Thermodynamics for Materials and Metallurgical Engineers

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Preface

There are four reasons to write another textbook on thermodynamics for students involved with materials.

First is to add a richer historical context for the subject than is normally found in texts. Often students think thermodynamics is a collection of formulas to be memorized devoid of practical meaning when, in fact, the subject is rich in practical historical significance. Thermodynamics is a beautiful subject with a rich history of clever people many who often had only practical reasons for their work. However, as it turned out they, along with theoreticians, provided tremendous insight into the fundamentals of what we now call thermodynamics. Even though the author has taught the subject nearly 50 times in the last 40 years, he is still finding new and fascinating insights into the historical underpinnings of the subject. This text attempts to keep these connections with the subject. By so doing, the student gains a richness that carries more meaning than just a rigorous treatment so commonly found in texts. The adding of historical context is not meant to denigrate the pure formal treatment of the subject. Indeed, that has its own appeal and place but more so for those first initiated in thermodynamics.

Second is to reduce the cost of the textbook for the student. This is accomplished by making this a digital text which is also available in hard copy through TMS for a modest charge. Reduced pricing for Material Advantage members promotes student membership in the student chapters.

Third is convenience. Many universities require laptop computers and nearly every student has one. So, it makes sense that a digital text is paired with the laptop. Special pricing is possible when universities preload software resources on laptops. Digital form also permits students to print selected chapters to carry to the classroom thereby reducing the load they need to carry from class to class. Also, digital form obviates the undesirable ritual of selling textbooks at semester's end.

Fourth is purely one of author preference. When one writes a text, it is exactly as the author prefers. Chances are small that the author's preferences match another professor's, but it is certainly *perfect* for the author. The good news is, however, that since the text is in digital form, arrangements can be made to rearrange and add content including changing notation with the *replace* command. This alludes to an eventual open source textbook, which is inherently uncontrollable but this is as it should be with a subject so beautifully and powerfully fundamental.

The author acknowledges considerable influence from three thermodynamic texts that have played a significant role in his learning of the subject: *Principles of Chemical Equilibrium* by Kenneth Denbigh and *Chemical Thermodynamics* by Irving M. Klotz. As young professor the author used for a few years *Physical Chemistry for Metallurgists* by J. Mackowiak and employed some ideas from Mackowiak in describing the First Law. For several decades up to the writing of this text, the author relied on David Gaskell's *Introduction to Thermodynamics for Materials Engineers* and editions preceding the current fifth edition.

Chapter 0
Basic Concepts
- **The Zeroth Law of Thermodynamics**
- **Definitions**
- **Mathematical Requirements**

The Zeroth Law of Thermodynamics was an after thought occurring after the First, Second, and Third Laws of Thermodynamics were stated. It acknowledges that thermal equilibrium occurs between bodies of the same degree of hotness, which in today's vernacular is equivalent to temperature. Before heat was known to be a form of energy and thought to be a caloric fluid that was somewhat mystically related to objects, the concept of thermal equilibrium involved more than degree of hotness or temperature. For example, when small metal chips were made during the boring of canons, *Caloric Fluid Theory* held that the metal chips were hot because the 'fluid' flowed into the smaller pieces. In view of the complex and long-abandoned caloric theory, the Zeroth Law observation that only degree of hotness fixes thermal equilibrium is elegant in its simplicity and validity.

The Zeroth Law of Thermodynamics
The Zeroth Law of Thermodynamics states that if two bodies, a and b, are each in thermal equilibrium with a third body, c, then they are in thermal equilibrium with each other and that the only germane property the bodies have in common is the *degree of hotness*. This is a simple Euclidean relationship is expressed as follows where the function *h* is the measure of hotness.

$$\text{If} \quad h(a) = h(c) \text{ and } h(b) = h(c),$$
$$\text{then} \quad h(a) = h(b).$$

Hotness and temperature are so intertwined in today's language that the terms are used interchangeably and one immediately thinks bodies with the same hotness are also at the same temperature. This is true but temperature is a defined measure not an observed natural property. Indeed, there was a time that temperature was unused, undefined and unknown but thermal equilibrium could still be defined through observable hotness. Temperature scales have been defined in many different ways including the first Fahrenheit scale that assigned zero to body temperature and 100 to a salt-ice-water eutectic mixture. This was later reversed so that 100 F was body temperature (actually 98.6 F) and salt-ice-water eutectic was 0 F (actually -6.0 F). This flexibility in the definition of temperature scales illustrates that as temperature scales were being established there was no inherent relationship between hotness and temperature. The laws of thermodynamics arise from observations of nature; consequently, the Zeroth Law does not rely on a defined temperature scale but only observable *hotness*. The *Absolute Thermodynamic Temperature Scale* is defined in Chapter 2.

Definitions
Other defined concepts that will be needed throughout this text are for *systems* and *variables*.

A system is defined as a part of the universe selected for consideration. Everything that has any interaction with the system is termed the surroundings. Systems may be *open*, *closed*, or *isolated*. Open systems can exchange both mass and energy with the surroundings; closed systems exchange energy but no mass; isolated systems exchange neither mass nor energy. A variable describing a particular piece of matter is said to be *extensive* if its value depends on the quantity of the matter being described. For example, total heat capacity and mass are both extensive variables as opposed to *intensive* variables such as density, specific heat capacity, and temperature, which are intrinsic to the matter and independent of quantity. In When Gibb's Phase rule is presented later in the text, it will be shown that fixing any two intensive variables for a pure material will fix all other intensive variables.

Throughout this text the terms variables and functions are often used interchangeably. A very important and mutually exclusive distinction is made between *path* and *state* functions. A function is said to be a state function if the change in the function while going from state *a* to state *b* is the same regardless of the path taken to move from state *a* to state *b*. The change in path functions do depend on the path taken. Illustrations of path functions will be given in Chapter 1 but suffice it to say here that most variables – but not all - are state functions including variables such as temperature, pressure, and volume. State functions are *exact* in the mathematical sense, which is to say that they may be differentiated in any order and the same result is obtained.

A process is said to be *reversible* while going from state *a* to state *b* if it could be returned to state *a* while leaving no more than a vanishingly small change in the surroundings. There is no requirement that the system actually return to the original state only that it could while leaving no more than a vanishingly small change in the surroundings. An *irreversible* process is one that requires some significant change in the surroundings were the system to be returned to its original state. This is illustrated by considering a compressed gas in a steel gas cylinder fitted with a frictionless piston. If the valve on the tank is opened so that the compressed gas (state *a*) inflates a balloon (state *b*), there is no way to return the gas to its original state without employing some substantial work to force it back into the high-pressure state inside the tank. Figure 1 shows in theory a way to reversibly take a compressed gas to a low-pressure. As the gas expands it lifts sand which is continuously moved to an infinite array of shelves. As the gas expands, the sand is lifted and deposited on the shelves. The accompanying gas expansion is reversible since the gas can be returned to its original state by moving the sand stored on the shelves back onto the plate originally holding the sand. Perhaps one additional grain of sand might need to be lifted at the top of the expansion to commence the compression. This one extra grain falling from the top to the bottom of the stroke could be said to be a *vanishingly small change* in the surroundings; therefore, the expansion process is said to be reversible. It is noteworthy that a gas compression process is inherently reversible because the work of compressing the gas is always available to return the surroundings to their original state. Also, friction necessarily causes a process to be irreversible since there is no way to reclaim the energy lost to friction for use for returning a system to its original state.
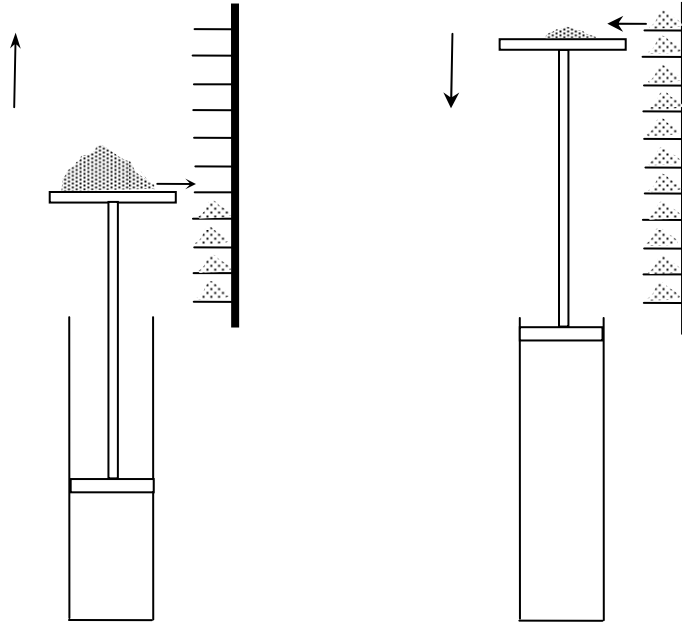
Figure 0.1 Reversible gas expansion process

Required Mathematical Tools
Mathematical tools from calculus required for the successful completion of this text are
  Differentiation and Integration of rudimentary functions
  Differentiation by the quotient rule and the product rule
  Integration by parts
  Total differentiation
  Properties of partial derivatives,
  Numerical integration using the trapezoid rule
  L'Hopital's Rule

Chapter 1
The First Law of Thermodynamics – Conservation of Energy

The word *thermodynamics* is from the Greek *therme* (heat) and *dynamis* (power). It was coined by Joule[1] in 1849 to describe the evolving use and understanding of the conversion of heat to produce mechanical power in steam engines. These engines drove the rapid industrial expansion of the industrial revolution. Characterized by a renewed spirit of inquiry and discovery in a political environment supporting such inquiry the industrial revolution required power beyond that available from manual labor, farm animals, water wheels, and wind mills. Near the end of the 17th century, inventions by Papin, and Savery pointed a way to use steam's expansion and condensation to perform useful work. In 1712 the marginally useful steam digester (Papin) and the water pump (Savery) were superseded by Thomas Newcomen's atmospheric engine that removed water from mines. Newcomen's engine was the first useful engine that produced work from heat.
http://en.wikipedia.org/wiki/Steam_engine

Practical advances in the steam engine increasingly drove the industrial revolution. Industry was being freed from the need for water wheels for industrial motive power. Industry could locate where ever there was a source of fuel. James Watt and Matthew Boulton in the late 18th century successfully marketed an improved efficiency steam engine by sharing the energy savings of their engines with their customers. Paralleling early advances in the practical advances in the steam engine was an ill-defined theoretical understanding of heat, work, and the maximum work attainable from heat that begged for definition. Clarity had to wait for several underlying principles: the true nature of heat as a form of energy, the Ideal Gas Law, and the absolute temperature scale.

Great effort was directed on producing the most work for the least heat since fuel was an expensive and limited resource. Many dubious theories were advanced: some claiming there was no theoretical limit on how much work could be extracted from heat – only practical limits. The quest for defining efficiency was finally realized, in the theoretical sense, by the work of Sadi Carnot in 1824 when he published and distributed in his ideas in an obscure booklet entitled *Reflections on the Motive Power of Fire.* This booklet was discovered by Claussius?? by chance at a news stand that stocked one of the few copies of Carnot's work. In the decades after his work became widely known, Carnot's ideas formed the basis of work by others including Classius and Claperyon. Carnot's accomplishment is remarkable because he did not have the advantage of the Ideal Gas Law advanced by Émile Clapeyron in 1834 or an absolute temperature scale defined by Lord Kelvin in 1848. Carnot was educated in Paris at the École polytechnique. He was a military engineer but after Napoleon's defeat in 1815, Carnot left military service and devoted himself to his publication (in England?). Carnot was a contemporary of Fourier of heat transfer fame, who held a chair at the École polytechnique.

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[1] Perrot, Pierre (1998). *A to Z of Thermodynamics*. Oxford University Press. ISBN 0-19-856552-6. OCLC 123283342 38073404

Carnot's short life (1796-1834) coincided with the period during which the Caloric Fluid Theory of heat was being debunked. In 1798 Count Rumford proposed that heat was not a fluid but rather a form of energy. Although Carnot lived in the world of controversy on these competing views of heat, the controversy, which ended with Joule's work in 1840, it did not prevent Carnot's progress. Today we accept heat to be a form of energy, not a caloric fluid, and it seems likely Carnot knew this as well. However, his thinking about steam engine efficiency was illustrated in fluid terms. He thought of heat as water driving a water wheel to produce work. The heat's temperature driving a steam engine was analogous to the water's height. The farther the water fell over the water wheel, the greater the work produced; the farther the temperature used to power a steam engine dropped, the greater the work produced.

Today's student arrives in the classroom with a better understanding of heat and work than the pioneers who built steam engines had. Trailing the builders by about a century, theoreticians eventually defined the theoretical limitations of the conversion of heat into work. Steam engines were followed by the internal combustion engine and the turbine engine. All convert the heat from fuel combustion into work and are now generalized as heat engines. They all have the same theoretical limitations described by the early thermodynamicists. The work of these early thermodynamicists are important for every engineer to know. Even more important for the materials and metallurgical engineer is that the analysis of heat engines leads to an understanding of entropy, the basis of predicting if a process is possible. Entropy is the arrow of time, but before it can be presented one must understand heat engines.

First Law of Thermodynamics
The First Law of Thermodynamics may be stated as follows:

In an isolated system of constant mass, energy may be distributed in different forms but the total energy is constant.

The term *system* means a region of space under consideration.
The term *isolated* means that no mass or energy is allowed to enter or leave the system.
The term *constant mass* precludes the occurrence of nuclear processes.

Figure 1.1 shows some of the many forms of energy. The First Law is a statement of conservation of energy. The analysis of heat engines involves only three of the many forms of energy shown in Figure 1.1: internal energy, heat, and work. The inclusion of heat (q) and work (w) are understandable since they are the forms of energy under consideration in heat engines. The internal energy, U, is needed to account for the change of the working fluid's (steam) energy. The internal energy is the total energy of all the molecular motion, bonding energy, etcetera, within the working fluid. As the working fluid's temperature is changed, by the addition or removal of heat, the working fluid's internal energy changes. Therefore, the change in the working fluid's internal energy is related to the amount of heat exchanged with the working fluid and the work performed by the working fluid. The First Law may be written

$$\Delta U = q - w \qquad\qquad\qquad\qquad (1\text{-}1)$$

The signs on the q and w terms are completely arbitrary, but once assigned, a sign convention is established. If heat is added to the working fluid, it will raise the working fluid's internal energy. Therefore, positive q is heat *into* the system. Likewise, since a system that performs work, will decrease the internal energy, positive w is work done *by* the system. One could change any sign in Equation (1.1x) and it would simply change the sign convention.
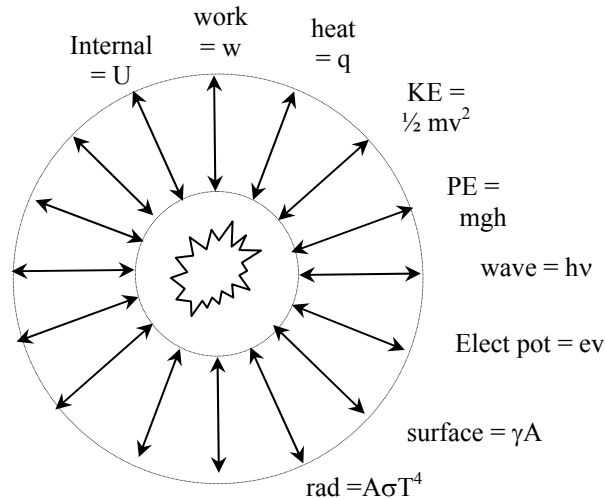

Figure 1.1 Conservation of Energy Forms

Throughout this text the sign convention set by Eq. (1.1x) will be used. Forms of energy other than heat, work, and internal energy are excluded from consideration in the First Law; however, when a system is encountered in which another form of energy is important, such as surface energy (surface tension) in nanoscience, the First Law can easily be amended. When kinetic energy, potential energy, and friction are included, the resulting equation is called the Overall Energy Balance used in the analysis of fluids in piping systems. Such amendments are beyond the scope of this text.

The focus of this chapter is the use of the First Law to analyze the behavior of gases undergoing selected processes so as to lay the foundation for understanding entropy – the arrow of time and basis of predicting by computation if a considered processes is at equilibrium, possible, or impossible. The typical processes selected for consideration are isothermal (constant temperature), isobaric (constant pressure), isochoric (constant volume), adiabatic (no heat exchange). Before such processes are considered, a review of ideal gases properties and definition of heat capacity is needed.

Ideal Gas

An ideal gas has the following properties:

- Small atoms that have volumes that are negligible compared to the volume of the container enclosing the gas
- Atoms that store energy by translation motion only ($\frac{1}{2}mv^2$), which excludes rotational, vibrational, and bond energies associated with molecules.
- Atoms that have perfectly elastic collisions with each other and with the container walls
- Atoms have no bonding interactions
- Atoms are randomly distributed within the container holding them

Ideal gases observe the Ideal Gas Law

$$PV = nRT$$

where P = pressure
V = volume
n = moles of gas
R = the gas constant
T = absolute temperature.

Energy added to an ideal gas can only be stored as kinetic energy. This energy is the internal energy of an ideal gas. As the energy of the gas increases, the velocity of the atoms increase. The internal energy is independent of the volume and, therefore, the pressure of the gas. It is a function of temperature only. A direct relationship between the internal energy of an ideal gas and temperature may be obtained from the properties of an ideal gas by considering an ideal gas with n atoms of gas having speed of c. The mass of one atom is m. If the atom with mass m moves inside a cube with edge of length L with velocity components v_x, v_y, and v_z, the force exerted by the atom in each direction is found from the rate of momentum change

$$F_x = \frac{2mv_x^2}{L}, \quad F_y = \frac{2mv_y^2}{L}, \quad F_z = \frac{2mv_z^2}{L} \tag{1-2}$$

The gas pressure is the sum of all these forces for all atoms divided by the cube's area of $6L^2$

$$P = \frac{2nmc^2}{6L^3} = \frac{2KE}{3V} \tag{1-3}$$

where the sum of the squares of the velocity components has been replaced by the atom speed squared, L^3 with volume, and nmc^2 with twice the total kinetic energy of the gas. This kinetic energy is also the internal energy of the ideal gas, which for one mole of gas gives

$$PV = \frac{2}{3}U = nRT \tag{1-4}$$

Work

It takes work to compress a gas. This work may be determined by integrating the definition of work

$$w \equiv \int_1^2 F \cdot ds \qquad (1\text{-}5)$$

The force, F, is the pressure P of the gas being compressed and A is the area of the piston compressing the gas as shown in Figure 1-2. The change in piston distance is related to the gas's volume change as shown. Substituting these expressions for F and ds in Equation (1.5) gives

$$w_C \equiv \int_1^2 P dV \qquad (1\text{-}6)$$

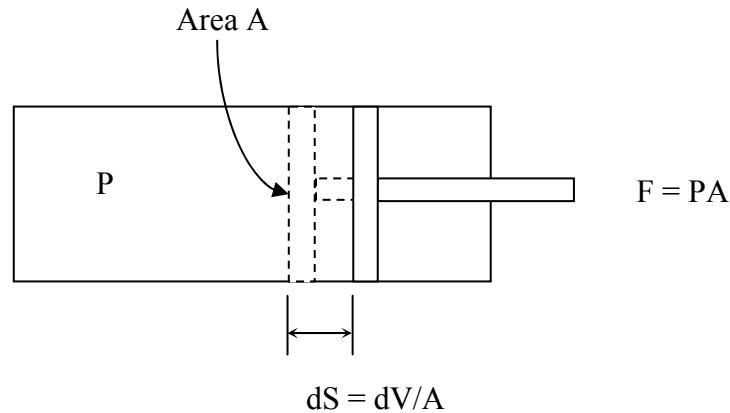Area A

P

F = PA

dS = dV/A

Figure 1.2 Relationship between pressure and force and piston distance and volume change during gas compression

If a gas undergoes expansion, the computation of work requires information about the restraining force in Equation (1.5). For example, it is possible to expand a gas without any restraining force. This is called *free expansion* and such expansion performs no work. Free expansion is rarely achieved since it requires that there is no atmospheric pressure, which requires work to displace. The opposite extreme to free expansion is *reversible* expansion. Under this condition, the restraining force is only infinitesimally less than the maximum force exerted by the gas; namely, PA. The reversible work is the maximum work that a gas can perform on expansion. Therefore the work exerted on expansion can range from maximum or reversible work all the way to the zero work of free expansion.

$$w_E \leq \int_1^2 P dV \qquad \begin{matrix} \textit{Irrev} \\ \textit{Re}\,v \end{matrix} \qquad (1\text{-}7)$$

No such range in work is needed for compression since the maximum work must always be performed on compression. For convenience and simplicity of writing equations, work will not be subscripted as either compression or expansion type work. Work will always be written as though it is maximum work and the student should must always exercise care when using the maximum work expression and make the required downward adjustments for expansion occurring under irreversible conditions. Of course, the same care must be used in computing heat during expansion since it is also a path function changing in concert with work to equal ΔU.

Equation (1.5) shows that the area under a plot of P versus V equals the work of compressing a gas as shown in Figure 1-3. If the compression proceeds along the path labeled *a*, the work required to compress the gas equals the cross-hatched area in accordance with Equation (1.6). The work done on the gas during compression is negative in agreement with the sign convention of the First Law. The sign is also fixed by the decrease in volume, which makes the change in volume negative: a good reason for First Law sign convention. This negative value for work is denoted in the figure with negatively sloped cross hatching. This convention will be observed throughout this text.
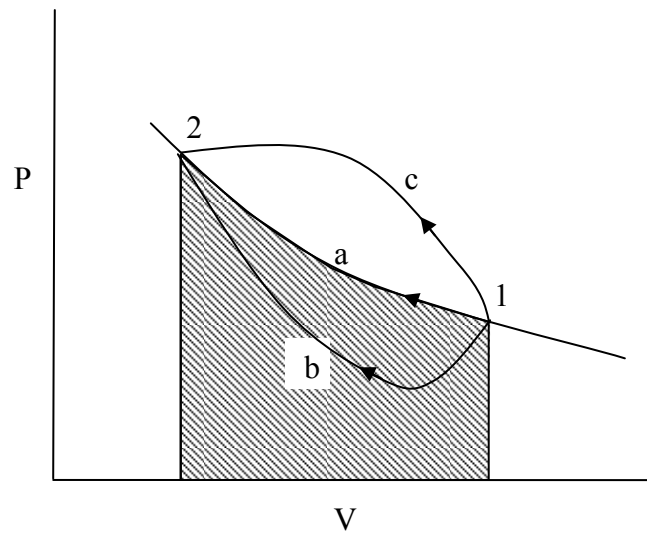

Figure 1-3 Work during gas compression.

If the compression proceeds from state 1 to state 2 along path *b*, the work as represented by the area under the P-V curve would be less than along path *a: p*roceeding along path *c* would require more work than along path *a*. Since the value of work depends on the path taken from state 1 to state 2, work is a *path function* as described in Chapter 0. This also has implications for heat because heat and work both appear in the First Law. Internal energy, which equals the difference in heat and work according to the First Law, depends only on the state of the system. Indeed, in the case of an ideal gas, the internal energy is a function of temperature only. The only way for the quality of the First Law to be maintained is for heat to change in concert with the work function of work so that their difference always equals the

change in internal energy, a state function. This means that both work and heat are path functions.

Enthalpy

Enthapy is term defined for convenience as

$$H \equiv U + PV \tag{1.7b}$$

Since all terms in the definition are state functions, enthapy is also a state function. The reason enthapy is convenient is that it is equals to the heat for a reversible isobaric process providing the only work performed is expansion type work (PdV). Friction is an example of possible other types of work. Isobaric processes are common since work occurring under atmospheric conditions is essentially isobaric. The derivation of this useful relationship begins by writing the definition in differential form

$$dH = dU + PdV.$$

Substitution of the incremental form of the First Law gives

$$dH = đq - đw + PdV \tag{ }$$

which for reversible and only expansion type work becomes

$$dH = đq_p \tag{ }$$

or

$$\Delta H = q_p \tag{ }$$

Work for selected processes

Equation (1.6) may be integrated for ideal gases under isothermal and isobaric conditions. To give

$$w_p = P(V_2 - V_1) = nR(T_2 - T_1) \tag{1-8}$$

$$w_T = \int_1^2 nRT \frac{dV}{V} = nRT \ln \frac{V_2}{V_1} \tag{1-9}$$

There can be no compression work under isochoric conditions since there is no volume change.

$$w_v = 0 \tag{1-10}$$

Under adiabatic conditions the heat is by definition zero. Therefore, according to the First Law, work is the negative of the change in internal energy.

$$w_{q=0} = -\Delta U \tag{1-11}$$

Heat Capacity

The heat capacity is the amount of heat required to raise the temperature of a material. If the heat capacity is for a specified amount of material, it is an intensive variable. Some texts distinguish between the extensive, or total, heat capacity and the intensive heat capacity. In this text the heat capacity will always refer to the intensive variable. The heat capacity is measured and reported for both isobaric and isochoric conditions as follows:

$$c_v \equiv \frac{1}{n}\left(\frac{\partial q}{\partial T}\right)_v \tag{1-12}$$

$$c_p \equiv \frac{1}{n}\left(\frac{\partial q}{\partial T}\right)_p \tag{1-13}$$

where q is the heat per gmole.

The value of c_v can be determined from Equation (1-4) since all the heat added to an ideal gas at constant volume becomes internal energy. Therefore,

$$c_v \equiv \frac{1}{n}\left(\frac{\partial q}{\partial T}\right)_v = \frac{1}{n}\left(\frac{\partial U}{\partial T}\right)_v = \frac{1}{n}\left(\frac{\partial KE}{\partial T}\right)_v = \frac{1}{n}\left(\frac{\partial (3/2)nRT}{\partial T}\right)_v = \frac{3}{2}R \tag{1-14}$$

The value for c_p for an ideal gas may be found by substituting the First Law into the definition of c_p and recognizing that kinetic energy depends on T only to give

$$c_p \equiv \frac{1}{n}\left(\frac{\partial q}{\partial T}\right)_p = \frac{1}{n}\left(\frac{\partial (U+w)}{\partial T}\right)_p = \frac{1}{n}\left[\left(\frac{\partial KE}{\partial T}\right)_p + \left(\frac{PdV}{\partial T}\right)_p\right] = c_v + R = \frac{5}{2}R \tag{1-15}$$

Heat for selected processes

The computation of heat for isochoric and isobaric processes flow directly from the definitions of c_v and c_p

$$q_v = nc_v\Delta T \tag{1-16}$$

$$q_p = nc_p\Delta T \tag{1-17}$$

For isothermal processes, the First Law requires that the heat associated with a process equals the sum of the work and internal energy. However, the internal energy of an ideal gas

is a function of temperature only making its change zero. Therefore, for isothermal processes involving ideal gases

$$q = w = nR \ln \frac{V_2}{V_1} \qquad \qquad (\ )$$

Of course, q = 0 for adiabatic processes.

ΔU and ΔH for selected processes
Both internal energy and enthalpy are state functions. Any equation that relates a change in a state function for a particular change in state is valid for any path. This means that a derivation for a change in a state function that relies on a certain path as part of the derivation does not encumber the result with the path constraints. For example, in the case of internal energy one may write based on the definition of c_v

$$đq = nc_v dT \qquad \qquad (\ )$$

but $đq = dU$ since $đw = 0$ for a constant volume process. Therefore,

$$dU = nc_v dT \qquad \qquad (\ )$$

Now the significance of state functions and the above comments come into focus. Even though the derivation relied on the assumption of constant volume, there is no such restriction on the resulting equation because internal energy is a state function. Therefore, the change in internal energy for any process can be computed from

$$\Delta U = nc_v \Delta T \qquad \qquad (\ )$$

In the case of enthapy

$$đq_p = nc_p dT \qquad \qquad (\ )$$

but $đq_p = dH$. Therefore,

$$\Delta H = nc_p \Delta T \qquad \qquad (\ )$$

for all processes.

Temperature-Pressure-Volume relationships for selected processes

For a specified number of moles, the Ideal Gas Law is a constraint between the three state variables V, P, and T. Specifying any two of the these three variables fixes the remaining state variable. If the system then undergoes a specified process (isothermal, isobaric, isochoric, adiabatic), only one final state variable needs to be specified to fix all state variables in the final state. Useful relationships for each of the specified relationships are now given.

Isothermal: $\qquad$ $PV = \text{constant}$ $\qquad$ $\dfrac{P_1}{P_2} = \dfrac{V_2}{V_1}$ $\qquad$ ( )

Isochoric: $\qquad$ $\dfrac{P}{T} = \text{constant}$ $\qquad$ $\dfrac{P_1}{P_2} = \dfrac{T_1}{T_2}$ $\qquad$ ( )

Isobaric: $\qquad$ $\dfrac{V}{T} = \text{constant}$ $\qquad$ $\dfrac{V_2}{V_1} = \dfrac{T_2}{T_1}$ $\qquad$ ( )

Reversible adiabatic:

Since this condition involves heat rather than any of the three terms in the Ideal Gas Law, an indirect method for arriving at T-P-V relationships is required. The derivation begins with the First Law with dq = 0

$$dU = -dw \qquad\qquad ()$$

Substitution for each term gives

$$nc_v dT = -PdV$$

Substitution of the Ideal Gas Law for P and rearranging gives

$$\frac{dT}{T} = -\frac{R}{c_v}\frac{dV}{V}$$

Upon integration the relationship between state 1 and state 2 temperatures and volumes is determined.

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{R}{c_v}}$$

The Ideal Gas Law can be used to replace either the temperatures or volumes with pressures to give

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{\frac{R}{c_p}} \qquad\qquad \left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{c_p}{c_v}}$$

P vs V Plots

The P versus V plot will be used throughout the early chapters of this text so additional discussion of them is warranted. Figure 1.4 shows paths for isobaric, isochoric, isothermal, and adiabatic compression of an ideal gas. The reversible-adiabatic process is steeper than an isothermal process since the work of compression increases the temperature of the gas whereas the temperature remains the same during an isothermal process.
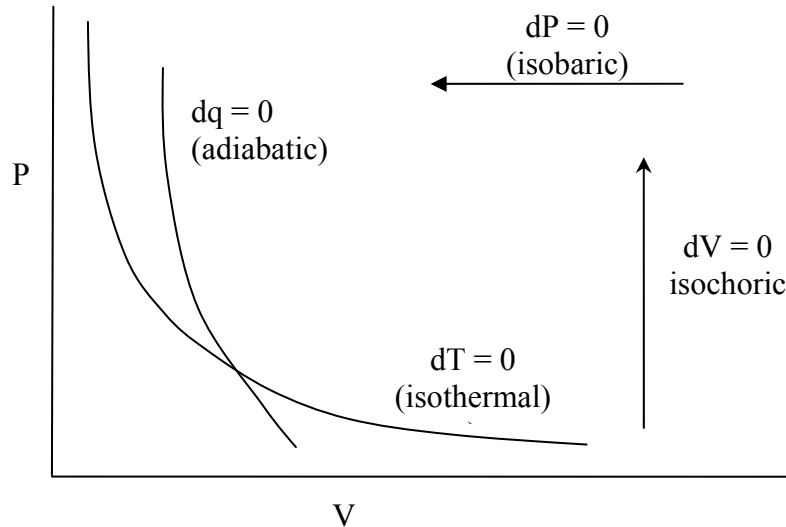

Figure 1-4 Paths for selected processes.

Summary

Table 1 summarizes the equations used to compute work, heat, and changes in internal energy and enthapy for selected processes as well as the associated T-P-V relationships. By the time students reach their upper-level classes, they should not navigate thermodynamics by attempting to memorize the contents of Table 1 but rather learn to use their previous knowledge to derive the contents of Table 1. The first method is memorization whereas the latter establishes a logical basis of learning that is more enduring than the results of memorization. To this end, the following table is the basis from which everything in Table 1 is obtained. Table 2 reduces to the Ideal Gas Law, work being the integral of PdV, the definitions of heat capacities, and the First Law. The student who can begin with these four fundamental ideas to obtain all of the equations enumerated in Table 1 will find mastering Chapters 1 and 2 greatly simplified compared to the student who tries to memorize or who must continually refer to Table 1.

Table 1 Summary equations for selected ideal gas compression processes

	dT=0	dP=0	dV=0	Rev adiabatic
w	$nRT\ln\dfrac{V_2}{V_1}$	$P(V_2-V_1)=nR(T_2-T_1)$	0	$-\Delta U$
q	w	$nc_v\Delta T$	$nc_v\Delta T$	0
ΔU	0	$nc_v\Delta T$	$nc_v\Delta T$	$nc_v\Delta T$
ΔH	0	$nc_p\Delta T$	$nc_p\Delta T$	$nc_p\Delta T$
T_2	T_1	$T_1\dfrac{V_2}{V_1}$	$T_1\dfrac{P_2}{P_1}$	$T_1\left(\dfrac{P_2}{P_1}\right)^{R/c_p}=T_1\left(\dfrac{V_2}{V_1}\right)^{R/c_v}$
P_2	$P_1\dfrac{V_1}{V_2}$	P_1	$P_1\dfrac{T_2}{T_1}$	$P_1\left(\dfrac{T_1}{T_2}\right)^{c_p/R}=P_1\left(\dfrac{V_2}{V_1}\right)^{c_p/c_v}$
V_2	$V_1\dfrac{P_1}{P_2}$	$V_1\dfrac{T_2}{T_1}$	V_1	$V_1\left(\dfrac{T_1}{T_2}\right)^{c_v/R}=V_1\left(\dfrac{P_2}{P_1}\right)^{c_v/c_p}$

Table 2 Summary of fundamental bases for the equations for selected ideal gas compression processes

	Originating concept	Additional information or result
w	$w=\displaystyle\int_1^2 PdV$;	$PV=nRT$
q	$c_v\equiv\dfrac{1}{n}\left(\dfrac{\partial q}{\partial T}\right)_v$;	dV=0; $q_v=nc_v\Delta T=\Delta U$
	$c_p\equiv\dfrac{1}{n}\left(\dfrac{\partial q}{\partial T}\right)_p$;	dP=0; $q_p=nc_p\Delta T=\Delta H$
	$\Delta U=q-w=0$;	dT=0; $q_T=w$
ΔU	$c_v\equiv\dfrac{1}{n}\left(\dfrac{\partial q}{\partial T}\right)_v=\dfrac{1}{n}\left(\dfrac{\partial U}{\partial T}\right)$;	$\Delta U=nc_v\Delta T$
ΔH	$c_p\equiv\dfrac{1}{n}\left(\dfrac{\partial q}{\partial T}\right)_p=\dfrac{1}{n}\left(\dfrac{\partial H}{\partial T}\right)$;	$\Delta H=nc_p\Delta T$
T_2, P_2, V_2	$\dfrac{P_2V_2}{T_2}=\dfrac{P_1V_1}{T_1}$	For $T_1=T_2$, $P_1=P_2$, or $V_1=V_2$
	$dU=-dw$; $nc_vdT=-PdV$	For reversible adiabatic processes

Example Problems

Problems

There are almost as many formulations of the second law as there have been discussions of it.
— Philosopher / Physicist P.W. Bridgman, (1941)

Chapter 2
The Second Law of Thermodynamics – The Arrow of Time
Basic Concepts
- **The Zeroth Law of Thermodynamics**
- **Definitions**
- **Mathematical Requirements**

If we see a film clip of a match being struck, bursting into flame, and slowing burning out, we think nothing beyond the process as viewed; however, if the clip is run in reverse we are immediately aware that we are observing something impossible. The impossibility of the process is precisely the reason the process grabs our attention. Rocks do not run up hill. Explosions do not collect tiny fractured bits of debris together through a huge fireball that continues to shrink into some undestroyed structure rigged with an explosive device. Each of us has learned from an early age that natural processes have a predictable sequence that is called in this text the *arrow of time*. Learning this arrow of time – the direction of natural processes - provides the predictability necessary to our functioning.

In the case of chemical reactions, we understand the direction of many processes but not all. Processes such as combustion of natural gas with air or the reaction of vinegar with baking soda are known, but few people would know by experience what, if any, reaction might occur if aluminum oxide is mixed with carbon and heated to 1000 °C. It turns out no reaction occurs at atmospheric pressure, but the more interesting question is *can one calculate if a reaction is favorable* and *what is the basis for making such a computation*. Often students suggest that predicting the down-hill direction of rocks involves nothing more than determining the direction for the reduction of potential energy. That works for rocks but potential energy has no value in trying to predict the direction of chemical reactions. In that case students often - and incorrectly – think that a reaction is favorable if it liberates heat, but if it were so simple then endothermic reactions would never occur: yet they do. Therefore, there must be more to the prediction of reactions than simply thermicity.

The Second Law of Thermodynamics defines a quantity called *entropy* that allows predicting the direction of chemical reactions, the direction rocks roll, and the direction of all physical processes. Figure 2.1 illustrates the direction of change in three systems. In Figure 2.1 a) a pendulum moves from position A towards B while at position B it moves toward A. At equilibrium it rests between A and B. In Figure 2.1 b) spontaneous change is shown in terms of ice and water, which is at equilibrium at ice's melting temperature. Figure c) shows a general spontaneous change and equilibrium in a system comprised of material A and B. In all processes, spontaneous change can be shown to be accompanied by an increase in total entropy.

For an unfamiliar reaction, the direction of the reaction is unknown so one assumes it proceeds as written. For example, a reaction might be assumed to proceed to the right when written as
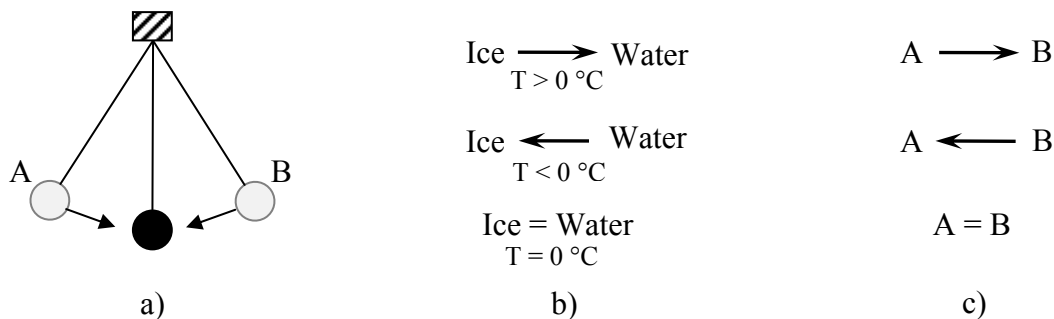
Figure 2.1 Three possible scenarios for a system involving State A and State B.

$$aA + bB \rightarrow cC \tag{2.1}$$

and the total entropy change computed. If the total entropy change > 0, then the assumed direction is correct. On the other hand if total entropy change < 0, then the actual spontaneous process direction is the opposite of the assumed direction and the direction of the reaction is to the left. A zero total entropy change indicates the reaction is at equilibrium. The arrow of time corresponds to increases in total entropy. Such processes are spontaneous or natural processes.

Now that the usefulness of the entropy is established, the value of the Second Law of Thermodynamics from which entropy arises should be greatly appreciated. The Second Law of Thermodynamics is based on observation of the natural world and permits the prediction of the processes direction through the computation of total entropy change. This direction corresponds to the *arrow of time*.

The Second Law of Thermodynamics in verbal form is stated as follows:

It is impossible to take a quantity of heat from a body at uniform temperature and convert it to an equivalent amount of work without changing the thermodynamic state of a second body.

Most students do not find much meaning in this statement of experimental observation. Figure 2.2 is the author's pedagogical device for making the Second Law more understandable. The figure consists of a tank of water at uniform temperature with a thermometer along the left side to measure the water's temperature. A weight on the right side is connected to a mixer inside the tank so that as the weight falls the mixer spins. In the normal course of events, the potential energy of the weight is converted to heat inside the tank of water and the water's temperature increases. However, the Second Law is stated for the impossible case in which heat from the water as indicated on the diagram by the falling water temperature, is converted to work that lifts the weight. This is impossible. It has never been observed and try as one might there has never been a reproducible experiment in which heat from a body at uniform temperature (the water in this case) has been converted to an equivalent amount of work (raising the weight in this case) without changing the

thermodynamic state of a second body. A second body is not needed in the example in Figure 2.2 since there is no change in any such body in the impossible case.
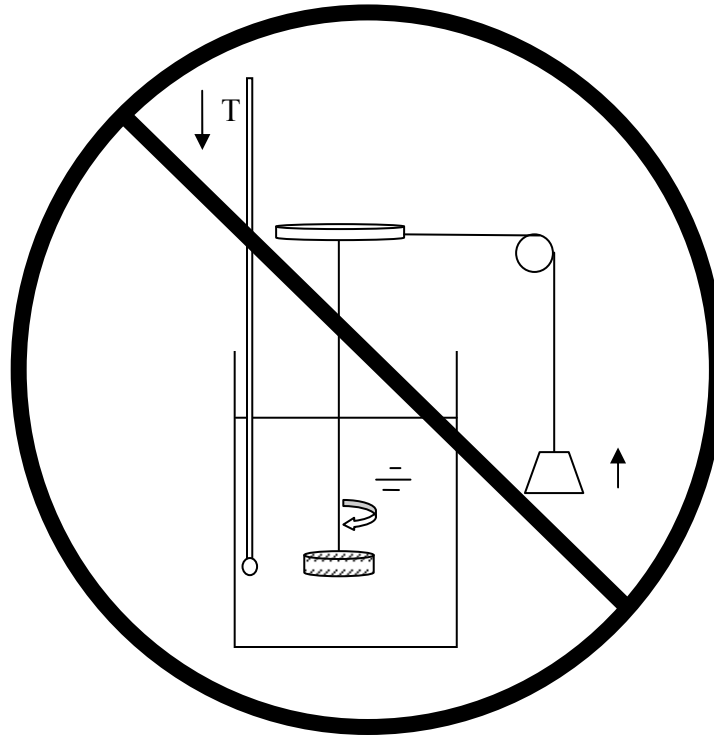

Figure 2.2 The Second Law of Thermodynamics in graphical format.

The mathematical statement of the Second Law is for a closed system

$$\frac{dq}{T}\bigg)_{Rev} \geq 0 \quad \square_{Rev}^{Irrev} \tag{2.2}$$

The left term is the definition of entropy change.

$$dS \equiv \frac{dq}{T}\bigg)_{Rev} \tag{2.3}$$

The definition requires that the change in entropy is computed under the constraint of reversible conditions. There are two primary processes that will be of interest in this chapter: heat transfer and gas expansion. Reversible means different conditions for each. For heat transfer the entropy change for a single body is computed using the body's temperature for the T in the denominator of the definition of entropy. In the case of gas expansion, reversible requires that the expansion occurs reversibly, which means that the gas performs maximum work during the expansion. It makes no difference if the actual expansion occurred

reversibly. Gas compression is always reversible so maximum work is always performed during compression.

When a gas undergoes expansion, the entropy change for the gas is the same regardless of whether maximum work was derived from the expansion or not. However, this does not mean that the total entropy change for the expansion is the same because the total entropy change includes the change in the heat sink, which undergoes a considerably different entropy change depending on how much work the gas actually does during the expansion. It is important to remember that reversible means different conditions for different kinds of processes. For the gas it means maximum work: for the heat sink it means the T in Equation (2.3) is the temperature of the heat sink and has nothing to do with the amount of heat transferred to the gas as it undergoes its expansion – reversibly or not.

Example 2.1: Find the total entropy change for 1000 joules of heat conducting from a massive body of copper at 500K to another massive body of iron at 400 K.
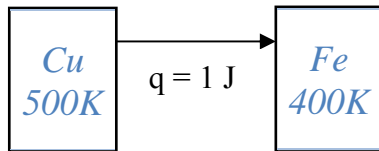
$$\Delta S_{Cu} = \int dS = \int \left(\frac{dq}{T}\right)_{Rev} = \int \frac{dq}{T_{Cu}} = \frac{q}{T_{Cu}} = \frac{-1000\,J}{500\,K} = -2.0\,\frac{J}{K}$$

$$\Delta S_{Fe} = \int dS = \int \left(\frac{dq}{T}\right)_{Rev} = \int \frac{dq}{T_{Fe}} = \frac{q}{T_{Fe}} = \frac{1000\,J}{400\,K} = 2.5\,\frac{J}{K}$$

$$\Delta S_{Total} = \Delta S_{Cu} + \Delta S_{Fe} = 0.5\,\frac{J}{K} > 0 \quad \text{Possible}$$

Example 2.2: Find the total entropy change for 1000 joules of heat conducting from a massive body of copper at 500K to another massive body of iron at 500 K.

$$\Delta S_{Cu} = \int dS = \int \left(\frac{dq}{T}\right)_{Rev} = \int \frac{dq}{T_{Cu}} = \frac{q}{T_{Cu}} = \frac{-1000\,J}{500\,K} = -2.0\,\frac{J}{K}$$

$$\Delta S_{Fe} = \int dS = \int \left(\frac{dq}{T}\right)_{Rev} = \int \frac{dq}{T_{Fe}} = \frac{q}{T_{Fe}} = \frac{1000\,J}{500\,K} = 2.0\,\frac{J}{K}$$

$$\Delta S_{Total} = \Delta S_{Cu} + \Delta S_{Fe} = 0\,\frac{J}{K} \quad \text{Equilibrium}$$

Example 2.3: Find the total entropy change for 1000 joules of heat conducting from a massive body of copper at 400K to another massive body of iron at 500 K, which is impossible.

$$\Delta S_{Cu} = \int dS = \int \left(\frac{dq}{T}\right)_{Rev} = \int \frac{dq}{T_{Cu}} = \frac{q}{T_{Cu}} = \frac{-1000\,J}{400\,K} = -2.5\,\frac{J}{K}$$

$$\Delta S_{Fe} = \int dS = \int \left(\frac{dq}{T}\right)_{Rev} = \int \frac{dq}{T_{Fe}} = \frac{q}{T_{Fe}} = \frac{1000\,J}{500\,K} = 2.0\,\frac{J}{K}$$

$$\Delta S_{Total} = \Delta S_{Cu} + \Delta S_{Fe} = -0.5\,\frac{J}{K} < 0$$

Impossible, The heat actually goes the other direction.

Example 2.4: Find the total entropy change when a rock rolls down a hill at 300 K. Assume the rock's potential energy change, which ends up as heat in the hill, equals 3000 Joules and that the rock (after some time) returns to its original temperature of 300 K.

$$\Delta S_{Hill} = \int dS = \int \left(\frac{dq}{T}\right)_{Rev} = \int \frac{dq}{T_{Hill}} = \frac{q}{T_{Hill}} = \frac{3000\,J}{300\,K} = 10\,\frac{J}{K}$$

$$\Delta S_{Rock} = \int dS = \int \left(\frac{dq}{T}\right)_{Rev} = 0$$

$$\Delta S_{Total} = \Delta S_{Hill} + \Delta S_{Rock} = 10\,\frac{J}{K} > 0 \quad \text{Possible}$$

Example 2.5: Find the total entropy change for the isothermal expansion of two moles of ideal gas at 10 atm and 500 K to 1 atm in contact with a heat sink at 500 K while performing a) maximum work, b) 70 percent of the maximum work, c) no work.

The entropy change for the gas is the same regardless of how the much work the gas actually does during the expansion.

$$\Delta S_{Gas} = \int dS = \int \left(\frac{dq}{T}\right)_{Rev} = \int \frac{dw_{Max}}{T_{Gas}} = \frac{w_{Max}}{T_{Gas}} = \frac{nRTln\left(\frac{10}{1}\right)}{T_{Gas}} = 2Rln(10)$$

The entropy change for the sink is the amount of heat from the sink divided by the sink's temperature. The amount of heat from the sink to the gas is the same as the work actually performed by the gas. The gas's heat gain is the sink's loss; therefore

$$q_{Sink} = -q_{Gas}$$

and

$$\Delta S_{Sink} = \int dS = \int \left(\frac{dq}{T}\right)_{Rev} = \int \frac{-dq_{Gas}}{T_{Sink}} = \frac{-q_{Gas}}{T_{Sink}} = \frac{-q_{Gas}}{300K}$$

a)   Maximum work

$$q_{Gas} = nRTln(10)$$

$$\Delta S_{Total} = \Delta S_{Gas} + \Delta S_{Sink} = 2Rln(10) - 2Rln(10) = 0$$

Reversible process conducted under equilibrium conditions.

b)   70 Percent maximum work

$$q_{Gas} = 0.7nRTln(10)$$

$$\Delta S_{Total} = \Delta S_{Gas} + \Delta S_{Sink} = 2Rln(10) - 1.4Rln(10) = 0.6Rln(10) > 0$$

Possible and conducted under irreversible conditions.

c)   No work

$$q_{Gas} = 0$$

$$\Delta S_{Total} = \Delta S_{Gas} + \Delta S_{Sink} = 2Rln(10) - 0 = 2Rln(10) > 0$$

Possible but conducted under irreversible conditions.

Example 2.6: Find the total entropy change for the same conditions as Example 2.5a except for a sink temperature of a) 700 K and b) 300 K.

The entropy change for the gas is the same regardless of how the much work the gas actually does during the expansion.

$$\Delta S_{Gas} = 2Rln(10)$$

The entropy change for the sink is as before

$$\Delta S_{Sink} = \int dS = \int \left(\frac{dq}{T}\right)_{Rev} = \int \frac{-dq_{Gas}}{T_{Sink}} = \frac{-q_{Gas}}{T_{Sink}} = \frac{-2R(300K)ln(10)}{T_{Sink}}$$

a)   S

ink T=700 K

$$\Delta S_{Total} = \Delta S_{Gas} + \Delta S_{Sink} = 2R\ln(10) - \frac{2R(300K)\ln(10)}{700\ K} = \frac{4R\ln(10)}{7} > 0$$

Possible but conducted under irreversible conditions.

a)   S

ink T=300 K

$$\Delta S_{Total} = \Delta S_{Gas} + \Delta S_{Sink} = 2R\ln(10) - \frac{2R(300K)\ln(10)}{300\ K} = -\frac{4R\ln(10)}{3} < 0$$

Impossible because heat cannot flow from a 300 K heat sink into a gas at 500 K; however, the process could occur in the opposite direction (i.e. - compression rather than expansion).

The Four Propositions
The Second Law of Thermodynamics is said to be stated as many ways as those writing about it. The statement used in this chapter is based on Denbigh[1]. Denbigh's treatment of thermodynamics in *Principles of Chemical Equilibrium* is beautifully concise and formal. It is recommended for students who have completed the corresponding subjects in this text. Denbigh presents four propositions arising from the Second Law statement. The proofs for these propositions are given in Appendix A. The propositions are stated here.

Proposition 1
>   For a Carnot cycle operating between a heat sink at hotness t_1 and hotter sink at hotness t_2 and exchanging the corresponding heats q_1 and q_2 to the working fluid that

$$\frac{q_2}{q_1} = f(t_2, t_1)$$

(2.4)

Proposition 2
>   The Thermodynamic Temperature Scale is defined by the ratio of heats exchanged in a Carnot cycle.

$$\frac{|q_2|}{|q_1|} = \frac{f(t_2)}{f(t_1)} = \frac{T_2}{T_1}$$

(2.5)

Proposition 3
>   Entropy defined as

$$dS \equiv \frac{dq}{T}\bigg)_{Rev}$$

(2.6)

>   is a state function.

Proposition 4

The change in entropy is zero for a reversible process and greater than zero for an irreversible process.

$$dS \geq 0 \quad \genfrac{}{}{0pt}{}{Irrev}{Rev}$$

(2.7)

Chapter 3
The Third Law of Thermodynamics
Basic Concepts
- **Heat capacity's variation with temperature**
- **Entropy of pure crystalline materials at absolute zero**

Experimental measurements for the heat capacity of a pure crystalline material have the form shown in Figure 3.1. As the temperature approaches absolute zero, the heat capacity not only approaches zero but so does its slope. The reason for this is that as the temperature is lowered towards absolute zero the crystalline structure has fewer and fewer ways of storing energy. At absolute zero there is no additional way to store or remove energy from the crystal. According to Eq (2.3), the zero slope of Cp as the temperature approaches absolute zero requires a constant value of entropy.

$$ dS = \lim_{T \to 0} \frac{dq}{T}\Big)_{Rev} = \lim_{T \to 0} \frac{C_p dT}{T} = \lim_{T \to 0} C_p d\ln(T) = 0 $$
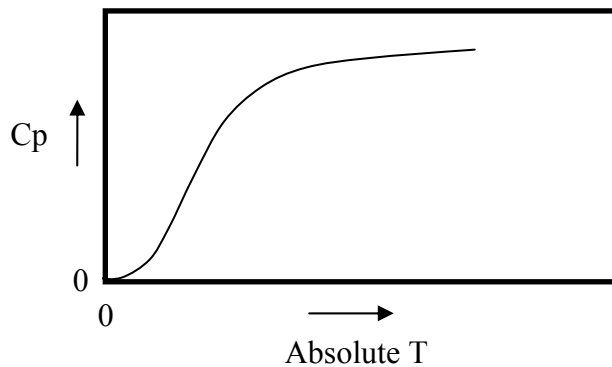
(3.1)

Figure 3.1 Heat capacity's variation with absolute temperature

In 1923 Gilbert N. Lewis and Merle Randall stated the Third Law of Thermodynamics as follows:

If the entropy of each element in some (perfect) crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances. http://en.wikipedia.org/wiki/Third_law_of_thermodynamics

The value of the Third Law is that the entropy is a material property that may be computed from experimental data. Since the entropy of a pure crystalline substance is zero at absolute zero, the absolute value of entropy may be computed at higher temperatures by integrating Eq (2.3) where $dq = C_p dT$ to give

$$S_T = \int_0^T \frac{C_p dT}{T}$$

(3.2)

Nice Web sites
http://mooni.fccj.org/~ethall/thermo/thermo.htm