

Chapter V

Thermodynamics

Day 1 Atomic Theory, Temperature and Thermal Expansion

Sections 13-1, 13-2 and 13-4

Atomic Theory

We step back to the atomic level where the atom, *ατομος*, is indivisible, that is, we are considering the atoms as units. When combining these atoms to form a particular compound, it is always in the same proportion by weight. For example, when water is formed from hydrogen and oxygen, it is always in the proportion, by weight, of 1:8. Similarly when carbon dioxide is formed from carbon and oxygen it is always in the proportion, by weight, of 3:8. This is known as *the law of definite proportions*. Using this, we were able to establish the relative weights of atoms.

In 1827, Robert Brown discovered that atoms were constantly in motion. He discovered this by observing the apparent random movement of pollen particles in water. This became known as *Brownian motion*.

In solids, atoms move relatively slowly (a vibration, generally), while in liquids they move more rapidly, and in gases more rapidly still.

We also know that the forces between atoms is generally attractive, unless they become too close, in which case it is repulsive.

Temperature

Temperature is a measure of how hot or cold something is. Thermometers, used to measure temperature, work on the basis of expansion of a material as the temperature increases. e.g. mercury or alcohol bulb thermometer, bimetallic strip, etc.

The SI units of temperature are Celsius degrees, which are based upon the freezing and boiling points of water (0°C and 100°C respectively). Fahrenheit is another common unit of measure with the freezing and boiling points of water being 32°F and 212°F respectively. The basis of the Fahrenheit scale is questionable, with many stories circulating as to its origin. Nevertheless, to convert between Celsius and Fahrenheit

$$T(^{\circ}\text{C}) = \frac{5}{9} [T(^{\circ}\text{F}) - 32] \quad (5.1)$$

and

$$T(^{\circ}\text{F}) = \frac{9}{5} T(^{\circ}\text{C}) + 32. \quad (5.2)$$

Thermal Expansion

Most substances will increase in length as heated. To a good approximation, the change in length, ΔL , is proportional to the length of the material, L_0 and to the change in temperature, ΔT . So

$$\Delta L = \alpha L_0 \Delta T.$$

The length of the object $L_0 + \Delta L$ can be written as

$$L = L_0(1 + \alpha \Delta T), \quad (5.3)$$

where $\Delta T = T - T_0$, and T is the temperature to which the substance is heated or cooled and T_0 is the original temperature of the material. See Table 13-1 for lists of α the linear expansion coefficient (p. 388).

For volume expansion,

$$\Delta V = \beta V_0 \Delta T, \quad (5.4)$$

where β is the coefficient of volume expansion. For isotropic solids (same properties in all directions), $\beta = 3\alpha$. (Approximately – see problem 21)

These equations are only accurate if ΔL or ΔV is small compared to L_0 and V_0 . Linear expansion has no meaning for liquids or gases as they have no fixed shapes. ΔV , however, varies greatly with T for liquids and especially for gases (and in fact β varies with temperature as well), so another means of dealing with gases is necessary.

Day 2 Ideal Gas Laws

Sections 13-7 to 13-9

For gases, volume expansion is meaningful only if we discuss a constant pressure, as gases naturally tend to expand to fill whatever container they are placed in (thereby reducing the pressure). So we must find a more convenient way to deal with gases.

Experimentally, at a constant temperature, the volume of a gas is approximately inversely proportional to the pressure, i.e.,

$$V \propto \frac{1}{P}. \quad [\text{constant } T]$$

This is known as Boyle's law, after Robert Boyle (1627-1691) who first discovered this. It can be rewritten as

$$PV = \text{constant}$$

or

$$P_1V_1 = P_2V_2 \quad (5.5)$$

Note this (and therefore everything else in this section) applies only when the pressure is not too great or the gas too close to the boiling temperature.

It was recognized that temperature also played a role in the volume of a gas, but the relationship was not found until about 100 years later by Jacques Charles. The relationship, known as Charles' law is that, to a good approximation, the volume of a gas at constant pressure is proportional to the absolute temperature, or

$$V \propto T. \quad [\text{constant } P]$$

This can be written as

$$\frac{V}{T} = \text{constant}$$

or

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}, \quad (5.6)$$

where T is in degrees Kelvin (K), and $1\text{K} = 1\text{C}^\circ$ and

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

The third gas law, known as Guy-Lussac's law (after Joseph Guy-Lussac, 1778-1850) relates pressure to temperature at constant volume. It states that the pressure of a gas is directly proportional to the absolute temperature at constant volume, or

$$P \propto T \quad [\text{constant } V]$$

This can be written as

$$\frac{P}{T} = \text{constant}$$

or

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}. \quad (5.7)$$

These three laws suggest a more general relationship,

$$PV \propto T.$$

Further experimental evidence shows that the volume of a gas increases in direct proportion to the mass, m , so

$$PV \propto mT$$

This can become an equation by inserting a proportionality constant. However, the constant is universal for all gases if we substitute the number of moles instead of the mass (where $n = \frac{\text{mass(g)}}{\text{molar mass(g/mol)}}$ and n is defined as the number of atoms which give a mass in grams equal to the atomic mass (i.e. 12.000 g for ^{12}C). The atomic mass is the molar mass.

In this case

$$PV = nRT \tag{5.8}$$

where R is the universal gas constant and is equal to 8.315 J/(mol·K) (see p. 395 for equivalent units).

This is called the ideal gas law, because real gasses do not behave this way exactly (at high pressures or near the liquefaction point). However, at less than a couple of atmospheres (1 atm = 101.325 kPa) and away from the liquefaction point, gasses follow this law fairly accurately.

Day 3 Boltzmann's Constant and the Kinetic Theory of Gases

Sections 13-10 to 13-11

Boltzmann's Constant

Using the ideal gas law, $PV = nRT$ we realize the number of moles, $n = \frac{N}{N_A}$, where N is the number of molecules and N_A is Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$). Combining these gives us

$$PV = \frac{N}{N_A}RT.$$

But both R and N_A are constants. Combining these constants, $k = \frac{R}{N_A}$ where k is known as Boltzmann's constant and is equal to $1.38 \times 10^{-23} \text{ J/K}$. This gives us

$$PV = NkT. \quad (5.9)$$

Kinetic Theory of Gases

The idea that matter is made up of molecules in continuous motion is known as kinetic theory. We make four assumptions about molecules in a gas. This is an oversimplification, but real gases match these well under our previously defined conditions. A gas which matches these assumptions is an ideal gas.

1. There are a large number of molecules, N , each of mass, m , moving in random directions in a gas.
2. The separation of the molecules is much greater than the diameter of the molecule (corresponds to relatively low pressure).
3. The molecules obey the laws of classical mechanics and only interact when they collide. (i.e. $KE \gg PE$ from attractive forces).
4. Collisions are all considered to be elastic (conservation of KE).

If pressure is considered to be the constant bombardment of molecules, we can see how these postulates explain Boyle's law (smaller V means greater number of molecules per unit V , therefore greater number of collisions and greater pressure). Using these postulates we can calculate the pressure exerted on a container by a gas.

Consider a container of length ℓ and area A . Assume A faces the $\pm x$ direction.

To strike the area A , a molecule must travel with a speed v_x (in the $-x$ direction). So the change in momentum of a molecule when it hits the face of the container must be

$$\Delta mv = mv_x - (-mv_x) = 2mv_x$$

Since $F = \frac{\Delta p}{\Delta t}$, the time it takes to travel across the box and back is $\frac{2\ell}{v}$, the number of collisions is large and the time between collisions is small, the average force per collision is equal to the force exerted during one collision, so

$$F = \frac{mv_x^2}{\ell}.$$

Since there are N molecules, the total force is equal to

$$F = \frac{m}{\ell} \sum_{i=1}^N v_{xi}^2.$$

But the average of the square of the velocities is equal to

$$\overline{v_x^2} = \frac{\sum_{i=1}^N v_{xi}^2}{N}$$

so the force can be written as

$$F = \frac{m}{\ell} N \overline{v_x^2}.$$

But in a 3-dimensional system, we must include v_y and v_z . Since $v^2 = v_x^2 + v_y^2 + v_z^2$, and $v_x = v_y = v_z$ on average,

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}.$$

So

$$F = \frac{m}{\ell} N \frac{\overline{v^2}}{3}.$$

But $P = \frac{F}{A}$ and $V = A\ell$, so

$$P = \frac{1}{3} \frac{Nm\overline{v^2}}{V}$$

but $\frac{1}{2}m\overline{v^2}$ is just the average KE of the molecules, so rearranging we get

$$3PV = 2N\overline{KE}.$$

Knowing $PV = NkT$ we get

$$\overline{KE} = \frac{3}{2}kT. \quad (5.10)$$

Therefore, the average KE is directly proportional to the absolute temperature. This is one of the triumphs of the kinetic theory.

Day 4 Heat and Temperature, Calorimetry

Sections 14-1 to 14-5

Definitions

Heat is energy transferred from one body to another due to a difference in temperature.

The unit of heat is the calorie (cal). This is the amount of heat necessary to raise the temperature of 1 g of water by 1°C.

Another common unit is the kilocalorie (kcal). This is the amount of heat necessary to raise the temperature of 1 kg of water by 1°C. This is also called the Calorie (Cal).

The British Thermal Unit (BTU) is a third common unit (for example barbeques). 1 BTU is the amount of heat necessary to raise the temperature of 1 lb of water by 1°F.

James Prescott Joule (a brewer) found that heat was related to energy. He found that 1 cal required 4.186 J of work (the mechanical equivalent to heat).

Thermal energy or **internal energy** is the sum of all the energy of all the molecules in an object.

Temperature refers to the average *KE* of the molecules in a substance. (2 objects may have the same *T*, but one has a greater internal energy).

Internal Energy of a Gas

The total internal energy of a monatomic ideal gas is given by

$$U = N\overline{KE} = N\left(\frac{1}{2}m\overline{v^2}\right) = \frac{3}{2}NkT = \frac{3}{2}nRT. \quad (5.11)$$

This is only true for monatomic ideal gases, since for polyatomic molecules, rotational and vibrational energies must also be taken into account. Internal energy of real gases is also dependent upon *P* and *V*.

Internal energy of liquids and solids must also take into account interactions between molecules and so is substantially more complicated.

Specific Heat

The amount of heat required to change the temperature of a body depends upon the mass of the body, the change in temperature and also the substance. Obviously, the greater the mass, the more heat is required and the greater the temperature change, the more heat is required. This relationship can be expressed

$$Q = mc\Delta T, \quad (5.12)$$

where *Q* is the amount of heat and *c* is the specific heat of the material. (See p. 421 for a table.)

The units for specific heat (in SI) are $\text{J}/(\text{kg}\cdot\text{C}^\circ)$ or $\text{kcal}/(\text{kg}\cdot\text{C}^\circ)$. For water at 15°C and 1 atm of pressure, $c = 1.00 \text{ kcal}/(\text{kg}\cdot\text{C}^\circ)$ or $4.19 \times 10^3 \text{ J}/(\text{kg}\cdot\text{C}^\circ)$.

Calorimetry

For an isolated system, energy can neither flow into it nor out of it, therefore the amount of energy is constant within the system. The flow of heat within an isolated system from one part to another is governed by

$$\text{heat lost} = \text{heat gained.}$$

Measuring this exchange of heat is done by a technique called calorimetry.

e.g. A 50 g ice cube at -5.0°C is placed in a Styrofoam cup, which is a good insulator of heat, full of water (250 mL) at 10.0°C . How much does the water cool as the ice warms to the melting point (not including melting the ice – this involves something called latent heat – another lesson)?

$$\begin{aligned} \text{heat lost by water} &= \text{heat gained by ice cube} \\ -m_w c_w \Delta T_w &= m_{ice} c_{ice} \Delta T_{ice} \\ (0.250 \text{ kg})(1.00 \text{ kcal}/\text{kg} \cdot \text{C}^\circ)(10^\circ\text{CT}) &= (0.050 \text{ kg})(0.50 \text{ kcal}/\text{kg} \cdot \text{C}^\circ)[0^\circ\text{C}(-5^\circ\text{C})] \\ (0.250 \text{ kcal}/\text{C}^\circ)(10^\circ\text{CT}) &= 0.125 \text{ kcal} \\ 10^\circ\text{CT} &= 0.500^\circ\text{C} \\ T &= 9.5^\circ\text{C} \end{aligned}$$

So the water cools by 0.50°C .

Day 5 Latent Heat and Heat Transfer

Sections 14-6 to 14-9

Latent Heat

When a substance changes phase (either between solid and liquid, or liquid and gas), during the phase change there is no increase or decrease in temperature, although there is a flow of heat in these changes. This flow of heat is called *latent heat*.

The heat required to change a solid to a liquid at the same temperature is called the *heat of fusion* (L_F), and is measured as heat per unit mass (i.e. kcal/kg or J/kg).

The heat required to change a liquid to a gas at the same temperature is called the *heat of vaporization* (L_V), and is measured as heat per unit mass (i.e. kcal/kg or J/kg).

The heat required for a phase change therefore is given by the equation

$$Q = mL. \quad (5.13)$$

Latent heats for several substances are given on p. 425, along with melting and boiling points.

It should be noted that these processes are reversible: If, in the process of changing from ice to water, 10 kcal are absorbed, then to change it back to ice 10 kcal of heat would need to be removed.

e.g. A 50 g ice cube at -5.0°C is placed in 250 mL of water at 10.0°C . What is the equilibrium temperature of the system?

The first question is whether there is actually enough heat in the system to fully melt the ice. From the question yesterday, we know that to take the ice cube to 0°C requires 0.125 kcal. To change 50 g of ice to water requires

$$\begin{aligned} Q &= mL \\ &= (0.050 \text{ kg})(79.7 \text{ kcal/kg}) \\ &= 3.99 \text{ kcal} \end{aligned}$$

The total heat to melt the ice, then is $3.985 \text{ kcal} + 0.125 \text{ kcal} = 4.11 \text{ kcal}$.

To cool the water from 10.0°C to 0°C requires a loss of

$$\begin{aligned} Q &= mc\Delta T \\ &= (0.250 \text{ kg})(1.00 \text{ kcal/kg} \cdot ^\circ\text{C})(-10.0^\circ\text{C}) \\ &= -2.50 \text{ kcal.} \end{aligned}$$

In this case, there is insufficient heat to melt all of the ice (in fact we can determine how much would melt!), so the system would be in equilibrium at 0°C with ice left in the water.

e.g. The 50 g ice cube is placed in 500 mL of water. What is the equilibrium temperature?

From example 1, the total heat to melt the ice is still 4.11 kcal. To cool twice as much water to 0°C would require a loss of twice as much heat, so the water would have to lose 5.00 kcal of heat. Evidently, there is enough heat to melt the ice. In this case

$$\begin{aligned}
 \text{heat lost by water} &= \text{heat gained by ice} \\
 -(0.500 \text{ kg})(1.00 \text{ kcal/kg} \cdot \text{C}^\circ)(T_f - 10.0^\circ\text{C}) &= 4.11 \text{ kcal} + (0.050 \text{ kg})(1.00 \text{ kcal/kg} \cdot \text{C}^\circ)(T_f - 0^\circ\text{C}) \\
 -0.500T_f + 5.00 \text{ kcal} &= 4.11 \text{ kcal} + 0.050T_f \\
 0.550T_f &= 0.89 \text{ kcal} \\
 T_f &= 1.6^\circ\text{C}.
 \end{aligned}$$

Note: p. 427 has some helpful problem solving tips.

Heat Transfer

There are three means of heat transfer:

1. Conduction - occurs as heat is transferred through an object, such as metal in a fire. If one end is placed in the fire, the other end soon gets warm. An object's ability to conduct heat is known as its thermal conductivity (k). The rate of heat flow is dependent upon this ability, as well as the size and shape of the object and the temperature differential.
2. Convection - is the process by which heat is transferred by the mass movement of molecules. An excellent example of this is wind chill. The body tends to cool more quickly when the air around it is moving faster. The air molecules strike the body and are heated by the body (i.e., heat is removed from the body). This air is quickly removed by the wind and replaced by cooler air.

Convection is also the process by which houses are heated and conventional ovens work. Convection currents in the atmosphere also produce a significant portion of the weather.

3. Radiation - As we learned before, objects radiate light based on their temperatures. The higher the temperature, the lower the peak wavelength. For objects at "normal" temperatures (say room temperature) this light is in the infrared region. The resting human body produces heat internally at a rate of about 100 W. Very little of this heat is carried away by conduction. Most is carried away by convection and by radiation, in the form of IR light.

Day 6 First Law of Thermodynamics

Sections 15-1 to 15-2

If U is the total internal energy of all the molecules of a system (or thermal energy) and Q is the heat flowing into a system, then it is easy to see by the conservation of energy that

$$\Delta U = Q + W \quad (5.14)$$

where W is the net work done *on* the system. (Note that this represents a change from your textbook, which states $\Delta U = QW$, but W is the work done *by* the system. This is to better correspond to the AP equation sheet.)

This is the first law of thermodynamics. It says, essentially, that the change in energy of a system is equal to the heat which flows into the system + the work done on the system. That is, it is simply a statement of conservation of energy.

For our equation:

Heat added is +

Heat lost is –

Work done on the system is +

Work done by the system is –

Simple Systems

An *isothermal* process is one in which the temperature is constant. Since $PV = NkT$, PV is constant. Since $U = \frac{3}{2}NkT$, $\Delta U = 0$, so in this case $Q = -W$. (Note: We are idealizing this process. We are assuming ideal gases, with the gas in a cylinder with a movable piston. This system is in contact with a heat reservoir - a body so large that its temperature does not change significantly with heat exchange. The expansion and compression also take place slowly, so that $\Delta T = 0$.)

An *adiabatic* process is one in which no heat flows into or out of the system ($Q = 0$). In this case, $\Delta U = W$. This happens if the process occurs so quickly that heat has no time to flow in or out of the system. In the process of adiabatic expansion of gas, the gas is doing work on the piston, so ΔU is negative. This indicates a decrease in temperature as well. Likewise, in adiabatic compression, we expect a rise in temperature.

An *isobaric* process is one in which the pressure is constant. In this case, $W = Fd = -P\Delta V$. It is therefore useful to note that in a plot of P vs. V , the area under the graph is equal to the work done by the system and is therefore negative. (As a gas expands, the gas is doing the work).

An *isochoric* process is one in which the volume is constant. In this case, no work is done on or by the system so $\Delta U = Q$. That is, the internal energy is changed only by a temperature change (since $Q = mc\Delta T$).

**Note: We will show $P - V$ graphs for all processes.

Day 7 Second Law of Thermodynamics and Heat Engines

Sections 15-4 to 15-5

Second Law of Thermodynamics

The law of conservation of energy says nothing about order. By conservation of energy, many processes could go both forward and backwards without violating the law. This led to a second law regarding heat transfer which states that *heat will naturally flow from a hot object to a cold object, but will not flow spontaneously from a cold object to a hot object.* [Clausius statement]

Of course this can be stated in other ways, more generally that *natural processes move toward a state of greater disorder.* [general statement]

The second law is essentially a way of underscoring the lack of reversibility of some processes.

Heat Engines

The basic idea behind a heat engine is that mechanical work can be obtained from thermal energy when heat is allowed to flow from a high temperature to a low temperature. That is heat, Q_H , at a high temperature, T_H , is transformed into mechanical energy and heat exhausted, Q_L , at a lower temperature, T_L .

By conservation of energy, $Q_H = W + Q_L$. Note in this case we take all values to be positive, with directions as shown in figure 5.1. Q_H and Q_L are known as operating temperatures.

Examples of these are steam engines and combustion engines. A steam engine heats water by burning coal or oil. This high pressure steam is used to expand a piston or turn a turbine, while lower pressure steam (and therefore lower energy) is exhausted. A combustion engine works by taking in a gas-air mixture, compressing it and igniting it raising the temperature, which causes expansion - this is the "power stroke" of the engine. The engine then exhausts the expanded gas through the exhaust valve.

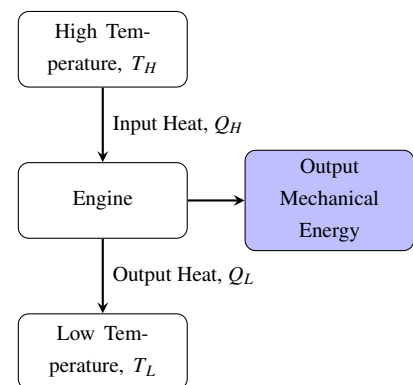


Figure 5.1: Flowchart of energy in a heat engine

The efficiency of an engine is defined as the ratio of the work produced compared to the thermal energy provided, i.e.,

$$e = \frac{W}{Q_H}. \quad (5.15)$$

Since $Q_H = W + Q_L$,

$$e = \frac{Q_H - Q_L}{Q_H}$$

or

$$e = 1 - \frac{Q_L}{Q_H}. \quad (5.16)$$

The Carnot Engine (The Ideal Engine)

The Carnot engine (see figure 5.2) is an ideal engine. First the gas is expanded isothermally, at T_H (A→B), through the addition of heat (Q_H). Then the gas is expanded adiabatically (B→C) by cooling the gas ($Q = 0$). The gas is then compressed isothermally at T_L (C→D) by removing heat Q_L and then it is compressed adiabatically back to its starting point (D→A).

It should be noted that no Carnot engine actually exists, but it is useful as an ideal comparison. For the Carnot engine, the processes are reversible. That is expansion and compression is done slowly so that it is essentially a series of equilibrium states. In reality the process occurs much more quickly and energy is lost to friction and turbulence.

For an idealized engine, Q_H and Q_L are directly proportional to the temperatures T_H and T_L respectively. The ideal efficiency then is

$$e_{ideal} = 1 - \frac{T_L}{T_H} \quad (5.17)$$

Real engines come nowhere close to this. Efficient engines might reach 80% of ideal efficiency.

Notice from this equation that since it is practically (if not theoretically) impossible to reach a temperature of absolute 0 that it is impossible to have an engine with 100% efficiency, which essentially is another statement of the second law of thermodynamics.

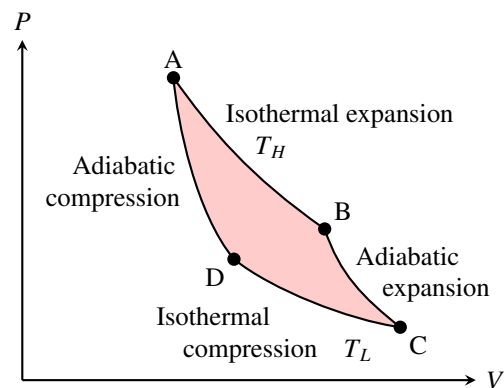


Figure 5.2: The Carnot Engine.