

## Chapter 10. Conservation of Energy and the First Law

### **Focus question:**

How does the total energy change when a hot brick is placed into a beaker of cold water?

### **Introduction**

To answer questions similar to the focus question requires an understanding of thermodynamics, which is the study of energy transfer in macroscopic systems. Energy, and energy transfer is an important area in any science, whether it is chemistry, biology, or physics. Every biological system exists because of energy transfer; without energy, all living things would die. How energy is used in a biological system depends on the laws of thermodynamics.

Thermodynamics is based solely upon observations of physical reality, and the laws of thermodynamics are the summation of human experience and are inviolate. There have been no instances in *normal* chemistry where the laws of thermodynamics are broken (the conversion of matter into energy in nuclear reactions is not *normal* chemistry). Because thermodynamics preceded quantum mechanics in its development, thermodynamics *does not depend* on quantum mechanics as its foundation. Thermodynamics is an area of investigation by itself, and in many instances, thermodynamics is taught before quantum mechanics. In our survey of thermodynamics, we will use quantum mechanics and statistical mechanics to understand the molecular nature of certain thermodynamic concepts and to bridge the gap between the microscopic and macroscopic worlds. Let's begin with some basic thermodynamic concepts and language.

### **Internal Energy**

In the previous chapter, we observed that molecules have translational, rotational, vibrational, and electronic energies. These molecular energies are determined by the molecular structure and, for an ensemble of molecules, the temperature. The ensemble of molecules is in constant random motion, and at higher temperatures, the ensemble has more energy. The sum total of all the molecular energies that the system possesses is called the **internal energy**, and the internal energy is symbolized by  $U$ . The internal energy is affected by anything that can modify the structure of the molecules or the distribution of molecules in their energy levels because any such changes will alter the molecular energy. As an example, if we heat the ensemble of molecules, we know from

Boltzmann's law that the molecules will occupy higher energy levels; therefore, the total energy (the internal energy) of the ensemble increases.

## **Systems and Surroundings, States and Processes**

As with any subject, thermodynamics has its own language. Since we will use this language throughout the next few chapters, let's take some time to discuss some common terminology. In thermodynamics, the universe is separated into two parts: the system and the surroundings. The system and surroundings are defined by the investigator. The **system** is the part of the universe under investigation. If you were to study the thermodynamics of this book, then the book would be the system. If you were to study the biochemistry of a rat, then the rat would be the system. If you were to study the workings of an automobile, the entire automobile – passengers, gasoline, wheels, etc., may be defined as the system.

The **surroundings** are objects in the universe that are not part of the system. If we study a rat and there is cheese nearby, we may consider the rat to be the system and the cheese is part of the surroundings. If we study the space shuttle, the shuttle is the system, and everything outside the shuttle is part of the surroundings. If we study an organic reaction contained in a flask, then everything in the flask is the system, and everything outside the flask is the surroundings. The system and surroundings are separated by a **boundary**, which may be real or imagined. The definition of system and surroundings is made by the investigator and is usually made for convenient calculation of thermodynamic properties of interest. For the example of the rat in a cage, we could have considered the rat, cheese, and everything in the rat's cage to be the system, and everything outside the cage is the surroundings; the cage would be the boundary.

Typically, we focus our attention on the system, and quantities, such as work, heat, and energy, are system-oriented. Anything that increases the energy of the system is considered a positive quantity, and anything that decreases the energy of the system is considered a negative quantity. Therefore, when heat flows into the system, it is a positive quantity. When a gaseous system expands, the system is working on the surroundings and the energy of the system decreases; therefore, the work of expansion is a negative quantity. ***Even though these quantities are system-oriented, these values are usually obtained from measurements in the surroundings.*** When we want to determine if work is produced during a chemical reaction, we measure the effect in the surroundings. In addition, we measure the temperature of the surroundings to determine if a system is producing heat during a reaction.

Systems may be either open or closed. An **open** system allows matter to enter or leave, while a **closed** system does not. A reaction carried out in a stoppered flask is a closed system, while a reaction in a beaker is an open system (even though nothing is transferred

from the beaker to the atmosphere, the potential for transfer exists; hence it is an open system). An *isolated* system prevents the transfer of both matter and energy.

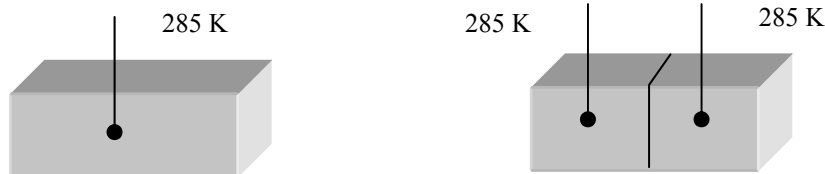
## Phase Rule

In thermodynamics, as in quantum mechanics, we speak of the state of the system. By state, we do not mean physical state, although that would be part of the description. The system is in a definite thermodynamic *state* when the thermodynamic properties of interest are specified for the system. As an example, if we consider argon to behave as an ideal gas, we have specified the state of this system when we specify the temperature, moles, and volume. Since pressure can be calculated from the other variables and the ideal gas law, it is not an independent variable. How many independent variables must be specified in order to define the state of a system? J. Willard Gibbs answered this question in the 19<sup>th</sup> century. Gibbs found that the number of variables needed to specify a state is given by the *phase rule*, which is:

$$F = C - P + 2$$

In the phase rule,  $P$  is the number of physical *phases* that exist in the system,  $C$  is the number of *components* in the system, and  $F$  is the number of independent intensive thermodynamic variables necessary to completely specify the state of the system.  $F$  is the number of independent thermodynamic variables, commonly called the *degrees of freedom*. From the phase rule, we can determine the number of variables we need to know to define the state of the system. If we have a sample of boiling water, is it enough to specify that the temperature is 373 K to completely define the system? If we have a sample of pure ice, do we need to specify only the temperature specify the state, or do we need to specify the temperature *and* the pressure? The phase rule answers these questions. Before we can use the phase rule, we need to amplify some of the terms used in it.

The phrase “independent intensive thermodynamic variables” is certainly intimidating, so let’s break it down into its parts. A thermodynamic variable is a quantity we can measure or calculate. Temperature, pressure, volume, and density are all examples of thermodynamic variables. These variables can be either intensive or extensive. An *intensive* variable does not depend on the amount of substance. Temperature and density are intensive variables, but volume and energy are not. Consider the figure below where we have a large object at a given temperature. If this object is sliced to make two separate parts, the temperature of each part is the same as in the original object. The temperature does not depend on the size (or amount) of the object; it is an intensive quantity.



Temperature is the same for the entire box and for each smaller part; therefore, temperature does not depend on the amount of material.

Quite obviously, the volume of material depends on how much material is present. Volume is an example of an *extensive* variable – one that does depend on the amount of substance. Looking at the previous figure, the volume changes as we change the amount of material. An extensive variable can be converted into an intensive variable by dividing the extensive variable by the amount of substance. The amount we will use is the mole (although we could use grams). Therefore, the extensive variable,  $V$ , can be converted into an intensive variable by dividing by the amount of material as in:

$$\bar{V} = \frac{V}{n}$$

In this relationship,  $\bar{V}$  is called the molar volume.

✎ **Exercise:** Is density intensive or extensive? 🙌

A *phase*,  $P$ , is a physically distinct, homogeneous, macroscopic piece of matter. Some examples of materials and the number of phases are:

1. Liquid water is one phase.
2. A solution of salt in water is also one phase because you cannot observe the ions (they are *microscopic* objects).
3. An aqueous solution of sugar *with solid sugar on the bottom of the beaker* is two phases – the solution and the solid sugar.
4. Oil and water are two phases because the liquids do not mix and you can easily detect the meniscus separating them.
5. Methylene chloride dissolved in hexane and mixed with water has two phases – one phase is the mixture of methylene chloride and hexane (a solution) while water is the other phase.

A *component* is a material whose amount can be *independently* varied. Independently is the key word. Water is a single component, as is iron, sugar or any other pure substance. In a sugar solution, there are two components (the sugar and the water) because both materials can be varied independently.

How many components exist in a sodium chloride solution? In this solution, there are (neglecting the ionization of water)  $\text{Na}^+$ ,  $\text{Cl}^-$ , water, and  $\text{NaCl}$ . Therefore, we may think that there are four components, but these four species are *not* independent because there are restrictions that connect them. Sodium ions and chloride ions are related by charge balance; the total concentration of sodium ion must equal the concentration of chloride ion for the solution to be electrically neutral:  $[\text{Na}^+] = [\text{Cl}^-]$ . This means that the concentration of sodium ions and concentration of chloride ions are not independent of each other, and they cannot be independently varied. Additionally, there is the restriction of mass balance; the initial concentration of salt is spread over the components of the salt, therefore:  $[\text{NaCl}]_0 = [\text{Na}^+] + [\text{Cl}^-]$ . The result is that the four species ( $\text{Na}^+$ ,  $\text{Cl}^-$ , water, and  $\text{NaCl}$ ) cannot be varied independently. For these four species, there are two restrictions placed on them (charge balance and mass balance); we therefore have  $4 - 2 = 2$  components. By the way, this number of components (two) is the same number of

components we would get by using common sense: we added salt (one component) to water (another component).

☞ **Example:** How many components exist in a solution of calcium chloride and potassium chloride?

*Solution:* The solution contains water,  $K^+$ ,  $Ca^{2+}$ , and  $Cl^-$ . The only restriction is:  $[K^+] + [Ca^{2+}] = [Cl^-]$ . The mass balance restriction,  $[KCl]_o = [K^+] + [Cl^-]$ , no longer applies because chloride ion is produced from both the potassium and calcium salts. There are  $4 - 1 = 3$  components. ☞

## Some Applications of the Phase Rule

The phase rule tells us the number of thermodynamic variables we need define in order to specify a system. If we have a pure substance that exists in the gas phase, how many variables do we need to specify the state of the system? Alternatively, how many degrees of freedom are there for a pure gaseous phase? We have one pure substance so we have one component, so  $C = 1$ . We also have one phase (gas), so  $P = 1$ . Since  $F = C - P + 2$ , we obtain  $F = 2$ . We need to specify two intensive variables such as  $T$  and  $P$ , or  $T$  and  $\bar{V}$  to completely specify the system. Again, you should see that this makes physical sense. If we know  $T$  and  $\bar{V}$  for instance, we can calculate  $P$  from the ideal gas law: the system is completely specified.

How many variables are needed to specify the state of the system if the pure substance exists in two phases such as a mixture of water vapor and liquid water? In this case there is one component in two phases, so  $C = 1$  and  $P = 2$ . Since  $F = C - P + 2$ , we obtain  $F = 1$ . We need only specify one variable. For instance, the vapor pressure of water is specified as soon as we specify the temperature; we need specify nothing else. This is why vapor pressure tables are simple; once we specify the temperature, the vapor pressure is known.

There is a point, called the **triple point**, where three phases can coexist. For a pure substance, how many variables can we change at the triple point? In this case,  $C = 1$  and  $P = 3$ . Since  $F = C - P + 2$ , we obtain  $F = 0$  at the triple point. There are no degrees of freedom or independent variables we can change at the triple point; therefore, the triple point is uniquely defined for a particular substance. For water, the triple point occurs at 273.16 K, and 4.56 mm Hg (0.006 bar). This is the only combination of temperature and pressure where all three phases of water coexist. Many pure substances have more than one triple point.

## Thermodynamic Processes

A thermodynamic **process** describes a *change in state* of the system. Compressing a gas, evaporating a liquid, or reacting chemicals are examples of thermodynamic processes because we have changed the state of the system in each case. Some typical thermodynamic processes are:

- Heating 5 g of water from 300 K to 325 K
- Melting 26 g of ice at 273 K
- Converting graphite to diamond under a high pressure
- Reacting hydrogen gas and chlorine gas to form hydrogen chloride.

Thermodynamics has its own language and we use specific words to describe common thermodynamic processes. Common processes can be:

- ***Isothermal***; the temperature is constant.
- ***Isobaric***; the pressure is constant.
- ***Isochoric***; the volume is constant.
- ***Adiabatic***; no heat is exchanged between system and surroundings.

☞ **Example** (Thermodynamic terms in italics): A person can be considered a *system* if that is what we wish to study. Everything else is the *surroundings*. As a person exercises, *energy* is expended. This energy may be transferred into the surroundings as heat or work. The system has undergone a *change in state* (Hopefully, the loss of a few pounds!). 🙌

**Ψ:** You react zinc metal with dilute hydrochloric acid in a stoppered Erlenmeyer flask. What is the chemical reaction that occurs? What is the system? What are the surroundings? Why is this procedure unsafe?

A common problem in the understanding of thermodynamics arises from the words heat and work. These words cause considerable confusion because they may be incorrectly used to describe the energy of a static system. A static system possesses energy; it does not possess heat or work. We cannot say that a system *has* heat, or that a system *has* work because heat and work exist only **during** a process – a change in state of the system. Heat flows from a higher to a lower temperature, and it flows during a change in state (the change in temperature as the hot object cools and the cool object warms). If two objects are at the same temperature, there is no heat flow.

## ***First Law of Thermodynamics***

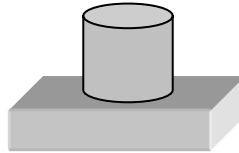
In a steam locomotive, coal is burned and water is heated in a boiler; the steam that is produced expands to drive a piston that is connected to the wheels. The heat produced by burning coal is converted to the work of moving the locomotive and the train. A nuclear power plant uses the heat of a nuclear reaction to convert liquid water to steam; this steam drives a turbine that works to produce electricity. Both of these processes demonstrate the importance of the conversion of heat into a work. The work is observed in the surroundings and the work only exists *during the process*. An understanding of the relationship between heat and work is necessary to understand energy transfer in real systems.

The first law of thermodynamics relates heat and work. The first law states that the sum total of the heat,  $q$ , and work,  $w$ , must equal the change in the internal energy,  $\Delta U$ , of the system. Mathematically, the first law is:

$$\Delta U = q + w \quad (10.1)$$

The first law dictates how we can change the internal energy. We can increase the internal energy in two ways: we can work on the system or we can heat the system. Alternatively, the internal energy may be used to produce work or to heat the surroundings. Before we discuss the nature of heat and work, let's show one very important aspect of the first law.

The first law is a **conservation law**; it states that energy cannot be created or destroyed. Consider a steel container of gas on a hot plate. When we turn on the hot plate, heat flows from it into the container. Because the container is rigid, the gas inside cannot expand and produce work. What happens to the energy?



If we consider the gas as the system then  $\Delta U = q + w$ , but the work is zero because the gas cannot expand, therefore  $\Delta U = q$ . The energy of the gas increases as heat is supplied to the system. The energy increases because at the higher temperature, molecules populate more energy levels and the partition function increases. There is no work done on the surroundings, but the surroundings lose heat,  $q$ , to the system; therefore  $\Delta U = -q$ . The net change for the system and surroundings is:

$$\Delta U_{total} = \Delta U_{sys} + \Delta U_{surr} = q + (-q) = 0$$

The total energy has not changed and energy is conserved. As another example, consider heating a balloon gently and allowing it to expand. If we define the balloon as the system, we see from the experiment that the temperature rises and heat is flowing into the system. The system is working because the balloon expands as it is heated (it is pushing back the atmosphere as it expands). Now look at the surroundings. Heat is transferred out of the surroundings (and into the balloon) and the balloon is working on the surroundings. Algebraically, we have,

|      | System | Surroundings |
|------|--------|--------------|
| Heat | $+q$   | $-q$         |
| Work | $-w$   | $+w$         |

The magnitude of the heat and work for the system and surroundings are the same, only the algebraic sign is different:  $w_{sys} = -w_{surr}$  and  $q_{sys} = -q_{surr}$ . Thus,  $\Delta U_{sys} = -\Delta U_{surr}$ , and

$\Delta U_{total} = \Delta U_{sys} + \Delta U_{surr} = 0$ . The total energy of system and surroundings does not change: energy is conserved. Also, don't forget that the First Law is the sum of human experience; there have been no examples of physical systems that violate the First Law.

We will need another form of equation (10.1), the differential form, for our mathematical work in thermodynamics. The differential form of equation (10.1) is:

$$dU = dq + dw \quad (10.2)$$

This equation defines an infinitesimal change in energy as the sum of infinitesimal changes in heat and work. The First Law of Thermodynamics deals with the interconversion of heat and work. Although there are many varieties of work including mechanical, gravitational, and electrical, let's focus on mechanical work at this time. From physics, mechanical work is defined as the application of an external force to an object, and that object moves through a distance. In calculus terms, work is:

$$dw = -f_{ext} dx \quad (10.3)$$

In this equation,  $f_{ext}$  is the external force and  $dx$  is an infinitesimal distance. The meaning of the negative sign will become clear shortly. For a constant external force, the integral becomes  $w = -f_{ext}\Delta x$ . When we apply a force to an object and we move it, we observe a work. The SI unit for force is a Newton ( $\text{kg m s}^{-2}$ ), so work has units of  $\text{N} \times \text{m} = \text{kg m}^2 \text{s}^{-2}$ , which is defined as a Joule.

## ***Ideal Gas as a Working Substance***

In order to understand thermodynamics, we need to apply the equations and relationships of thermodynamics to physical substances. Although any substance can be used, it is convenient to use an ideal gas as the working substance. Thermodynamic equations for an ideal gas are generally easy to derive and to interpret, while equations for real gases, solids, and liquids are more complicated, and relationships between the thermodynamic variables are sometimes obscured. We will introduce other working substances, most commonly real gases, as we go along. For now, we will focus on an ideal gas.

Recall that an ideal gas is defined as a gas that obeys the equation:

$$PV = nRT \quad (10.4)$$

In this equation, the units for the variables  $P$ ,  $V$ , and  $T$  depend on the units for the gas constant,  $R$ . Typically,  $R$  is  $0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$ , so  $P$  is in bar,  $V$  is in liters and  $T$  is in kelvins. A bar is the SI unit of pressure and it is equal to  $101\,325$  Pascals ( $\text{N m}^{-2}$ ). An atmosphere (atm) is approximately 1 bar ( $1 \text{ atm} \equiv 10^5$  Pascals, so the difference between a bar and an atm is  $1325 \text{ Pa}$  or  $1325/10^5 = 0.013 \sim 1.3\%$ ).

On a molecular level, an ideal gas is one in which there are no intermolecular forces; therefore, the gas particles behave as independent particles. Additionally, all molecular collisions are assumed elastic, so no energy is gained or lost during collisions. Finally, the volume of the individual molecules is assumed to be zero in an ideal gas.

## Expansion or Compression Work

In chemical systems, we normally do not use expression (10.3) for work because we do not consider moving beakers or flasks as interesting chemical processes. Instead, we are interested in the work that occurs during a chemical reaction. One type of work, called  $PV$  work, is produced by expansion or compression of gases.

Consider a gas, with an internal pressure,  $P_{int}$ , trapped in a piston of area  $A$  ( Figure 10-1). Arbitrarily, let's say that  $P_{int}$  is greater than the outside pressure, which we will denote as  $P_{ext}$ . If the piston is free to move, the gas expands (because the internal pressure is greater than the external pressure). During the expansion, the piston moves a distance,  $\Delta x$ . What work is observed for this process?

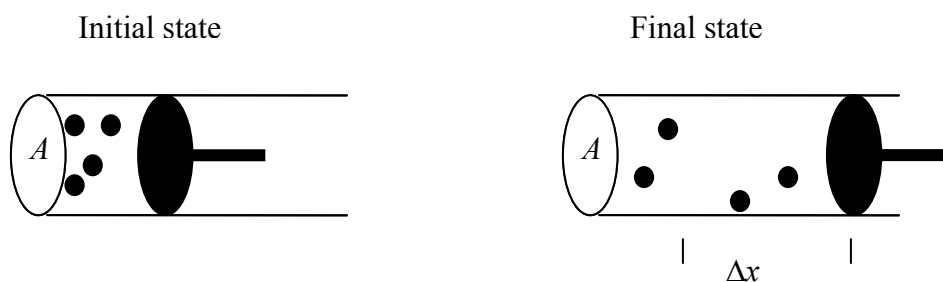


Figure 10-1

Recall that work is caused by the external force applied to an object. Use the definition for work, equation (10.3),  $dw = -f_{ext} dx$ . Recall that  $P = f/A$ , so

$$w = -\int f_{ext} dx = -\int P_{ext} A dx$$

The cylinder has a cross-sectional area of  $A$ . From the figure, the volume is related to the area by  $dV = A dx$  (the area is fixed; only the distance,  $x$ , can change),

So the equation for  $PV$  work becomes:

$$w = -\int P_{ext} dV \quad (10.5)$$

All examples of  $PV$  work are specific cases of equation (10.5). If the external pressure is constant, we can remove it from inside the integral. We will no longer use the subscript

'int' to denote the pressure of the gas; the gas pressure will be denoted by  $P$ . Note that if  $P > P_{\text{ext}}$ , the gas expands, and if  $P < P_{\text{ext}}$ , the gas is compressed. This is the reason for the negative sign in equation (10.3). Expansion occurs when the system is working; the work is negative due to the sign convention that anything lost from the system is a negative quantity.

☞ **Example:** If the space shuttle had developed a hole while orbiting the earth, what would be the work in expanding the gas from inside the shuttle to outer space?

*Solution:* Certainly, a great deal of work would be done by the astronauts repairing the hole, but we wish to consider the  $PV$  work. Space is a virtual vacuum, thus the external pressure is zero. Since  $w = -\int P_{\text{ext}} dV = -P_{\text{ext}} \int dV = 0 \int dV = 0$ , there is no  $PV$  work. ☞

Ψ: Why can we write  $w = -\int P_{\text{ext}} dV = -P_{\text{ext}} \int dV$ ?

☞ **Exercise:** You are blowing up a balloon for your sister's birthday party. What would be the expression for the  $PV$  work? ☞

☞ **Exercise:** In thermochemical studies, a reaction are often carried out in a bomb calorimeter, which is a sealed, 1/4 inch stainless steel container and is quite inflexible. What would be  $PV$  work for the reaction,  $\text{N}_2 + \text{O}_2 \rightarrow \text{N}_2\text{O}$  in a bomb calorimeter? ☞

Thermodynamic variable are either path variables or state variables (see later). Work is a thermodynamic variable that depends on the *path* we choose to get from the initial to the final state. One way to see that work is a path variable is to recall that an integral is the area between the curve and the horizontal axis. Since work is  $w = -\int P_{\text{ext}} dV$ , we can view work as an area on a  $PV$  diagram. A typical  $PV$  plot may look like Figure 10-2 for a constant temperature.

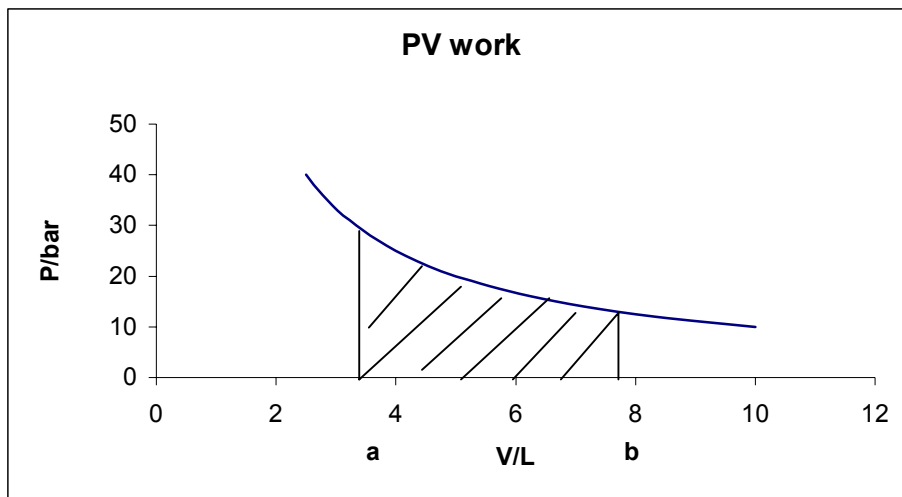
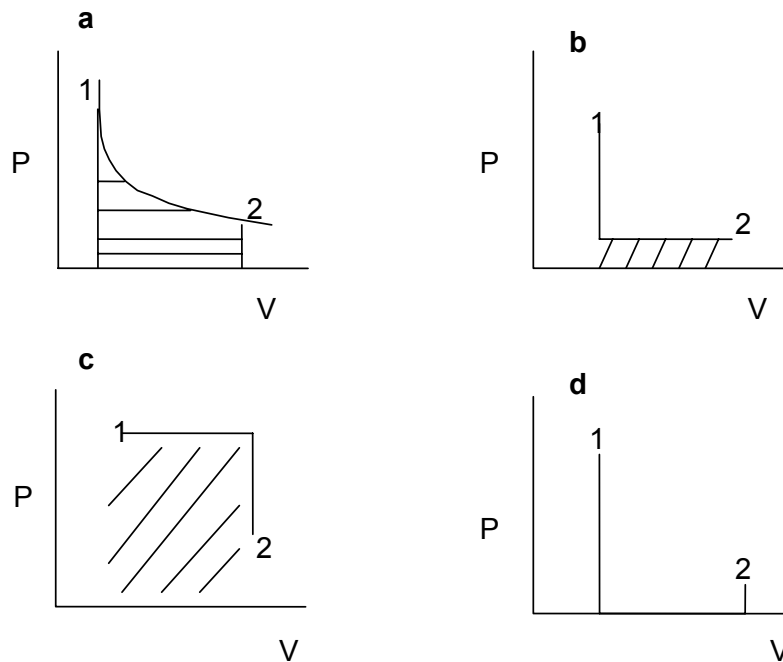


Figure 10-2

The work produced when the volume changes from  $V_a$  to  $V_b$  is the negative of the shaded area. *The work depends on the path we choose between these two states.* To see this, let's assume we take a gas from state 1 ( $P = 10$  bar,  $V = 2$  L) to state 2 ( $P = 1$  bar,  $V = 20$  L). Imagine four different possibilities for this change as shown in Figure 10-3.

- Follow the constant temperature path (Boyle's law);
- Reduce the pressure at constant volume, then expand the volume;
- Increase the volume at constant pressure, then decrease the pressure;
- Decrease the pressure to zero, expand the volume, and increase the pressure to 1 bar.

What is the work in each case?



Hatched area represents the work

Figure 10-3

It is apparent from the figure that the work depends on the path we choose to get from 1 to 2. In case (b), the work is less than in case (a) because the area in (b) is less than the area in (a). In case (c), the work is greatest and, in case (d), the work is zero. Work is an example of a **path variable** because it depends on the path between the two states.

## Reversibility

Reversibility is one of the most important concepts in thermodynamics. In many cases, we are interested in reversible work or reversible energy because (as we will see later) it is the *maximum* obtainable value. To get some sense of the concept of reversibility, consider a gas contained in a piston in which the external and internal pressures are identical. A weight is placed on the movable piston. This weight produces an extra pressure on the gas, and the gas below the piston is compressed. When the weight is

removed, the gas will expand and the piston will rise in one fell swoop. This is an irreversible process (Figure 10-4).

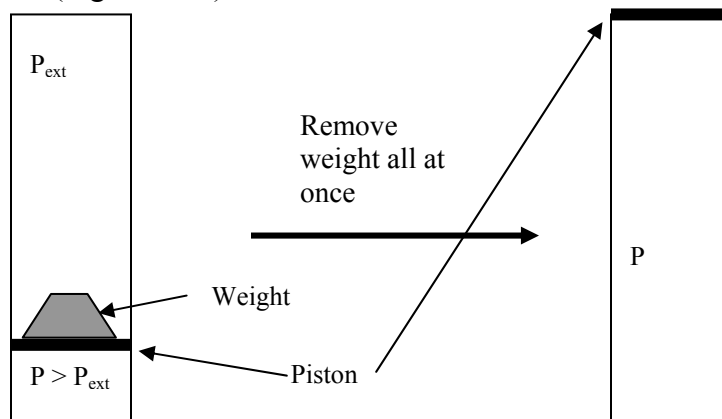


Figure 10-4

Let's use the same gas under the same conditions as in Figure 10-4, but this time there is not one massive weight, but a series of smaller weights that compress the gas. We remove these small weights one by one and the gas expands incrementally (Figure 10-5).

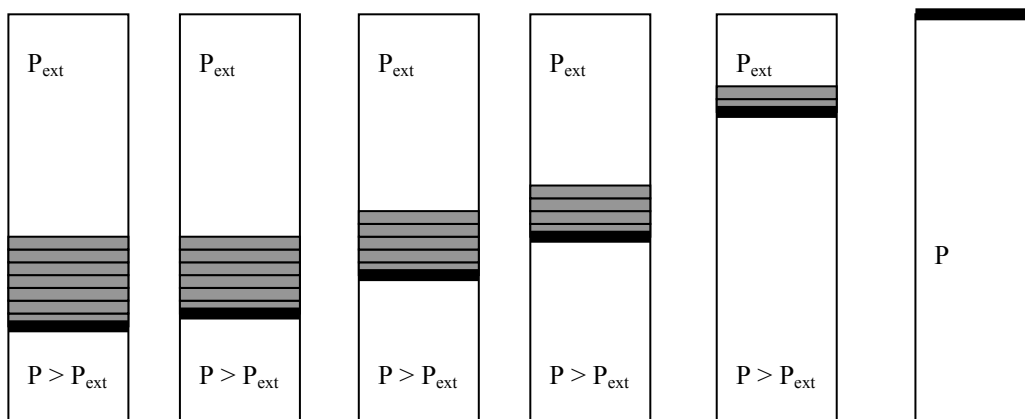


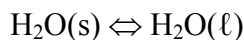
Figure 10-5

If each of the weights have a very small mass, then the piston will move in very small steps; the smaller the masses, the smaller the increments that the piston will move (Figure 10-5). This example approximates a reversible process. If the weights are infinitesimally small, then the internal and external pressures would differ by an infinitesimal amount and this would be a true reversible process.

In a **reversible** process, traveling the same path in reverse restores the system to its original state, *and* restores all parts of the surroundings to their original conditions. Reversible processes are characterized by **infinitesimal** changes in thermodynamic variables. In a truly reversible process involving pressure, the internal and external pressure would differ by an infinitesimal amount ( $P_{\text{ext}} = P + dP$ ), and the change would not be measurable due to the infinitesimal change in pressure. Since  $dP$  is infinitesimally

small, we routinely omit the  $dP$  term and write  $P_{\text{ext}} = P$  for a reversible process. *A synonym for reversible is equilibrium.* The direction of a reversible (equilibrium) process can be changed by a slight (infinitesimal) change in a thermodynamic variable.

Melting of water at 273.15 K and 1 bar is a reversible physical process. The normal melting point of ice is 273.15 K, so at this temperature water can be forced to go from solid to liquid or from liquid to solid by an infinitesimal change in temperature. We write this process as:



The double arrow ( $\rightleftharpoons$ ) denotes a reversible, or equilibrium, process. Increasing the temperature by a small amount forces the reaction to go in the forward direction, whereas decreasing the temperature by a small amount causes the reaction to reverse – a reversible process. Note that these changes occur with no change in the surroundings. A piece of ice placed in contact with a large reservoir at 273.16 K would cause the ice to melt but the reservoir, since it has a large heat capacity, would not change.

Let's get an expression for the  $PV$  work for a reversible process. From equation (10.5), we can write:

$$w = -\int P_{\text{ext}} dV$$

Since the process is reversible, we can replace  $P_{\text{ext}}$  by  $P$ :

$$w = -\int P dV$$

To proceed, we must specify the relationship between  $P$  and  $V$ . Assuming the gas obeys the ideal gas law ( $PV = nRT$ ), we substitute for  $P$  to obtain;

$$w = -\int \frac{nRT}{V} dV$$

If we assume an isothermal process, we can remove  $T$  from within the integral:

$$w = -nRT \int \frac{dV}{V}$$

**Ψ:** Why can we remove  $T$  from the integral?

Integrating between initial and final volumes,  $V_i$  and  $V_f$ , we obtain:

$$w = -nRT \ln \left( \frac{V_f}{V_i} \right) \quad (10.6)$$

Equation (10.6) is the work for an isothermal reversible expansion or compression of an ideal gas. Notice the assumptions that we made in order to evaluate the integral; such assumptions are common in physical chemistry.

☞ **Example:** What is the work when 1.0 mole of ideal gas is reversibly compressed from 25 L to 3.0 L at 300 K?

*Solution:* The process is isothermal ( $T = 300$  K) and reversible.

$$w = -(1.0 \text{ mol}) (300 \text{ K}) (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln(3.0 \text{ L}/25 \text{ L}) = 5300 \text{ J or } 5.3 \text{ kJ.}$$

The work is positive meaning it is done *on* the system. ☞

☞ **Exercise:** Two moles of neon at a pressure of 1.5 bar are enclosed in a rigid container with a movable piston that is latched. The entire apparatus is thermostated at 325 K.

What happens to the gas when the latch is released? Is this a reversible process? What is the expression for the work for this process? Answers and hints: the gas expands, no,

$$w = -P_{ext} \Delta V. ☞$$

## Maximum Work of Expansion

What is the maximum expansion work that a system can do? Obviously, this quantity is important for the design of engines such as steam or gasoline engines because they work by expanding gases. It would be useful, in designing these engines, to know the maximum work we can expect to get from them. Any real engine would produce less work because of friction, design restrictions, and the like. Let's attempt to find the maximum work for 1.0 mole of our ideal gas in an isothermal process. Arbitrarily we will start at 10 bar and 300 K.

Ψ: First, complete this table:

| State | P/bar | V/L  |
|-------|-------|------|
| 1     | 10    | 2.46 |
| 2     | 8     |      |
| 3     | 5     |      |
| 4     | 3     |      |
| 5     | 1     |      |

Consider three separate processes:

- Start in state 1 and go directly to state 5.
- Start in state 1 and go to state 3 and then go from state 3 to state 5.
- Start in state 1 and go to state 2 then go from 2 to 3, then 3 to 4, and finally 4 to 5.

**Ψ:** Are any of the processes (A, B, C) reversible? Explain. Complete this table for processes A, B, and C.

| Process | Number of expansion steps | Work /J |
|---------|---------------------------|---------|
| A       | 1                         |         |
| B       |                           |         |
| C       |                           |         |

**Ψ:** What is the correlation between the magnitude (excluding sign) of the work and the number of steps in the process?  
 If the process were carried out in 20 steps, would the magnitude of the work be greater or smaller than if the process had 50 steps?  
 How many steps do you think would represent the maximum work?

Maximum work is produced when the number of steps is infinite, and therefore the pressure changes infinitesimally from the previous pressure. This is a reversible process, and consequently, reversible processes produce the maximum work. Reversible processes would also take an infinite amount of time since the pressure changes are infinitesimal and the volume changes would also be infinitesimal. Therefore, these reversible expansions do not correspond to real physical expansions but they provide a theoretical limit to the maximum work we can achieve. Figure 10-6 is a graph of the expansion of a gas from 8.0 bar and 12.0 L to 1.0 bar (and 96.0 L) at constant temperature for both reversible and irreversible cases. Since work is represented by the area between the curve and the x-axis, it is clear that the reversible case (smooth line) produces a larger work than the irreversible case (stepped line).

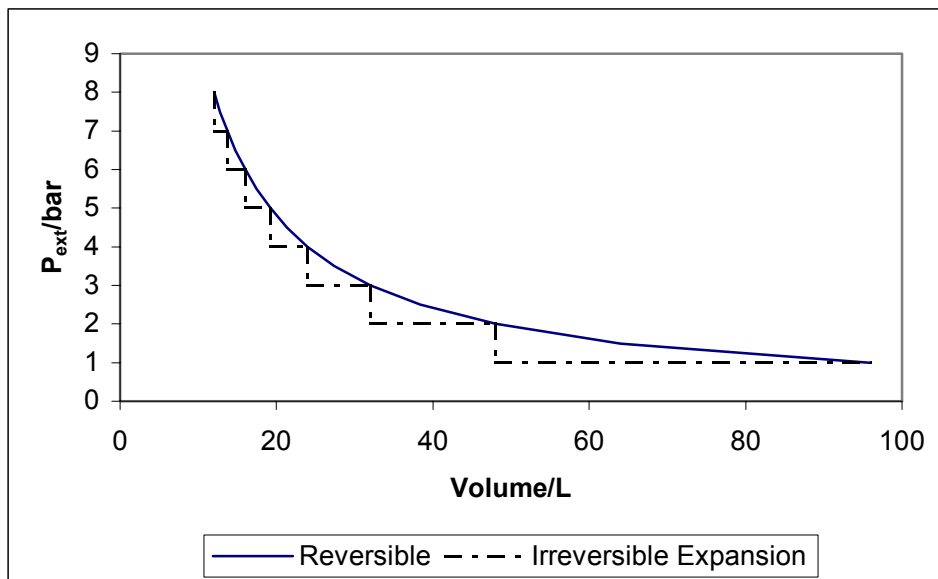


Figure 10-6

If we now irreversibly compress the gas from 96.0 L and 1.0 bar back to the initial point of 12.0 L and 8.0 bar, we obtain the graph shown in Figure 10-7. The compression steps are shown as dashed lines while the previous expansion is the solid line. Recall that the work is the negative of the area under the curve, it is clear that the work of expansion and the work of compression are not equal. Work depends on the path we choose; work is a path variable.

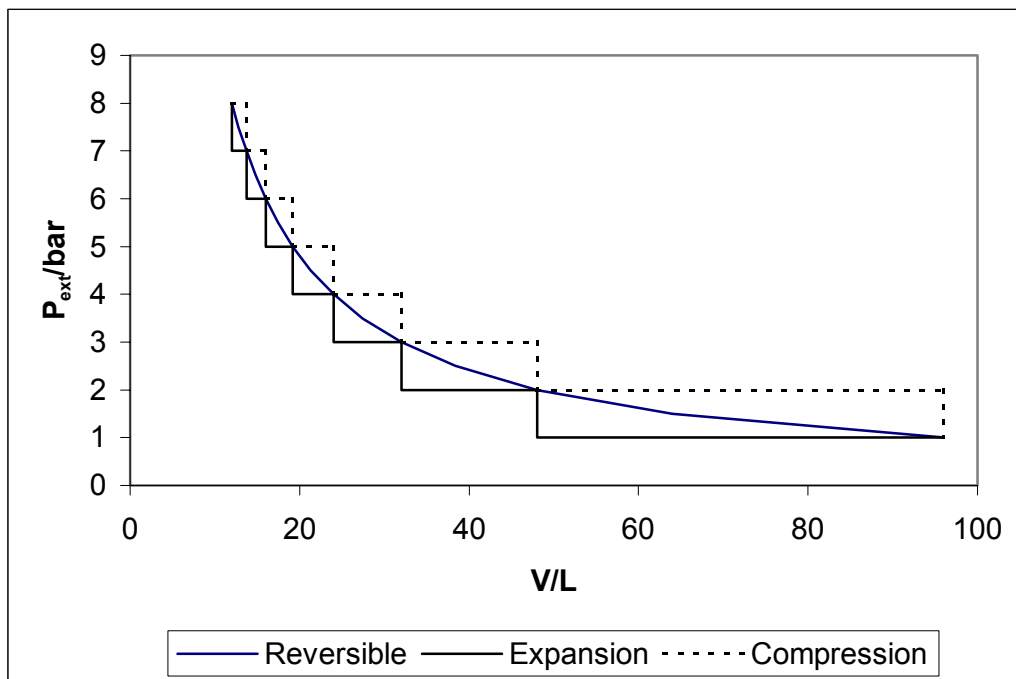


Figure 10-7

## van der Waals and Other Equations of State

The ideal gas equation is a first approximation to the behavior of gases and other, more sophisticated equations describe the behavior of gases better than the ideal gas equation. One of these equations is the van der Waals equation:

$$\left( P + \frac{a}{\bar{V}^2} \right) (\bar{V} - b) = RT$$

The van der Waals equation is an example of a two-parameter equation because the equation contains the two parameters,  $a$  and  $b$ , in addition to the variables,  $P$ ,  $\bar{V}$ , and  $T$ . These parameters correct for some of the inadequacies in the ideal gas equation. The parameter  $a$  is related to a correction for pressures while the parameter  $b$  is a correction for volume. The parameters can be obtained by fitting  $P$ ,  $V$ , and  $T$  data for a gas. The van der Waals parameters are different for each gas and can be found in standard references.

The supplementary section on critical points shows one method of obtaining the van der Waals parameters.

**Table 10-1 Van der Waals Parameters**

|                        | $a/\text{dm}^6 \text{ bar mol}^{-2}$ | $b/\text{cm}^3 \text{ mol}^{-1}$ |
|------------------------|--------------------------------------|----------------------------------|
| $\text{C}_2\text{H}_6$ | 5.489                                | 63.80                            |
| $\text{CH}_4$          | 2.253                                | 42.78                            |
| $\text{CO}$            | 1.485                                | 39.85                            |
| $\text{H}_2$           | 0.2444                               | 26.61                            |
| $\text{H}_2\text{O}$   | 5.464                                | 30.49                            |
| $\text{He}$            | 0.03412                              | 23.70                            |
| $\text{N}_2$           | 1.390                                | 39.13                            |
| $\text{NH}_3$          | 4.170                                | 37.07                            |
| $\text{O}_2$           | 1.360                                | 31.83                            |
| $\text{CO}_2$          | 3.59                                 | 42.7                             |

What is the expression for the reversible isothermal work for a van der Waals gas and how would it differ for the work of an ideal gas? The work is still defined as:

$$w = -\int_{\bar{V}_i}^{\bar{V}_f} P_{\text{ext}} d\bar{V}$$

Solve the van der Waals equation for  $P$  and substitute,

$$w = -\int_{\bar{V}_i}^{\bar{V}_f} \underbrace{\left( \frac{RT}{V-b} - \frac{a}{V^2} \right)}_P d\bar{V}$$

Now we have to integrate.

**Ψ:** What assumptions are necessary to integrate this equation and what is the result of the integration?

**Exercise:** Calculate the work done by reversibly isothermally expanding 1.0 mole of ammonia from 1.2 L to 12.5 L at 325 K assuming:

- ammonia is an ideal gas;
- ammonia is a van der Waals gas.

*Answers:* Ideal work = -6.3 kJ; van der Waals work = -6.7 kJ. 🙌

Under the conditions of the above exercise, the ideal result is different from the van der Waals result by ~ 6%  $((6.7 - 6.4)/6.7 \times 100\%)$ . We use the van der Waals equation, or any other equation of state for a gas, when the ideal gas law does not adequately describe

the behavior of gases. A measure of nonideal behavior of a gas is the compressibility factor,  $Z$ , which is defined as:

$$Z = \frac{P\bar{V}}{RT} \quad (10.7)$$

For an ideal gas,  $Z$  is always one, regardless of the pressure, but for a real gas,  $Z$  can deviate quite significantly from one. These deviations usually occur at high pressures and/or low temperatures (Figure 10-8). These deviations are caused by intermolecular interactions that the ideal gas law neglects, and the deviations are most apparent at higher pressures and lower temperatures. Although the interactions produce negative deviations in Figure 10-8, positive deviations, where  $Z > 1$ , are also common.

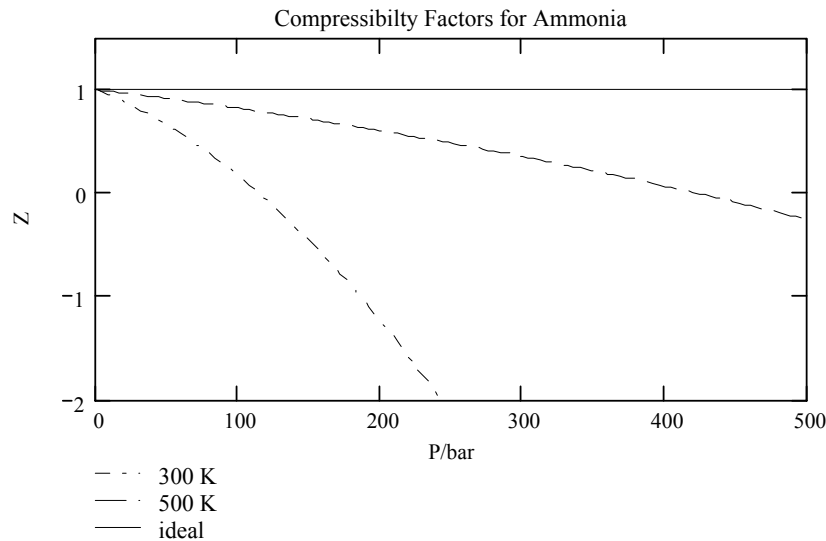


Figure 10-8

The low-pressure region of Figure 10-8 is expanded and shown in Figure 10-9. Even at 300 K and a modest pressure of 20 bar, ammonia has  $Z = 0.87$ , which is a 13% deviation from ideal behavior. It would be unwise to use the ideal gas law at any pressure greater than 20 bar for this gas unless you are willing to accept errors of approximately 13% or greater. Also note that the deviation from ideal behavior is smaller at the higher temperature of 500 K; at 20 bar and 500 K,  $Z = 0.97$  and that is more ideal behavior than at 300 K.

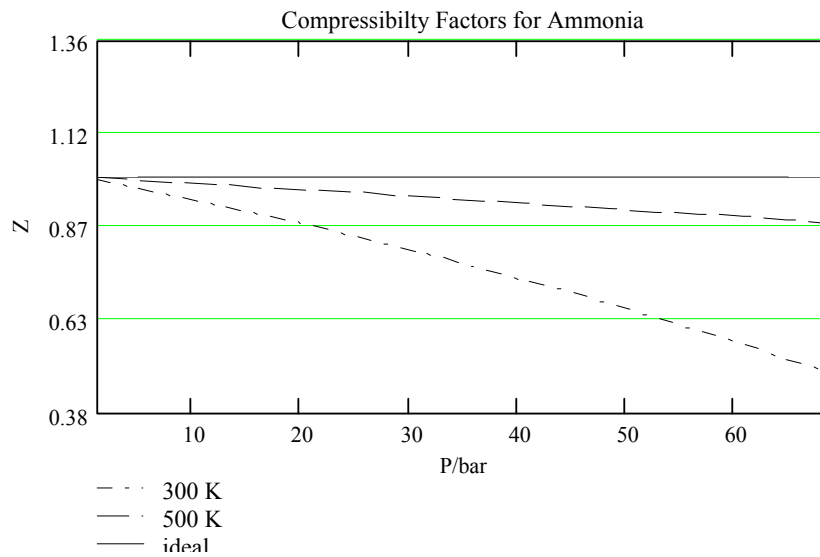


Figure 10-9

Figure 10-10 shows experimental data (solid line) for carbon dioxide at 250 K, and you can see that the van der Waals equation fits the experimental data better than the ideal gas law ( $Z = 1$ ). At very high pressures (in this case, more than  $\sim 150$  bar), even the van der Waals equation fails to reproduce the experimental data.

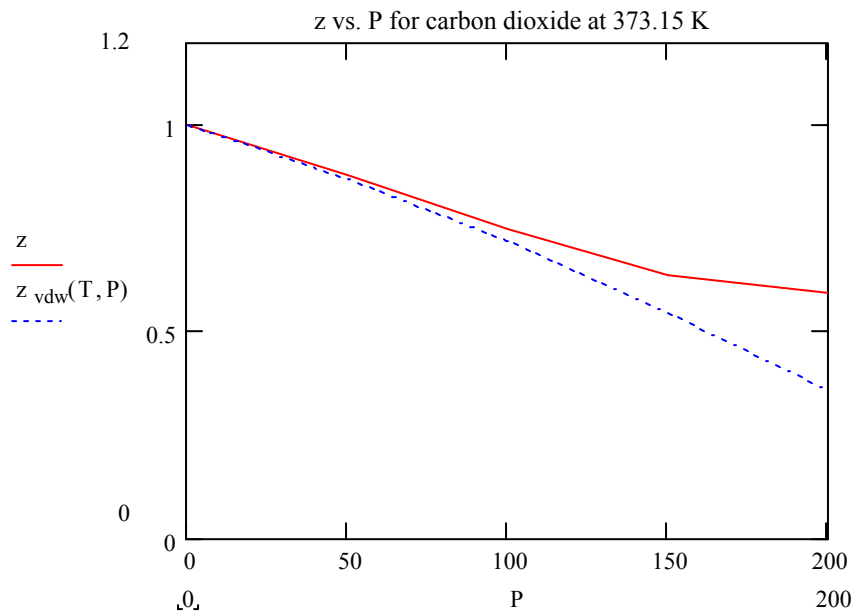


Figure 10-10

At lower pressures, up to 100 bar, the van der Waals equation reproduces the experimental data quite precisely (Figure 10-11).

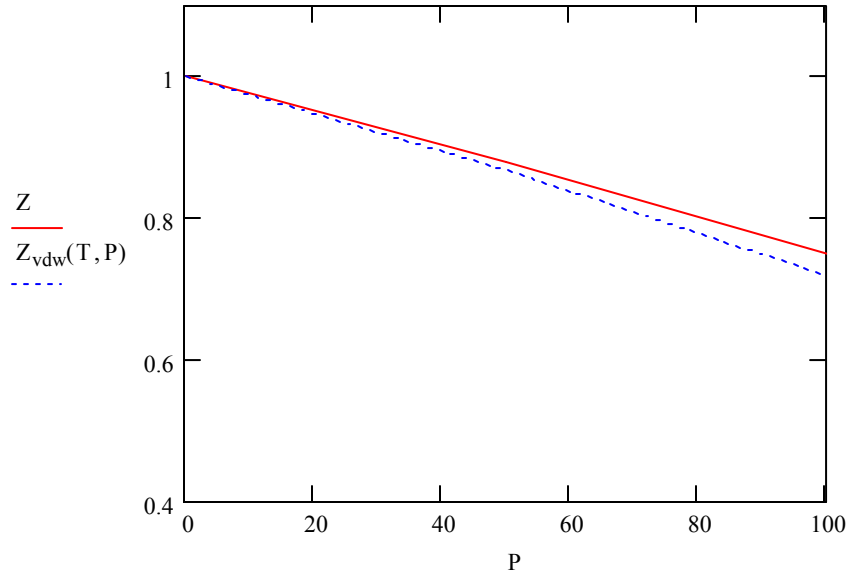


Figure 10-11

As an example of using the van der Waals equation, and as a comparison of calculation methods, let's calculate the molar volume of carbon dioxide at 80 bar and 373 K.

a) Ideal gas law: 
$$\bar{V} = \frac{RT}{P} = \frac{0.08134 \text{ L bar mol}^{-1} \text{ K}^{-1} \times 373 \text{ K}}{80 \text{ bar}} = 0.39 \text{ L mol}^{-1}$$

b) Van der Waals: for  $\text{CO}_2$ ,  $a = 3.59 \text{ dm}^6 \text{ bar mol}^{-2}$  and  $b = 42.7 \text{ cm}^3 \text{ mol}^{-1}$ . Rearrange the van der Waals equation,

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

into:

$$\bar{V} = \frac{RT}{P + \frac{a}{\bar{V}^2}} + b$$

We can solve the latter equation by successive approximations. Use the ideal gas law volume as the initial guess for the volume on the right-hand-side:

$$\bar{V} = \frac{0.08314 \times 373}{80 + \frac{3.59}{0.39^2}} + 0.0427.$$

An Excel spreadsheet produces a molar volume of  $0.30 \text{ L mol}^{-1}$  after 7 iterations:  
0.39 0.342028 0.322867 0.313686 0.308927 0.306363 0.304953 0.304169

Therefore, the van der Waals volume is  $0.30 \text{ L mol}^{-1}$ .

c) Finally, from the graph in Figure 10-10, we determine that  $Z = 0.81$  at 80 bar. Given that

$$Z = \frac{P\bar{V}}{RT}, \text{ then } \bar{V} = \frac{ZRT}{P},$$

and we calculate  $\bar{V} = \frac{0.81 \times 0.08314 \times 373}{80} = 0.31 \text{ L mol}^{-1}$ . This result is essentially the same as the van der Waals result.

**Exercise:** Use the van der Waals equation to calculate the molar volume of  $\text{CO}_2$  at 373 K and 300 bar. Estimate the actual molar volume from Figure 10-10. Why is your agreement not as good as the agreement of the previous example?

## Other Equations of State

Two other common equations of state for gases are the Berthelot and Redlich-Kwong equations. These equations are not necessarily superior to the van der Waals equation and they are introduced to give you some other possibilities for equations of state. Both of the equations are two-parameter equations; that is, they contain the parameters  $a$  and  $b$ . **The  $a$  and  $b$  parameters are different for each equation of state and you must find the values for the specific equation you are using.**

Berthelot: 
$$P = \frac{RT}{\bar{V} - b} - \frac{a}{T\bar{V}^2}$$

Redlich-Kwong 
$$P = \frac{RT}{\bar{V} - b} - \frac{a}{T^{1/2}\bar{V}(\bar{V} + b)}$$

## Microscopic Description of Work and Heat

Thermodynamics deals with macroscopic systems containing large numbers of particles and its laws do not depend on the theories we have developed for microscopic phenomena. However, we can use the information for microscopic systems to help us to understand some thermodynamic concepts.

As a useful example of this approach, let's use the information from statistical mechanics to distinguish between heat and work on a molecular level. We begin by defining a process where we do not allow heat during a process. In this process,  $q = 0$ , therefore  $\Delta U = w$ ; the internal energy changes solely due to work. For ease of calculation, let's use a monatomic gas such as helium as the system. Helium has no vibrational or rotational energy; it only has electronic energy and translational energy. There is no specific equation for electronic energy, but the electronic energy can be obtained from detailed molecular orbital calculations and is a constant. We can always add this constant to our


results if we wish. The translational energy of helium can be obtained from the equation for a particle in a box. We do not need the exact equations for partition functions in this discussion; the Boltzmann Law will be sufficient to illustrate the concepts.

Let's look at two different one-dimensional boxes filled with helium (we could use three-dimensional boxes with the same result). One box has a length of 2 nm, while the other box is 1 nm long. The energy levels for a one-dimensional box are given by the expression:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (10.8)$$

If we evaluate this expression for the different size boxes, we obtain the energy level diagrams in Figure 10-12.

In both cases, the energy gaps between levels are much smaller than the thermal energy at ambient temperature; therefore, the Boltzmann law tells us that *all* of the translational energy levels are populated with helium atoms.

**✎ Exercise:** Show that  $\Delta E$  for helium in a 5 mm box is smaller than  $k_b T$  at room temperature. 

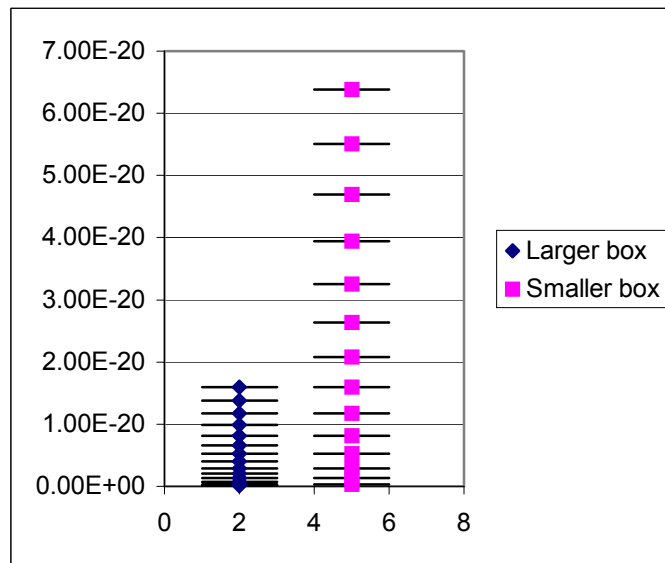


Figure 10-12

We have tabulated 15 energy levels in each case. The total energy of the smaller box is  $\sim 3 \times 10^{-19}$  J while the larger box has a total energy of  $\sim 8 \times 10^{-20}$  J. We observe that as the box gets larger, the total energy decreases. How is this concept translated to the macroscopic scale? To increase the length (or volume in three dimensions) of the box, the system would have to work. The helium atoms would have to collide with a moveable

wall of the container and force it to move, thus increasing the size of the box. In this process, the energy levels are changing, but there is no change in the population of atoms in each level. We conclude that:

***Work is a manifestation of changing the energy levels of the microscopic system.***

To investigate heat transfer, we will not allow any work to be involved in the process;  $w = 0$ , therefore  $\Delta U = q$ . The internal energy changes solely due to heat,  $q$ . What happens on the microscopic scale? For a collection of atoms or molecules, heat effect is explained by the Boltzmann distribution equation (10.9).

$$\frac{N_i}{N_0} = \frac{g_i}{g_0} e^{-\Delta\epsilon_i/kT} \quad (10.9)$$

Since there is no work being done, the energy levels of the system do not change. The only other variable that can be changed is the temperature. What happens to the to the number of atoms in each energy level as we change the temperature?

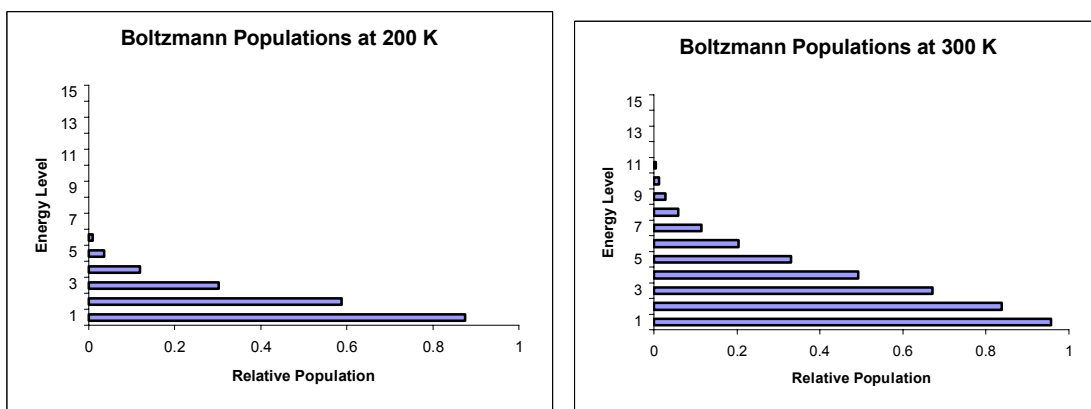


Figure 10-13

In Figure 10-13, we graph the populations of helium atoms at 200 K and 300 K for a one-dimensional box. As you can see, the populations in the upper energy levels increase as we increase the temperature. More energy levels are occupied at the higher temperature, and the internal energy increases. This increase in internal energy is called thermal energy. We immediately see that thermal energy and temperature are related and that thermal energy can be increased through the heat added to the system.

***Heat is a manifestation of changing the populations in the energy levels of the microscopic system.***

The upshot of this discussion is that heat and work are both forms of the same thing – energy. The difference between them is that heat is related to population changes of the energy levels and is intimately connected to temperature, while work is related to changing the energy levels of the microscopic system

## Heat Capacity

The concepts of heat, temperature, and heat capacity are intimately related and often confused. We need to know the precise connection among the quantities. Experience shows that when two objects at different temperatures are placed in contact, their temperatures change. Observations show that the hot object *always* gets colder and the cold object *always* gets hotter until the two temperatures are equal. We describe this process by saying that heat flows from the hot object to the cold object. These observations are summarized by stating that **heat** is a form of energy that always moves from hot to cold.

Temperature is a measure *intensity* of heat – of *how* hot or *how* cold an object is. An iron nail at 555 K is said to be hotter than an iron nail at 315 K. Although temperature is not heat, the temperature and heat are related. Let's separately heat 10 g of water and 10 g of copper. During the heating process, we transfer 40 J of thermal energy to each substance. What happens to the temperature of the water and the copper? For water, the temperature changes by 0.95 K, but for copper, the temperature changes by 10 K. The same quantity of heat does not produce the same temperature change for each substance because each substance has its own capacity to absorb thermal energy. We say that water has a greater heat capacity than copper because water absorbs heat and produces a smaller temperature change than copper. This heat capacity is related to  $q/\Delta T$ . More precisely, the **molar heat capacity** is defined as the amount of heat needed to raise the temperature of exactly 1 mole of a substance by exactly 1 K. The relationship between heat capacity, temperature and heat is:

$$\bar{C} = \frac{q}{n \Delta T}$$

Where  $\bar{C}$  is the molar heat capacity and  $n$  is the number of moles. A substance with a large heat capacity can be heated with little temperature change; conversely, a material with a small heat capacity will have a large temperature change if heated the same way.

☞ **Example:** 5.00 kJ of thermal energy is supplied to 2.0 moles of aluminum. What is the temperature change?  $\bar{C}=0.90 \text{ J mol}^{-1}\text{K}^{-1}$ .

$$\text{Solution: } \Delta T = \frac{q}{n \bar{C}} \text{ so } \Delta T = \frac{5000 \text{ J}}{(2.0 \text{ mol})(0.90 \text{ J mol}^{-1}\text{K}^{-1})} = 2778 \text{ K} = 2.8 \times 10^3 \text{ K}.$$

The temperature of aluminum changes by a large amount because the heat capacity is small. This makes aluminum useful for cooking because the thermal energy from the stove is not absorbed by the metal but instead transferred to the food. 🙌

**Ψ:** Would the temperature change for 2.0 moles of water be greater than or less than the change in aluminum if the same 5.00 kJ of heat flows into each substance? Explain.

A more precise definition of heat capacity accounts for the fact that heat capacity changes with temperature. The heat capacity at a given temperature is a limiting case of

$\bar{C} = \frac{q}{n\Delta T}$ , written as  $\bar{C}(T) = \frac{1}{n} \left( \frac{dq}{dT} \right)$ . The heat capacity per gram of material is also quite commonly used (called the specific heat). The symbol for specific heat is  $C$ , and  $\bar{C} = C \times MW$ . Heat capacities are related to many thermodynamic variables and we will use heat capacity later in this chapter.

On a molecular level, the thermal energy is absorbed and is used to activate translational, rotational, and vibrational motions in the molecule. Since translational energy levels are closely spaced, any thermal energy will increase the population in the upper levels; this produces increased motion – the molecules move faster. The same is true for rotational motion; the levels are closely spaced and any thermal energy populates the higher rotational levels; therefore, the molecules rotate faster. Most molecules are nonlinear and have three rotational and three translational modes, so the heat capacities behave similarly if we look at only rotational and translational modes. It is vibrational motion that causes distinct differences in heat capacities of molecules.

Vibrational modes are different from translation and rotation in two ways: a) vibrational modes are not closely spaced, and b) the number of vibrational modes is quite different for different molecules. Additionally, the vibrational modes of a molecule with low vibrational frequencies are easily activated while the modes of a molecule with high frequencies are not easily activated.

The vibrational partition function *for a diatomic molecule* is:

$$q = \frac{1}{1 - e^{-hc\bar{\omega}/k_B T}}$$

with the corresponding vibrational energy:

$$E = Nhc\bar{\omega} \frac{e^{-hc\bar{\omega}/k_B T}}{1 - e^{-hc\bar{\omega}/k_B T}}$$

Represent the quantity,  $\frac{hc\bar{\omega}}{k_B}$  by the symbol,  $\Theta_v$  and then form  $\frac{\partial E}{\partial T}$ :

$$\frac{\partial E}{\partial T} = \frac{R\Theta_v^2 e^{\Theta_v/T}}{\left( e^{\Theta_v/T} - 1 \right)^2 T^2}$$

Since  $\left( \frac{\partial E}{\partial T} \right)_v = C_v$ , we have:

$$C_v = \frac{R\Theta_v^2 e^{\Theta_v/T}}{\left(e^{\Theta_v/T} - 1\right)^2 T^2} \quad (10.10)$$

for the vibrational contribution to the heat capacity. For the total heat capacity, we add the vibrational contribution to the translational ( $3/2 RT$ ) and rotational ( $RT$  for linear molecules;  $3/2 RT$  for nonlinear molecules) to obtain the total heat capacity. These vibrational modes make the greatest difference in heat capacities of gaseous molecules. At the high temperature limit ( $T \rightarrow \infty$ ),  $C_v$  approaches  $R$ , the equipartition value.

For polyatomic molecules, there is more than one vibrational mode; the heat capacity relation, equation (10.10), becomes:

$$C_v = \sum_i^n \frac{R\Theta_i^2 e^{\Theta_i/T}}{\left(e^{\Theta_i/T} - 1\right)^2 T^2} \quad (10.11)$$

In equation (10.11),  $n$  is the total number of vibrational modes, and  $i$  is an index for a specific mode. Carbon dioxide has four vibrational modes,  $666 \text{ cm}^{-1}$ ,  $1386 \text{ cm}^{-1}$ , and  $2347 \text{ cm}^{-1}$ . At 298 K, these vibrational modes contribute 7.9 of the total  $28.5 \text{ J mol}^{-1} \text{ K}^{-1}$  heat capacity. Hypothetically changing the frequency at  $666 \text{ cm}^{-1}$  to  $1360 \text{ cm}^{-1}$  changes the vibrational contribution from 7.9 to  $4.47 \text{ J mol}^{-1} \text{ K}^{-1}$ .

**Ψ:** Compare the vibrational contributions of the CH stretch and the CO stretch to the heat capacity of formaldehyde,  $\text{H}_2\text{CO}$ . You need to look up the vibrational spectrum or the vibrational frequencies of the CH and CO stretches.

**Ψ:** Graph  $C_v(T)$  vs.  $T$  for a vibrational frequency of  $700 \text{ cm}^{-1}$ . Extend the graph from 1 K to 800 K. Comment on the shape and behavior of the graph. What happens to  $C_v$  at high temperatures? Compare this graph to a graph of  $C_v$  for a vibration of  $1700 \text{ cm}^{-1}$  and comment on the differences. Which graph approaches the equipartition value more rapidly? What is the reason for this behavior?

## State Functions and Their Mathematical Properties

Did you notice that in equation (10.1), the internal energy,  $U$ , is written with uppercase lettering? This is a convention in thermodynamics and the uppercase lettering is used to denote a state function. The change in a **state function** depends only on the initial and final states of the system; it does not depend on the path taken to get from the initial state to the final state.

As an example of a state function, consider a person who wants to get to the top of Pike's Peak (14,110 ft or 4300.5 m). The person can walk along the paved highway (a distance of 21 km), or can follow the hikers' trail through the woods (a distance of 43 km). Walking along the paved highway, the person would travel fewer kilometers to ascend to the peak than if the hikers' trail were followed. Although the same altitude (4300.5 m) would be achieved in each case, the distance traveled would be different (43 vs. 21 km). In this example, the altitude is a state function, and the distance, which depends on the choice of path, is a path function. In thermodynamics, path functions are written in lowercase.

✍ **Exercise:** Identify the state and path functions in the first law. 🙌

State functions have mathematical properties that are useful in deriving or manipulating thermodynamic equations. These properties help us to convert many thermodynamic equations into more useable forms. Let's look at some of these mathematical properties.

### **Exact Differential**

State functions have exact differentials, and exact differentials have specific mathematical properties. How do we know if we have an exact differential? There is a basic mathematical definition for exact differentials. Let's write the differential of  $z$  in the form:

$$dz = M(x, y) dx + N(x, y) dy \quad (10.12)$$

where  $M(x, y)$  and  $N(x, y)$  are unspecified functions that may depend on  $x$  and  $y$ . **The differential,  $dz$ , is exact if:**

$$\frac{\partial M(x, y)}{\partial y} = \frac{\partial N(x, y)}{\partial x} \quad (10.13)$$

We can also write the differential of  $z$ , equation (10.12), as:

$$dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy \quad (10.14)$$

$\updownarrow$   
 $M$

$\updownarrow$   
 $N$

Using equation(10.14), notice that condition (10.13) implies that:

$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y} \quad (10.15)$$

(Note the order of differentiation is different for each case.)

The differential is exact if the mixed second partial derivatives are equal as shown in (10.15). To make these mathematical statements more concrete, let's look at some examples.

☞ **Example:** Is the function,  $z = y/x$  exact?

*Solution:* To be exact,  $\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$ .

$$\frac{\partial z}{\partial x} = \frac{-y}{x^2} \text{ and therefore } \frac{\partial^2 z}{\partial y \partial x} = \frac{-1}{x^2}$$

$$\frac{\partial z}{\partial y} = \frac{1}{x} \text{ and therefore } \frac{\partial^2 z}{\partial x \partial y} = \frac{-1}{x^2}$$

The mixed partial derivatives are equal, so  $dz$  is an exact differential. ☞

☞ **Example:** Is the function  $z = xy$  exact?

*Solution:*

$$\frac{\partial z}{\partial x} = y \therefore \frac{\partial^2 z}{\partial y \partial x} = 1$$

$$\frac{\partial z}{\partial y} = x \therefore \frac{\partial^2 z}{\partial x \partial y} = 1$$

The mixed partial derivatives are equal, so  $dz$  is an exact differential. ☞

☞ **Example:** Is the function,  $dw = -PdV$  exact?

*Solution:* Since this function is already a differential, we use equation (10.13) directly:

$$dw = -PdV + 0dP$$

$$\frac{\partial(-P)}{\partial P} \neq \frac{\partial 0}{\partial V}$$

These derivatives are not equal, so  $dw$  is not exact. Notice that since work is not an exact differential, then work is not a state function. ☞

For an exact differential, the integral depends only on the initial and final limits and not on the path:

$$\int_{z_1}^{z_2} dz = z_2 - z_1$$

For an inexact differential:

$$\int_{z_1}^{z_2} dz \neq z_2 - z_1$$

In this case, the integral depends on the specific path chosen between the points  $z_1$  and  $z_2$ ; this integral is called a line integral. The usefulness of an exact differential (or state variable) is that we do not need to specify the path between the initial and final states. ***The integral of an exact differential will have the same value for any path.***

## **Total Differential**

In this discussion, we will use the variables associated with the internal energy in the examples. Typically, we will write thermodynamic equations using the “natural” variables for a specific function. For instance, the internal energy is usually written as a function of volume and temperature  $U = f(V, T)$ . We choose  $V$  and  $T$  as variables rather than  $P$  and  $T$  or some other pair of variables because the equations and relationships that are produced are simpler and more succinct. Although we will use  $U$ ,  $T$ , and  $V$  to illustrate the concepts, remember that the relationships are valid for any of state function. If  $U = f(V, T)$  and is exact, then, for a closed system, we can express the total differential of  $U$  in terms of the differentials in  $T$  and  $V$ :

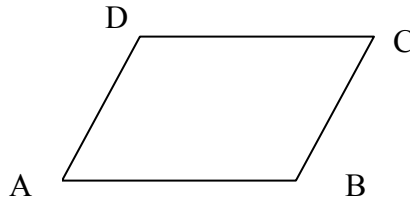
$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad (10.16)$$

This equation represents how the internal energy changes as temperature and volume change. The term  $\left( \frac{\partial U}{\partial T} \right)_V$  is a partial derivative (Appendix: Mathematics); that is, a derivative with respect to one variable while the other variable is held constant. In this specific case,  $V$  is constant as we observe how  $U$  changes with  $T$ . The partial derivative,  $\left( \frac{\partial U}{\partial T} \right)_V$ , tells us how  $U$  changes with  $T$  at a constant volume. This relationship, equation (10.16), is a specific case of the general mathematical relationship for any set of variables  $x, y, z$ :

$$dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy$$

## Cyclic Integral

A cyclic integral is an integral around a closed path, and the symbol  $\oint$  represents a cyclic integral. Consider the figure below:



What is the change in the internal energy as we follow the path:  $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$ ? This is a cyclic path because we start at A, travel around a closed pathway, and return to A. Since a state function depends only on the initial and final states, we have:

$$\oint dU = \Delta U = U_{final} - U_{initial} = U_A - U_A = 0$$

The cyclic integral of any state function around a closed path is zero:  $\oint dU = 0$ .

## Chain Rule

The chain rule for partial derivatives is the same as the chain rule for full derivatives.

$$\left(\frac{\partial U}{\partial V}\right)_P \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P$$

Notice that in the chain rule, the constant variable (the one denoted as a subscript on the partial derivative) is always the same in all the partial derivatives. This fact distinguishes the chain rule from the cyclic rule.

## Cyclic Rule

The cyclic rule relates the different partial derivatives of exact differentials. The cyclic rule involves three variables; in this example, they are  $U$ ,  $T$ , and  $V$ . The easy way to remember the order of variables is to notice that the rule is a permutation of the variables in order. As an example, if we write  $U$ ,  $T$ ,  $V$ , then the order in the derivatives is  $U$ ,  $T$ ,  $V$ . in the first term,  $T$ ,  $V$ ,  $U$  in the second term, and  $V$ ,  $U$ ,  $T$  in the last term. The cyclic rule for this case is:

$$\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial V}{\partial U}\right)_T = -1$$

The chain rule and cyclic rule are used in deriving various thermodynamic equations.

## **Internal Energy Changes for Some Processes**

Now that we've listed some mathematical properties, let's get into the first law. Some typical questions we might ask are:

- How does the energy of a system change for certain processes?
- How do we use the first law to calculate the heat and work for different changes in state?

Our first task is to see how the internal energy changes with temperature. A good place to start is the differential form of the first law, equation (10.2),  $dU = dq + dw$ . If we equate this expression to equation (10.16), which represents the total differential of the internal energy, we get:

$$\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = dq + dw$$

Since we are interested in temperature, let's eliminate the work term. In an isochoric process, both  $dV$  and  $dw$  are zero (explain why) and the equation reduces to:

$$\left(\frac{\partial U}{\partial T}\right)_V dT = dq_V$$

The  $V$  subscript on  $q$  is a reminder that we have imposed constant volume. Notice that we have isolated the temperature effect on the internal energy. Divide both sides of this equation by  $dT$  to obtain:

$$\left(\frac{\partial U}{\partial T}\right)_V = \frac{dq_V}{dT}$$

Now,  $dq_V/dT$  can be written as  $(\partial q/\partial T)_V$  so we rewrite this equation as:

$$\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial q}{\partial T}\right)_V$$

Recall that a change in heat as temperature changes is a heat capacity, so  $(\partial q/\partial T)_V$  is a heat capacity:

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \quad \text{or if we use molar quantities} \quad \left(\frac{\partial \bar{U}}{\partial T}\right)_V = \bar{C}_V \quad (10.17)$$

where  $C_V$  is the heat capacity at constant volume. Note that (10.17) is the definition of  $C_V$ , which is the change in internal energy as the temperature changes. If we substitute equation (10.17) for  $\left(\frac{\partial U}{\partial T}\right)_V$  in equation (10.16), we get:

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (10.18)$$

Equation (10.18) is valid for all processes and all substances because we made no assumptions to obtain it. You may say that we assumed constant volume, and you are correct. We did make that assumption, but now that we have the result, we can drop the assumption of constant volume. Why? Because  $U$  is a state function and **independent** of the path we choose. We chose a constant volume path to derive the equation. After the derivation is complete, the equation is valid for **any** path because the equation contains only state variables. This approach is common in thermodynamics; assumptions are made to derive equations, but the assumptions are removed in the result **if** the result contains only state variables.

Equation(10.18) can be written in terms of molar quantities. All we need do is divide by the number of moles,  $n$  and use molar variables:

$$d\bar{U} = \bar{C}_V dT + \left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T d\bar{V}$$

You should note that equation (10.18) is an improved version of equation (10.16). It is improved because we eliminated a partial derivative and replaced it with an experimentally determined quantity, in this case,  $C_V$ . The replacement of partial derivatives by experimentally determined quantities is usually advantageous in thermodynamics because we can substitute numbers into the equations and calculate values.

The partial derivative term that is left in equation (10.18) is a bit more troublesome to deal with because there is no simple replacement for it. Later, we will see that the partial derivative,  $\left(\frac{\partial U}{\partial V}\right)_T$  can be replaced by:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

If we use this information in equation (10.18), we obtain:

$$dU = C_V dT + \left[ T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \quad (10.19)$$

Equation(10.19) is a thermodynamic equation of state; it expresses the change in a thermodynamic function (internal energy in this case) in terms of experimentally measurable quantities.

**Ψ:** Show that for an *ideal gas*,  $\left(\frac{\partial U}{\partial V}\right)_T = 0$  and therefore  $dU = C_V dT$ .

**Ψ:** Is  $dU = C_V dT$  for a van der Waals gas? Hint: You need to evaluate  $\left(\frac{\partial U}{\partial V}\right)_T$ . Second hint: What is equal to  $\left(\frac{\partial U}{\partial V}\right)_T$  ?

For an ideal gas,  $dU = C_V dT$ . The internal energy of an ideal gas is *solely* a function of temperature. To simplify our discussions, we will consider an ideal gas as the working substance in the system. All of our calculations will focus on the differential forms of the first law, equations (10.2), (10.16), or (10.18). Some useful tips on solving problems are collected in the next section. We will use some of these as we work through some examples.

## **Strategies for Solving Thermodynamic Problems**

Students often get confused when attempting to solve thermodynamics problems. There is a new language to learn, there are new concepts to apply, and sometimes, a new approach has to be learned for problem solving. Everybody has a unique style for solving problems, but if you find yourself in difficulty, this approach may help you:

1. **Read the problem carefully.**
2. Write down useful information.
3. Don't make assumptions that may not be valid; think before you write.
4. Choose the appropriate equations to use.
5. Solve your equations and check your units.
6. Check the order of magnitude of your result.

In my years of teaching, I have observed students who fail to follow this simple approach, and they often get incorrect answers. While this method doesn't guarantee a correct answer, it should get you moving in the right direction. What is important about these steps? Let's elaborate on some of them.

1. Many useful ideas are missed on a cursory reading of a question. Make notes of the physical states of matter described in the problem. In some cases, a simplifying assumption can be made and you fail to notice it. This oversight makes the question more difficult than it was intended to be.
2. Writing things down accomplishes two things: You have a synopsis of important ideas in front of you, and you start thinking about these ideas.
3. This is very important. The number of times students assume that copper is an ideal gas is amazing! Be careful with your assumptions; think about them *before* you apply them. Do not make poor assumptions just to get a result.
4. This point is related to #3. Don't use equations just because you have used them before. Check to see if the equation is *valid* under the conditions of the problem. As an example of this point, if there is nothing in the question that implies the process is reversible, do not use equations designed for reversible processes – they will not work for your problem.
5. Checking units is useful. If your units don't work out, then you have made a mistake. Go back and fix it.
6. Orders of magnitude are important to give you a sense that you have correctly answered the question. If you calculate the mass of an atom to be 37 g, you know you have made an error. In order to use this idea, you need to have a sense of how large or small typical quantities are: A bond energy is  $\sim 400 \text{ kJ mol}^{-1}$ , a bond length is  $\sim 100 \text{ pm}$ . As you work examples, get a sense of the order of magnitude for typical chemical quantities such as  $\Delta U$  and  $\Delta H$ .

Let's put some of these ideas into practice in an example.

☞ **Example:** 5.0 moles of an ideal gas, with  $\bar{C}_V = \frac{3}{2}R$ , expand isothermally and reversibly from 350 K and 2.0 L to a final volume of 13 L. Calculate  $q$ ,  $w$ , and  $\Delta U$  for this process.

*Solution:* An analysis of this example is:

**Steps 1 and 2:**

Use molar quantities here. We have an isothermal process, ideal gas, and a reversible process  $\Rightarrow d\bar{U} = \bar{C}_V dT$

**Step 3:**

Make no other assumptions.

**Step 4:**

Because  $\bar{C}_V$  is a constant we can immediately integrate  $d\bar{U} = \bar{C}_V dT$  to obtain  $\Delta\bar{U} = \bar{C}_V \Delta T$ . Additionally, the process is isothermal and reversible, and equation (10.6) applies:  $w = -nRT \ln(V_f/V_i)$ .

**Step 5:**

Since it is an isothermal process,  $dT = 0$ ; therefore,  $\Delta U = 0$ . We can use equation (10.6) for the work:  $w = -nRT \ln(V_f/V_i)$ . We know the values of  $V_f$ ,  $V_i$ , and  $T$ , so we can calculate the work:  $w = -27$  kJ.

Since  $\Delta U = q + w$  and  $\Delta U = 0$ , we know that  $q = -w = 27$  kJ.

#### Step 6:

The units are correct and the order of magnitude is about right.

*Comment:* Note that since  $\Delta U = 0$ , the work is produced from the heat flow; we heat the system and the system works. 🙌

✎ **Exercise:** An ideal gas with  $\bar{C}_V = 12.9$  J mol<sup>-1</sup>K<sup>-1</sup> is isothermally and irreversibly compressed from 300 K, 1.1 bar, and 2.7 L to 4.5 bar. Calculate  $q$ ,  $w$ , and  $\Delta U$ . 🙌

Note that in isothermal processes,  $\Delta U$  is zero for an ideal gas. This means that any work done by the system must come from heat absorbed by the system. In the exercise you just completed, is  $q$  positive or negative? Explain your reasons for the algebraic sign.

✎ **Exercise:** A certain gas does *not* obey the ideal gas law. What are  $q$ ,  $w$ , and the change in internal energy when one mole of this gas is heated from 250 K to 325 K at constant volume?  $\bar{C}_V$  is 12.5 J mol<sup>-1</sup>K<sup>-1</sup>. (Hint: Read carefully, this problem is easier than it seems.) 🙌

## Adiabatic Processes

What takes place when there is no heat flow during a process? This situation is analogous to a thermos container where the coffee or other liquid in the thermos remains either hot or cold. This type of process is an adiabatic process, and for an adiabatic process,  $q = 0$ . From the first law, equation (10.2), we know that  $dq = 0$  and so  $dU = dw$  for any adiabatic process. We need to specify the system to proceed. As usual, we use an ideal gas.

For an adiabatic process (and one a mole basis):

$$dU = dw$$

or, considering only  $PV$  work:

$$dU = -P_{\text{ext}} dV$$

For an ideal gas, we know that:

$$dU = C_V dT$$

Equating the last two expressions for  $dU$ :

$$C_V dT = -P_{\text{ext}} dV \quad (10.20)$$

This equation is a general equation for the adiabatic processes of ideal gases. Equation (10.20) can now be modified to fit different physical situations.

If the process is reversible, we replace  $P_{\text{ext}}$  by  $P$ :

$$C_V dT = -PdV$$

Substitute for  $P$  Using the ideal gas law produces,

$$C_V dT = -\frac{nRT}{V} dV$$

This is a differential equation and we need to integrate the equation to use it. To integrate, we separate the variables (the same procedure we used in Chapter 3). Rearrange the expression to put temperature terms on one side of the equation and volume terms on the other:

$$C_V \frac{dT}{T} = -\frac{nRdV}{V}$$

Now integrate this equation, assuming a constant  $C_V$ ,

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -nR \int_{V_1}^{V_2} \frac{dV}{V}$$

$$C_V \ln\left(\frac{T_2}{T_1}\right) = -nR \ln\left(\frac{V_2}{V_1}\right) \quad (10.21)$$

This is the working equation for reversible adiabatic expansions (or compressions) of ideal gases. What is the physical interpretation of this equation? In an adiabatic expansion, there is no heat transfer, so the internal energy of the gas is used to produce the work for expansion. In any adiabatic ideal gas expansion, the system works, the internal energy decreases, and therefore, the temperature of the system decreases. In an adiabatic compression, the surroundings work on the system, the internal energy increases, and the temperature of the system increases.

☞ **Example:** 2.3 moles of an ideal gas at 327 K and 1.25 L are allowed to reversibly and adiabatically expand to 2.51 L. What are  $q$ ,  $w$ , and  $\Delta U$  for this process?  
 $\bar{C}_V$  is  $14.5 \text{ J mol}^{-1}\text{K}^{-1}$

*Solution:*

The process is reversible and adiabatic so we can use equation (10.21). We know everything in this equation except for the final temperature, so we plug and chug:

*Note:* we first divided both sides of (10.21) by  $n$ , so we have molar heat capacity:

$$\bar{C}_v \ln\left(\frac{T_2}{T_1}\right) = -R \ln\left(\frac{V_2}{V_1}\right)$$

$$14.5 \text{ J mol}^{-1} \text{ K}^{-1} \ln\left(\frac{T_2}{327 \text{ K}}\right) = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln\left(\frac{2.51 \text{ L}}{1.25 \text{ L}}\right)$$

$\ln\left(\frac{T_2}{327}\right) = -0.3997$ . Solve for  $T_2$ . We find that  $T_2 = 219 \text{ K}$ .

An adiabatic process has  $q = 0$ ; therefore,  $\Delta U = nC_v\Delta T$ .

$$\Delta U = 2.3 \text{ mole} \times 14.5 \text{ J mol}^{-1} \text{ K}^{-1} \times (219 \text{ K} - 327 \text{ K}) = -3.6 \text{ kJ}.$$

Since  $q = 0$ ,  $\Delta U = w \Rightarrow w = -3.6 \text{ kJ}$ . 🙌

Note that the temperature decreased, as it should for an adiabatic expansion.

**Ψ:** Explain why the temperature must decrease for an adiabatic expansion of an ideal gas.

How is an adiabatic process depicted on a  $PV$  diagram? An adiabat is the line of pressure vs. volume that connects two isotherms (Figure 10-14).

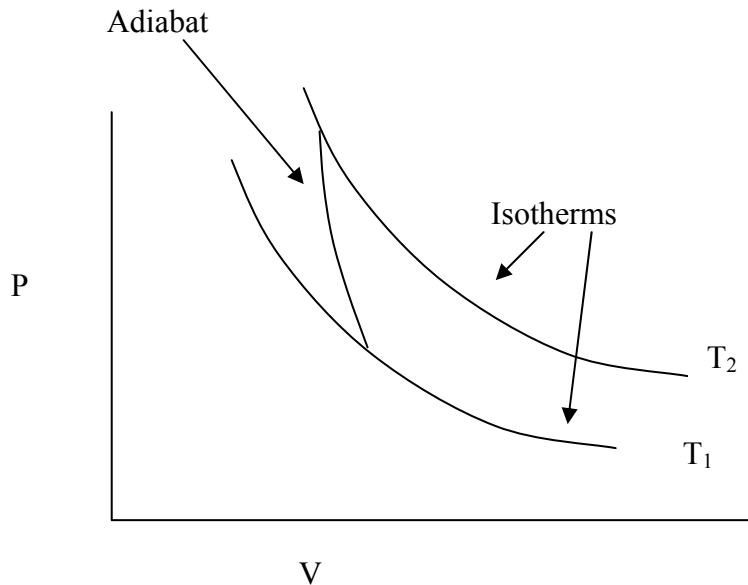


Figure 10-14

**Ψ:** Now that you have seen the approach taken to obtain relationships for a reversible adiabatic process, you should derive an equation for an irreversible adiabatic process. (Hint: Irreversible means that  $P \neq P_{\text{ext}}$  (which is constant and equal to the final pressure)). Use your equation to solve this problem: 1.1 mole of ideal gas with  $\bar{C}_v = 21.2 \text{ J mol}^{-1} \text{ K}^{-1}$  is placed in a container at a pressure of 11.5 bar. The temperature of the gas is 355 K. The gas quickly expands to a pressure of 1.3 bar. What is the final temperature of the gas and  $q$ ,  $w$ , and  $\Delta U$ ?

## Enthalpy

It is apparent from equations (10.18) and (10.16) that the internal energy,  $U$ , is a function of volume and temperature. In chemistry, volume is a less important variable than pressure, because we typically run reactions at constant pressure and not at constant volume. Therefore, we would like to have a thermodynamic quantity that depends on pressure and temperature. Let's produce this new state variable.

The first law is:

$$dU = dq + dw$$

If we assume only  $PV$  work, we obtain:

$$dU = dq - P_{\text{ext}} dV$$

We further assume a reversible process, then  $P_{\text{ext}} = P$ , and

$$dU = dq - PdV$$

Put all state variables on one side:

$$dU + PdV = dq$$

Finally, assume a constant pressure so that  $PdV = d(PV)$ :

$$d(U + PV) = dq_p$$

Everything on the left side of this equation is a state function. We define this combination of variables,  $U + PV$ , as a new state function: the **enthalpy**,  $H$ :

$$H \equiv U + PV \quad (10.23)$$

With this definition, we then produce:

$$dH = dq_p$$

or, if we integrate:

$$\Delta H = q_p$$

Enthalpy is the heat absorbed or released at constant pressure when there is only  $PV$  work. This statement is true whether the process is reversible or irreversible because enthalpy is a state function. This equality is often misinterpreted by stating that the enthalpy is the heat at constant pressure. This is not quite correct. If you have a battery switched on to run a motor, the system does electrical work in addition to  $PV$  work ; we can measure  $q_p$  for this process, but  $q_p$  would not equal  $\Delta H$  in this case.

**Ψ:** Show that  $PdV = d(PV)$  at constant pressure.

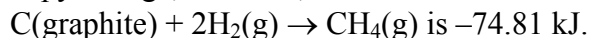
Chemical reactions are generally run at constant pressure, and we can measure the heat absorbed or released; therefore, we know  $\Delta H$ . If we can relate  $\Delta U$  to  $\Delta H$ , we can calculate one quantity when we know the other one. From the definition of enthalpy, equation (10.23), we obtain, at constant pressure:  $\Delta H = \Delta U + P\Delta V$ . Since we are applying this to a chemical reaction, all of the changes are defined as products minus reactants (final – initial). The volume change upon reaction is generally caused by changes in the moles of gas because volume changes of solids and liquids are negligibly small. Furthermore, if we consider that any gases behave ideally, we can write:  $P\Delta V = \Delta n_g RT$ ; therefore,

$$\Delta_r H = \Delta_r U + \Delta n_g RT$$

where  $\Delta n_g$  is the change in the number of moles of gas in the reaction and the subscript  $r$  means for the reaction..

**Ψ:** Compare the molar volume of liquid water ( $d = 1.0 \text{ g mL}^{-1}$ ) to the molar volume of gaseous water. Can you see why liquid and solid volumes are negligible compared to gas volumes?

**Exercise:** The enthalpy change, at 300 K, for the reaction:



What is  $\Delta U$  for the reaction?

*Solution:*  $\Delta U = \Delta H - \Delta n_g RT$ .  $\Delta U = -74810 \text{ J} - (1 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K}) = -72316 \text{ J} = -72.32 \text{ kJ}$ . Notice that  $\Delta n_g$  for the reaction is  $1 - 2 = -1$  (graphite is not a gas and not included in the calculation of  $\Delta n_g$ ). 🙌

## Enthalpy Changes with Temperature and Pressure

Enthalpy is a function of pressure and temperature just as internal energy is a function of volume and temperature. Let's see what useful equations we can derive for changes in enthalpy when pressure or temperature change. The total differential of enthalpy is:

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP \quad (10.24)$$

*Aside:* Notice the similarity of this equation to the equation for internal energy, equation (10.16). Also, notice how the manipulations we are about to perform parallel those we did to equation (10.16). This type of similarity is another common thread in thermodynamics.

At constant pressure,  $dH = dq_P$ , so from equation (10.24) we obtain:

$$dq_p = \left( \frac{\partial H}{\partial T} \right)_p dT$$

Divide both sides by  $dT$ ,

$$\left( \frac{\partial q}{\partial T} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p$$

The first term,  $\left( \frac{\partial q}{\partial T} \right)_p$ , is a heat capacity, but a heat capacity at constant pressure. We define this new heat capacity as:

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad (10.25)$$

or, on a molar basis,

$$\bar{C}_p = \frac{1}{n} \left( \frac{\partial H}{\partial T} \right)_p$$

Equation (10.24) now can be rewritten as:

$$dH = C_p dT + \left( \frac{\partial H}{\partial P} \right)_T dP \quad (10.26)$$

Since equation (10.26) contains only state variables, it is universally true. Note the similarity between equations (10.18) and (10.26); also, notice that we have eliminated a partial derivative in equation (10.24) and substituted an experimental quantity,  $C_p$ , into the enthalpy equation.

Can equation (10.26) be simplified for certain materials? Recall that for an ideal gas, we said that  $\left( \frac{\partial U}{\partial V} \right)_T = 0$ . Is there a similar relation for the enthalpy? In other words, can we replace  $\left( \frac{\partial H}{\partial P} \right)_T$ ?

We start with the definition of  $H$ ,

$$H = U + PV$$

We want  $\left( \frac{\partial H}{\partial P} \right)_T$ , so differentiate the definition of  $H$  with respect to  $P$  at constant  $T$ .

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial PV}{\partial P}\right)_T$$

For an ideal gas, the product  $PV$  is independent of  $P$ , that is:

$$\left(\frac{\partial PV}{\partial P}\right)_T = 0$$

Therefore, the expression for  $\left(\frac{\partial H}{\partial P}\right)_T$  reduces to:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T$$

To proceed further, we need  $\left(\frac{\partial U}{\partial P}\right)_T$ . For an ideal gas, we don't know  $\left(\frac{\partial U}{\partial P}\right)_T$  but we do know that  $\left(\frac{\partial U}{\partial V}\right)_T = 0$ , so we have to relate  $\left(\frac{\partial U}{\partial P}\right)_T$  to  $\left(\frac{\partial U}{\partial V}\right)_T$ . Notice that  $T$  is constant in both derivatives; this is an indication to try the chain rule. We write:

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

Since  $\left(\frac{\partial U}{\partial V}\right)_T = 0$ , we have shown that  $\left(\frac{\partial U}{\partial P}\right)_T = 0$

Therefore;

$$\left(\frac{\partial H}{\partial P}\right)_T = 0$$

**The internal energy and the enthalpy of an ideal gas depend solely on the temperature.**

**Ψ:** Why is the product  $PV$  independent of  $P$  for an ideal gas?

☞ **Example:** 3.0 moles of chlorine ( $\bar{C}_p = 33.91 \text{ J/mol K}$ ) at 365 K are irreversibly cooled to 308 K at 1.0 bar. What are  $\Delta U$ ,  $\Delta H$ ,  $q$ , and  $w$  for this process? Assume ideal behavior.

*Solution:* Since this is a constant pressure process, it seems reasonable to focus on enthalpy. For an ideal gas,  $d\bar{H} = \bar{C}_p dT$ ; integrating, we get  $\Delta\bar{H} = \int \bar{C}_p dT$ . Since the heat capacity is constant, we obtain  $\Delta\bar{H} = \bar{C}_p \Delta T$ .

Consequently,  $\Delta H = 3.0 \text{ mol} \times 33.91 \text{ J mol}^{-1}\text{K}^{-1} \times (308 \text{ K} - 365 \text{ K}) = -5.8 \text{ kJ}$ . Since this is a constant pressure process,  $\Delta H = q$ ; so that  $q = -5.8 \text{ kJ}$ .

From the ideal gas law,  $V_i = (3.0 \text{ mol} \times 0.0831 \text{ J mol}^{-1}\text{K}^{-1} \times 365 \text{ K})/1.0 \text{ bar} = 89.8 \text{ L}$  and  $V_f = 75.8 \text{ L}$ .  $w = -P\Delta V = 14 \text{ L}\cdot\text{bar} = 1.4 \text{ kJ}$ .

Finally,  $\Delta U = q + w = -5.8 \text{ kJ} + 1.4 \text{ kJ} = -4.4 \text{ kJ}$ . The temperature decrease and since the internal energy of an ideal gas depends solely on temperature, the internal energy decreases and molecular energy decreases. 🙌

✎ **Exercise:** An ideal gas at 315 K absorbs 6.5 kJ of thermal energy in a constant volume container. What are  $\Delta U$ ,  $\Delta H$ ,  $q$ , and  $w$  for this process?  $\bar{C}_v = 12.5 \text{ J mol}^{-1}\text{K}^{-1}$  and  $\bar{C}_p = 21.0 \text{ J mol}^{-1}\text{K}^{-1}$ . 🙌

## Temperature Variation of the Enthalpy

In the previous examples, we assumed that the heat capacity is constant, but in reality, this approximation generally is not valid. We must account for the changes in heat capacities as the temperature changes for more realistic results. The temperature dependence of heat capacities are generally presented in two ways:

- The heat capacity is given as tabular data;
- The heat capacity is given in a functional form.

### Case a:

Quite often, we can find tables of experimental heat capacity data such as:

| $T/\text{K}$ | $\bar{C}_p / \text{J mol}^{-1} \text{K}^{-1}$ |
|--------------|---|
| 300          | 25.44   |
| 400          | 26.89   |
| 600          | 28.33   |
| 700          | 28.75   |
| 900          | 28.99   |

How do we calculate the enthalpy change from this tabular data? We know that  $d\bar{H} = \bar{C}_p dT$ ; if we integrate, we obtain:

$$\Delta\bar{H} = \int_{T_1}^{T_2} \bar{C}_p dT$$

The integral is the area under the curve of  $\bar{C}_p$  vs.  $T$ . Let's evaluate the integral for the change from 400 K to 700 K (note that we don't have to use all the data). A graph of this heat capacity data is shown in Figure 10-15.

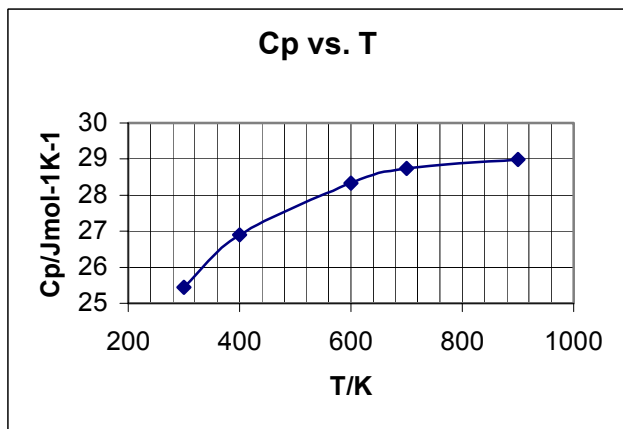
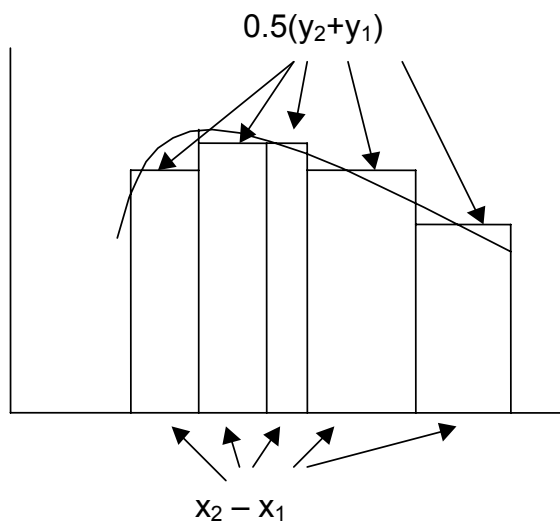


Figure 10-15

The simplest, though not the most accurate, way to obtain the area is by the trapezoidal rule ( Mathematics Appendix). The trapezoidal rule approximates the area between two pairs of  $x,y$  points as:  $0.5(y_2+y_1)*(x_2-x_1)$ . Note that this assumes the area is a rectangle where  $0.5(y_2+y_1)$  is the average height of the rectangle and  $(x_2-x_1)$  is the width of the rectangle (see figure below). By summing these rectangles, we can obtain the area over a set of data points. Although there are better methods of estimating the integral, the trapezoidal rule is more general because it places no restrictions on the data interval in the function. Simpson's rule, for example, requires equally spaced data along the x-axis.



**Exercise:** Graph the data and use the trapezoidal rule to estimate the enthalpy change from 400 K to 700 K. *Answer:* 14.1 kJ. 🙌

### Case b:

If we are given a functional form for the heat capacity, we have to integrate the function to obtain the enthalpy change. Various equations exist to describe the temperature dependence of the heat capacity, and one equation is:

$$\bar{C}_p / (\text{J mol}^{-1} \text{K}^{-1}) = a + bT + \frac{c}{T^2}$$

To obtain the enthalpy change using this heat capacity equation, we integrate:

$$\Delta\bar{H} = \int_{T_1}^{T_2} \left[ a + bT + \frac{c}{T^2} \right] dT$$

**Example:** What is the enthalpy change in cooling 1 mole of methane, from 415 K to 325 K at 1 bar?

*Solution:* Look up the heat capacity function for methane (Table 10-2).

$$\bar{C}_p / \text{Jmol}^{-1} \text{K}^{-1} = 23.67 + 0.04786T - \frac{1.92 \times 10^5}{T^2}$$

Integrate:

$$\begin{aligned} \Delta\bar{H} &= \int_{415}^{325} \left[ 23.67 + 0.04786T - \frac{1.92 \times 10^5}{T^2} \right] dT \\ \Delta\bar{H} &= 23.67T + \frac{0.04786}{2} T^2 + \frac{1.92 \times 10^5}{T} \Bigg|_{415}^{325} \end{aligned}$$

Evaluate the expression at the upper and lower limits:  $\Delta\bar{H} = 1.081 \times 10^4 - 1.441 \times 10^4 = -3.60 \times 10^3 \text{ J mol}^{-1}$ , or for 1 mol of gas,  $-3.60 \text{ kJ}$ . Note that the enthalpy change is negative because we are cooling methane. 🙌

Do not memorize this equation or the answer because the result depends on the original heat capacity equation, which changes for each substance. The process or method is important. Situation change and you must adapt your process to the situation. Often we assume that the heat capacity is constant and therefore  $\Delta H = C_p \Delta T$ ; at other times, as in this example, the heat capacity is a function of temperature and has to be integrated.

**Exercise:** What is the enthalpy change necessary to heat 3 moles of carbon dioxide from 215 K to 400 K a) assuming a constant heat capacity of  $58.1 \text{ J mol}^{-1} \text{K}^{-1}$  b) using the heat capacity equation from Table 10-2? 🙌

Table 10-2

$$\bar{C}_p / (\text{Jmol}^{-1}\text{K}^{-1}) = a + bT + \frac{c}{T^2}$$

| <b>Gases</b>     | a     | b/10 <sup>3</sup> | c/10 <sup>-5</sup> | <b>Liquids</b>                 | a     | b/10 <sup>3</sup> | c/10 <sup>-5</sup> |
|------------------|-------|-------------------|--------------------|--------------------------------|-------|-------------------|--------------------|
| H <sub>2</sub>   | 27.28 | 3.26              | 0.50               | I <sub>2</sub>                 | 80.33 | —                 | —                  |
| O <sub>2</sub>   | 29.96 | 4.18              | -1.67              | H <sub>2</sub> O               | 75.48 | —                 | —                  |
| N <sub>2</sub>   | 28.58 | 3.77              | -0.50              | C <sub>10</sub> H <sub>8</sub> | 79.50 | 407.5             | —                  |
| CO               | 28.41 | 4.10              | -0.46              |                                |       |                   |                    |
| Cl <sub>2</sub>  | 37.03 | 0.67              | -2.85              |                                |       |                   |                    |
| Br <sub>2</sub>  | 37.32 | 0.50              | -1.26              |                                |       |                   |                    |
| I <sub>2</sub>   | 37.40 | 0.59              | -0.71              |                                |       |                   |                    |
| CO <sub>2</sub>  | 44.23 | 8.79              | -8.62              |                                |       |                   |                    |
| H <sub>2</sub> O | 30.54 | 10.29             | —                  |                                |       |                   |                    |
| H <sub>2</sub> S | 32.68 | 12.38             | -1.92              |                                |       |                   |                    |
| NH <sub>3</sub>  | 29.75 | 25.10             | -1.55              | <b>Solids</b>                  | a     | b/10 <sup>3</sup> | c/10 <sup>-5</sup> |
| CH <sub>4</sub>  | 23.67 | 47.86             | -1.92              | C (graphite)                   | 16.86 | 4.77              | -8.54              |
|                  |       |                   |                    | Al                             | 20.67 | 12.38             | —                  |
|                  |       |                   |                    | Cu                             | 22.64 | 6.28              | —                  |
|                  |       |                   |                    | Pb                             | 22.13 | 11.72             | 0.96               |
|                  |       |                   |                    | I <sub>2</sub>                 | 40.12 | 49.79             | —                  |
|                  |       |                   |                    | C <sub>10</sub> H <sub>8</sub> | -116  | 937               | —                  |
|                  |       |                   |                    | Al <sub>2</sub> O <sub>3</sub> | 114.8 | 12.8              | -35.4              |
|                  |       |                   |                    | CuO                            | 38.8  | 20.1              | —                  |
|                  |       |                   |                    | Ag                             | 21.3  | 8.54              | -1.5               |
|                  |       |                   |                    | AgCl                           | 62.26 | 4.18              | -11.3              |

For gases the constants apply from 298 K to 2000 K

For liquids, the constants apply at 1 bar from melting point to boiling point.

For solids constants apply at 1 bar from 298 K to melting point or 2000 K.

Source: G.N. Lewis, M. Randall, K. Pitzer, and L. Brewer, *Thermodynamics*, 1961: New York, McGraw-Hill Book Co. (and miscellaneous others).

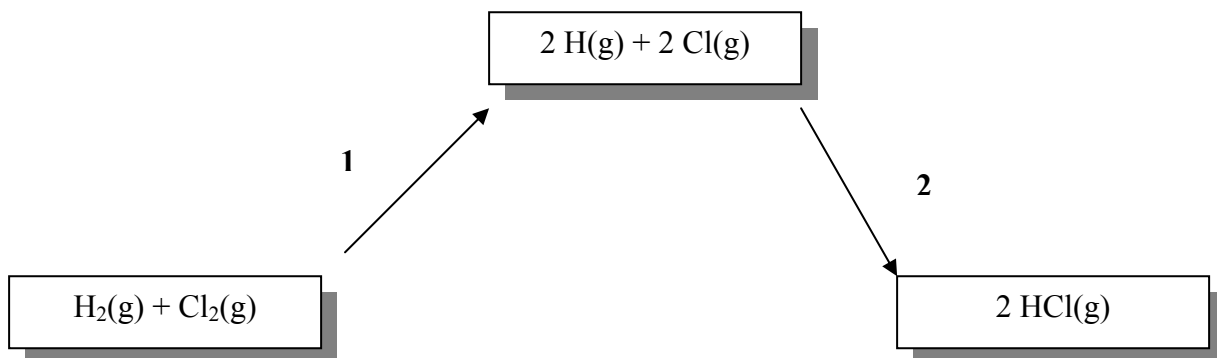
## Reaction enthalpy

Our final issue concerns a concept that is most useful to chemists: How much heat is absorbed or released during a chemical reaction? The quantity of heat is an important commodity for practical reasons. In our society, fossil fuels (coal, oil, natural gas) are typically burned to produce thermal energy for heating houses. How much natural gas is needed to heat a house of a particular size? Is one type of fuel more efficient than another type in providing the requisite heat? All of these questions involve the heat associated with chemical reactions and therefore we need to investigate the enthalpy of chemical reactions.

To answer questions like this one, we will use the state function properties of the enthalpy. Consider a typical reaction:



Since enthalpy is a state function, we can *imagine* the path from reactants to products occurring in two steps.

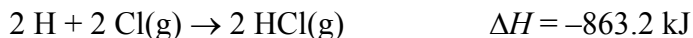


In step 1, energy is supplied to break bonds and to form atoms. In step 2, energy is released as new chemical bonds are made by combining atoms. The enthalpies for step 1 are the bond dissociation energies for  $\text{H}_2$  and  $\text{Cl}_2$  respectively:

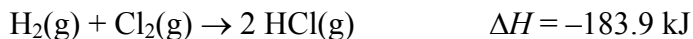


Therefore, it requires 679.03 kJ to dissociate one mole of hydrogen and one mole of chlorine into their atoms.

In step 2, we combine these atoms, make the bonds in hydrogen chloride, and release energy:



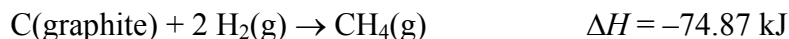
So the total enthalpy change is  $679.30 \text{ kJ} - 863.2 \text{ kJ} = -183.9 \text{ kJ}$ . Therefore:



This reaction *does not really proceed* the way we have diagrammed it, and the actual sequence of steps is more complicated. However, the enthalpy change we calculated is valid no matter what sequence of steps is required to produce the product because enthalpy is a state function and is independent of path. We can choose any path we desire

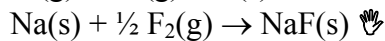
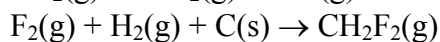
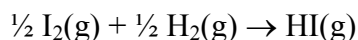
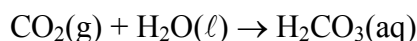
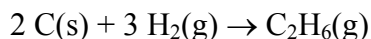
to calculate the enthalpy. This procedure of taking a reaction and breaking it up into a series of steps in order to calculate  $\Delta H$  is referred to as Hess's Law.

Where do we obtain the enthalpies of substances so that we can use them in reaction enthalpy calculations? Generally, these enthalpies are listed in tables, but before we introduce these tables, consider a specific reaction:



This reaction is an example of a formation reaction. A **formation reaction** is a reaction that produces **one** mole of **one** product from the **elements** in their most stable forms at 1 bar. Formation reactions are the foundation for the data in enthalpy tables.

✎ **Exercise:** Which of these are formation reactions?



Every element and compound has an absolute enthalpy but we have no way of measuring it. Instead, we use a relative scale based on the standard enthalpy of formation,  $\Delta_f H^\circ$ . The **standard enthalpy of formation** is the enthalpy of a substance at 1 bar. Furthermore, the reference point for this enthalpy scale is set by the condition that the standard enthalpy of formation of any element in its most stable form is zero. Additionally, these enthalpies are reported at the conventional temperature of 298.15 K. These standard enthalpies of formation are listed in the NIST Chemistry Webbook at <http://webbook.nist.gov/chemistry/>.

For any chemical reaction, the reaction enthalpy is obtained by the sum of the standard enthalpies of formation of reactants minus the sum of the standard enthalpies of formation of products, or mathematically,

$$\Delta H^\circ = \sum_i n_i \Delta_f H^\circ(i)$$

In this equation, the index,  $i$ , labels chemical  $i$ , while  $n_i$  is the molar coefficient of chemical  $i$  in the balanced equation ( $n_i$  is defined to be positive for products and negative for reactants).  $\Delta_f H^\circ(i)$  is the enthalpy of formation of chemical  $i$ . For the formation reaction of methane,  $\text{C}(\text{graphite}) + 2 \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$ , we would write:

$$\Delta H^\circ = \underbrace{\Delta_f H^\circ(\text{CH}_4)}_{\text{products}} - \underbrace{[\Delta_f H^\circ(\text{C}) + 2\Delta_f H^\circ(\text{H}_2)]}_{\text{reactants}}$$

Since carbon and hydrogen are in their most stable forms, their enthalpies of formation are zero. Thus,  $\Delta H^\circ = \Delta_f H^\circ(\text{CH}_4)$ , and the enthalpy we measured for this reaction,  $-74.81$  kJ, is the enthalpy of formation of methane.

☞ **Example:** Calculate the enthalpy for the reaction:



*Solution:* The equation is balanced (always check to see that the equation is balanced), therefore, we have:

$$\Delta H^\circ = \underbrace{\left[ \Delta_f H^\circ(\text{CH}_3\text{COOH}) + \Delta_f H^\circ(\text{H}_2\text{O}) \right]}_{\text{products}} - \underbrace{\left[ \Delta_f H^\circ(\text{C}_2\text{H}_5\text{OH}) + \Delta_f H^\circ(\text{O}_2) \right]}_{\text{reactants}}.$$

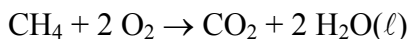
We look up the enthalpies of formation and substitute to obtain:

$$\Delta H^\circ = [1 \text{ mol} \times -484.5 \text{ kJ mol}^{-1} + 1 \text{ mole} \times -285.83 \text{ kJ mol}^{-1}] - [1 \text{ mole} \times -277.6 \text{ kJ mol}^{-1} + 1 \text{ mole} \times 0 \text{ kJ mol}^{-1}] = -492.2 \text{ kJ.} \text{☞}$$

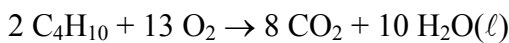
☞ **Exercise:** Calculate the enthalpy for the reaction  $\text{C}_2\text{H}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell)$ .

☞ **Example:** Which fuel produces more heat of combustion per mole,  $\text{CH}_4$  or  $\text{C}_4\text{H}_{10}$ ?

*Solution:* The balanced equations are:



And



$$\Delta H^\circ = \left[ \underbrace{\Delta_f H^\circ(\text{CO}_2)}_{-393.51} + \underbrace{2\Delta_f H^\circ(\text{H}_2\text{O})}_{2 \times -285.83} \right] - \left[ \underbrace{\Delta_f H^\circ(\text{CH}_4)}_{-74.81} + \underbrace{2\Delta_f H^\circ(\text{O}_2)}_{2 \times 0} \right] = -890.36$$

$$\Delta H^\circ = \left[ \underbrace{8\Delta_f H^\circ(\text{CO}_2)}_{8 \times -393.51} + \underbrace{10\Delta_f H^\circ(\text{H}_2\text{O})}_{10 \times -285.83} \right] - \left[ \underbrace{2\Delta_f H^\circ(\text{C}_4\text{H}_{10})}_{2 \times -127.1} + \underbrace{13\Delta_f H^\circ(\text{O}_2)}_{13 \times 0} \right] = -5752$$

The methane reaction produces 890 kJ/mole of methane while the butane reaction produces  $5752/2 = 2876$  kJ/mole of butane. On a mole basis, butane is more efficient at producing the thermal energy. On a gram basis, we have 55.6 kJ/g methane and 99.2 kJ/g butane. Butane is still more efficient.

☞ **Exercise:** Calculate the energy per mole for octane and decane and compare the values with those for methane and butane. Is there a trend in these four values? If so, what is the trend? ☞

## Relationship between $C_P$ and $C_V$

There is a relationship between the two heat capacities,  $C_V$  and  $C_P$ , and this relationship is useful because we can convert one type of heat capacity into the other. Let's try to find the connection. This derivation is not to be memorized, but as in the previous example derivations, it will demonstrate some typical manipulations used in thermodynamics.

Let's use the difference between the heat capacities as a starting point; if  $C_V$  and  $C_P$  are not different, we should get zero as a result. From the definitions of the heat capacities, we have:

$$\bar{C}_P - \bar{C}_V = \left( \frac{\partial \bar{H}}{\partial T} \right)_P - \left( \frac{\partial \bar{U}}{\partial T} \right)_V$$

Substitute the definition:  $H \equiv U + PV$  into the first term on the right hand side of the equation,

$$\bar{C}_P - \bar{C}_V = \left( \frac{\partial (\bar{U} + P\bar{V})}{\partial T} \right)_P - \left( \frac{\partial \bar{U}}{\partial T} \right)_V$$

Expand the  $U + PV$  term:

$$\bar{C}_P - \bar{C}_V = \left( \frac{\partial \bar{U}}{\partial T} \right)_P + \left( \frac{\partial P\bar{V}}{\partial T} \right)_P - \left( \frac{\partial \bar{U}}{\partial T} \right)_V$$

Take the derivative  $\left( \frac{\partial P\bar{V}}{\partial T} \right)_P$  (Note: Use the product rule for derivatives and remember that the pressure is constant). Substitute this derivative into the above equation:

$$\bar{C}_P - \bar{C}_V = \left( \frac{\partial \bar{U}}{\partial T} \right)_P + P \left( \frac{\partial \bar{V}}{\partial T} \right)_P - \left( \frac{\partial \bar{U}}{\partial T} \right)_V \quad (10.27)$$

The term  $\left( \frac{\partial \bar{V}}{\partial T} \right)_P$  is the change in volume with temperature, and we certainly can measure it; the last term is  $C_V$ , which is also measurable. However, what can we do with the first term  $\left( \frac{\partial \bar{U}}{\partial T} \right)_P$ ? It is certainly not something we have seen previously. We have to relate it

to something more useful or eliminate it. *Aside:* This is not the heat capacity; the constant variable is  $P$  and not  $V$ .

Since this term contains  $U$ , let's start with the total differential of  $U$ .

$$d\bar{U} = \left( \frac{\partial \bar{U}}{\partial T} \right)_V dT + \left( \frac{\partial \bar{U}}{\partial \bar{V}} \right)_T d\bar{V}$$

Divide through by  $dT$  at constant pressure to produce the term we want,  $\left( \frac{\partial \bar{U}}{\partial T} \right)_P$ .

$$\left( \frac{\partial \bar{U}}{\partial T} \right)_P = \left( \frac{\partial \bar{U}}{\partial T} \right)_V \underbrace{\left( \frac{\partial T}{\partial T} \right)_P}_{=1} + \left( \frac{\partial \bar{U}}{\partial \bar{V}} \right)_T \left( \frac{\partial \bar{V}}{\partial T} \right)_P$$


Now substitute this expression for  $\left( \frac{\partial \bar{U}}{\partial T} \right)_P$  into equation (10.27) to produce:


$$\bar{C}_P - \bar{C}_V = \left( \frac{\partial \bar{U}}{\partial T} \right)_V + \left( \frac{\partial \bar{U}}{\partial \bar{V}} \right)_T \left( \frac{\partial \bar{V}}{\partial T} \right)_P + P \left( \frac{\partial \bar{V}}{\partial T} \right)_P - \left( \frac{\partial \bar{U}}{\partial T} \right)_V$$

The first and last terms in this equation cancel, and we can factor  $\left( \frac{\partial \bar{V}}{\partial T} \right)_P$  out of the middle two terms to obtain the relationship:

$$\bar{C}_P - \bar{C}_V = \left( \frac{\partial \bar{V}}{\partial T} \right)_P \left[ \left( \frac{\partial \bar{U}}{\partial \bar{V}} \right)_T + P \right] \quad (10.28)$$

Equation (10.28) is the equation that we sought. It is the connection between the two heat capacities and it is valid for any substance. All other relations between the heat capacities are special cases of equation (10.28).

**✎ Exercise:** Show that for an ideal gas  $\bar{C}_P - \bar{C}_V = R$ . (Hints: Recall what  $\left( \frac{\partial \bar{U}}{\partial \bar{V}} \right)_T$  becomes for an ideal gas, and evaluate  $\left( \frac{\partial \bar{V}}{\partial T} \right)_P$  from the ideal gas law.) 

**✎ Exercise:** 5 moles of ideal gas with  $\bar{C}_V = \frac{1}{2}R$  are heated from 225 K to 315 K. What is the change in the internal energy and the enthalpy? 

**Ψ:** What is the relationship of  $\bar{C}_p$  to  $\bar{C}_v$  for a van der Waals gas?

## ***Application of Adiabatic Processes***

Earlier, we derived an equation for adiabatic processes that related temperature to volume:

$$\bar{C}_v \ln\left(\frac{T_2}{T_1}\right) = -R \ln\left(\frac{\bar{V}_2}{\bar{V}_1}\right)$$

We will now derive an expression that relates temperature to pressure and then use the expression to discuss thunderclouds. Thunderclouds are generally very large systems with altitudes of  $\sim 50\,000$  to  $70\,000$  feet. There is a large temperature differential in these clouds and this temperature change produces either rain or hail. A common approximation is to assume that the temperature changes within a thundercloud are the result of adiabatic processes. First, we need an expression that relates temperature to pressure for the adiabatic process.

Begin with the first law,

$$dU = dq + dw$$

For an adiabatic process this becomes:

$$dU = dw$$

Assume only  $PV$  work, and a reversible process:

$$dU = -PdV$$

Insert the definition of enthalpy:

$$d(H - PV) = -PdV$$

or

$$dH - PdV - VdP = -PdV$$

Canceling terms produces:

$$dH = VdP$$

Assume an ideal gas, so that  $dH = C_p dT$

$$C_p dT = \frac{nRT}{P} dP$$

Divide by  $n$ , separate the variables, and integrate (assuming a constant heat capacity):

$$\bar{C}_p \ln \frac{T_2}{T_1} = R \ln \frac{P_2}{P_1} \quad (10.29)$$

Equation (10.29) is a relationship between the temperature and pressure for a reversible adiabatic process. Note that this equation is analogous to equation (10.21).

Atmospheric pressure varies with height (or altitude) according to the barometric formula:

$$P = P_0 e^{-Mgh/RT}$$

where:

$M$  is the molar mass of the gas (kg/mol);

$g$  is the acceleration of gravity;

$h$  is the altitude

$R$  is the gas constant

$T$  is the Kelvin temperature

And  $P_0$  is the pressure at zero altitude.

Let's assume that the atmospheric pressure is 1.00 bar at 35 °C. Air has an average molar mass of 29.1 g/mol. We can calculate the pressure at the top of a 50 000 foot (15.1 km) thundercloud is 0.183 bar. The heat capacity of air is 29.4 J mol<sup>-1</sup> K<sup>-1</sup>. What is the estimated temperature at 50 000 feet?

$$29.4 \text{ J mol}^{-1} \text{ K}^{-1} \ln \frac{T_2}{308 \text{ K}} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \ln \frac{0.183 \text{ bar}}{1 \text{ bar}}$$

The estimated temperature is 191 K! This is well below the freezing point of water and you can see why hail (large ice) is easily formed in thunderclouds.

## ***What Have We Learned?***

This chapter has introduced you to the First Law of Thermodynamics. You have also learned the language of thermodynamics. Remember that this language is very important when you do problems. If you don't understand the meaning of adiabatic, you can't calculate data for adiabatic processes because you won't know which equations are useful. You have also seen different processes and how thermal energy, work effect, and energy change during these processes. Finally, you have seen how to calculate enthalpy changes for chemical reactions.

## Useful Equations

|   |  |
|---|--|
| First law                                     | $dU = dq + dw$   |
| Work  | $w = -\int P_{\text{ext}} dV$  |
| Reversible work for ideal gas                 | $w = -nRT \ln\left(\frac{V_f}{V_i}\right)$   |
| Van der Waals equation                        | $\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$                                     |
| Compressibility factor                        | $Z = \frac{P\bar{V}}{RT}$  |
| Heat capacity (constant volume)               | $\left(\frac{\partial \bar{U}}{\partial T}\right)_V = \bar{C}_V$                             |
| Dependence of internal energy on $T$ and $V$  | $dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$                              |
| Reversible adiabatic expansion or compression | $\bar{C}_V \ln\left(\frac{T_2}{T_1}\right) = -R \ln\left(\frac{\bar{V}_2}{\bar{V}_1}\right)$ |
| Enthalpy                                      | $H \equiv U + PV$  |
| Heat capacity (constant pressure)             | $\bar{C}_P = \frac{1}{n} \left(\frac{\partial H}{\partial T}\right)_P$                       |
| Dependence of internal energy on $T$ and $P$  | $d\bar{H} = \bar{C}_P dT + \left(\frac{\partial \bar{H}}{\partial P}\right)_T dP$            |
| Typical heat capacity temperature dependence  | $\bar{C}_P / (\text{J mol}^{-1} \text{K}^{-1}) = a + bT + \frac{c}{T^2}$                     |
| Ideal gas $C_P - C_V$ relation                | $\bar{C}_P - \bar{C}_V = R$  |

**Summary Problem:** 25 g of nitrogen gas, originally at 300 K and 3.6 bar, adiabatically expand to 1 bar. Calculate  $\Delta U$ ,  $\Delta H$ ,  $q$ , and  $w$ . The same amount of the gas, under the same initial conditions, expands isothermally to 1 bar. Calculate  $\Delta U$ ,  $\Delta H$ ,  $q$ , and  $w$ . Explain why your answers are different from the adiabatic case.

## Additional Information – Critical Points and the van der Waals Parameters

Consider a set of experimental isotherms for carbon dioxide (Figure 10-16). The isotherm at 323 K follows Boyle's law, and an increase in pressure produces a decrease in volume. Isotherms at some of the lower temperatures show deviation due to intermolecular forces in the fluid. The isotherm at 293 K shows condensation of the fluid because the volume is identical in the region from 60 to 90 atm. This region, labeled, as AB in the graph, is the region of liquefaction. In this region, increasing in pressure produces no noticeable volume change; instead, the gas liquefies.

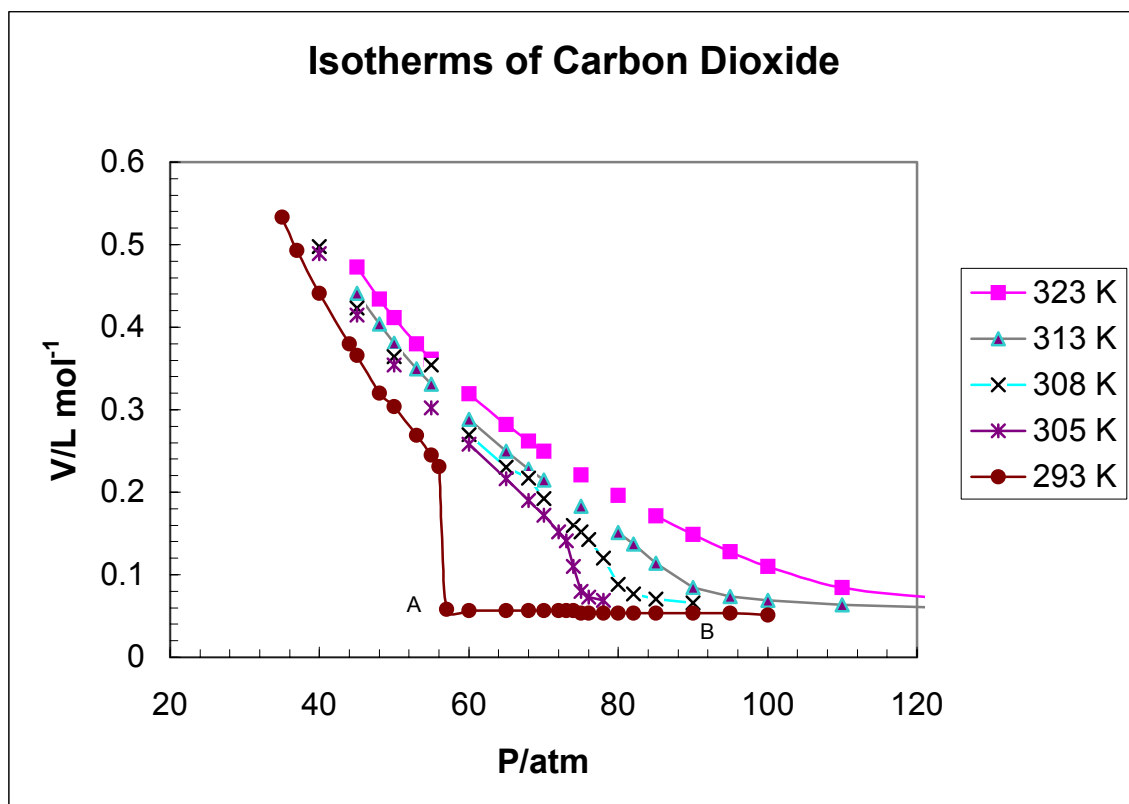


Figure 10-16

The isotherm at 305 K is unique. At any temperature below this isotherm, the gas will liquefy as we increase the pressure; we will observe two phases. At any temperature above 305 K, the gas will not liquefy regardless of the pressure. This temperature is called the **critical temperature** of the gas. There is an inflection point on this isotherm at approximately 70 atm. The inflection point on this isotherm is called the **critical point**. Since the critical point is a horizontal inflection point, the first and second derivatives are zero at this point. We can use this information to obtain the van der Waals parameters,  $a$  and  $b$ .

We begin with the van der Waals equation:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \quad (10.30)$$

At the critical point, the first derivative is zero:

$$\frac{dP}{d\bar{V}} = \frac{-RT}{(\bar{V} - b)^2} + \frac{2a}{\bar{V}^3} = 0 \quad (10.31)$$

The second derivative is also zero:

$$\frac{d^2P}{d\bar{V}^2} = \frac{RT}{(\bar{V} - b)^3} - \frac{6a}{\bar{V}^4} = 0 \quad (10.32)$$

Rearrange (10.31)

$$\frac{RT}{(\bar{V} - b)^2} = \frac{2a}{\bar{V}^3} \quad (10.33)$$

and rearrange (10.32):

$$\frac{RT}{(\bar{V} - b)^3} = \frac{6a}{\bar{V}^4} \quad (10.34)$$

Divide (10.33) by (10.34) to produce:  $\bar{V} - b = \frac{\bar{V}}{3}$ , or

$$\bar{V}_c = 3b \quad (10.35)$$

The subscript  $c$  means the critical molar volume. We substitute (10.35) into (10.33) for each volume to obtain:

$$\frac{RT}{(3b - b)^2} = \frac{2a}{(3b)^3}$$

Solving this equation:

$$T_c = \frac{8a}{27Rb} \quad (10.36)$$

Finally, we substitute (10.35) and (10.36) into (10.30):

$$P = \frac{R\left(\frac{8a}{27Rb}\right)}{3b-b} - \frac{a}{(3b)^2}$$

Simplifying:

$$P_c = \frac{a}{27b^2} \quad (10.37)$$

We can now use the experimental data for  $T_c$ ,  $P_c$ , and  $\bar{V}_c$  to calculate the van der Waals parameters  $a$  and  $b$ . The  $a$  and  $b$  are over specified in that we have three equations to calculate two parameters. The usual procedure is to calculate  $a$  and  $b$  from  $T_c$  and  $P_c$  because these two quantities are determined with greater precision than  $\bar{V}_c$ . The algebra used to obtain the van der Waals parameters can be used for any two-parameter equation of state for a gas.

