Chapter 14A Thermal Energy

14A.1 Thermal Energy, Heat and Temperature

On a cold winter day, suppose you want to warm up by drinking a cup of tea. You start by filling up a kettle with water from the cold water tap (water heaters tend to add unpleasant contaminants and reduce the oxygen level in the water). You place the kettle on the heating element of the stove and allow the water to boil briefly. You let the water cool down slightly to avoid burning the tea leaves or creating bitter flavors and then pour the water into a pre-heated teapot containing a few teaspoons of tea; the tea leaves steep for a few minutes and then you enjoy your drink.

When the kettle is in contact with the heating element of the stove, energy flows from the heating element to the kettle and then to the water. The conduction of energy is due to the contact between the objects. The random motions of the atoms in the heating element are transferred to the kettle and water via collisions. We shall refer to this conduction process as '*energy transferred thermally*'. The term *heat refers to* energy transformed thermally has traditional been called *heat.* The energy associated with the random motions of the water molecules (and also the potential energy associated with the vibrational interactions intrinsic to water molecules and between molecules) is called *thermal energy*.

The thermal unit for heat is the *calorie* and is defined to be the amount of heat required to raise the temperature of one gram of water from $14.5\,^0C$ to $15.5\,^0C$ (where we have yet to properly define the Celsius, a unit of temperature.) Another common unit is the Btu (British Thermal Unit), which is the amount of heat necessary to raise one pound of water from $63\,^\circ\mathrm{F}$ to $64\,^\circ\mathrm{F}$. Note that $1\,\mathrm{Btu} = 252\,\mathrm{cal}$.

We can attribute different degrees of "hotness" (based on our experience of inadvertently touching the kettle and the water). Temperature is a measure of the "hotness" of a body. When two isolated objects that are initially at different temperatures are put in contact, the "colder" object heats up while the "hotter" object cools down, until they reach the same temperature, a state we refer to as *thermal equilibrium*. Temperature is that property of a system that determines whether or not a system is in thermal equilibrium with other systems.

14A.1.1 Internal Energy

More generally, the *internal energy* U of a physical system is defined to be the sum of all contributions to the total energy of the system in a reference frame in which the center of mass of the system is at rest. For example the internal energy of a gas consist of the kinetic energy of the gas molecules, arising from the center-of-mass motions of the molecules relative to a container that is at rest in the reference frame, and kinetic energy of rotational motion of the molecules. These two motions have no potential energies associated to them. At sufficiently high temperatures, diatomic and polyatomic atoms also have vibrational motions due to interatomic forces, which like a spring have both kinetic and potential energies. Intermolecular forces contribute to the internal energy for solids and liquids, but make negligibly small contributions for gases.

The internal energy also includes contributions due to the rest–mass energy of the constituents, and atomic and nuclear binding energies associated with the structure of the constituents. The internal energy includes does not include potential energies that are due to external interactions, for example the gravitational potential energy due to the interaction between the system and an external body such as Earth. **Thermal energy is the sum of all the internal energies except the binding energies and rest energies.**

14A.1.2 Internal Energy of a Solid or Liquid:

Generally, the potential energy of the intermolecular interaction between molecules is repulsive for small r and attractive for large r, where r is the separation between molecules. At low temperatures, when the average kinetic energy is small, the molecules can form bound states with negative energy $E_{\text{internal}} < 0$ and condense into liquids or solids. The intermolecular forces act like restoring forces about an equilibrium distance between atoms, a distance at which the potential energy is a minimum. For energies near the potential minimum, the atoms vibrate like springs. For larger (but still negative) energies, the atoms still vibrate but no longer like springs and with larger amplitudes, undergoing thermal expansion. At higher temperatures, due to larger average kinetic energies, the internal energy becomes positive, $E_{\text{internal}} > 0$. In this case, molecules have enough energy to escape intermolecular forces and become a gas.

14A.2 Zeroth Law of Thermodynamics

Temperature is a measure of the thermal energy of a system. At absolute zero temperature, the thermal energy of a gas is zero even though the internal energy is still a positive constant due the binding energies and rest energies.

Consider two systems A and B that are separated from each other by an adiabatic boundary (*adiabatic = no heat passes through*) that does not allow any thermal contact. Both A and B are placed in thermal contact with a third system C until thermal equilibrium is reached. If the adiabatic boundary is then removed between A and B, no energy will transfer thermally between A and B. Thus

> *Zeroth Law of Thermodynamics*: Two systems in thermal equilibrium with a third system are in thermal equilibrium with each other.

Temperature T is that property of a system that determines whether or not a system is in thermal equilibrium with other systems.

14A.3 Gas

We begin our analysis of energy transformations by considering a vessel containing a *gas*; a system consisting of a very large number of particles (typically 10^{24} or many orders of magnitude more) occupying a volume of space that is very large compared to the size (10^{-10} m) of any typical atom or molecule. The state of the gas can be described by a few macroscopically measurable quantities that completely determine the system. The volume of the gas in a container can be measured by the size the container. The pressure of a gas can be measured using a pressure gauge. The temperature can be measured with a thermometer. The mass, or number of moles or number of molecules, is a measure of the quantity of matter.

14A.3.1 Macroscopic vs. Atomistic Description of a Gas

How can we use the laws of mechanics that describe the motions and interactions of individual atomic particles to predict macroscopic properties of the system such as pressure, volume, and temperature? In principle, each point-like atomic particle can be specified by its position and velocity (neglecting any internal structure). We cannot know exactly where and with what velocities all the particles are moving so we must take averages. In addition, we need quantum mechanical laws to describe how particles interact. In fact, the inability of classical mechanics to predict how the heat capacity of a gas varies with temperature was the first experimental suggestion that a new set of principles (quantum mechanics) operates at the scale of the size of atoms. However, as a starting point we shall make some simplifying assumptions about the properties of a gas, a model which we shall refer to as an *ideal gas.*

14A.3.2 Ideal Gas

Consider a gas consisting of a large number of molecules inside a rigid container. We shall assume that the volume occupied by the molecules is small compared to the volume occupied by the gas, that is, the volume of the container (dilute gas assumption). We also assume that the molecules move randomly and satisfy Newton's Laws of Motion. The gas molecules collide with each other and the walls of the container. We shall assume that all the collisions are instantaneous and any energy converted to potential energy during the collision is recoverable as kinetic energy after the collision is finished. Thus the collisions are elastic and have the effect of altering the direction of the velocities of the molecules but not their speeds. We also assume that the intermolecular interactions contribute negligibly to the internal energy.

An ideal monatomic gas atom has no internal structure, so we treat it as point particle. Therefore there are no possible rotational degrees of freedom or internal degrees of freedom; the ideal gas has only three degrees of freedom, and the internal energy of the ideal gas is

$$E_{\text{internal}} = N\frac{3}{2}kT \,. \tag{14A.1}$$

Eq. (14A.1) is called the *thermal equation of state* of a monatomic ideal gas. The average kinetic energy of each ideal gas atom is then

$$\frac{1}{2}m(v^2)_{\text{ave}} = \frac{3}{2}kT \tag{14A.2}$$

where $(v^2)_{\text{ave}}$ is the average of the square of the speeds and is given by

$$(v^2)_{\text{ave}} = \frac{3kT}{m} \ . \tag{14A.3}$$

The temperature of this ideal gas is proportional to the average kinetic of the ideal gas molecule. It is an incorrect inference to say that temperature is defined as the mean kinetic energy of gas. At low temperatures or non-dilute densities, the kinetic energy is no longer proportional to the temperature. For some gases, the kinetic energy depends on number density and a more complicated dependence on temperature than that given in Eq. (14A.2).

14A.3.3 Pressure of an Ideal Gas

Consider an ideal gas consisting of a large number N of identical gas molecules, each of of mass m, inside a container of volume V and pressure P. The number of gas molecules per unit volume is then $n = N / V$. The density of the gas is $\rho = nm$. The gas molecules collide elastically with each other and the walls of the container. The pressure that the gas exerts on the container is due to the elastic collisions of the gas molecules with the walls of the container. We shall now use concepts of energy and momentum to model collisions between the gas molecules and the walls of the container in order to determine the pressure of the gas in terms of the volume V, particle number N and Kelvin temperature T.

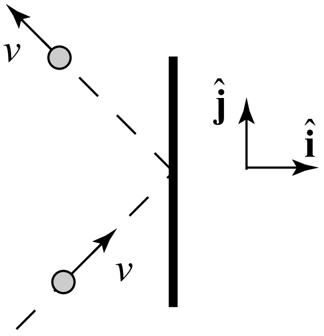

Figure 14A.1 Collision of a gas molecule with a wall of a container

We begin by considering the collision of one molecule with one of the walls of the container, oriented with a unit normal vector pointing out of the container in the positive $\hat{\mathbf{i}}$-direction (Figure 14A.1). Suppose the molecule has mass m and is moving with velocity $\vec{\mathbf{v}} = v_x\,\hat{\mathbf{i}} + v_y\,\hat{\mathbf{j}} + v_z\,\hat{\mathbf{k}}$. Because the collision with the wall is elastic, the y-and z-components of the velocity of the molecule remain constant and the x-component of the velocity changes sign (Figure 29.2), resulting in a change of momentum of the gas molecule;

$$\Delta \vec{\mathbf{p}}_m = \vec{\mathbf{p}}_{m,f} - \vec{\mathbf{p}}_{m,i} = -2mv_x\,\hat{\mathbf{i}}\,. \tag{14.1.4}$$

Therefore the momentum transferred by the gas molecule to the wall is

$$\Delta \vec{\mathbf{p}}_w = 2mv_x\,\hat{\mathbf{i}}\,. \tag{14.1.5}$$

Now, let's consider the effect of the collisions of a large number of randomly moving molecules. For our purposes, "random" will be taken to mean that any direction of motion is possible, and the distribution of velocity components is the same for each direction.

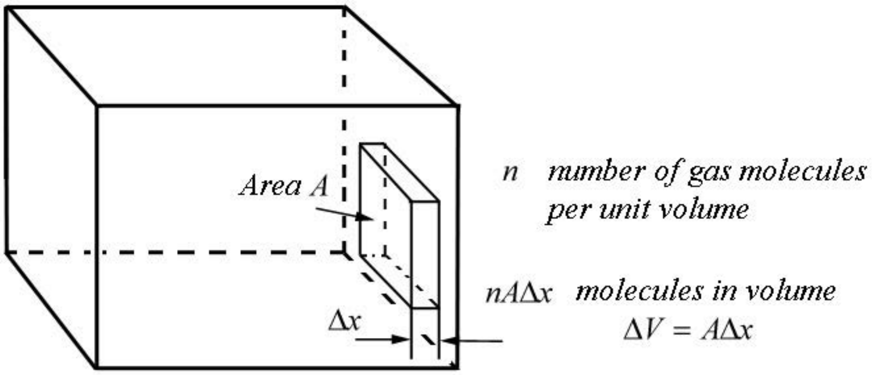

Figure 14A.2 Small volume adjacent to the wall of container

Consider a small rectangular volume $\Delta V = A\Delta x$ of gas adjacent to one of the walls of the container as shown in Figure 14A.2. There are $nA\Delta x$ gas molecules in this small volume. Let each group have the same x-component of the velocity. Let n_j denote the number of gas molecules in the j^{th} group with x-component of the velocity $v_{x,j}$. Because the gas molecules are moving randomly, only half of the gas molecules in each group will be moving towards the wall in the positive x-direction. Therefore in a time interval $\Delta t_j = \Delta x / v_{x,j}$, the number of gas molecules that strike the wall with x-component of the velocity $v_{x,j}$ is given by

$$\Delta n_j = \frac{1}{2} n_j A \Delta x\,. \tag{14.1.6}$$

(During this time interval some gas molecules may leave the edges of the box, but because the number that cross the area per second is proportional to the area, in the limit as $\Delta x \to 0$, the number leaving the edges also approaches zero.) The number of gas molecules per second is then

$$\frac{\Delta n_j}{\Delta t_j} = \frac{1}{2} n_j A \frac{\Delta x}{\Delta t_j} = \frac{1}{2} n_j A v_{x,j} . \tag{14.1.7}$$

The momentum per second that the gas molecules in this group deliver to the wall is

$$\frac{\Delta \vec{\mathbf{p}}_j}{\Delta t_j} = \frac{\Delta n_j}{\Delta t_j} 2 m v_{x,j} \hat{\mathbf{i}} = n_j m A v_{x,j}^2 \hat{\mathbf{i}} . \tag{14.1.8}$$

By Newton's Second Law, the average force on the wall due to this group of molecules is equal to the momentum per second delivered by the gas molecules to the wall;

$$(\vec{\mathbf{F}}_{j,w})_{\text{ave}} = \frac{\Delta \vec{\mathbf{p}}_j}{\Delta t_j} = n_j m A v_{x,j}^2 \hat{\mathbf{i}} . \tag{14.1.9}$$

The pressure contributed by this group of gas molecules is then

$$P_j = \frac{\left|(\vec{\mathbf{F}}_{j,w})_{\text{ave}}\right|}{A} = n_j m v_{x,j}^2 . \tag{14.1.10}$$

The pressure exerted by all the groups of gas molecules is the sum

$$P = \sum_{j=1}^{j=N_g} (P_j)_{\text{ave}} = m \sum_{j=1}^{j=N_g} n_j v_{x,j}^2 . \tag{14.1.11}$$

The average of the square of the x-component of the velocity is given by

$$(v_x^2)_{\text{ave}} = \frac{1}{n} \sum_{j=1}^{j=N_g} n_j v_{x,j}^2 , \tag{14.1.12}$$

where n is the number of gas molecules per unit volume in the container. Therefore we can rewrite Eq. (14.1.11) as

$$P = mn(v_x^2)_{\text{ave}} = \rho (v_x^2)_{\text{ave}} , \tag{14.1.13}$$

where ρ is the density of the gas. Because we assumed that the gas molecules are moving randomly, the average of the square of the x-, y- and z-components of the velocity of the gas molecules are equal,

$$(v_x^2)_{\text{ave}} = (v_y^2)_{\text{ave}} = (v_z^2)_{\text{ave}} . \tag{14.1.14}$$

The average of the square of the speed $(v^2)_{\text{ave}}$ is equal to the sum of the average of the squares of the components of the velocity,

$$(v^2)_{\text{ave}} = (v_x^2)_{\text{ave}} + (v_y^2)_{\text{ave}} + (v_z^2)_{\text{ave}} . \tag{14.1.15}$$

Therefore

$$(v^2)_{\text{ave}} = 3(v_x^2)_{\text{ave}} . \tag{14.1.16}$$

Substituting Eq. (14.1.16) into Eq. (14.1.13) for the pressure of the gas yields

$$P = \frac{1}{3}\rho(v^2)_{\text{ave}} . \tag{14.1.17}$$

The square root of $(v^2)_{\text{ave}}$ is called the **root-mean-square** ("rms") speed of the molecules. Substituting Eq. (14A.3) into Eq. (14.1.17) yields

$$P = \frac{\rho kT}{m} . \tag{14.1.18}$$

Recall that the density of the gas

$$\rho = \frac{M}{V} = \frac{Nm}{V} . \tag{14.1.19}$$

Therefore Eq. (14.1.18) can be rewritten as

$$P = \frac{NkT}{V} . \tag{14.1.20}$$

Eq. (14.1.20) can be re-expressed as

$$PV = N\,kT . \tag{14.1.21}$$

Eq. (14.1.21) is known as the *ideal gas equation of state* also known as the *Perfect Gas Law* or *Ideal Gas Law*.

The total number of molecules in the gas $N = n_{\text{m}} N_A$ where n_{m} is the number of moles and N_A is the Avogadro constant. The ideal gas law becomes

$$PV = n_{\text{m}} N_A\, kT . \tag{14.1.22}$$

The *universal gas constant* is $R = k\,N_A = 8.31\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The ideal gas law can be re-expressed as

$$PV = n_{\text{m}}\, RT . \tag{14.1.23}$$

Although we started with atomistic description of the collisions of individual gas molecules satisfying the principles of conservation of energy and momentum, we ended up with a relationship between the macroscopic variables pressure, volume, number of moles, and temperature that are measurable properties of the system.

One important consequence of the Ideal Gas Law is that equal volumes of different ideal gases at the same temperature and pressure must contain the same number of molecules,

$$N = \frac{1}{k}\frac{PV}{T}. \tag{14.1.24}$$

When gases combine in chemical reactions at constant temperature and pressure, the numbers of each type of gas molecule combine in simple integral proportions. This implies that the volumes of the gases must always be in simple integral proportions. Avogadro used this last observation about gas reactions to define one mole of a gas as a unit for large numbers of particles.

14A.3.3 Atoms, Moles, and Avogadro's Number

The *Avogadro number* was originally defined as the number of molecules in one gram of hydrogen. The number was then redefined to be the number of atoms in 12 grams of the carbon isotope carbon-12. Now the Avogadro number is the fixed numerical value of the *Avogadro constant* N_A when expressed in the unit mol^{-1}

$$N_A = 6.022\,140\,76 \times 10^{23}\ \text{mol}^{-1}. \tag{14A.25}$$

Recall that the mole is a base unit in the SI system of units for an amount of substance with symbol $[\text{mol}]$. Based on the new definition of Avogadro constant N_A, one mole contains $6.022\,140\,76 \times 10^{23}$ elementary entities:

$$1\,\text{mol} = \frac{N_A}{6.02214076 \times 10^{23}} \tag{14A.26}$$

14A.4 Degrees of Freedom

An individual gas molecule can translate in any spatial direction. Multi-atomic gas molecules may undergo rotational motions associated with the structure of the molecule. Additionally, there may be intermolecular vibrational motion between nearby gas particles, and vibrational motion arising from intramolecular forces between atoms that form the molecules. Each of these independent contributions to the internal energy motions are called *degree of freedoms*.

For gas molecules, there are three translational degrees of freedom associated with the center of mass motion in each direction. For diatomic gases like oxygen molecule (O_2) or carbon monoxide (CO), there are additional degrees of freedom: two rotational degrees of freedom corresponding to independent rotations about axes that are perpendicular to the line connecting the centers of the two atoms, and two degrees of freedom corresponding to the kinetic and potential energies associated with vibrational motion about the center of mass, resulting in a total of seven degrees of freedom. Note the extra factor of two for the vibrational modes can be understood by modeling the vibrational motion of the molecules as an oscillating spring in one-dimension with two contributions to the internal energy, $E_{vibrational} = (1/2)mv^2 + (1/2)kx^2$. For linear triatomic linear molecules like carbon dioxide $(\mathrm{CO_2})$: there are also two rotational degrees of freedom, and six degrees of freedom associated with the three vibrational modes of the molecule, totaling eleven degrees of freedom. For non-linear triatomic molecules, there is an extra rotational degree of freedom compared to the linear case, hence twelve degrees of freedom. For polyatomic molecules, there are many vibrational modes, so the number of degrees of freedom is greater than twelve.

14A.5 Equipartition of Energy

We shall make our first assumption about how the internal energy distributes itself among N gas molecules, as follows:

Each independent degree of freedom has an equal amount of energy equal to $(1/2)kT$,

where the constant k is called the **Boltzmann constant** and is defined by

$$k = 1.380649 \times 10^{-23}\ \mathrm{J \cdot K^{-1}}\ .$$

The total internal energy U of the ideal gas is then

$$U = N(\#\text{ of degrees of freedom})\,\frac{1}{2}kT\ . \qquad (14A.27)$$

This equal division of the energy is called the ***equipartition of the energy.***

14A.5.1 Boltzamnn constant

Recall that the Boltzmann constant is now one of the seven defining constants that determine the SI units and along with the constants h, c *and* $\Delta\nu_{\mathrm{Cs}}$ determine the unit kelvin.

> *The kelvin, symbol* K, *is the SI unit of thermodynamic temperature. It is defined by taking the fixed numerical value of the Boltzmann constant* k *to be* 1.380649×10^{-23} *when expressed in the unit* $\mathrm{J\cdot K^{-1}}$, *which is equal to* $\mathrm{kg\cdot m^2\cdot s^{-2}K^{-1}}$, *where the kilogram, meter and second are defined in terms of* h, c *and* $\Delta\nu_{\mathrm{Cs}}$.

This definition implies the exact relation $k = 1.380649\times10^{-23}\,\mathrm{J\cdot K^{-1}}$. *Its effect is that one kelvin is equal to the change of thermodynamic temperature T that results in a change of thermal energy kT by* $1.380649\times10^{-23}\,\mathrm{J}$. *[1]*

Therefore the unit kelvin is defined as

$$1\,\mathrm{K} = \frac{1.380649\times10^{-23}}{k}\cdot\mathrm{kg\cdot m^2\cdot s^{-2}} \tag{14A.28}$$

Using the SI definitions for the kilogram, meter and second, Eq. (14A.28) becomes

$$\begin{aligned}1\,\mathrm{K} &= \left(\frac{1.380649\times10^{-23}}{k}\right)\cdot\left(1.4755214\times10^{40}\,\frac{h\Delta\nu_{\mathrm{Cs}}}{c^2}\right)\\ &\cdot\left(30.663\,314\,9\,\frac{c}{\Delta\nu_{\mathrm{Cs}}}\right)^2\cdot\left(\frac{9\,192\,631\,770}{\Delta\nu_{\mathrm{Cs}}}\right)^{-2}\end{aligned} \tag{14A.29}$$

One kelvin is then equal to

$$1\,\mathrm{K} = 2.266\,665\,265\,\frac{h\Delta\nu_{\mathrm{Cs}}}{k} \tag{14A.30}$$

14A.5.2 Freezing out Degrees of Freedom

Vibrational modes generally do not occur at room temperature. At higher temperatures, a diatomic gas molecule has a potential energy associated with the interaction between the two molecules. This potential energy acts like a spring between the two atoms contributing to a vibrational mode along the -axis. Analogous to a spring connected two objects, there are two degrees of freedom associated with a vibrational mode, the potential energy stored in the interaction and the kinetic energy associated with the vibration. Thus there are seven total degrees of freedom for the energy to partition among. So in principle of all of these energy modes are accessible, then the total internal energy U for a diatomic gas consisting N molecules is

$$U = N(\#\ of\ deg)((1/2)kT) = N(7/2)kT \tag{14A.31}$$

According to our classical theory of the gas, all these modes should be equally occupied at all temperatures but in fact they are not! This important deviation from classical physics was the first place that a more detailed model of the atom is needed to correctly describe experimental observations.

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[1] https://www.bipm.org/en/measurement-units/base-units.html

14A.5.3 Example Diatomic Nitrogen Gas

What is the internal energy of the diatomic N_2 gas at room temperature?

Solution: At room temperature, the internal energy is due to only the five degrees of freedom associated with the three translational and two rotational degrees of freedom,

$$U = \frac{5}{2} NkT \,. \tag{14A.32}$$

As discussed above, at temperatures well above room temperature, but low enough for nitrogen to form diatomic molecules, there is are two additional vibrational degree of freedoms. Therefore there are seven degrees of freedom and so the internal energy is

$$U = N(\#\text{ of degrees of freedom})\frac{1}{2}kT = \frac{7}{2}N\,kT \,. \tag{14A.33}$$

14A.6 Temperature, Scales, and Thermometers

14A.6.1 Temperature

In our discussion so far, we have not defined precisely how we can measure temperature. In particular, we have not determined how the flow of thermal energy into a system raises its temperature. We begin with a macroscopic characterization of the temperature of a body.

To measure the temperature of a system, we need to measure a *thermometric* property of the system, one that varies with its hotness or coldness. There are many such properties; for example, electrical resistance of a filament, pressure of a gas, thermal electromotive force, radiant emittance, or magnetic susceptibility. Let X be any thermometric property of a material. Then we define the temperature scale so that the temperature θ is linear proportional to X

$$\theta(X) = aX \,. \tag{14A.34}$$

where a is a constant of proportionality. By this linearity, the ratio of temperatures between any two states of the system is then the ratio of the thermometric properties of those states,

$$\frac{\theta_1}{\theta_2} = \frac{X_1}{X_2} \,. \tag{14A.35}$$

Traditionally, to determine temperature for any state, we need to define temperature for a standard state. The standard fixed state for thermometry is the *triple point of water*. This is the state in which ice, water, and water vapor coexist.

This occurs at 0.01°C and at a water-vapor pressure of $610\ \text{Pa}$. For historical and scientific reasons to be explained, we define the temperature of the triple point of water to be $273.16\ \text{K}$ on the Kelvin scale, which fixes the constant a as follows. Let X_{TP} be the value of the thermometric property X at the triple point. Then

$$a = \frac{273.16\ \text{K}}{X_{TP}} . \tag{14A.36}$$

Hence the temperature at any value of X is then

$$\theta(X) = aX = a\frac{273.16\ K}{X_{TP}} . \tag{14A.37}$$

14A.6.2 Temperature Scales

We use the Kelvin scale as a measure of absolute temperature. The commonly used Celsius scale employs the same size for each degree as the Kelvin scale, but the zero point is shifted by 273.15 degrees so that the triple point of water has a Celsius temperature of 0.01°C,

$$T(^{\circ}\text{C}) = \theta(\text{K}) - 273.15\ ^{\circ}\text{C} , \tag{14A.38}$$

and the freezing point of water at standard atmospheric pressure to be 0°C. The Fahrenheit scale is related to the Celsius scale by

$$T(^{\circ}\text{F}) = \frac{9}{5}T(^{\circ}\text{C}) + 32\ ^{\circ}\text{F} . \tag{14A.39}$$

The freezing point of pure water at standard atmospheric pressure occurs at 0°C and $32\ ^{\circ}\text{F}$. The boiling point of pure water at standard atmospheric pressure occurs at 100°C and $212\ ^{\circ}\text{F}$.

14A.6.3 Example Gas Thermometer

The gas thermometer measures temperature based on the pressure of a gas at constant volume and is used as the standard thermometer, because the variations between different gases can be greatly reduced when low pressures are used. A schematic device of a gas thermometer is shown in Figure 14A.3. The volume of the gas is kept constant by raising or lowering the mercury reservoir so that the mercury level on the left arm in Figure 14A.3 just reaches the point I. When the bulb is placed in thermal equilibrium with a system whose temperature is to be measured, the difference in height between the mercury levels in the left and right arms is measured. The bulb pressure is atmospheric pressure plus the pressure in mercury a distance h below the surface (Pascal's Law). A thermometer needs to have two scale points, for example the height of the column of mercury (the height is a function of the pressure of the gas) when the bulb is placed in thermal equilibrium with ice water and in thermal equilibrium with standard steam.

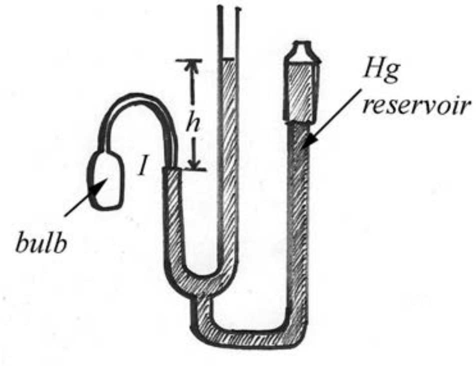

Figure 14A.3 Constant volume gas thermometer

At constant volume, and at ordinary temperatures, the pressure of gases is proportional to the temperature,

$$T \propto P\,. \tag{14A.40}$$

We define a linear scale for temperature based on the pressure in the bulb by

$$T = a\,P \tag{14A.41}$$

where a is a positive constant. In order to fix the constant a in Eq. (14A.41), a standard state must be chosen as a reference point. The standard fixed state for thermometry is the *triple point of water*, the state in which ice, water, and water vapor coexist. This state occurs at only one definite value of temperature and pressure. By convention, the temperature of the triple point of water is chosen to be exactly 273.16 K on the *Kelvin scale*, at a water-vapor pressure of 610 Pa. Let P_{TP} be the value of the pressure P at the triple point in the gas thermometer. Set the constant a according to

$$a = \frac{273.16\text{ K}}{P_{\text{TP}}}\,. \tag{14A.42}$$

Hence the temperature at any value of P is then

$$T(P) = a\,P = \frac{273.16\text{ K}}{P_{\text{TP}}}\,P\,. \tag{14A.43}$$

The ratio of temperatures between any two states of a system is then measured by the ratio of the pressures of those states,

$$\frac{T_1}{T_2} = \frac{P_1}{P_2}\,. \tag{14A.44}$$

14A.7 Conservation of Energy and Energy Transformations

When we do work on a system, for example we can increase the speed of an object by pushing it, and the kinetic energy increases. We can do work compressing a spring, and the potential energy increases. We can also do work on a system in such a way that the mechanical energy stays constant, but we generate thermal energy. For example, we can slide an object along a surface at constant speed. If we consider the object and the surface as our system, then we do work on the sliding object, and increase the thermal energy of the system.

We can also decrease both the kinetic energy and potential energy of a system, and increase the thermal energy. Consider the interaction between water falling over a waterfall and the earth. Between the top and bottom of a waterfall, there is a net loss in mechanical energy. As the water falls, it accelerates, an amount of gravitational potential energy transforms into kinetic energy. When the falling water strikes the surface, much of that kinetic energy is lost from the mechanical system. However the temperature of the water at the bottom of the fall will be higher than the temperature at the top. We can also increase or decrease the energy of a system by heating or cooling as we observed with warming a kettle of water. We shall study types of energy transformations due to interactions both inside and across the boundary of a system.

14A.7.1 System, Boundary and Surroundings

Recall in Chapter 13, when we specify a system, we also specified the surroundings (everything else) and a boundary between the system and the surroundings. The boundaries are interfaces through which energy can be transferred. The above examples suggest that we can change the energy of the system by doing work on the system, or by the flow of "heat" into the system.

Recall that a system is *open* if both energy and matter can enter of leave the system. A system is *closed* if only energy can be transferred to or from the surroundings. A closed system in which energy is constant may not be isolated. For example consider a compressed spring in which one end is attached to a cart and the other end attached to a wall. The cart is held in place on a frictionless air track. Choose as the system the cart and spring. Then release the cart. While the spring is expanding and the cart is accelerating, there is an external force of the wall on the spring so the system is not isolated but there is no transfer of energy to or from the system. The potential energy of the spring is transformed into kinetic energy of the cart. So the energy of the system is constant but it is not isolated.

For a closed system, the change in energy of the system and the surroundings sum to zero,

$$\Delta E^{\text{total}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0 \qquad (14A.45)$$

When a system undergoes a change from state A, to state B, the sum of the kinetic and potential energy (mechanical energy $\Delta E_{\text{mechanical}}$) may change, and the kinetic energy associated with random motions, (thermal energy $\Delta E_{\text{thermal}}$), may also change. In addition there may be other forms of energy ΔE_{other} that may change as well. So the total change in energy of the system is the sum of these changes

$$\Delta E_{\text{system}} = \Delta E_{\text{mechanical}} + \Delta E_{\text{thermal}} + \Delta E_{\text{other}} . \tag{14A.46}$$

If the total energy of the system changes, then the total energy of the surrounding must change by the opposite amount,

$$\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}} \tag{14A.47}$$

If the energy is a system changes, then energy must flow across the boundary. We shall study two different types of energy flows across the boundaries of a system. The first type is when the surroundings do work on the system (or the system does work on the surroundings). Consider a closed cylinder of gas with a piston at one end. Identify the gas as the system. If an external force pushes the piston inwards, then the surroundings do (external) work on the system, and the total energy of the system changes,

$$\Delta E^{(1)}_{\text{system}} = W_{\text{external}} . \tag{14A.48}$$

A second type of energy flow through the boundary involves the flow of thermal energy, which we denote by Q. We adapt the convention that $Q > 0$ means that a positive amount of heat flows into the system, the energy of the system increases, therefore

$$\Delta E^{(2)}_{\text{system}} = Q . \tag{14A.49}$$

14A.8 First Law of Thermodynamics

The energy of a closed system can increase or decrease either through external work done on or by the system, and by the flow of thermal energy into or out of the system.

Let $Q > 0$ represent a positive amount of thermal energy that flows into a system. If $Q < 0$, then thermal energy flows from the system to the surroundings.

Let $W_{ext} > 0$ denote the work done by the surroundings on a system. (If $W_{ext} < 0$ then the system is doing work on the surroundings.)

In what follows we shall denote the total change in internal energy of a system by ΔU. Then the *first law of thermodynamics* describes the sum of the change in energy due to heating and the work done by the surroundings on the system,

$$\Delta U = W_{ext} + Q \ . \tag{14A.50}$$

Whenever a closed system is divided into a system (1) and surroundings (2) that are in thermal contact, and there is a thermal energy flow from (1) to (2), then the thermal energy lost from (1) is gained by (2),

$$Q_1 = -Q_2 \tag{14A.51}$$

14A.8.1 Mechanical Equivalent of Heat

We have already used the joule as the unit for mechanical energy; we would like to determine the constant of proportionality k between the rate of loss of mechanical energy as measured in watts and the rate of the flow of thermal energy as measured in calories per sec

$$\frac{dE_{mech}}{dt} = -k\frac{dQ}{dt} \ . \tag{14A.52}$$

James Joule in 1847 first measured this connection between mechanical energy and heat and found that $4.2\ \mathrm{J} = 1\ \mathrm{cal}$. The modern result at $15^{\circ}\mathrm{C}$ is $4.186\ \mathrm{J} = 1\ \mathrm{cal}$.

When a mass slides along the table, work done by the contact friction generates thermal energy that is absorbed by both the mass and the table. So we must include the mass and the table as part of our system. In fact, the gas molecules near the table absorb some thermal energy, so strictly speaking they must also be included in the closed system. Is mechanical energy really 'lost' in a system? If we examine the individual molecules in our system, and we discover that their average kinetic energy increases along with an increase in the potential energy associated with their molecular interactions. Microscopically, energy is conserved!

If we immerse a light bulb in water, the electrical power delivered to the light bulb is dissipated into the water causing the thermal energy of the water to increase. Macroscopically we could measure this increased thermal energy by measuring the rise in the temperature of the water.

14A.9 States of Matter

14A.9.1 Heat Capacity and Specific Heat

When thermal energy $Q > 0$ flows into a system, the temperature of the system may or may not undergo a change. When the temperature does rise by an amount $\Delta T > 0$, as we can observe by heating water with a light bulb, the *average heat capacity* of the system is defined to be the total amount of thermal energy that flows into the system divided by the rise in temperature,

$$C = \frac{Q}{\Delta T} \qquad (14A.53)$$

If we were to divide our system precisely in half, the same flow of thermal energy will induce double the temperature change, hence halving the heat capacity. If we divide heat capacity by the amount of mass present, then we have a property of the system that will not change when we halve the system. Thus we define the *average specific heat* as the heat capacity per mass,

$$c = \frac{Q}{m\Delta T} \ . \qquad (14A.54)$$

The units for specific heat are $\left[\mathrm{J \cdot kg^{-1} \cdot K^{-1}}\right]$. For water, the specific heat varies as a function of temperature. Figure 14A.4 shows the specific heat of water plotted as a function of temperature for the range $\left[0\ ^{\circ}\mathrm{C},\ 100^{\circ}\mathrm{C}\right]$.

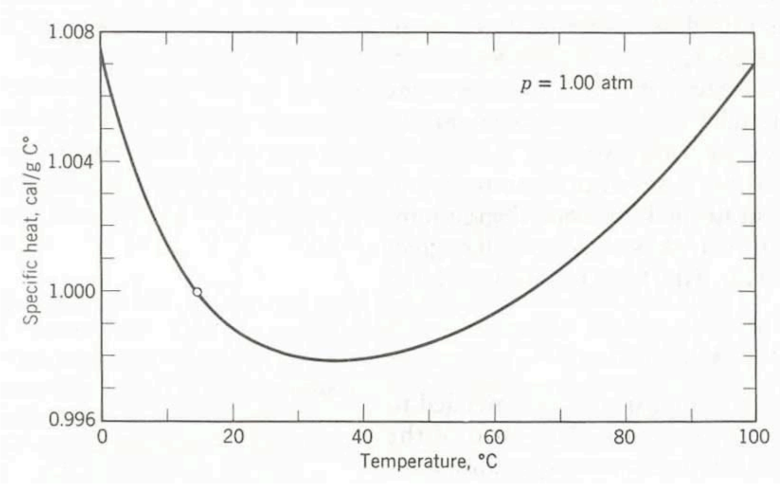

Figure 14A.4 Specific heat of water as a function of temperature.

For the range 14.5 ^{0}C to 15.5 ^{0}C, the value is

$$c_{\mathrm{H_2O}} = 4.1860 \times 10^3 \ \mathrm{J \cdot kg^{-1} \cdot K^{-1}} \ . \qquad (14A.55)$$

14A.9.2 Specific Heats of an Ideal Gas

The specific heat of a substance is the amount of heat required per unit mass per unit temperature change. When the unit of mass is the mole, the specific heat is called the molar heat capacity. A gas can have two types of molar heat capacities: at constant pressure, C_P, or at constant volume, C_V.

Consider n_m moles of an ideal gas that is in thermal contact with a reservoir of thermal energy. The temperature of the reservoir is slowly raised. The volume of the gas does not change during the process. Therefore no work is done on the gas. From the first law of thermodynamics, the change in the internal energy of the gas is due entirely to the flow of thermal energy into the gas,

$$\Delta U = Q \ . \tag{14A.56}$$

The amount of thermal energy required is equal to

$$Q = n_m C_V \Delta T \ . \tag{14A.57}$$

Therefore the change in internal energy is given by

$$\Delta U = n_m C_V \Delta T \ . \tag{14A.58}$$

For an ideal gas, the change in internal energy only depends on the temperature change

$$\Delta U = \frac{3}{2} n_m R \Delta T \ . \tag{14A.59}$$

Therefore comparing these expressions shows that the molar heat capacity at constant volume is

$$C_V = \frac{3}{2} R \ . \tag{14A.60}$$

For a gas molecule with D degrees of freedom, the change in internal energy is

$$\Delta U = \frac{D}{2} n_m R \Delta T \tag{14A.61}$$

and so the heat capacity is

$$C_V = \frac{D}{2} R \ . \tag{14A.62}$$

Table 14A.1 shows the molar specific heats for different gases at 15°C and $1\,\text{atm}$ pressure..

Table 14A.1 Constant Volume Molar Specific Heats for Different Gases.

Gas	Molar Specific Heat C_V	C_V / R
Ar	12.5	1.50
He	12.5	1.50
CO	20.7	2.49
H_2	20.4	2.45
HCl	21.4	2.57
N_2	20.6	2.49
NO	20.9	2.51
O_2	21.1	2.54
Cl_2	24.8	2.98
CO_2	28.2	3.40
CS_2	40.9	4.92
H_2S	25.4	3.06
N_2O	28.5	3.42
SO_2	31.3	3.76

Figure 14A.5 shows the variation in the hydrogen molar specific heat at constant volume as a function of the temperature. The temperature scale is logarithmic. The classical theory does not agree with experiment!

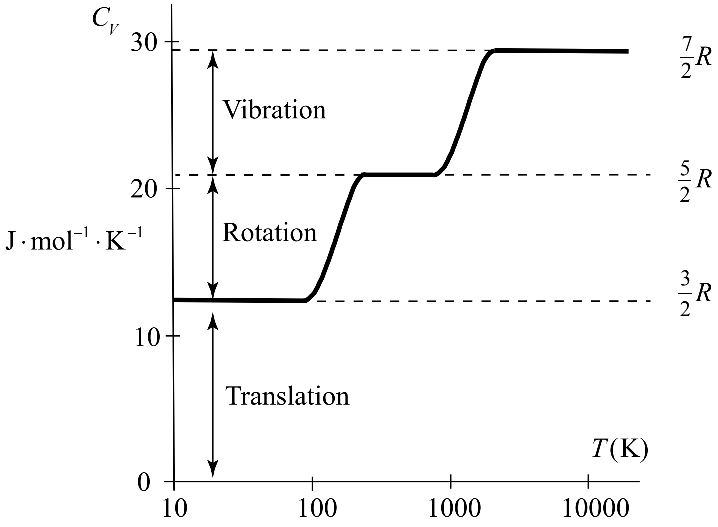

Figure 14A.5 Hydrogen molar specific heat at constant volume as a function of temperature.

14A.9.3 Example Molar heat capacities of an ideal gas

Consider an ideal gas undergoing a constant pressure expansion, with a temperature change ΔT. The gas does work on the surroundings, $W = P\Delta V$, and hence the surroundings do negative work on the gas. From the ideal gas law, the external work done is then

$$W_{ext} = -P\Delta V = -n_m R\Delta T \ . \tag{14A.63}$$

According to the first law of thermodynamics, the change in the internal energy of the gas is

$$\Delta U = Q + W_{ext} = Q - P\Delta V \ . \tag{14A.64}$$

The amount of thermal energy that flowed into the gas is then

$$Q = n_m C_P \Delta T \ . \tag{14A.65}$$

So the change in internal energy for the constant pressure expansion is

$$\Delta U = n_m C_P \Delta T - n_m R\Delta T \ . \tag{14A.66}$$

For an ideal gas, the change in internal energy only depends on the temperature change

$$\Delta U = \frac{3}{2} n_m R\Delta T \ . \tag{14A.67}$$

Therefore the change in internal energy is,

$$\Delta U = n_m C_V \Delta T = n_m C_P \Delta T - n_m R\Delta T \ . \tag{14A.68}$$

The two molar heat capacities are related by solving this equation to yield

$$C_P = C_V + R \ . \tag{14A.69}$$

Using the fact that $C_V = (3/2)R$, we find that the molar heat capacity at constant pressure for an ideal gas is then

$$C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R \ . \tag{14A.70}$$

Let $\gamma = C_P / C_V$ denote the ratio of the heat capacities. Then for the ideal gas

$$\gamma = C_P / C_V = 5/3 \ . \tag{14A.71}$$

The ideal gas law establishes a proportional of the product of the pressure with the volume to the temperature according to

$$PV = n_m RT \ . \tag{14A.72}$$

The internal energy of the gas is

$$U = (3/2) n_m RT \ . \tag{14A.73}$$

.

Thus combining these equations yields

$$PV = \frac{2}{3} U \ . \tag{14A.74}$$

We can rewrite this last equation is terms of the ratio of the heat capacities,

$$PV = (\gamma - 1) U \tag{14A.75}$$

14A.9.4 Example Adiabatic compression of an ideal gas

Suppose we compress the gas by an amount $dV < 0$ so that there is no loss of energy as heat through the container, adiabatic compression. The work that is done on compressing the gas,

$$dW = -PdV = \Delta U > 0 \ , \tag{14A.76}$$

will increase the internal energy. Note that the minus sign ensures that the work done on the gas is positive. Since the volume of the gas is decreasing, the pressure of the gas must increase. So using Eq. (14A.75), the differential rate of change of the internal energy of the gas is given by

$$(\gamma - 1)\Delta U = dPV + PdV \tag{14A.77}$$

Thus substituting Eq. (14A.76) into Eq. (14A.77), yields

$$(\gamma - 1)(-PdV) = dPV + PdV \ . \tag{14A.78}$$

Collecting terms yields

$$-\gamma PdV = dPV \tag{14A.79}$$

This equation is separable

$$-\gamma \frac{dV}{V} = \frac{dP}{P} \ . \tag{14A.80}$$

.

which can then be integrated

$$-\gamma \int_{V_i}^{V_f} \frac{dV}{V} = \int_{P_i}^{P_f} \frac{dP}{P} \tag{14A.81}$$

resulting in

$$\gamma \ln(V_i / V_f) = \ln(P_f / P_i) . \tag{14A.82}$$

Exponentiating both sides then yields

$$(V_i / V_f)^{\gamma} = (P_f / P_i) \ . \tag{14A.83}$$

Thus the product of the pressure and the volume raised to the power γ is a constant for the adiabatic compression of the gas,

$$PV_i^{\gamma} = P_f V_f^{\gamma} \tag{14A.84}$$

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Spring 2022