to increase the temperature of the gas. Thus, we expect the specific heat at constant pressure to exceed that at constant volume, as indicated by the previous formula.

The ratio of the two specific heats, C_P/C_V, is conventionally denoted γ. We have

$$\gamma \equiv \frac{C_P}{C_V} = 1 + \frac{R}{C_V} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (37)$$

for an ideal gas. In fact, γ is easy to measure experimentally because the speed of sound in an ideal gas takes the form

$$u = \sqrt{\frac{\gamma p}{\rho}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (38)$$

Where ρ is the mass density.

Helmholtz Free Energy

Suppose that *T* and *V* are the are the two independent parameters that specify the system. Because

$$\mathbf{T\,dS = d(T\,S) - S\,dT} \quad \text{……(39)}$$

we can rewrite Equation (*dE = T dS − p dV*) in the form

$$\mathbf{dF = -S\,dT - p\,dV} \quad \text{…….(40)}$$

where

$$\mathbf{F = E - T\,S} \quad \text{…….(41)}$$

is termed the *Helmholtz free energy*.
Proceeding as before, we write

***F = F(T, V)* …….(42)**
which implies that

$$dF = \left(\frac{\partial \mathrm{F}}{\partial \mathrm{T}}\right)_V dT + \left(\frac{\partial \mathrm{F}}{\partial \mathrm{V}}\right)_T dV \ldots\ldots\ldots\ldots\ldots\ldots\ldots (43)$$

Comparison of Equations (40) and (43) yields

$$\left(\frac{\partial \mathrm{F}}{\partial \mathrm{T}}\right)_V = -S \ldots\ldots\ldots\ldots\ldots\ldots\ldots (44)$$

$$\left(\frac{\partial \mathrm{F}}{\partial \mathrm{V}}\right)_T = -P \ldots\ldots\ldots\ldots\ldots\ldots (45)$$

$$\frac{\partial^2 F}{\partial V\,\partial T} = \frac{\partial^2 F}{\partial T\,\partial V} \ldots\ldots\ldots\ldots (46)$$

Or

$$\left(\frac{\partial}{\partial \mathrm{v}}\right)_T \left(\frac{\partial \mathrm{F}}{\partial \mathrm{T}}\right)_V = \left(\frac{\partial}{\partial \mathrm{T}}\right)_V \left(\frac{\partial \mathrm{F}}{\partial \mathrm{V}}\right)_T \ldots\ldots\ldots\ldots\ldots\ldots (47)$$

Thus, it follows from Equations (44) and (45) that

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \ldots\ldots\ldots\ldots (48)$$

Gibbs Free Energy

Suppose, finally, that *T* and *p* are the are the two independent parameters that specify the system. Because

T dS = d(T S) − S dT ……..(49)

we can rewrite Equation

***dH = T dS + V dp* ……..(50)**

in the form

dG = −S dT + V dp ……(51)

where

G = H − T S = E − T S + PV ……..(52)

is termed the *Gibbs free energy*.
Proceeding as before, we write

G = G(T, p) ……(53)

which implies that

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \ldots\ldots\ldots (54)$$

Comparison of Equations (51) and (54) yields

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \ldots\ldots\ldots (55)$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \text{ …… (56)}$$

We also know that

$$\frac{\partial^2 G}{\partial P\, \partial T} = \frac{\partial^2 G}{\partial T\, \partial P} \ldots\ldots\ldots\ldots (57)$$

Or

$$\left(\frac{\partial}{\partial P}\right)_T \left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial}{\partial T}\right)_P \left(\frac{\partial G}{\partial T}\right)_P \ldots\ldots(58)$$

Thus, it follows from Equations (55) and (56) that

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial S}{\partial T}\right)_P \ldots\ldots\ldots\ldots\ldots(59)$$

Equations (48), and (59) are known collectively as Maxwell relations.

General Relation Between Specific Heats

Consider a general homogeneous substance (not necessarily a gas) whose volume, *V*, is the only relevant external parameter. Let us find the general relationship between this substance's molar specific heat at constant volume, C_V, and its molar specific heat at constant pressure, C_P.

The heat capacity at constant volume is given by

$$C_V = \left(\frac{dQ}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(60)$$

Likewise, the heat capacity at constant pressure is written

$$C_P = \left(\frac{dQ}{dT}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(61)$$

Experimentally, the parameters that are most easily controlled are the temperature, *T*, and the pressure, *p*. Let us consider these as the independent variables. Thus, *S* = *S* (*T*, *p*), which implies that

$$dQ = TdS = T\left[\left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP\right] \ldots\ldots\ldots(62)$$

in an infinitesimal quasi-static process in which an amount of heat *dQ* is absorbed. It follows from Equation (60) that

$$dQ = TdS = C_P\, dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \ldots\ldots\ldots(63)$$

Suppose that p = p (T, V).

The previous equation can be written

$$\boldsymbol{dQ = TdS = C_P\, dT + T\left(\frac{\partial S}{\partial P}\right)_T\left[\left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV\right]} \ldots\ldots\ldots (64)$$

At constant volume, $dV = 0$. Hence, Equation (60) gives

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = C_p + T\left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V \quad \ldots\ldots\ldots\ldots\ldots\ldots (65)$$

This is the general relationship between C_V and C_P. Unfortunately, it contains quantities on the right-hand side that are not readily measurable.

Combinatorial Analysis for Statistical Thermodynamics

Distinguishable Objects

Combinatorial analyses for distinguishable objects encompass three significant cases. Each case can be considered by posing and answering a different fundamental query.

1. In how many ways may *N* identical, distinguishable objects be placed in *M* different containers with a limit of one object per container?

The limitation of one object per container requires $N \leq M$. The first object may be placed in any of *M* available containers, the second in $(M-1)$ available containers, and so on. Hence the number of ways for this case becomes

$$W_1 = M\,(M-1)(M-2)\cdots(M-N+1) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Or

$$W_1 = \frac{M!}{(M-N)!} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

2. In how many ways may *N* identical, distinguishable objects be placed in *M* different containers such that the *i*th container holds exactly N_i objects?

The total number of permutations for *N* objects is *N*! However, within each container, permutations are irrelevant as we are concerned only with their number rather than their identity. Hence, the number of permutations, *N*!, overcounts the number of ways by the number of permutations, N_i!, for each container. Therefore, the number of ways is

$$W_2 = \prod_{i=1}^{M} N_i! \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

3. In how many ways may *N* identical, distinguishable objects be placed in *M* different containers with no limitation on the number per container?

Because no limit exists, each object can be placed in any of the *M*containers.Therefore,

$$W_3 = M^N \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Indistinguishable Objects

Combinatorial analyses for indistinguishable objects encompass two rather than three

cases of significance. Each case can again be considered by posing and answering a fundamental query.

4. In how many ways may *N* identical, indistinguishable objects be placed in *M* different containers with a limit of one object per container?

A similar query for distinguishable objects previously led to Eq. (2). For indistinguishable objects, however, any rearrangement among the *N* objects is unrecognizable. Hence, W_1 overcounts the number of ways for indistinguishable objects by a factor of *N*! Therefore,

$$W_4 = \frac{M!}{N!\,(M - N)!} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

5. In how many ways may *N* identical, indistinguishable objects be placed in *M* different containers with no limitation on the number per container?

This fully unconstrained case (indistinguishable objects, no limitation) mandates a totally different approach from that used for W_4. We begin by initially assuming distinguishable objects labeled 1, 2, 3, . . . , *N*. Let us now arrange these *N* objects in a row, with the *M* containers identified and separated by partitions. As an example,

1, 2, 3 | 4, 5 | 6 | . . .| N − 1, N

Specifies that objects 1, 2, and 3 are in the first container, objects 4 and 5 are in the second container, object 6 is in the third container, and so on. Now, regardless of their actual arrangement, the maximum number of rearrangements among the *N* objects and *M* − 1 partitions is (*N* + *M* − 1)! However, interchanging the partitions produces no new arrangements; thus, we have overcounted by a factor of (*M* − 1)! Similarly, because the *N* objects are actually indistinguishable, we have again overcounted by a factor of *N*!, as in query 4. Therefore, the number of ways for this case becomes

$$W_5 = \frac{(N + M - 1)!}{N!\,(M - 1)!} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

The combinatorial analyses conducted for Cases 3–5 will prove to be of most interest to us for practical calculations. As we will see in the following chapter, Eq. (4) corresponds to Boltzmann statistics, Eq. (5) corresponds to Fermi–Dirac statistics, and Eq. (6) corresponds to Bose–Einstein statistics.

EXAMPLE

Determine the number of ways of placing two balls in three numbered containers for (a) Boltzmann statistics, (b) Fermi–Dirac statistics, and (c) Bose–Einstein statistics. Construct a table that identifies each of the ways for all three cases.

Solution

(a) For Boltzmann statistics, the balls are distinguishable with no limit on the number per container. Hence, from Eq. (4),

$$W_3 = M^N = 3^2 = 9$$

Way	Container 1	Container 2	Container 3
1	●○		
2		●○	
3			●○
4	●	○	
5	○	●	
6	●		○
7	○		●
8		●	○
9		○	●

(b) For Fermi–Dirac statistics, the balls are indistinguishable, but with a limit of one ball per container. Therefore, Eq. (5) yields

$$W_4 = \frac{M!}{N!\,(M - N)!} = \frac{3!}{2!\,1!} = 3$$

If only closed circles are used to enumerate the indistinguishable balls, these three distributions are as follows:

Way	Container 1	Container 2	Container 3
1	●	●	
2	●		●
3		●	●

(c) For Bose–Einstein statistics, the balls are indistinguishable, with no limit on the number of balls per container. Hence, using Eq. (6), we have

$$W_5 = \frac{(N+M-1)!}{N!(M-1)!} = \frac{(2+3-1)!}{2!(3-1)!} = \frac{4!}{2!2!} = 6$$

Way	Container 1	Container 2	Container 3
1	••		
2		••	
3			••
4	•	•	
5	•		•
6		•	•

In physics, a microstate is defined as the arrangement of each molecule in the system at a single instant. A macrostate is defined by the macroscopic properties of the system, such as temperature, pressure, volume, etc. For each macrostate, there are many microstates which result in the same macrostate.

The M–B Method: Microstates and Macrostates

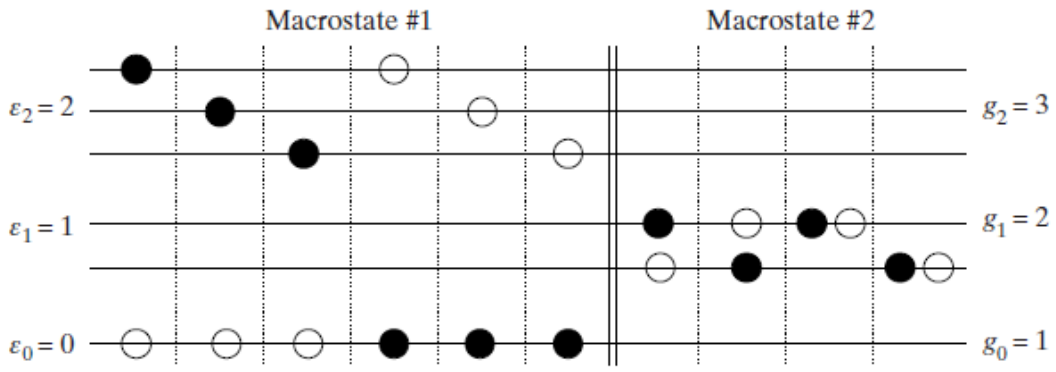
that a particle distribution is ordinarily specified by the number of particles in each *energy level,* $N_j(\varepsilon_j)$.
Because of its importance for the M–B method, this particle distribution is called a *macrostate*.
We could, of course, consider
more directly the influence of degeneracy and specify instead the number of distinct particles in each *energy state,* $N_j(\varepsilon_j)$. This more refined distribution is called a *microstate*.
Clearly, for each separate macrostate, there are many possible microstates owing to the potentially high values of the degeneracy, g_j . Hence, the most probable distribution of particles over **energy levels should correspond to that macrostate associated with the greatest number of microstates.**
Based on the above notions of microstate and macrostate, we may recast the two basic postulates of statistical thermodynamics in forms suitable for application to the M–B method. Therefore, for an isolated system of independent particles, we now have the following:
1. The time average for a thermodynamic variable is equivalent to its average over all possible microstates.
2. All microstates are equally probable; hence, the relative probability of each macrostate is given by its number of microstates.

EXAMPLE

Consider an isolated system of independent particles with the following allowed energy levels and associated degeneracies: $\varepsilon_0 = 0$, $g_0 = 1$; $\varepsilon_1 = 1$, $g_1 = 2$; $\varepsilon_2 = 2$, $g_2 = 3$. If the system holds only two particles and the total energy is two units, determine (a) the number of macrostates, (b) the number of microstates for distinguishable particles, and (c) the number of microstates for indistinguishable particles. For simplicity, assume no limit on the number of particles per energy state.

Solution
(a) If only two independent particles are available, they must be distributed among the three allowed energy levels either with one particle at $\varepsilon_0 = 0$ and the other at $\varepsilon_2 = 2$ or with both at $\varepsilon_1 = 1$. Indeed, given two particles, these two particle distributions represent the only ways by which the total energy can be two units. Therefore, this isolated system contains only two macrostates.
(b) The following table identifies the possible microstates for each macrostate when the particles are distinguishable. Macrostate #1 has six microstates and macrostate #2 has four microstates. Hence, the total number of microstates is 10. In this case, macrostate

#1 is the most probable macrostate.



(c) For indistinguishable particles, the distinguishable open and closed circles are irrelevant.
Hence, the number of microstates in both macrostate #1 and macrostate #2 is three, for a total of six microstates.

Bose–Einstein and Fermi–Dirac Statistics

We now proceed to identify mathematically the most probable macrostate for an isolated system of independent particles by investigating thoroughly both Bose–Einstein and Fermi–Dirac statistics. Bose–Einstein statistics describe the behavior of indistinguishable particles with no limit on the number of particles per energy state. Such particles are called *bosons*. In comparison, Fermi–Dirac statistics describe the behavior of indistinguishable particles with a limit of one particle per energy state. These particles are called *fermions*. For each particle type, we derive a general expression for the number of microstates per macrostate. We then determine the extremum for this expression, including constraints imposed by an isolated system, so as to identify the most probable particle distribution. The mathematical procedure that we will employ is called the method of Lagrange,

Method of Lagrange Multipliers

Consider a continuous function, *f* (*x*, *y*, *z*), which depends on the three independent variables, *x*, *y*, and *z*. To determine the maximum or minimum of this function, we normally invoke

$$df = \left(\frac{\partial f}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y}\right) dy + \left(\frac{\partial f}{\partial z}\right) dz = 0 \qquad \textbf{(D.1)}$$

Which simply requires

$$\left(\frac{\partial f}{\partial x}\right) = \left(\frac{\partial f}{\partial y}\right) = \left(\frac{\partial f}{\partial z}\right) = 0$$

Now, suppose that *x*, *y*, and *z* are not independent variables but are instead related through two independent and continuous constraints,

$$g_1(x, y, z) = 0 \qquad \textbf{(D.2)}$$

$$g_2(x, y, z) = 0 \qquad \textbf{(D.3)}$$

Since g_1 and g_2 are each constant, the differential of each must be zero so that

$$\left(\frac{\partial g_1}{\partial x}\right) dx + \left(\frac{\partial g_1}{\partial y}\right) dy + \left(\frac{\partial g_1}{\partial z}\right) dz = 0 \qquad \textbf{(D.4)}$$

$$\left(\frac{\partial g_2}{\partial x}\right) dx + \left(\frac{\partial g_2}{\partial y}\right) dy + \left(\frac{\partial g_2}{\partial z}\right) dz = 0 \qquad \textbf{(D.5)}$$

Multiplying Eqs. (D.4) and (D.5) by the constants λ_1 and λ_2, respectively, and adding the results to Eq. (D.1) yields the combined requireme

$$\left(\frac{\partial f}{\partial x}+\lambda_1\frac{\partial g_1}{\partial x}+\lambda_2\frac{\partial g_2}{\partial x}\right)dx+\left(\frac{\partial f}{\partial y}+\lambda_1\frac{\partial g_1}{\partial y}+\lambda_2\frac{\partial g_2}{\partial y}\right)dy+\left(\frac{\partial f}{\partial z}+\lambda_1\frac{\partial g_1}{\partial z}+\lambda_2\frac{\partial g_2}{\partial z}\right)dz=0 \quad \textbf{(D.6)}$$

Given the two applied constraints, two of the three variables, say *x* and *y*, must depend on the remaining variable, *z*. Consequently, the first two terms of Eq. (D.6) can be zero only by choosing λ_1 and $\lambda_2$so that

$$\left(\frac{\partial f}{\partial x}+\lambda_1\frac{\partial g_1}{\partial x}+\lambda_2\frac{\partial g_2}{\partial x}\right)=0 \quad \textbf{(D.7)}$$

$$\left(\frac{\partial f}{\partial y}+\lambda_1\frac{\partial g_1}{\partial y}+\lambda_2\frac{\partial g_2}{\partial y}\right)=0 \quad \textbf{(D.8)}$$

Having selected λ_1 and λ_2, the only way that Eq. (D.6) can be zero for any arbitrary value of *dz* is for its coefficient to be identically zero, or

$$\left(\frac{\partial f}{\partial z}+\lambda_1\frac{\partial g_1}{\partial z}+\lambda_2\frac{\partial g_2}{\partial z}\right)=0 \quad \textbf{(D.9)}$$

Analogous arguments hold for any arbitrary choice of the independent variable. Hence, in general, the extremum is defined in all cases by the same three expressions, namely, Eqs. (D.7), (D.8), and (D.9). Including the two constraints, Eqs. (D.2) and (D.3), we have finally five equations in the five unknowns, x_0 , y_0, z_0, λ_1, and λ_2, where (x_0 y_0, z_0) defines the extremum condition.

The parameters λ_1 and λ_2 are called Lagrange multipliers. In essence, the maximum or minimum with constraints is obtained from the above procedure by finding the extremum of the auxiliary function.

$$\psi = f + \lambda_1 g_{1+} \lambda_2 g_{2+} \ldots\ldots + \lambda_n g_n$$

where $\lambda_1, \lambda_2, \ldots, \lambda_n$ are the unknown Lagrange multipliers, the number of which must, of course, be less than the number of system variables.

Bose–Einstein Statistics

For each case, we begin by deriving an expression for the number of microstates per macrostate, which represents the total number of ways an arbitrary particle distribution can arise when accounting for all possible energy levels. Let us first consider one energy level. The number of ways in which N_j bosons in a single energy level, ε_j , may be distributed among g_j energy states is equivalent to the number of ways in which N_j identical, indistinguishable objects may be arranged in g_j different containers, with no limitation on the number of objects per container. Hence, we have

$$W_j = \frac{(N_j + g_j - 1)!}{N_j!\,(g_j - 1)!} \dots\dots\dots\dots\dots\dots\dots\dots (1)$$

W_j: number of ways

Because each energy level represents an independent event, the total number of ways of obtaining an arbitrary particle distribution becomes

$$W_{BE} = \prod_j W_j = \prod_j \frac{(N_j + g_j - 1)!}{N_j!\,(g_j - 1)!} \dots\dots\dots\dots\dots\dots (2)$$

In other words, W_{BE} identifies the generic number of microstates per macrostate for Bose–Einstein statistics.

Taking the natural logarithm of Eq. (2), we obtain

$$\ln W_{BE} = \sum_j \{\ln(N_j + g_j)! - \ln N_j! - \ln g_j!\} \dots\dots\dots\dots\dots (3)$$

where we have neglected the unity terms since $g_j >> 1$.

Applying Stirling's approximation,

i.e., ln N! = N ln N − N, we find that

$$\ln W_{BE} = \sum_j \{(N_j + g_j)\ln(N_j + g_j) - N_j \ln N_j! - g_j \ln g_j\} \dots\dots\dots\dots\dots (4)$$

Or

$$\ln W_{BE} = \sum_j \left\{(N_j \ln \frac{g_j + N_j}{N_j} + g_j \frac{g_j + N_j}{g_j}\right\} \dots\dots\dots\dots\dots (5)$$

Fermi–Dirac Statistics

We again develop an expression for the number of microstates per macrostate, but this time for fermions. The number of ways in which N_j fermions in a single energy level, ε_j, may be distributed among *gj* energy states is equivalent to the number of ways in which N_j identical, indistinguishable objects may be arranged in g_j different containers, with no more than one object per container. Hence, employing Eq. (*W4*), we have

$$W_J = \frac{g_J!}{N_J!(g_J - N_J)!} \text{.....(1)}$$

where the N_J ! term in the denominator accounts for particle indistinguishability. The total number of ways of obtaining an arbitrary particle distribution then becomes

$$W_{FD} = \prod_j W_j = \prod_j \frac{g_J!}{N_J!(g_J - N_J)!} \text{.....(2)}$$

so that W_{FD} denotes the generic number of microstates per macrostate for Fermi–Dirac statistics.
Taking the natural logarithm of Eq. (2), we obtain

$$ln\, W_{FD} = \sum_j ln\, g_J! - \ln N_J! - \ln(g_J - N_J)! \text{.....(3)}$$

Applying Stirling's approximation, we find that

$$ln\, W_{FD} = \sum_j \{g_J\, ln\, g_J - N_J \ln N_J - (g_J - N_J)\ln(g_J - N_J)\}$$

Or

$$ln\, W_{FD} = \sum_j \left\{ N_J \ln \frac{g_J - N_J}{N_J} - g_J \ln \frac{g_J - N_J}{g_J} \right\}$$

EXAMPLE
A thermodynamic assembly consists of five independent particles having access to two energy levels. A particular particle distribution for this system and the associated degeneracies
for each energy level are as follows: (1) *N*1 = 2, *g*1 = 4; (2) *N*2 = 3, *g*2 = 6. Determine

the number of microstates for this macrostate if the particles are (a) bosons and (b) fermions.

Solution
(a) For bosons, the number of ways that a single energy level can be constructed is

$$W_j = \frac{(N_j + g_j - 1)!}{N_j!\,(g_j - 1)!}$$

Thus, for each energy level, $W1 = 5!\,/\,(2!\,3!) = 10$ and $W2 = 8!\,/\,(3!\,5!) = 56$. As a result, the number of microstates for this macrostate is $W = W1 \times W2 = 560$.

(b) For fermions, the number of ways that a single energy level can be constructed is

$$W_j = \frac{g_j!}{N_j!\,(g_j - N_j)!}$$

Hence, for each energy level, $W1 = 4!\,/\,(2!\,2!) = 6$ and $W2 = 6!\,/\,(3!\,3!) = 20$. Consequently, the number of microstates for this macrostate is $W = W1 \times W2 = 120$.

Corrected Maxwell–Boltzmann Statistics

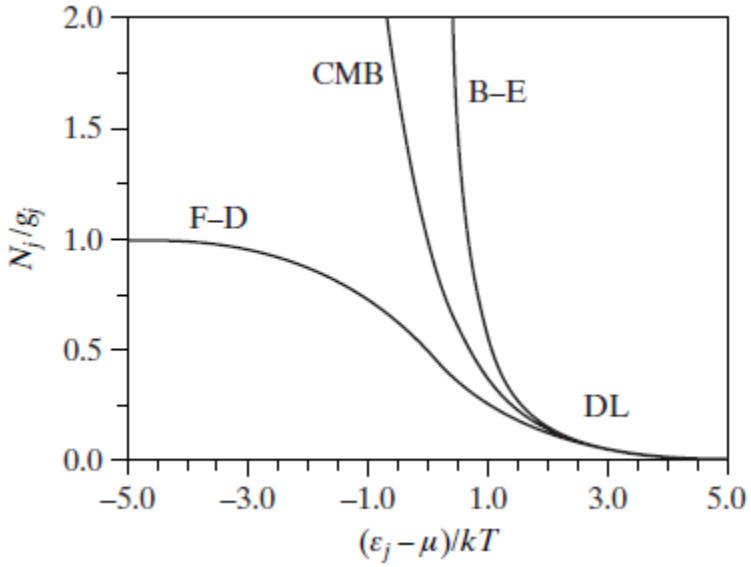
We begin as usual by developing an expression for the number of microstates per macrostate. Specifically, for classical particles, the number of ways in which N_j boltzons (such particles are said to follow Maxwell–Boltzmann (M–B) statistics, and may be called *boltzons*) in a single energy level, ε_j , may be distributed among g_j energy states is equivalent to the number of ways in which $N_j$identical, distinguishable objects may be arranged in g_j different containers, with no limitation on the number of objects per container.
We have

$$W_j = g_j^{N_j} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

So that the total number of ways of obtaining an arbitrary particle distribution for distinguishable particles, when considering all possible energy levels, appears to be

$$W_a = \prod_j W_j = \prod_j g_j^{N_j} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In comparison to our previous analyses for bosons and fermions, however, we recognize that, for distinguishable particles, a new microstate is formed when particles are exchanged among energy levels. To account for this classical complication, we must determine the number of possible particle distributions for distinguishable particles. This quantity is equivalent to the number of ways that *N* identical, distinguishable objects may be arranged among available shelves (energy levels) such that N_j objects occupy the *j*th shelf.



The dilute limit (DL) for Fermi–Dirac (F–D) and Bose–Einstein (B–E) statistics as compared to corrected M–B (CMB) statistics.

We have

$$W_b = \frac{N!}{\prod_j N_j!} \quad \text{.....(3)}$$

Therefore, multiplying Eqs. (3) and (2), we obtain the number of microstates per macrostate for M–B statistics,

$$W_{MB} = N! \prod_j \frac{g_j^{N_j}}{N_j!} \quad \text{.....(4)}$$

We have

$$W_{DL} = \prod_J \frac{g_j^{N_j}}{N_j!} \quad \text{.....(5)}$$

If we now compare Eq. (4), based on classical M–B statistics for distinguishable particles, with Eq. (5), based on the dilute limit for indistinguishable particles, we note that

$$W_{DL} = \frac{W_{MB}}{N!} \text{.....(6)}$$

Owing to the transparency of Eq. (6), the dilute limit is often referred to as *corrected Maxwell–Boltzmann statistics*.