

Thermodynamics of Natural Systems

Theory and Applications in Geochemistry
and Environmental Science

Third Edition
G.M. ANDERSON



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The First Law of Thermodynamics

3.1

Temperature and Pressure Scales

3.1.1

Temperature

One of the early milestones in the development of thermodynamics was the demonstration that there is an absolute zero of temperature. Nevertheless there are several different temperature scales, for historical reasons. All you need to know about this is that the Kelvin scale (named after William Thompson, Lord Kelvin) has an absolute zero of 0 K and a temperature of 273.16 K at the triple point where water, ice, and water vapor are at equilibrium together. The melting point of ice at one atmosphere pressure is 0.01 degrees less than this, at 273.15 K (Figure 3.1). The Celsius scale (named after Anders Celsius, a Swedish astronomer) has a temperature of 0 °C at the ice point (273.15 K) and absolute zero at -273.15°C . This gives almost exactly 100 °C between the freezing and boiling points of water at one atmosphere, so water boils at 100°C (373.15 K). Thus the numerical conversion between the two scales is

$$T\text{ K} = T^{\circ}\text{C} + 273.15$$

Remember that all equations in thermodynamics use the absolute or Kelvin temperature scale, so that, if you have temperatures in °C, you must convert them to the Kelvin scale before using them in equations. The “standard” temperature of 25°C for example is 298.15 K. Standard IUPAC¹ usage is to refer to temperatures on the Kelvin scale as so many kelvins, not degrees kelvin or °K. One kelvin is defined as the fraction 1/273.16 of the temperature of water at the triple point. More detail on temperature scales can be found in Anderson and Crerar (1993, Section 4.3).

3.1.2

Pressure

Force is measured in newtons (N), where 1 newton will give a mass of 1 kg an acceleration of 1 m s^{-2} . Pressure is defined as force per unit area, and a pressure of 1 newton per square meter (1 N m^{-2}) is called 1 pascal (1 Pa). This is a very small pressure, and older, larger pressure units are still in use. The bar, for example, is 10^5 Pa and is almost equal to the standard atmosphere ($1 \text{ atm} = 1.01325 \text{ bar}$). Weather reports in many countries give the atmospheric pressure in kilopascals (kPa), and it is usually close to 101 kPa, or 1 atm, or 1 bar. These units are summarized in Appendix A.

¹ International Union of Pure and Applied Chemistry.

3.2 Internal Energy

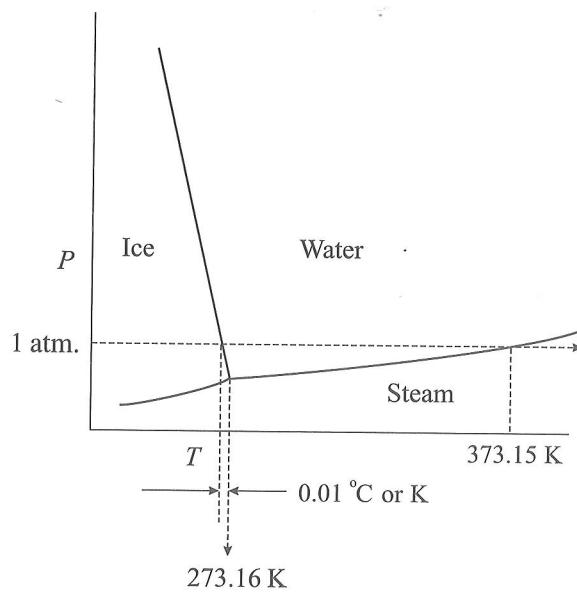


Figure 3.1 Schematic P - T phase diagram for the system H_2O . The temperature of the triple point is defined as 273.16 K. Illustrative, not to scale.

3.2

Internal Energy

In everyday conversation we use words like heat, work, and energy quite frequently, and everyone has a sufficiently good idea of their meaning for our ideas to be communicated. Unfortunately, this type of understanding is not sufficient for the construction of a quantitative model of energy relationships like thermodynamics. To get quantitative about anything, or, in other words, to devise equations relating measurements of real quantities, you must first be quite sure what it is you are measuring. This is not too difficult if you are measuring the weight of potatoes and carrots; it is a more subtle problem when you are measuring heat, work, and energy. Historically, it took several decades of effort by many investigators in the nineteenth century to sort out the difficulties that you are expected to understand by reading this chapter!

3.2.1

Energy

Everyone knows what energy is, but it is an elusive topic if you are looking for a deep understanding. In fact, a Nobel Prize-winning physicist has affirmed that

It is important to realize that in physics today, we have no knowledge of what energy *is*.

Feynman *et al.* (1963), p. 4–2

An eminent French scientist said

As we cannot give a general definition of energy, the principle of the conservation of energy simply signifies that there is *something* which remains constant.

Poincaré (1952), p. 166

If you consult a dictionary as to the meaning of energy, you find that the scientific meaning is “*the ability to do work, i.e., move a body.*” In physics, work is not what you do from 9 to 5 every day, but the action of a force moving through a distance. So, if you lift a book from the floor and put it on the table, you are performing work (the mass of the book, multiplied by the acceleration due to gravity, times the distance from the floor to the table), and we say that we expended energy to lift the book. It has proved tremendously useful to take the view that the energy we expended has not disappeared, but has been transferred to the book. In other words, the book on the table has more energy (potential energy) than it had on the floor, and the increase is exactly equal to the work we did in lifting it. Thus we can use energy to do work, and we can do work on a system to increase the energy of that system. Work and energy are thus very closely related concepts (note that they have the same dimensions in Appendix A).

If only things were that simple! However, we know that they are not, because the energy in a stick of dynamite on the table is not equal to the work expended in lifting it from the floor. Similarly, the energy in water is not the same as that in ice, irrespective of whether it is on the floor or on the table. These complications are actually of two types.

1. There are many ways of doing work, because there are many kinds of forces. We are particularly concerned with the work involved in chemical reactions.
2. Although work and energy are indeed closely related, doing work is not the only way of changing the energy of something, and changing the energy of something does not always produce work. For example, we could change the energy in our book by warming or cooling it.

We have to consider both work (in all its forms) and heat to get a consistent picture of energy changes.

3.2.2 Absolute Energy

In discussing energy, we always seem to be talking about *changes* in energy. The book has more energy on the table than on the floor, and presumably more energy on the roof than on the table. And we can add energy by warming the book too. But how much energy does the book have in any particular state – say, on the table at 25 °C? What is the absolute energy content of the book? This was a difficult question until 1905, when Einstein proposed the essential equivalence of mass and energy in his famous equation

$$E_r = mc^2 \quad (3.1)$$

where E_r is the rest energy of a system, m is the mass, and c is the speed of light. Therefore, the energy contained in any macroscopic system is extremely large, and adding energy to a system (for instance by heating it) will in fact increase its mass. However, ordinary

3.2 Internal Energy

(i.e., non-nuclear) energy changes result in extremely small and unmeasurable changes in mass, so that relativity theory is not very useful to us, except in the sense that it gives energy an absolute kind of meaning, which is sometimes helpful in trying to visualize what energy *is*.

So, in considering ordinary everyday kinds of changes and chemical reactions, we will continue to deal with energy *changes* only, never with how much energy is in any particular equilibrium state. This is entirely sufficient for our needs, but it does introduce some complications that would be avoided if we had a useful absolute energy scale.

3.2.3 The Internal Energy

Thermodynamics does not use the term E_r , but it does have a term for the energy in a system. All that is required to develop our model of energy relationships is that every equilibrium state of a system has a fixed but unknown energy content, which is called the *internal energy*, U . The numerical value of this energy content is not known, and not needed. It could be thought of as identical to the rest energy E_r , if that helps, or as some small subset of E_r ; it doesn’t really matter. All that matters is that, when the system is at equilibrium, its energy content or energy level is constant. Since we do not use absolute values of U or U , we cannot use absolute values of any of the several quantities having the internal energy in their equations of definition.

Notice that, although we have been illustrating energy and work by using the ball-in-valley idea (Chapter 2) and the book-and-table idea (this chapter), which emphasizes *potential* energy, this particular kind of energy/work is actually irrelevant in thermodynamics, except as an analogy. We will define the energy content of systems of importance to us to be the same whether they are on the floor or the table. Thermodynamics is concerned only with the internal energy U or its molar form U , no matter where the system is. This gets a little more complicated if we are considering a magma rising rapidly through the Earth’s gravitational field, but for now we will stick to U and its changes due to work and heat. For the role of gravity as well as electric and magnetic fields in thermodynamics see Guggenheim (1959) and Pippard (1966).

The Meaning of ΔU

Although the principles of thermodynamics are independent of any assumptions regarding the atomic and molecular structure of matter, it is helpful to think of internal energy as the summation of the kinetic and potential energies of the molecules of a substance. The kinetic energy of the molecules is associated with the translational, rotational, and vibratory motions of molecules, which increase as heat is added. Potential energy is related to the forces between the atoms, ions, and molecules, being large in solids, smaller in liquids and gases. A chemical reaction causes the atoms, molecules, and ions in a system to rearrange themselves, breaking some bonds and forming others, resulting in changes in their potential and kinetic energies, and therefore changes in U .

If the system is *isolated* (Section 2.2.2) this will result in a rise or fall in pressure and temperature, which are simply manifestations of the average kinetic energy of the particles (McQuarrie and Simon, 1997, Chapter 27), but the total energy U of the system does not

change. In a *closed* system, energy is permitted to enter or leave the system, so changes in the particle energies might result in energy leaving or entering the system as heat (as when the heat flow is measured in a calorimeter, Section 5.3) or as work (as when a system expands against an external pressure, Section 3.5.1).

The Internal Energy Paradox

Somewhat paradoxically, in spite of being one of the most fundamental of thermodynamic quantities, changes in U or U are little used in geochemical applications. It is never listed in tables of thermodynamic values such as those in Appendix B, for example, and one rarely needs to calculate ΔU . The reason for this will become apparent as we proceed. It has to do with the fact that we, the users of thermodynamics, have a great predilection for using temperature, pressure, and volume as our principal constraints or measured system parameters. It turns out that this requires that we use ΔU in slightly modified forms, that is, ΔU modified by what are often relatively small correction factors (such as $P \Delta V$), and these modified forms are given different names and symbols. It is then quite possible to rarely think about ΔU , since it seems only to arise in the development of the first law. For a better understanding of the subject, however, it is best to realize that, in most energy transfers in the real problems that we will be considering, ΔU is by far the largest term involved. The fact that we do not usually calculate its value does not mean it is not important.

3.3

Energy Transfers

In the discussions in the previous chapters, we proposed the idea that changes or reactions occur because systems can lower some kind of energy by such changes. However, we mentioned that the most obvious kind of energy, heat energy, was not the right kind of energy. There is another very common kind – energy expended as *work*, as when dynamite is used to break rock. However, work energy is not the answer to our questions either, nor is the combination of heat and work. Nevertheless, they are extremely important, and together form the basis of the first law.

- *Heat (q)* is energy that crosses a system boundary in response to a temperature gradient.
- *Work (w)* is energy that crosses a system boundary in response to a force moving through a distance (such as happens when a system changes volume).

These statements describe heat and work as energy transfers, but are not good definitions. In fact it has proved quite difficult to provide a rigorous definition of heat in this respect. According to the experts (e.g., Canagaratna, 1969), there is really only one. Heat is that part of any energy transfer which is not accounted for by mechanical work (which has a satisfactory definition: force \times distance), and assuming that other forms of energy transfer are negligible. That is,

$$q = \Delta U - w$$

This turns out to be not very different from the way we actually do think about heat in thermodynamics, as when we subtract a $P \Delta V$ term from some calorimetry results, and describe the remaining energy term as heat.

We use q and w for increments or amounts of heat and work in joules. If this heat or work is related to a chemical reaction we could use q and w (J mol^{-1}), but this is rarely necessary. Normally total heat and work (q and w) are measured quantities which are used to calculate the change in some state variable such as ΔU or ΔH . These state variables are then converted to their molar forms, ΔU and ΔH , for use in calculations. An example of the use of q is given on page 117, where q is measured in a calorimeter for small amounts of solid Al and Al(OH)_3 , then converted into q_P , which is enthalpy (Equation (3.32)). See the boxes on pages 46 and 49 for (total) work calculations.

The Pond Analogy

Heat and work are forms of energy that is transferred in different ways. An enlightening analogy has been offered by Callen (1985). In Figure 3.2 we consider the water in a very deep pond. The amount of water in the pond is quite large, but finite, and could in principle be measured, but is in fact unknown. It corresponds to the internal energy U of a system.

Water may be added and subtracted from the pond either in the form of stream water (heat) or precipitation/evaporation (work). Both the inlet and the outlet stream water can be monitored by flow gauges, and the precipitation can be measured by a rain gauge. Evaporation would be trickier to measure, but we may assume that we have a suitable measure for it. Now, if the volume of stream inlet water over some period of time is q_i , with volumes for the stream outlet water of q_o , for the rain of w_r , and for the evaporation of w_e , then, if there are no other ways of adding or subtracting water, clearly

$$\Delta U = (q_i - q_o) + (w_r - w_e)$$

where ΔU is the change in the amount of water in the pond, which could be monitored by a level indicator as shown. Thus

$$\Delta U = q + w \quad (3.2)$$

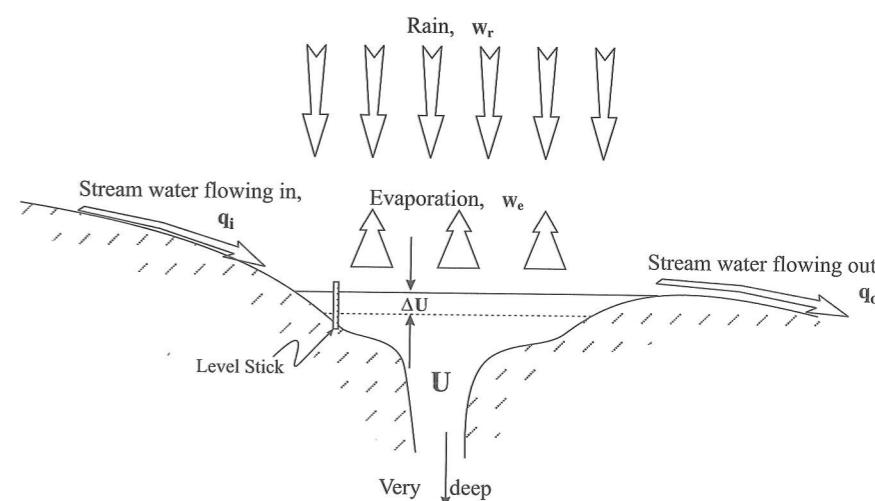


Figure 3.2 The pond analogy for the first law.

where $q = q_i - q_o$ and $w = w_r - w_e$, so changes in internal energy ΔU is given by $\Delta U = q + w$.

Once water has entered the pond, it loses its identity as stream or rain water. The pond does not contain any identifiable stream water or rain water, simply water. Similarly systems do not contain so much heat or work, just energy. Just as the water level in the pond can be raised *either* by stream water alone *or* by rain water alone, Joule showed in the nineteenth century that a temperature rise in a water bath of so many degrees can be caused *either* by heating (transferring energy due to a temperature difference) *or* by thrashing a paddle wheel about in it (transferring energy by doing work on the system).

Another implication or assumption in our pond analogy is that water is conserved; that is, it cannot simply appear or disappear as if by magic. The same proposition regarding energy is known as the first law of thermodynamics. We invoked this principle when we said that the energy expended in lifting a book from the floor to the table was not lost, but transferred to the book.

Internally Generated Energy

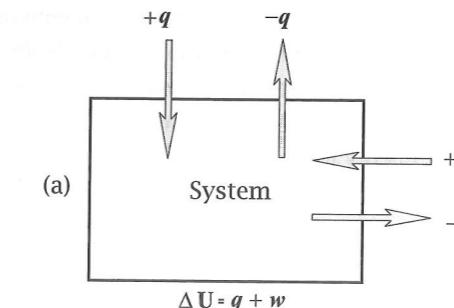
Note finally that in our pond model water enters and leaves the pond from the environment; there is no provision for water (energy) to be generated *within* the pond. However, in real systems energy *can* be generated or absorbed within a system due to chemical reactions. We will have to develop some way to take care of this. We noted in Section 2.6.1 that Prigogine and Defay (1954) refer to this energy as uncompensated heat, but that's because they specifically exclude work energy, other than whatever work is done by a change in the system volume. It is actually just energy, which does not become work or heat until it leaves the system.

3.4

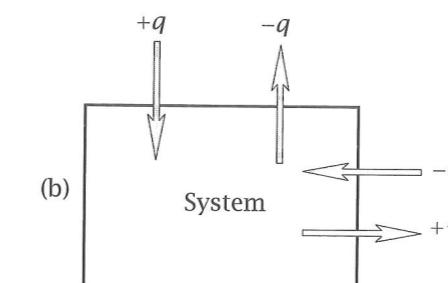
The First Law of Thermodynamics

The first law of thermodynamics is the law of conservation of energy. If U is the energy content of a system, and it may gain or lose energy only by the flow of heat (q) or work (w), then clearly, as in the pond analogy, ΔU must be the algebraic sum of q and w . In order to express this algebraically, we must have some convention as to what direction of energy flow $+q$, $-q$, $+w$, and $-w$ refer to. In the pond analogy we assumed implicitly that addition of water to the pond was positive, whether as stream water or rain water. Thus heat added *to* a system is positive, and work done *on* a system is positive. This convention may be represented as in Figure 3.3(a) and is what we call the "scientific" convention – scientists like it because it is internally consistent. It results in the equation previously found,

$$\Delta U = q + w \quad (3.3)$$



$$\Delta U = q + w$$



$$\Delta U = q - w$$

Figure 3.3 The two commonly used conventions for the sign of q and w , leading to two formulations of the first law.

3.5

3.5.1

Work

Types of Work

There are many different ways of doing work on a system depending on what kinds of forces are available, and many different ways of having a system do work. For example, consider the following examples.

Note that we have not "proved" the first law. It is a principle that has been deduced from the way things work in our experience, but the fact that it has never been known to fail does not constitute a proof. Neither does the fact that the sun has never failed to rise in the east constitute a proof that it will rise in the east tomorrow, but I wouldn't bet against it.

- The force of gravity means that we have to do work to lift objects, as mentioned above. If the mass is m , the acceleration due to gravity is g , and the distance is dh , the work w is $w = mg \cdot dh$. As mentioned in Section 3.2.3, if this work is just used to change the potential energy of the system, it is not usually of interest in thermodynamics, but in rare cases it can be used to transfer energy to a system, as when Joule used a falling weight to drive a paddle wheel in a tank of water.
- Tensile force can be used to stretch a wire. If the tensile force is f and the increase in length is dl , $w = f \cdot dl$, assuming the wire deforms elastically.
- Tensile force can be used to increase the area of a soap film. If the surface tension is γ and the increase in surface area is dA , $w = \gamma \cdot dA$.
- Expansion due to the heating of a gas, or indeed of anything at all, produces a force. This case is of special interest to us, because the work done by expansion or contraction of systems cannot be avoided. We can choose to eliminate other forms of work, but not this one (unless we consider only constant-volume systems, which is useful in theory but not very practical). It is treated in more detail below.
- Chemical work. For example, a battery can be used to do work, because a chemical reaction occurs in it, which produces a voltage. The work done by chemical reactions is of course a principal focus of chemical thermodynamics, and the equations for it will be developed in later chapters.

There are others, such as work done by centripetal and frictional forces, that you can review in a physics text. Thermodynamics can accommodate all kinds of forces and types of work, but, because they are in principle all the same, and are treated in the same way, it is simpler to develop the subject by considering only those forms of work that we cannot

Box 3.1 Other Forms of Work

A block weighing 10.0 kg is lifted 4 m at a place where $g = 9.80 \text{ m s}^{-2}$. The work done is

$$\begin{aligned} w &= mg \cdot dh \\ &= 10.0 \times 9.80 \times 4 \\ &= 98.0 \text{ newtons} \times 4 \text{ meters} \\ &= 392 \text{ joules} \end{aligned}$$

A film of water has a surface tension of $\gamma = 72 \times 10^{-3} \text{ N m}^{-1}$. The work done in expanding its area by $1 \text{ cm}^2 (= 10^{-4} \text{ m}^2)$ is

$$\begin{aligned} w &= \gamma \cdot dA \\ &= 72 \text{ N m}^{-1} \times 10^{-4} \text{ m}^2 \\ &= 72 \times 10^{-4} \text{ joules} \end{aligned}$$

avoid. Therefore the basic structure of thermodynamics is always developed using heat and pressure–volume work, and other forms of work considered afterward. In our case, the only other form of work of any importance is chemical reaction work.

3.5.2 Pressure–Volume Work

Work in natural environments is for the most part only of one kind – the work of expansion, or pressure–volume work. Pressure–volume work is always discussed using a piston–cylinder arrangement as shown in Figure 3.4. This seems natural to engineers, but may seem rather artificial or even useless to someone interested in processes that happen in nature or in the environment. You have to realize that virtually *all* processes in *all* natural systems involve some change in volume, and therefore work is done against the pressure on the system, whatever that is (it is very often atmospheric pressure). We use a piston–cylinder arrangement for convenience – any system that changes volume could be used. Once we have found the appropriate equations for pressure–volume work, we can use them in our models of any system, irrespective of whether or not the system has pistons and cylinders.

The piston–cylinder arrangement as shown in Figure 3.4 is not a real piston in a real cylinder, of course, but a conceptual one, so we can give it whatever properties we like. We must be careful about this, however, otherwise the results will be useless. The cylinder is fitted with some devices that can hold the piston in position at various levels. When the piston is held stationary, the forces tending to move the piston are balanced (force pushing up equals force pushing down). If this were not the case, the piston would move. The two forces are acting on opposite sides of the same piston, having the same area (and force/area = pressure), so the pressure of the gas, P_{int} , is exactly balanced by the external pressure, P_{ext} . The external pressure is provided partly by the stops that are holding the piston in place and partly by the weight of the piston itself, plus any weights on the piston. If the stops are removed, then all of a sudden P_{ext} is reduced to that produced by the piston

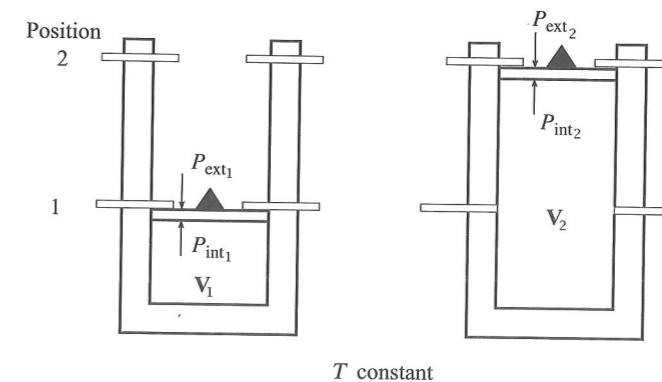


Figure 3.4 Irreversible expansion of a gas from external pressure $P_{\text{ext}1}$ to $P_{\text{ext}2}$. Expansion occurs when the stops holding the piston at position 1 are released. During expansion, the external pressure is fixed by the weight of the piston plus the weights on the piston.

and weights only, $P_{\text{int}} \gg P_{\text{ext}}$, and the piston moves up until it encounters more stops – WHAP! – and all of a sudden $P_{\text{int}} = P_{\text{ext}}$ once more, though at a different (lower) pressure (the experiment has been arranged such that the gas pressure is 10 pressure units at the upper stops, which is position 2, and 20 pressure units at the lower stops, position 1). Real gases tend to cool during expansion, so, if we want the initial and final states to be at the same temperature, some heat must flow into the cylinder from the surroundings.

At this stage, one normally says something like “If the piston is well-lubricated and well-constructed, we can ignore friction effects, . . .,” but we know we are conducting a model experiment, so we just say there is no friction in our model. The pressure–volume history of the change can be illustrated as in Figure 3.5. The external pressure during expansion is constant, since it is fixed by the mass of the piston plus whatever weights are on it. The work done during the expansion is

$$\begin{aligned} -w &= \text{force} \times \text{distance} \\ &= (\text{total mass} \cdot g) \cdot \Delta h \\ &= (P_{\text{ext}} \cdot A) \cdot \Delta h \\ &= P_{\text{ext}}(A \cdot \Delta h) \\ &= P_{\text{ext}} \cdot \Delta V \end{aligned} \quad (3.4)$$

where A is the area of the piston and Δh the distance it travels, so $-w$ is the area under the path of expansion or expansion curve in Figure 3.5. The minus sign is because the system is doing work. If we repeat the process, but this time we place a larger weight on the piston, exactly the same thing will happen, but more work is done because a greater mass was lifted through the same volume.

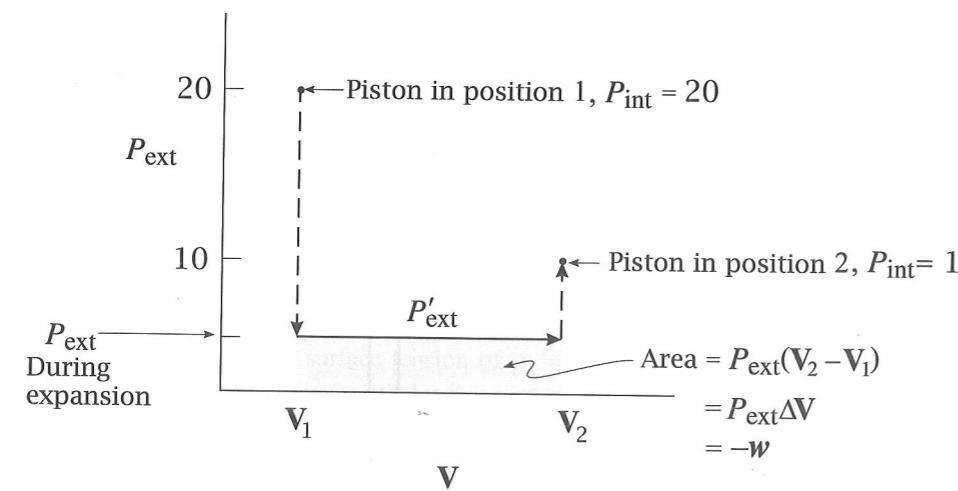


Figure 3.5 External pressure (P_{ext}) versus volume (V) plot for the irreversible expansion of the gas in Figure 3.4. The vertical dashed lines indicate an instantaneous change in pressure. The solid horizontal lines indicate change in volume at constant pressure.

Box 3.2 $P \Delta V$ Work

In Figure 3.5, suppose the pressure units are bars, $V_1 = 1000 \text{ cm}^3$ of ideal gas, and during expansion P_{ext} is 5 bars. Assume T is constant. How much work is done?

The pressure on the gas is halved (from 20 to 10 bars), so the (ideal) gas will expand to twice its volume ($PV = \text{constant}$), so $V_2 = 2000 \text{ cm}^3$. Then, from Equation (3.4),

$$\begin{aligned} -w &= P_{\text{ext}}(V_2 - V_1) \\ &= 5 \times (2000 - 1000) \\ &= 5000 \text{ bar cm}^3 \end{aligned}$$

To convert this to joules, Appendix A gives the conversion $1 \text{ bar} = 0.10 \text{ J cm}^{-3}$, so

$$-w = 500 \text{ J or } w = -500 \text{ J}$$

Note the minus sign, which indicates the system is doing work. If V_2 were less than V_1 , ΔV would be negative and w would be positive, meaning work is done on the system.

If another weight is added for the next expansion, we may have a total weight that is too great to allow the piston to reach the upper stops (position 2) and it will come to rest (equilibrium) somewhere in between. Then, if the second weight is removed, the piston will proceed upward again as before, giving an expansion path as shown in Figure 3.6. If we use a lot of weights and remove them one at a time, letting the piston come to rest after each step, we will get a path such as the one shown in Figure 3.7.

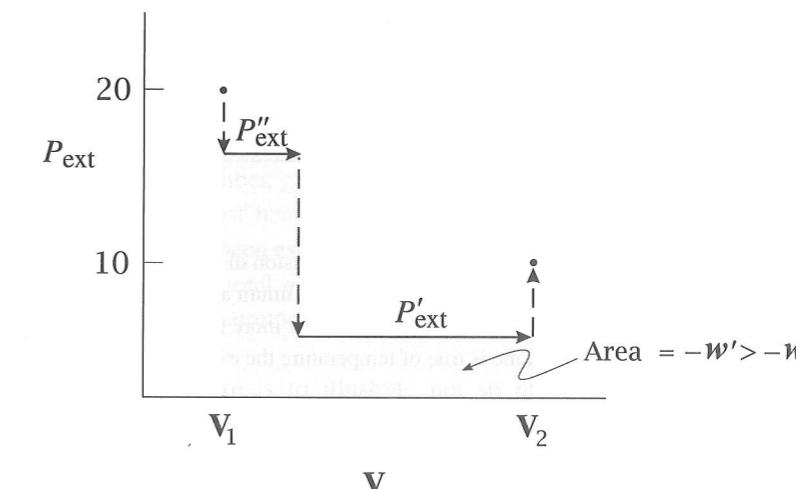


Figure 3.6 External pressure (P_{ext}) versus volume (V) for a two-stage expansion of gas. After an initial expansion at P''_{ext} , some weight was removed from the piston and the expansion continued at P'_{ext} .

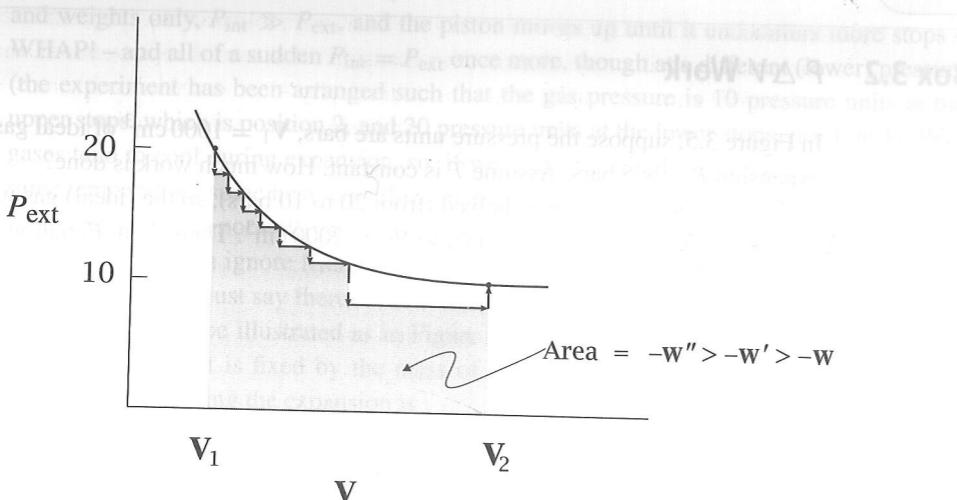


Figure 3.7 External pressure (P_{ext}) versus volume (V) for a multistage expansion of gas. After each constant- P_{ext} expansion, some weight was removed, allowing a further expansion. If in each stage the weight was added rather than removed, each little arrow would be reversed, work would be done *on* the system, and the work variable would be w instead of $-w$.

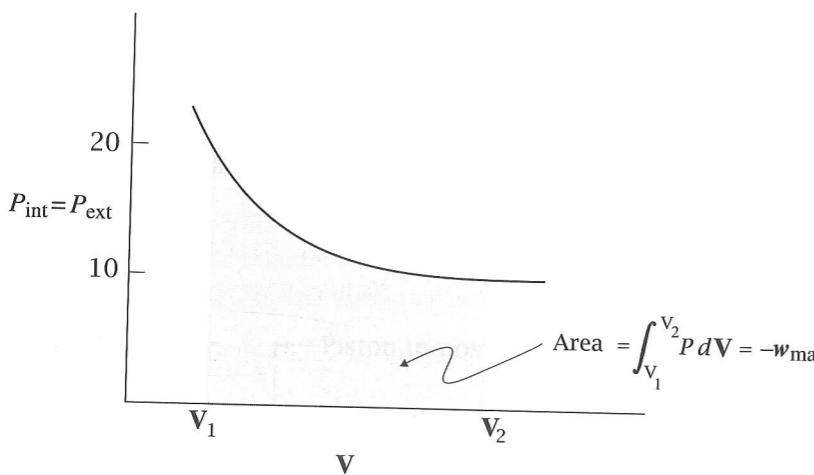


Figure 3.8 Pressure versus volume for the reversible expansion of a gas. The limiting case in which infinitely many constant- P_{ext} steps are taken gives the maximum area under the curve. During the expansion, internal pressure and external pressure are never more than infinitesimally different, or $P_{\text{int}} = P_{\text{ext}}$ at all times. If the same is true of temperature the expansion is isothermal, and the curve in the figure is an *isotherm*.

Clearly we are approaching a limit of maximum work obtainable from the expansion of our gas, and clearly too, the maximum will be when we take an infinite number of infinitesimally small incremental steps from V_1 to V_2 , resulting in the curve in Figure 3.8.

Since we have been letting the piston come to rest or equilibrium after every weight removal, in the limit we will have an infinite number or continuous succession of

equilibrium states, giving us an example of a reversible process. The name “reversible” is appropriate since at any stage in the expansion the direction of movement can be reversed by changing the external pressure infinitesimally – the piston is in a balanced condition. After each increment of movement of the piston we have been allowing heat to flow into the cylinder so that the initial and final temperatures are the same. In the limit we have also achieved a perfect *isothermal* expansion, where the temperature difference is never more than infinitesimal. We could perform the same reversible expansion or compression using a cylinder having *adiabatic* walls which prevent any heat flow to or from the gas. The resulting curve (Figure 3.8) is then an *adiabat* rather than an isotherm, and the work done is different because the functional relationship between P and V in Equation (3.5) is different.

In the limit when infinitesimal increments of V are taken, the work of expansion is (see Figure 3.8)

$$-w_{\text{rev}} = -w_{\text{max}} = \int_{V_1}^{V_2} P dV \quad (3.5)$$

Here we need make no distinction between P_{ext} and P_{int} because they are never more than infinitesimally different in our continuous succession of equilibrium states. Again, note the negative sign required to comply with the scientific sign convention. In general, considering both reversible and irreversible expansions,

$$-w \leq \int_{V_1}^{V_2} P dV \quad (3.6)$$

Since the end positions 1 and 2 of our expansion in every case consisted of our gas at stable equilibrium at a fixed P and T , according to the first law there is a fixed energy difference ΔU between the two states. We have gone to some length to show that there is no fixed “difference in work,” or work available from the change from one state to the other. The work done depends on what values of P_{ext} are in effect at all stages of the expansion. In the example we used only two different values, P'_{ext} and P''_{ext} , but there could be any number, giving any value of the total work done. Thus we are led to believe that the amount of heat flowing into our thermostatted cylinder must at all times, once equilibrium had been established, have compensated for the variations in work performed, giving the same total $q + w$ in every case. We could verify this, of course, by making calorimetric measurements, but this is basically what Joule and many other workers have already done.

Our intent here is to illustrate not so much the constant energy change between equilibrium states, but that this energy change, while accomplished by heat and work, can be made up of an infinite variety of combinations of heat and work. When the process is made reversible, we get the maximum work of expansion, and this will be given by Equation (3.5), but even so, we are unable to calculate this amount of work (evaluate the integral) without more information (we need to know P as a function of V so that we can integrate Equation (3.5)).

The integration of (3.5) at a constant external pressure results in

$$-w = P_{\text{ext}}(V_2 - V_1) \quad (3.7)$$

$$= P_{\text{ext}} \Delta V \quad (3.8)$$

as in Equation (3.4). The *internal* pressure necessarily varies during this (irreversible) expansion, as discussed above.

A point worth emphasizing is that in any real expansion, which is necessarily irreversible, the work obtained is always less than the maximum obtainable (from a reversible expansion). This can also be expressed as

$$-w \leq -w_{\text{max}} \quad (3.9)$$

or

$$-w \leq -w_{\text{rev}} \quad (3.10)$$

For the opposite case of compressing the gas from position 2 back to position 1, the inverse series of steps can be employed. Thus, if at position 2 a heavy weight is placed on the piston, it will ~~WAP~~ down to the stops at position 1, describing a path such as in Figure 3.9. Obviously, much more work has had to be done in compressing the gas than we obtained, even in the reversible case, from expansion. However, by adding a larger number of smaller weights one at a time we can reduce the amount of work required for the compression, gradually approaching the stable equilibrium curve from above, rather than from below as before. In the limit, of course, we find that for a reversible compression the work required is exactly the same as the work available from a reversible expansion.

Considering this work stuff in such detail may make it look complex, but it really is not. Just remember that, if you need to calculate work (which happens surprisingly little

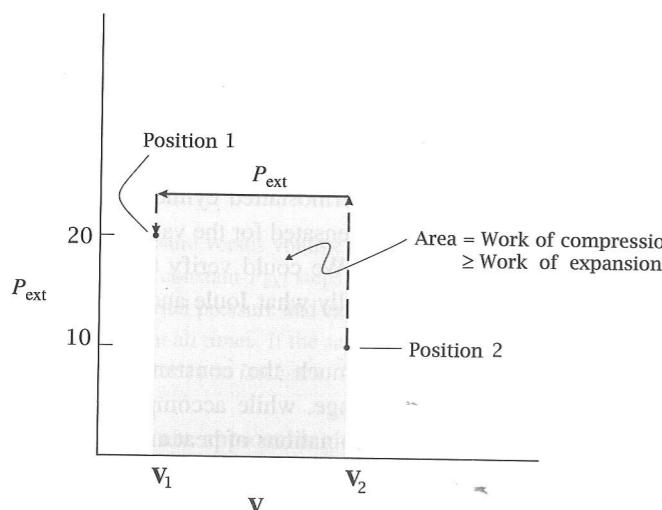


Figure 3.9 External pressure (P_{ext}) versus volume for the irreversible compression of gas at constant P_{ext} .

in geochemistry), you need either a constant pressure process, or a reversible one (so you can integrate). More important is the fact that any real work done is always less than the theoretical maximum (Equation (3.9)), usually much less, and usually of more interest to engineers than to geochemists.

3.5.3 An Inexact Differential

The limitless sequence of small increments of movement of the piston (and hence of work done) in Figure 3.7 resulting in Figure 3.8 might suggest an integration. Why not integrate dw ? We can consider w to be made up of small or infinitesimal increments δw , then sum up all the increments between states 1 and 2, giving (McQuarrie and Simon, 1997, p. 773)

$$\int_1^2 \delta w = w \text{ not } \Delta w \text{ or } w_2 - w_1 \quad (3.11)$$

This introduces the subject of inexact differentials. Integration of δw does not result in Δw because the differential of w is not the exact differential dw but the inexact differential δw . w does not have an exact differential because there is no function from which we could derive dw as we did for dy in the example in Section 1.4.1. As shown in Figures 3.4–3.8 all numerical values of w depend on the path followed by the piston during the expansion. This path is infinitely variable, and even if we had a function for one such path it would only be valid for that one path. w is a *path variable*, not a state variable. Change in a path variable depends on the series of states occupied between its initial and final states (its path), and its differential is therefore inexact. Change in a state variable depends only on the initial and final states (Section 2.4) and its differential is exact. We use δ rather than d for inexact differentials.

After every increment of change in Figures 3.4–3.8 some heat was exchanged, so this amount of heat will also depend on the path followed. q is also a path variable, and

$$\int_1^2 \delta q = q \text{ not } \Delta q \text{ or } q_2 - q_1 \quad (3.12)$$

At each point on the isotherm in Figure 3.8 the small (or infinitesimal) change in work done (δw_{rev}) at pressure P (where $P_{\text{int}} = P_{\text{ext}}$) is

$$-\delta w_{\text{rev}} = P dV \quad (3.13)$$

If we integrate this expression keeping P constant we have a constant *internal* pressure expansion

$$-\int_1^2 \delta w_{\text{rev}} = \int_1^2 P dV$$

$$-w_{\text{rev}} = P \Delta V \quad (3.14)$$

where in this case, because w is reversible, P is the reversible pressure, i.e., $P_{\text{int}} = P_{\text{ext}}$ at all times.