

Chapter 1

Introduction and Zeroth Law

Much like other scientific disciplines, thermodynamics also has its own vocabulary. For instance, while dealing with objects composed of very large numbers of particles, one might use terms like: thermodynamic system; adiabatically isolating and adiabatically enclosing walls; adiabatic and non-adiabatic enclosures; conducting and/or diathermal walls; isothermal, isobaric, isochoric, quasi-static, reversible, and irreversible processes; state functions and state variables; thermodynamic equilibrium; and, of course, temperature in its various representations.

Central to the understanding of temperature and its relationship to thermodynamic equilibrium is the Zeroth Law of thermodynamics.

Just as driving an automobile gets one much farther than walking, thermodynamics is greatly helped by the use of mathematics. And there are a few simple mathematical techniques that are particularly useful.

An attempt at treating the foregoing issues is made in the current chapter. For instance, Sect. 1.1 deals with definitions of the terms that are often used; Sect. 1.2 with the need for large numbers in thermodynamic systems and their effect on the most probable state; Sect. 1.3 with the zeroth law; Sect. 1.4 with helpful mathematical procedures; Sect. 1.5 deals with the cyclic identity, with exact and inexact differentials, and their relevance to state variables and state functions; Sect. 1.6 with the use of simple Jacobian techniques; and finally, Sect. 1.7, with the re-derivation of the cyclic identity and the introduction of other well known identities.

1.1 Some Definitions

1.1.1 A Thermodynamic System

A thermodynamic system – sometime also called an “object” – comprises a collection of very large numbers of atoms and/or electromagnetic field quanta. In general, in addition to being subject to internal effects, a system may also be

affected from the outside. Further, it may be of liquid, solid, gaseous, or even some other exotic form.

1.1.2 Adiabatic Enclosure

Generally the walls of an enclosure in which a system is placed allow for the transfer and exchange of translational momentum, electro-magnetic and gravitational fields, heat energy, and sometime even molecules, etc. It is, however, possible to build walls that greatly reduce such transfers and exchanges. Exceptionally, one can imagine the construction of walls that reduce all of the aforementioned transfers and exchanges a 100%. These are called “adiabatic” walls.

Built entirely from such adiabatic walls, an enclosure, that completely encloses a (thermodynamic) system, is called an “adiabatic” enclosure.

1.1.3 Adiabatically Isolated System

An adiabatically isolated system exists within an adiabatic enclosure and it interchanges no energy, and no information, with the environment(meaning, the rest of the universe).

1.1.4 Adiabatically Enclosed System

While an adiabatically enclosed system does not interchange any energy with the environment, unlike an adiabatically isolated system it may be subject to interchanging some information with the environment.

1.1.5 Conducting Walls

Walls that are not adiabatic and freely allow for the transfer of momentum, energy, etc., are called “conducting.” In a word, they are “open.” This open-ness can take several forms. Particularly relevant to the study of thermodynamics is the open-ness to the transfer and exchange of “thermal energy,” “mass,” “electromagnetic fields and charges, etc.,” and momentum.

1.1.6 Diathermal Walls

If a wall allows for the transfer of heat energy, it is called a “diathermal,” or equivalently, a “heat energy conducting,” or a “thermally open,” wall.

1.1.7 Isobaric Process

A process that occurs while the pressure remains unchanged is called an “isobaric process.”

1.1.8 Isochoric Process

An “isochoric process” occurs at constant volume.

1.1.9 Thermal Equilibrium

We all know when we feel “hot” or “cold.” Also that given two objects, one “hot” and the other “cold,” bringing them into contact generally cools-down the hot object and warms-up the cold object.

When a thermometer is used to take a reading of the hot object “ h ,” it registers a number, T_h , that is higher than that, that is, T_c , registered for the cold object “ c .”

Let identical thermometers be placed in two objects as they are brought into “thermal contact.” Now let both the objects, with their thermometers, be placed inside an adiabatic enclosure. Assume that the thermometer readings can be observed. These readings, T_h and T_c , begin to move toward an intermediate number. Indeed, as the contact time increases, the readings move ever closer. Eventually, they stop changing and attain – what should be – the same reading. When that happens we say that the thermometers and the systems have reached – both by themselves and with each-other – a state of “thermal equilibrium.”

1.1.10 Quasi-Static Process

A quasi-static process proceeds extremely – in principle, infinitely – slowly: almost as if it were static when in fact it is proceeding. Generally, it passes through a very long – in principle, infinitely long – series of equilibrium states that are infinitesimally close to each other. In contrast, real processes proceed at finite speeds and pass through states that depart from the equilibrium.

For instance, during a quasi-static transfer of heat energy, both the relevant thermodynamic systems – that is, the one delivering the heat energy as well as the one receiving it – pass through only those states that are in thermodynamic equilibrium.

In contrast, a real process both proceeds at non-zero speed and the intermediate states that it passes through may often depart from the equilibrium. Thus a quasi-static process is an idealization and, in practice, is at best achieved only approximately. Yet, in thermodynamics, the concept is of great theoretical value.

1.1.11 *Reversible and Irreversible Processes*

A reversible process is one that occurs with such little “enthusiasm” that it can be reversed with merely an infinitesimal amount of effort. A signature example of such a process would be provided by quasi-static transfer of heat energy from a reservoir to an object that is almost exactly at the same temperature. In this way, the process can proceed in either direction with only an infinitesimal change in the temperature. Note, a reversible process is necessarily quasi-static.

1.2 Thermodynamics: Large Numbers

Thermodynamics deals with macroscopic systems. Any such system comprises very large number of particles. For instance, one gram of hydrogen has approximately 6×10^{23} atoms. Considering that the age of the Universe is thought to be less than $\approx 10^{18}$ seconds, 6×10^{23} is a very large number.

Owing to inter-particle interaction, theoretical analysis of most such systems is very complicated and can at best be carried out only approximately. Indeed, unlike statistical mechanics, thermodynamics itself does not even attempt to perform “a priori” theoretical calculations. Rather, it deals with inter-relationships of observed physical properties of macroscopic systems. In so far as such knowledge can often help relate easily measurable physical properties to those that are hard to measure, thermodynamics plays an important role in scientific disciplines.

1.2.1 *Remark: Most Probable State*

As elucidated in appendix A, large numbers are fundamental to the accuracy of thermodynamic relationships. Indeed, systems with small numbers of atoms do not satisfy thermodynamic identities.

Macroscopic systems contain very large number of particles. For large numbers, the most probable occurrence is overwhelmingly so. As such, the result of any thermodynamic – that is, a “macroscopic” – measurement is extremely well described by the configuration that refers to the most probable state. Therefore, quite appropriately, thermodynamics focuses primarily on the most probable state.

1.3 Zeroth Law of Thermodynamics

Insert identical thermometers into three different objects (that is, systems) called *A*, *B* and *C*. Place the trio in an adiabatic enclosure.

Bring *A* into thermal contact separately with *B* and *C*. But make sure that the objects *B* and *C* are not placed in direct mutual thermal contact.

Let the two contacts – namely $A \rightarrow B$ and $A \rightarrow C$ – last for an extended period of time. As noted before, this causes the objects A and B , as well as the duo A and C , to reach mutual thermal equilibrium.

The zeroth law now makes a seemingly un-surprising prediction: namely that the above two equilibrating processes also ensure that B and C – which are not in direct thermal contact with each other – will also have reached mutual thermal equilibrium. Considering that elementary rules of algebra require B to be equal to C whenever $A = B$ and $A = C$, one might laughingly assert that there is nothing special about this prediction!

But this assertion is fallacious, because we are not dealing with the rules of algebra here. For instance, consider two persons, “a” and “b,” who are good friends. If “a” is also good friends with another person named “c,” then is it always the case that “b” is good fiends with “c”? Indeed, if that should be the case, then the trio may be thought to have some common “chemistry” together!

Below we follow an argument, given by Pippard, to show that the zeroth law predicts the trio A , B , and C to have a common state variable. The relevant common state variable is normally called the “temperature.”^{1,2}

1.3.1 Empirical Temperature

A “simple” system is defined such that a given amount – say, a single mole^{3,4} – can be⁵ completely specified by two state variables: pressure p and volume v . Further, with appropriate effort, the magnitude of either, or indeed both, of these variables may be changed. Consider three such systems – one mole each – labeled A , B , and C . What happens if all three are placed within the same adiabatic enclosure in such a way that A is separately in thermal contact with B , on one side, and C , on the other. In this fashion, because B and C themselves remain physically separated from each other, they are not in direct thermal contact.

Over time, the pressures and volumes settle down at three pairs of values – say, (p_A, v_A) , (p_B, v_B) , and (p_C, v_C) – that are relevant to the achieved state of mutual thermal equilibrium of A separately with B and C .

¹A. B. Pippard in “Classical Thermodynamics,” pages 7–11, Cambridge University Press, 1957.

²Pippard, Alfred Brian (9/7/1920)–(9/21/2008).

³By international agreement, the relative atomic mass of N_A carbon-12 atoms is chosen to be exactly equal to 12. Note that a carbon-12, that is, $^{12}\text{C}_6$, atom has six protons, and six neutrons. The Avogadro’s number, N_A , is so chosen that the mass of N_A carbon-12 atoms is exactly equal to 12 grams. Measured, thus, N_A is equal to $6.02214179(30) \times 10^{23} \text{ mol}^{-1}$. References to one mole always specify N_A particles whether they be atoms or molecules.

⁴Avogadro, Lorenzo Romano Amadeo Carlo (8/9/1776)–(6/9/1856).

⁵Note that both carbon and helium molecules are monatomic.

An interesting result is that now the values (p_A, v_A) , (p_B, v_B) , (p_C, v_C) arbitrarily cannot be adjusted. It is important to note that such an inability did not exist when A and B , and A and C , were not in thermal contact. In fact, it is now found that only three of the four variables of a pair of systems in thermal equilibrium can be chosen arbitrarily. The fourth variable is then completely specified.

In other words, the two pairs (p_A, v_A) and (p_B, v_B) – or similarly, the pairs (p_A, v_A) and (p_C, v_C) – have only three independent variables. The fourth variable is dependent on the other three.

Mathematically, this fact can be expressed as follows.⁶

$$p_A = f_1(v_A, p_B, v_B). \quad (1.1)$$

Let us treat next the second pair of systems in thermal equilibrium: namely, A and C . Again, noting that of the four variables (p_A, v_A) and (p_C, v_C) only three are independent, we can write⁷

$$p_A = f_2(v_A, p_C, v_C). \quad (1.2)$$

Equating p_A in (1.1) and (1.2) yields

$$f_1(v_A, p_B, v_B) = f_2(v_A, p_C, v_C). \quad (1.3)$$

Let us now remind ourselves of the assertion made by the zeroth law. Because the objects A and B , as well as A and C , are in mutual thermal equilibrium; therefore, it is asserted that B and C must also be in mutual thermal equilibrium.

Should the above assertion – namely that B and C are also in mutual thermal equilibrium – be correct, then much as noted earlier, of the four variables (p_B, v_B) and (p_C, v_C) , only three would be independent. Thus, any of these four variables depends on the other three: for example,⁸

$$p_B = f_3(v_B, p_C, v_C). \quad (1.4)$$

Equation (1.4) is more conveniently written as follows:

$$\begin{aligned} G(p_B, v_B, p_C, v_C) &= f_3(v_B, p_C, v_C) - p_B \\ &= 0. \end{aligned} \quad (1.5)$$

⁶Although we have chosen to represent p_A as a function of (v_A, p_B, v_B) , any other of these four variables could equally well have been chosen as a function of the remaining three.

⁷It bears noting that $f_1(x, y, z)$ and $f_2(x, y, z)$ are, in all likelihood, not the same functions. This is especially true if B and C are physically different systems.

⁸Note $f_3(x, y, z)$, a function of the three variables x, y and z , is in all likelihood different from $f_1(x, y, z)$ and $f_2(x, y, z)$ encountered in (1.3) above.

1.3.2 Taking Stock

Let us take stock of what has been achieved so far. Equation (1.3) acknowledges the fact that the pairs, (A, B) as well as (A, C) , have been brought into mutual thermal equilibrium while the systems B and C have been kept physically separated. Consequent to this happenstance, (1.5) records the prediction – which is actually an assertion – of the zeroth law.

In other words, the zeroth law asserts that (1.5) – which signifies mutual thermal equilibrium for systems B and C – follows from (1.3).

But how can this be true considering (1.3) is a function of five variables, v_A , (p_B, v_B) , and (p_C, v_C) , while (1.5) depends only on the four variables (p_B, v_B) and (p_C, v_C) ? In order for this to happen, in (1.3), there must occur a complete self-cancellation of the fifth variable, v_A . The most general choice for f_1 and f_2 that satisfies this requirement is the following:

$$\begin{aligned} f_1(v_A, p_B, v_B) &= \alpha(v_A)J(p_B, v_B) + \beta(v_A); \\ f_2(v_A, p_C, v_C) &= \alpha(v_A)K(p_C, v_C) + \beta(v_A). \end{aligned} \quad (1.6)$$

It is important to note that the functions $J(x, y)$ and $K(x, y)$ are neither required, nor are they expected to be the same.

The equality of $f_1(v_A, p_B, v_B)$ and $f_2(v_A, p_C, v_C)$, demanded by (1.3), that is,

$$\alpha(v_A)J(p_B, v_B) + \beta(v_A) = \alpha(v_A)K(p_C, v_C) + \beta(v_A), \quad (1.7)$$

yields

$$J(p_B, v_B) = K(p_C, v_C) \equiv T_{B-C}(\text{empirical}). \quad (1.8)$$

Equation (1.8) is of central importance. The assertion of the zeroth law that systems B and C are also in thermal equilibrium demands that both B and C lead to a common value of a parameter, $T_{B-C}(\text{empirical})$, that we shall call their empirical temperature.⁹

Analogously, we can conclude that because we started with the knowledge that A and B are in thermal equilibrium, they too must lead to the existence of a common empirical temperature. Let us call that $T_{A-B}(\text{empirical})$.

Equivalently, the same must be true for the duo A and C who also were stated to be in thermal equilibrium. As a result we must have an empirical temperature, $T_{A-C}(\text{empirical})$, that is common to the two systems A and C .

Therefore, using basic rules of algebra, all of the three systems, A , B , and C , have in common the same empirical temperature $T(\text{empirical})$. That is

⁹Such an empirical temperature could be defined by any appropriate thermometric property that both the systems share.

$$\begin{aligned}
T(\text{empirical}) &= T_{A-B}(\text{empirical}) \\
&= T_{A-C}(\text{empirical}) \\
&= T_{B-C}(\text{empirical}).
\end{aligned}
\tag{1.9}$$

1.3.3 Isothermal Process

A process that occurs at constant temperature is called an “isothermal process.”

1.3.4 Equation of State

Relationships of the type given in (1.8), for example,

$$J(p, v) = T(\text{empirical}), \tag{1.10}$$

where $J(p, v)$ represents a function of the pressure p and the volume v , are often referred to as equations of state of a simple thermodynamic system.

1.3.5 Remark

The zeroth law leads to a result that equates a function of the pressure and the volume of a “simple”¹⁰ thermodynamic system to a single parameter that is the same for any two systems in thermal equilibrium. This parameter can be labeled the “empirical temperature.” Note that there are also other important consequences of the zeroth law. Under the heading: “Zeroth Law Revisited,” these consequences are discussed in detail in Chap. 9 that in the table of contents is titled “Zeroth Law; Motive Forces; Stability.”

1.4 Useful, Simple Mathematical Procedures

Readers of this text are likely to be familiar with elementary differential and integral calculus. Many will also have been introduced to partial differentiation and possibly also to the use of Jacobians. Experience suggests that at least for some the

¹⁰It should be noted that the implications of the zeroth law are not limited to just simple thermodynamic systems. Systems with an arbitrary number of thermodynamic state variables also obey the zeroth law equally well.

knowledge will have become rusty. Therefore, a quick review of the mathematical procedures, that are most needed for an adequate study of Thermodynamics, is often helpful. Salient features of such a review are recorded below. In order to keep the review simple, proofs are not provided and issues of mathematical rigor are not tackled.

1.5 Exact Differential

Thermodynamics deals with macroscopic systems that can be described in terms of state variables. For a given amount – such as one mole, for example – of a simple system, there are three such variables: pressure p , volume v , and temperature T . As mentioned above, in general, these three variables are related through an equation of state of the form

$$f(p, v, T) = 0, \quad (1.11)$$

making only two of them independent. For notational convenience let us denote the two independent variables X and Y .

Given Z is a function of X and Y ,

$$Z = Z(X, Y),$$

and dZ is an exact differential,¹¹ then the line integral in the (X, Y) plane,

$$\int_{(X_i, Y_i)}^{(X_f, Y_f)} dZ(X, Y),$$

depends only on the initial, $i \equiv (X_i, Y_i)$, and the final, $f \equiv (X_f, Y_f)$, positions and thereby is totally independent of the path traversed between i and f .

1.5.1 Exercise I-a

Show that

$$\begin{aligned} dZ(X, Y) = & (2AXY^2 + BY^2 + 2CXY + D) dX \\ & + (2AX^2Y + 2BXY + CX^2 + E) dY, \end{aligned} \quad (1.12)$$

is an exact differential.

¹¹Note: some authors – for example, D. ter Haar and H. Wergeland, op. cit. – prefer to use the term total differential.

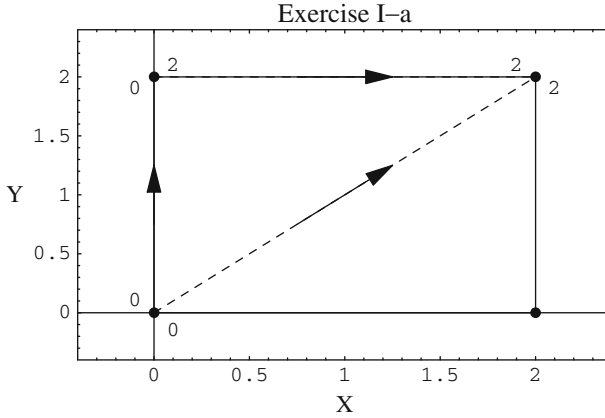


Fig. 1.1 Paths traveled. The paths traveled are: (*First*): From the point (0,0) up to (0,2) and then to (2,2). (*Second*): Another possibility is to travel directly from (0,0) across to the point (2,2)

1.5.1.1 Solution

Let us try to determine whether the line-integral,

$$\int_{(X_1, Y_1)}^{(X_2, Y_2)} dZ(X, Y),$$

between any two points, (X_1, Y_1) and (X_2, Y_2) , is path independent. To this end, set $(X_1, Y_1) = (0, 0)$ and $(X_2, Y_2) = (2, 2)$. A simple check is provided by choosing two different paths – as in Fig. 1.1 – that use straight-lines. Because, in principle, there are infinitely many different paths in the (X, Y) plane that can connect the given two points, the use of only two paths, while being indicative of the result, can by no means be considered a proof. A convincing proof is provided in Exercise I-b below.

Route I: First travel from (0, 0) to (0, 2) and then from (0, 2) to (2, 2). According to (1.12) we get

$$\begin{aligned} \int_{(0,0)}^{(0,2)} dZ(X, Y) &= \int_{(0,0)}^{(0,2)} (2AXY^2 + BY^2 + 2CXY + D) dX \\ &\quad + \int_{(0,2)}^{(2,2)} (2AX^2Y + 2BXY + CX^2 + E) dY \\ &= 0 + \int_0^2 (E) dY = 2E. \end{aligned} \tag{1.13}$$

Note, in the above, $X = 0$, and also $dX = 0$.

Next, we need the integral from $(0, 2)$ to $(2, 2)$, that is,

$$\begin{aligned}
 \int_{(0,2)}^{(2,2)} dZ(X, Y) &= \int_{(0,2)}^{(2,2)} (2AXY^2 + BY^2 + 2CXY + D) dX \\
 &\quad + \int_{(0,2)}^{(2,2)} (2AX^2Y + 2BXY + CX^2 + E) dY \\
 &= \int_0^2 (8AX + 4B + 4CX + D) dX + 0 \\
 &= (16A + 8B + 8C + 2D).
 \end{aligned} \tag{1.14}$$

Note, in the above, $Y = 2$. Additionally, $dY = 0$. Thus, the total value of the line integral along route I is

$$\begin{aligned}
 \int_{(0,0)}^{(2,2)} dZ(X, Y) &= \int_{(0,0)}^{(0,2)} dZ(X, Y) + \int_{(0,2)}^{(2,2)} dZ(X, Y) \\
 &= (2E + 16A + 8B + 8C + 2D).
 \end{aligned} \tag{1.15}$$

Route II: Travel directly along the straight line from $(0, 0)$ to $(2, 2)$. In order to work out the line integral – as always – we need to arrange things so that any of the integrals used involves only one variable. Because the equation for the relevant path is $X = Y$, and also because both X and Y extend from 0 to 2, one gets:

$$\begin{aligned}
 \int_{(0,0)}^{(2,2)} dZ(X, Y) &= \int_{(0,0)}^{(2,2)} (2AXY^2 + BY^2 + 2CXY + D) dX \\
 &\quad + \int_{(0,0)}^{(2,2)} (2AX^2Y + 2BXY + CX^2 + E) dY \\
 &= \int_0^2 (2AX^3 + BX^2 + 2CX^2 + D) dX \\
 &\quad + \int_0^2 (2AY^3 + 2BY^2 + CY^2 + E) dY \\
 &= (16A + 8B + 8C + 2D + 2E).
 \end{aligned} \tag{1.16}$$

As expected, this result is identical to that noted in (1.15).

1.5.2 Notation

Because for an exact differential

$$\int_{(X_i, Y_i)}^{(X_f, Y_f)} dZ(X, Y) = \alpha(X_f, Y_f) - \alpha(X_i, Y_i),$$

and similarly

$$\int_{(X_f, Y_f)}^{(X_i, Y_i)} dZ(X, Y) = \alpha(X_i, Y_i) - \alpha(X_f, Y_f),$$

therefore, adding the two gives

$$\begin{aligned} \int_{i \rightarrow f} dZ(X, Y) &= \int_{(X_i, Y_i)}^{(X_f, Y_f)} dZ(X, Y) + \int_{(X_f, Y_f)}^{(X_i, Y_i)} dZ(X, Y) \\ &= \alpha(X_f, Y_f) - \alpha(X_i, Y_i) + \alpha(X_i, Y_i) - \alpha(X_f, Y_f) \\ &= 0. \end{aligned} \quad (1.17)$$

This is valid for all paths of the integration, which lie within the (X, Y) plane, and form a closed loop. Such a loop starts off at some arbitrary initial location i within the X, Y plane, travels within the plane to some arbitrary final point f , and at the end returns to the initial location i .

Accordingly, the usual notation for displaying an exact differential dZ is the following:

$$\oint dZ(X, Y) = \oint dZ = 0. \quad (1.18)$$

In general, such an exact differential can be expressed as

$$dZ = dZ(X, Y) = N(X, Y)dX + M(X, Y)dY, \quad (1.19)$$

where $N(X, Y)$ and $M(X, Y)$ are functions of X and Y and obey the so called “integrability” requirement

$$N(X, Y) = \left(\frac{\partial Z}{\partial X} \right)_Y; \quad M(X, Y) = \left(\frac{\partial Z}{\partial Y} \right)_X, \quad (1.20)$$

which holds if the second mixed derivatives of Z are equal. That is:¹²

$$\frac{\partial^2 Z}{\partial Y \partial X} = \left(\frac{\partial N}{\partial Y} \right)_X = \left(\frac{\partial M}{\partial X} \right)_Y = \frac{\partial^2 Z}{\partial X \partial Y}. \quad (1.21)$$

Thus, the standard representation for an exact differential – in two dimensions – is

$$dZ = \left(\frac{\partial Z}{\partial X} \right)_Y dX + \left(\frac{\partial Z}{\partial Y} \right)_X dY. \quad (1.22)$$

¹²Beginners usually benefit by being reminded that the operation $\left(\frac{\partial Z}{\partial X} \right)_Y$ consists in finding a derivative of Z with respect to X while holding the variable Y constant.

1.5.3 Exercise I-b

Rigorous method to show that

$$\begin{aligned} dZ(X, Y) = (2AXY^2 + BY^2 + 2CXY + D) dX \\ + (2AX^2Y + 2BXY + CX^2 + E) dY, \end{aligned} \quad (1.23)$$

is an exact differential.

1.5.3.1 Solution

Calculus tells us that a necessary and sufficient condition for

$$dZ(x, y) = M(x, y)dx + N(x, y)dy \quad (1.24)$$

to be an exact differential is the requirement that the following equality hold:

$$\left(\frac{\partial M(x, y)}{\partial y} \right)_x = \left(\frac{\partial N(x, y)}{\partial x} \right)_y.$$

Thus, for $dZ(X, Y)$ to be an exact differential, we must have

$$\left(\frac{\partial (2AXY^2 + BY^2 + 2CXY + D)}{\partial Y} \right)_X = 4AXY + 2BY + 2CX,$$

equal to

$$\left(\frac{\partial (2AX^2Y + 2BXY + CX^2 + E)}{\partial X} \right)_Y = 4AXY + 2BY + 2CX.$$

Which is the case.

1.5.4 Inexact Differential

Let us look at the differential

$$\begin{aligned} dZ(X, Y) &= (BY^2 + 2CXY + D) dX \\ &\quad + (2AX^2Y + 2BXY + CX^2 + E) dY \\ &\equiv N(X, Y) dX + M(X, Y) dY. \end{aligned} \quad (1.25)$$

Clearly, this differential is inexact because

$$\begin{aligned} \left(\frac{\partial N}{\partial Y} \right)_X &= 2BY + 2CX \\ &\neq \left(\frac{\partial M}{\partial X} \right)_Y = 4AXY + 2BY + 2CX. \end{aligned} \quad (1.26)$$

Of course, information about the inexactness of this differential can also be obtained by integrating along route I – similar to the way it was done in (1.15) – and route II – much as was done in (1.16). As behaves an inexact differential, these two results are not the same. Being equal to $(8B + 8C + 2D + 2E)$ and $(8A + 8B + 8C + 2D + 2E)$, respectively, they differ by an amount equal to $8A$.

1.5.5 State Function and State Variables

Any thermodynamics function, Z , which admits of an exact differential, dZ , is vested with the special title: state function.

As mentioned earlier, for a “simple” thermodynamic system, variables X and Y may represent any of the three pairs p, v ; p, t ; or v, t . These pairs are called state variables. An obvious property of these variables is that their differentials $dp = dp(v, t)$; $dv = dv(p, t)$; or $dt = dt(p, v)$, are also exact.

An essential attribute of a state function $Z(X, Y)$ (for a simple thermodynamic system), therefore, is that for any thermodynamic equilibrium state, the state function depends only on the value of the given pair of state variables, X and Y . As a result, when a thermodynamic system travels from an initial position specified by a given initial value of the relevant state variables, namely (X_i, Y_i) , to another position specified by a given final value, say (X_f, Y_f) , of the same two state variables, the resultant change in any state function, namely $Z(X_f, Y_f) - Z(X_i, Y_i)$, is independent of the path taken. Furthermore, as a necessary consequence, any travel that takes the system completely around a closed loop, leaves the value of the state function, Z , unchanged.

1.5.6 Cyclic Identity

Much of the work involved in the study of elementary thermodynamics consists in deriving relationships between quantities that are easy to access experimentally and others that are less so. This is not an idle exercise. Specific heat, compressibility, expansivity, etc., are quantities that are readily measurable under most ambient experimental environments. Their relationships to various derivatives of important thermodynamic state functions, that may not be so easy to measure, help in the

evaluation of these functions. Examples of these are the system internal energy, enthalpy, entropy, etc.

The establishment of such relationships can often be accomplished by the use of exact differentials of the state functions themselves as well as those of the relevant state variables. Such procedures involve the use of (1.22).

Noting that $dp(v, t)$ and $dv(p, t)$ are exact differentials, we can use (1.22) and write

$$\begin{aligned} dp &= \left(\frac{\partial p}{\partial v} \right)_t dv + \left(\frac{\partial p}{\partial t} \right)_v dt; \\ dv &= \left(\frac{\partial v}{\partial p} \right)_t dp + \left(\frac{\partial v}{\partial t} \right)_p dt. \end{aligned} \quad (1.27)$$

Eliminating dv between these two equations yields:

$$\left[1 - \left(\frac{\partial p}{\partial v} \right)_t \left(\frac{\partial v}{\partial p} \right)_t \right] dp = \left[\left(\frac{\partial p}{\partial v} \right)_t \left(\frac{\partial v}{\partial t} \right)_p + \left(\frac{\partial p}{\partial t} \right)_v \right] dt. \quad (1.28)$$

Consider two neighboring equilibrium states of a simple thermodynamic system at temperature t . Recall that the thermodynamics of a simple system depends only on three state variable p, v and t . The fixing of one of these specifies the interdependence of the other two. For example, given any two neighboring equilibrium states that are both at the same temperature, that is, $dt = 0$, then according to (1.28),

$$\left[1 - \left(\frac{\partial p}{\partial v} \right)_t \left(\frac{\partial v}{\partial p} \right)_t \right] dp = 0.$$

And unless the two “neighboring” states are identical – in which case dp, dv are both vanishing – generally dp and dv are $\neq 0$. Therefore, in general, we must have:

$$1 - \left(\frac{\partial p}{\partial v} \right)_t \left(\frac{\partial v}{\partial p} \right)_t = 0.$$

This, of course, is the un-surprising statement that

$$\left(\frac{\partial p}{\partial v} \right)_t = \frac{1}{\left(\frac{\partial v}{\partial p} \right)_t}. \quad (1.29)$$

Next, consider two neighboring states with the same pressure. Here $dp = 0$ but dv and dt are in general not equal to zero. Therefore, (1.28), namely

$$\left[1 - \left(\frac{\partial p}{\partial v} \right)_t \left(\frac{\partial v}{\partial p} \right)_t \right] \times 0 = \left[\left(\frac{\partial p}{\partial v} \right)_t \left(\frac{\partial v}{\partial t} \right)_p + \left(\frac{\partial p}{\partial t} \right)_v \right] dt,$$

leads to the result

$$0 = \left(\frac{\partial p}{\partial v} \right)_t \left(\frac{\partial v}{\partial t} \right)_p + \left(\frac{\partial p}{\partial t} \right)_v. \quad (1.30)$$

Using (1.29), (1.30) can also be written as

$$\left(\frac{\partial p}{\partial v} \right)_t \left(\frac{\partial v}{\partial t} \right)_p \left(\frac{\partial t}{\partial p} \right)_v = -1. \quad (1.31)$$

Equation (1.31) – or, equivalently (1.30) – will be referred to as the “cyclic identity.”

1.5.7 Exercise II-a

(1) Instead of dv , eliminate dp from the two equations in (1.27), and re-derive the cyclic identity. (2) Also, do the same by eliminating dt .

1.5.7.1 Remark

In the following chapters, we shall make much use of the cyclic identity and the formula introduced in (1.22). Also, occasionally we shall work with an easy to use “Jacobian Determinant” – (JD) – procedure.

1.6 Jacobians: A Simple Technique

The (JD) offers an easy, and often-time an efficient, procedure for establishing thermodynamic inter-relationships. Below we describe its use in treating state functions $A(X, Y)$ and $B(X, Y)$ of a simple thermodynamic system where X and Y are any two of the three state variables. The relevant (JD) makes use of a 2×2 Jacobian of the general form $\frac{\partial(A, B)}{\partial(X, Y)}$. That is:

$$\begin{aligned} \frac{\partial(A, B)}{\partial(X, Y)} &= \begin{vmatrix} \left(\frac{\partial A}{\partial X} \right)_Y & \left(\frac{\partial A}{\partial Y} \right)_X \\ \left(\frac{\partial B}{\partial X} \right)_Y & \left(\frac{\partial B}{\partial Y} \right)_X \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial A}{\partial X} \right)_Y & \left(\frac{\partial B}{\partial X} \right)_Y \\ \left(\frac{\partial A}{\partial Y} \right)_X & \left(\frac{\partial B}{\partial Y} \right)_X \end{vmatrix} \\ &= \left(\frac{\partial A}{\partial X} \right)_Y \left(\frac{\partial B}{\partial Y} \right)_X - \left(\frac{\partial A}{\partial Y} \right)_X \left(\frac{\partial B}{\partial X} \right)_Y. \end{aligned} \quad (1.32)$$

Clearly, therefore, by exchanging A and B , and/or X and Y , we find the relationships:

$$\frac{\partial(A, B)}{\partial(X, Y)} = -\frac{\partial(B, A)}{\partial(X, Y)} = \frac{\partial(B, A)}{\partial(Y, X)} = -\frac{\partial(A, B)}{\partial(Y, X)}. \quad (1.33)$$

In other words, a single reversal in the order of the entries at the top or the bottom of $\frac{\partial(A, B)}{\partial(X, Y)}$ causes a (single) change of sign of the Jacobian. Similarly, if the number of reversals is two it causes (two changes in sign which amounts to) no change in sign. An important property of the Jacobian determinant, that will be found very useful, is the following:

$$\frac{\partial(A, B)}{\partial(X, Y)} = \frac{\partial(A, B)}{\partial(C, D)} \cdot \frac{\partial(C, D)}{\partial(X, Y)}. \quad (1.34)$$

An easy way to remember this is the following: what you add at the bottom here, you add “next-door” at the top.

It is clear that in a fashion similar to (1.34), we can extend the process further. That is:

$$\begin{aligned} \frac{\partial(A, B)}{\partial(C, D)} \cdot \frac{\partial(C, D)}{\partial(X, Y)} &= \frac{\partial(A, B)}{\partial(C, D)} \cdot \frac{\partial(C, D)}{\partial(E, F)} \cdot \frac{\partial(E, F)}{\partial(X, Y)} \\ &= \frac{\partial(A, B)}{\partial(C, D)} \cdot \frac{\partial(C, D)}{\partial(E, F)} \cdot \frac{\partial(E, F)}{\partial(G, H)} \cdot \frac{\partial(G, H)}{\partial(X, Y)} \\ &= \text{etc., etc.} \end{aligned} \quad (1.35)$$

1.6.1 Exercise II-b

Prove the following equality (which is similar to (1.34)).

$$\frac{\partial(x_1, x_2)}{\partial(z_1, z_2)} = \frac{\partial(x_1, x_2)}{\partial(y_1, y_2)} \cdot \frac{\partial(y_1, y_2)}{\partial(z_1, z_2)}. \quad (1.36)$$

1.6.1.1 Solution

Here, x_1 and x_2 depend on two variables z_1 and z_2 , each of which also happens to depend on two other variables y_1 and y_2 . For such a case the “chain rule” of differential calculus tells us that:¹³

¹³See any text on Differential Calculus, or see M. L. Boas in “Mathematical Methods in the Physical Sciences,” John Wiley, Publishers.

$$\left(\frac{\partial x_i}{\partial z_1}\right)_{z_2} = \left(\frac{\partial x_i}{\partial y_1}\right)_{y_2} \left(\frac{\partial y_1}{\partial z_1}\right)_{z_2} + \left(\frac{\partial x_i}{\partial y_2}\right)_{y_1} \left(\frac{\partial y_2}{\partial z_1}\right)_{z_2}, \quad (1.37)$$

and

$$\left(\frac{\partial x_i}{\partial z_2}\right)_{z_1} = \left(\frac{\partial x_i}{\partial y_1}\right)_{y_2} \left(\frac{\partial y_1}{\partial z_2}\right)_{z_1} + \left(\frac{\partial x_i}{\partial y_2}\right)_{y_1} \left(\frac{\partial y_2}{\partial z_2}\right)_{z_1}, \quad (1.38)$$

where $i = 1$, or 2 . Equations (1.37) and (1.38) prove the desired equality 1.36.¹⁴

1.6.2 Jacobian Employed

As noted earlier, partial derivatives of the form $\left(\frac{\partial Z}{\partial X}\right)_Y$ play an important role in the study of thermodynamics. The (JD) provides a convenient representation for such derivatives. For example, in (1.32), simple notational change A to Z and B to Y yields

$$\frac{\partial(Z, Y)}{\partial(X, Y)} = \begin{vmatrix} \left(\frac{\partial Z}{\partial X}\right)_Y & \left(\frac{\partial Z}{\partial Y}\right)_X \\ \left(\frac{\partial Y}{\partial X}\right)_Y & \left(\frac{\partial Y}{\partial Y}\right)_X \end{vmatrix}. \quad (1.39)$$

Because

$$\left(\frac{\partial Y}{\partial X}\right)_Y = 0; \left(\frac{\partial Y}{\partial Y}\right)_X = 1,$$

equation (1.39) gives

$$\frac{\partial(Z, Y)}{\partial(X, Y)} = \begin{vmatrix} \left(\frac{\partial Z}{\partial X}\right)_Y & \left(\frac{\partial Z}{\partial Y}\right)_X \\ 0 & 1 \end{vmatrix} = \left(\frac{\partial Z}{\partial X}\right)_Y. \quad (1.40)$$

The significance of (1.40) should be emphasized: it connects the typical partial derivative, $\left(\frac{\partial Z}{\partial X}\right)_Y$, that is often used in thermodynamics, with a simple (JD), $\frac{\partial(Z, Y)}{\partial(X, Y)}$, which is easy to manipulate. An aid to memory:

¹⁴Note, in order to convince oneself of the above statement one needs first to write down the two 2×2 determinants on the right hand side of (1.36); next to multiply them and write the result naturally as a 2×2 determinant. This resultant determinant consists of the four terms given as (1.37) and (1.38). It should be identical to the 2×2 determinant on the left hand side of (1.36).

The essential feature of the derivative $\left(\frac{\partial Z}{\partial X}\right)_Y$, is that Z is being varied as a function of X , while Y is being kept constant. Accordingly, in $\frac{\partial(Z,Y)}{\partial(X,Y)}$, Z occurs at the top left, X at the bottom left, and Y occurs to the right both at the top and the bottom.

1.7 Useful Identities

Consider variables X, Y and Z where only two are independent. According to (1.40)

$$\frac{\partial(X, Z)}{\partial(X, Z)} = \left(\frac{\partial X}{\partial X}\right)_Z. \quad (1.41)$$

Following the procedure described in (1.34), the left-hand side of (1.41) can be extended to

$$\begin{aligned} \frac{\partial(X, Z)}{\partial(Y, Z)} \cdot \frac{\partial(Y, Z)}{\partial(X, Z)} &= \frac{\partial(X, Z)}{\partial(X, Z)} \\ &= \left(\frac{\partial X}{\partial X}\right)_Z = 1. \end{aligned} \quad (1.42)$$

Indeed, we can continue to extend the left hand side and write:

$$\frac{\partial(X, Z)}{\partial(Y, Z)} \cdot \frac{\partial(Y, Z)}{\partial(X, Y)} \cdot \frac{\partial(X, Y)}{\partial(X, Z)} = 1.$$

Now, as explained earlier, if we reverse the order in three of the six factors, the overall sign will get reversed three times – which is equivalent to a single reversal of sign, that is,

$$\frac{\partial(X, Z)}{\partial(Y, Z)} \cdot \frac{\partial(Z, Y)}{\partial(X, Y)} \cdot \frac{\partial(Y, X)}{\partial(Z, X)} = -1. \quad (1.43)$$

1.7.1 Cyclic Identity: Re-Derived

Using the transliteration embodied in (1.40), the above can be represented as follows:

$$\left(\frac{\partial X}{\partial Y}\right)_Z \cdot \left(\frac{\partial Z}{\partial X}\right)_Y \cdot \left(\frac{\partial Y}{\partial Z}\right)_X = -1.$$

The mutual interchange of the last two terms makes this equation easier to memorize. That is,

$$\left(\frac{\partial X}{\partial Y}\right)_Z \cdot \left(\frac{\partial Y}{\partial Z}\right)_X \cdot \left(\frac{\partial Z}{\partial X}\right)_Y = -1. \quad (1.44)$$

Aid to memory: think of the cyclical order, v

$$(X \rightarrow Y \rightarrow Z \rightarrow X \rightarrow Y)$$

Often, it is helpful to recast the cyclic identity in the following form:

$$\left(\frac{\partial X}{\partial Y}\right)_Z = - \left(\frac{\partial X}{\partial Z}\right)_Y \cdot \left(\frac{\partial Z}{\partial Y}\right)_X. \quad (1.45)$$

The cyclic identity given in (1.44) and (1.45) is identical to that given earlier in (1.31) and (1.30). Recall that this identity represents an important relationship and will be put to good use in this text.

1.7.2 Simple Identity

Another identity that is worth noting is obtained straight forwardly when Jacobian representation is employed.

$$\frac{\partial(A, G)}{\partial(B, G)} = \frac{\partial(A, G)}{\partial(\Sigma, G)} \cdot \frac{\partial(\Sigma, G)}{\partial(B, G)}. \quad (1.46)$$

Equivalently, it reads

$$\left(\frac{\partial A}{\partial B}\right)_G = \left(\frac{\partial A}{\partial \Sigma}\right)_G \cdot \left(\frac{\partial \Sigma}{\partial B}\right)_G. \quad (1.47)$$

We shall call this the simple identity.¹⁵

1.7.3 Mixed Identity

As stated earlier, all thermodynamic functions that refer to (a given quantity of) a simple system depend on the variables P , V and T . While only two of these three variables are linearly independent, occasionally it is useful to work with all three. For instance, consider a function A

¹⁵Some students may prefer to use (1.47) as a calculus identity and work backwards to (1.46) as a useful Jacobian identity.

$$A = A(X, Y, Z).$$

Treating the pair X and Y as the independent variables we have

$$dA = \left(\frac{\partial A}{\partial X} \right)_Y dX + \left(\frac{\partial A}{\partial Y} \right)_X dY. \quad (1.48)$$

Because Y and Z can also, just as well, be treated as the independent pair, X can be represented in terms of them.

$$X = X(Y, Z).$$

Thus,

$$dX = \left(\frac{\partial X}{\partial Y} \right)_Z dY + \left(\frac{\partial X}{\partial Z} \right)_Y dZ.$$

When introduced on the right hand side of (1.48) this gives

$$dA = \left[\left(\frac{\partial A}{\partial X} \right)_Y \left(\frac{\partial X}{\partial Y} \right)_Z + \left(\frac{\partial A}{\partial Y} \right)_X \right] dY + \left(\frac{\partial A}{\partial Z} \right)_Y dZ.$$

Comparing this relationship with one where Y, Z are treated as the independent pair, that is,

$$dA = \left(\frac{\partial A}{\partial Y} \right)_Z dY + \left(\frac{\partial A}{\partial Z} \right)_Y dZ,$$

we get an identity

$$\left(\frac{\partial A}{\partial Y} \right)_Z = \left(\frac{\partial A}{\partial Y} \right)_X + \left(\frac{\partial A}{\partial X} \right)_Y \left(\frac{\partial X}{\partial Y} \right)_Z. \quad (1.49)$$

By making a cyclic change of the variables – such that, Y goes to Z , Z goes to X , and X goes to Y – we get two other equivalent relationships:

$$\left(\frac{\partial A}{\partial Z} \right)_X = \left(\frac{\partial A}{\partial Z} \right)_Y + \left(\frac{\partial A}{\partial Y} \right)_Z \left(\frac{\partial Y}{\partial Z} \right)_X, \quad (1.50)$$

and

$$\left(\frac{\partial A}{\partial X} \right)_Y = \left(\frac{\partial A}{\partial X} \right)_Z + \left(\frac{\partial A}{\partial Z} \right)_X \left(\frac{\partial Z}{\partial X} \right)_Y. \quad (1.51)$$

For future reference, these will be called mixed identities.

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