

Chapter 12

Gases

Introduction

The study of systems of many particles is facilitated by the introduction of the concept of temperature. We will do this by successive approximations. We will start with a definition of temperature that is not very rigorous. With the help of this definition, however, we will be able to study a number of systems and improve our definition of temperature. Eventually, we will provide the most rigorous definition, but this will have to await the introduction of the concept of entropy in Chapter 13.

Temperature

The concept of temperature is associated with the sensations of “hot” and “cold.” “Cold” corresponds to low temperature, “hot” to high temperature. In addition, we know that if two objects, initially at different temperatures, are placed in contact, they eventually reach the same final temperature. These characteristics of temperature make it a very useful quantity. From the point of view of physics, however, the concept of temperature presents a problem because it is not obvious how to define it in terms of elementary quantities. After all, we have specific definitions for quantities like momentum, angular momentum, energy, etc. All these quantities can be expressed in terms of elementary particle properties, such as mass, velocity, etc. We said at the very beginning of this course that if we know the initial positions and velocities of the particles in our system, plus the forces that act among them, we have everything we need to calculate any property of that system. That includes temperature. The problem is how. Our definition of temperature must correspond to the sensations of “hot” and “cold,” and must also reflect the phenomenon of equalization of temperatures when two objects are brought into thermal contact. It turns out that this problem is very complicated, so that we will address it following more of less the historical path. To understand the properties of temperature and do experiments, we need a scale of temperatures. It is difficult to come out with a scale if we still don’t have a rigorous definition of temperature, but we can hope to find a reasonable scale with which we might later find a better scale and eventually solve the entire problem. The

obvious choice for an “initial” scale of temperature is some material property that changes with temperature.

Temperature-dependent properties of materials

Many material properties depend on temperature: the length of an object, its electrical resistance, the volume of a gas, etc. Any of these properties can be used to build a **thermometer**. Once we settle on a given property, we must choose a scale. This is done by arbitrarily defining two “fixed” points. For example, in the **Celsius** scale the value of 100 °C is assigned to the temperature of boiling water at the pressure of 1 atm, whereas the value of 0 °C corresponds to the temperature of melting ice.

Of course, the problem with the above thermometers is that their measurements may not agree. This is because there is no reason why all thermal properties should be linear with respect to each other. In other words, suppose we compare a thermometer based on the length of a column of mercury with a resistance thermometer. Of course, the two thermometers agree on what is 100 °C and 0 °C, since these two points are defined in terms of the properties of water. But they may disagree at intermediate temperatures: the mercury thermometer might read 40 °C when the resistance thermometer reads 42 °C. Many experiments done in the XIXth century lead scientists to the conclusion that by choosing gases as their thermometers the results of temperature measurements could be made much more consistent.

The gas thermometer

It was recognized by Boyle that for a fixed amount of gas the product of its volume times its pressure remains constant if the temperature remains constant. This can be written as

$$pV = N f(T), \quad (1)$$

where N is the total number of molecules in a gas and $f(T)$ a certain function of temperature. This can be plotted in a p - V diagram, as shown in Fig. 1.

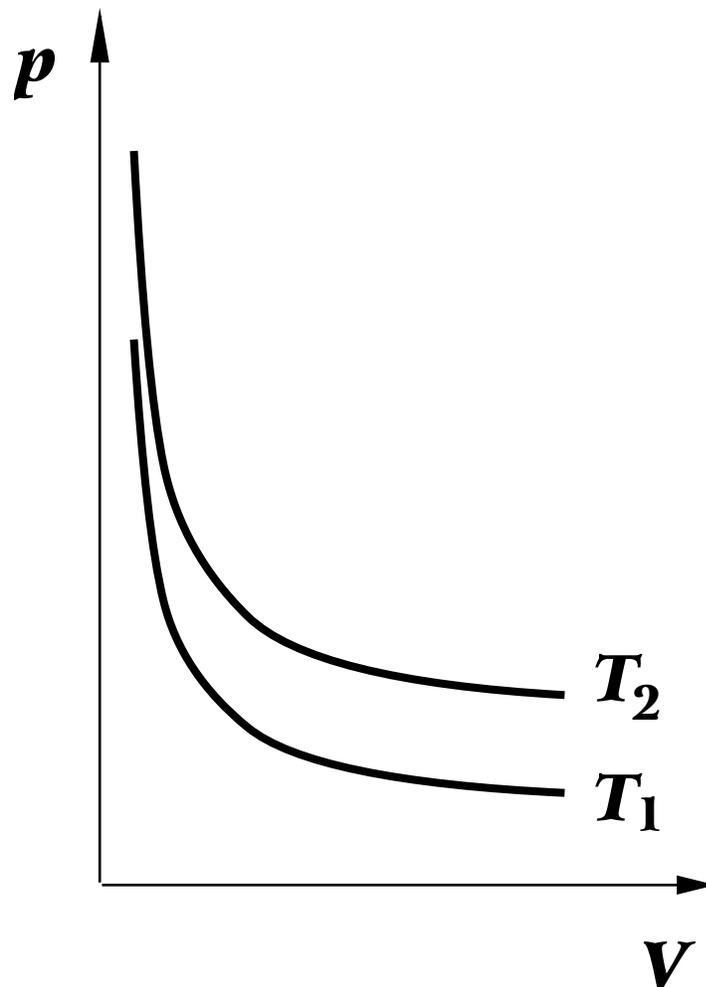


Figure 1 Boyle's law

The way to establish a temperature scale based on this property is to *define* the temperature T such that $f(T)$ is given by kT , where k is a constant. In other words, the product of the pressure and the volume of a given mass of gas is taken as the material property to be used as a thermometer. Notice that by taking this product as our thermometer we can no longer define “zero” temperature arbitrarily. This temperature corresponds to $pV = 0$. The conditions under which this product becomes zero depend on the properties of the gas and have nothing to do with other “zeros” such as the zero of the Celsius scale, which represents the temperature of melting ice. However, we still are free to select the constant k so that the difference between the temperature of

melting ice and the temperature of boiling water is 100 units. Let us call T_0 the temperature of melting ice and $T_1 = T_0 + 100$ the temperature of boiling water. According to Boyle's law $p_0V_0 = NkT_0$ and $p_1V_1 = NkT_1$. Combining these relationships we obtain

$$T_0 = \frac{100 p_0 V_0}{p_1 V_1 - p_0 V_0} \quad (2)$$

The value of T_0 can be determined experimentally by measuring the pressure and volumes of a given amount of gas in equilibrium with melting ice and boiling water. The value so obtained is $T_0 = 273.15$ K, where we have introduced the name "Kelvin" to indicate this scale of temperature. By definition, the separation between degrees in the **Kelvin** scale is the same as in the **Celsius** scale, but the zero is shifted by 273.15 degrees.

Of course, the values of T_0 obtained by using Eq. (1) might depend on the gas being used, reflecting again the fact that different materials have properties that do not scale linearly with each other. However, for many elementary gases one obtains very similar values. This indicates that there is something universal and fundamental about this scale of temperature.

The equation of state of a gas

The relationship

$$pV = NkT \quad (3)$$

is called the **equation of state of an ideal gas**. Notice that so far the product Nk appears as a combination, so that we do not have a way of finding the number of molecules in a gas unless we find independently the value of k , which is known as **Boltzmann's constant** (today's accepted value is $k = 1.3805 \times 10^{-23}$ J/K.). This was a crucial search for early chemists, since it could be used to determine the weight of single molecules. These early chemists used Eq. (3) in a different form:

$$pV = nRT \quad (4)$$

where N is the number of **moles** of a given substance. By definition, one mole is the number of atoms in 12 g of carbon. By studying chemical reactions the chemists were able to determine the relative weights of different atoms. This made it possible to select a given number of moles of any substance. For example, if an element is three times heavier than carbon, one mole of this element has a weight of 36 g. With the above definition of mole, the constant R , called the **ideal gas constant**, can be determined experimentally. Its value is $R = 8.34144 \text{ J K}^{-1} \text{ mol}^{-1}$.

The ratio $R/k = N_A$, called **Avogadro's number**, gives the number of particles in a mole of a substance. The accepted value today is $N_A = 6.0225 \times 10^{23} \text{ mol}^{-1}$. This means that a molecule is very small!

The mechanical interpretation of the equation of state

To gain insight into the concept of temperature we will study to what extent we can derive an expression similar to the equation of state of a gas based solely on mechanical considerations. For that, we need a *model* of an ideal gas. We will assume that our gas is a collection of non-interacting point masses. Since the particles do not interact, their internal potential energy is constant and can be chosen to be zero. By “point masses” we mean that the particles occupy no volume. These assumptions are not unreasonable for normal gases at room temperature: the average distance between molecules is much larger than the size of the molecules, so that the interactions are reduced. In addition, there is so much empty volume between molecules that one can neglect the volume occupied by the molecules themselves.

Let us consider first the average force exerted on the walls of a container by a stream of particles. The situation is depicted in Fig. 2.

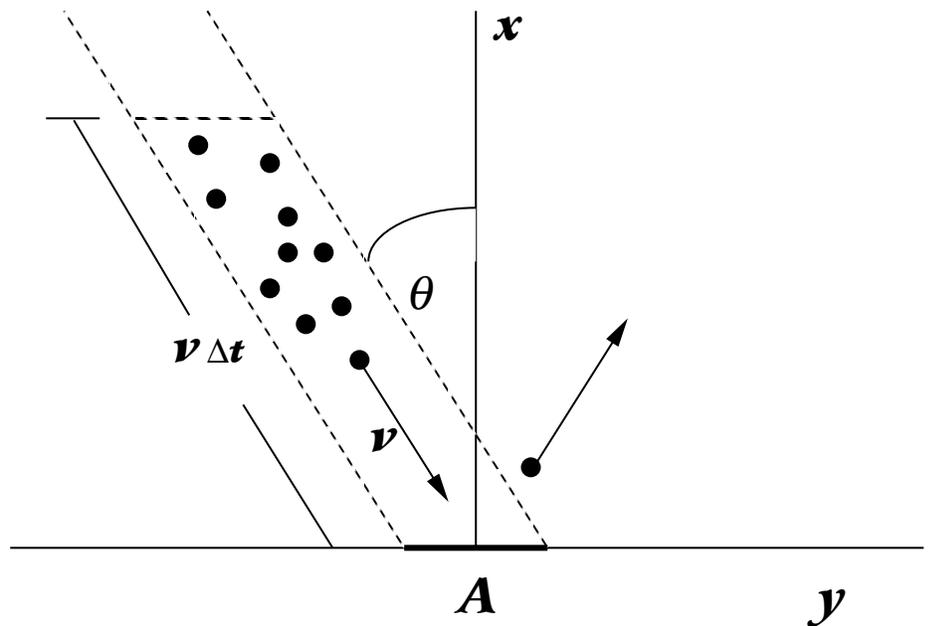


Figure 2 A stream of particles colliding with the container's wall.

Let us assume that v is the average velocity of the particles. If a particle is reflected elastically from the wall, its change in momentum is given by $\Delta p = 2mv_x$. During a time Δt , the average force exerted on a section of the wall of area A is therefore

$$\overline{F} = \frac{(\# \text{ of particles that hit wall in } \Delta t) \times 2mv_x}{\Delta t} \quad (5)$$

The particles that hit the wall are those contained in the slanted cylinder of volume $(A \cos \theta)(v \Delta t)$. If we call n_x the number of particles per unit volume whose x -component of the velocity is towards the wall, we obtain

$$\overline{F} = \frac{(n_x A v \cos \theta \Delta t)(2mv_x)}{\Delta t} = 2n_x m v_x^2 A \quad (6)$$

The pressure exerted on the wall is the average force per unit area, so that we obtain

$$p = 2n_x m v_x^2 \quad (7)$$

For a gas in equilibrium, one-half of the molecules move in the $+x$ direction, while the other half moves in the $-x$ direction. Hence $n_x = n/2$, where n is the number of particles per unit volume. The velocity term can be rewritten by noting that on the average $v_x^2 = v_y^2 = v_z^2$. On the other hand, $v^2 = v_x^2 + v_y^2 + v_z^2$, so that we can write

$$p = \frac{1}{3} n m v^2 . \quad (8)$$

By noting that $n = N/V$, we obtain

$$pV = \frac{1}{3} N m v^2 = \frac{2}{3} N E_{k,\text{ave}} , \quad (9)$$

where $E_{k,\text{ave}} = 1/2 m v^2$ is the average kinetic energy per particle. Comparing with the equation of state of an ideal gas, $pV = NkT$, we find that we obtain this result if we define the temperature as

$$E_{k,\text{ave}} = \frac{3}{2} kT \quad (10)$$

This is a very appealing definition because it is made in terms of fundamental particle properties, regardless of the properties of any thermometer used to measure the temperature. It is also intuitive in that it associates high temperatures with higher kinetic energies: the molecules are moving faster when the gas is hotter. On the other hand, it is not clear how this definition can be applied to real systems, not ideal gases, where the interactions between atoms cannot be neglected. Moreover, even within the realm of ideal gases, we have not yet provided an explanation for the fundamental property of temperature: the fact that two systems in thermal contact eventually attain the same final temperature. If two otherwise isolated ideal gases are in contact, we know that the sum of their energies remains constant. However, no mechanics principle requires that the average kinetic energy per particle be the same. If one of the gases is hot and the other is cold, nothing in the laws of mechanics prevents the hot gas from getting hotter while the cold gas gets colder. The only constraint is that the energy gained by one of the gases comes from the other gas. Clearly, this is not what happens in real systems. Hence we still need to

“fine tune” our definition of temperature so that we account for this behavior. A satisfactory definition will be provided in the next chapter when we introduce the concept of entropy.

Since the internal potential energy in an ideal gas is zero, the internal energy can be written as

$$U = \frac{3}{2} NkT \quad (11)$$

This energy will change if external work is done on the system, according to $\Delta U = W_{\text{ext}}$.

Energy, work, and heat

A small volume of gas may contain an extraordinarily high number of particles. The calculation of W_{ext} for such a system appears to be impossible, since we must compute an integral of $\mathbf{F} \cdot d\mathbf{r}$ for each particle. Under certain conditions, however, the calculation of the external work can be extremely simple. These conditions correspond to cases where some macroscopic parameter of the system changes. Let us consider for example the container in Fig. 3

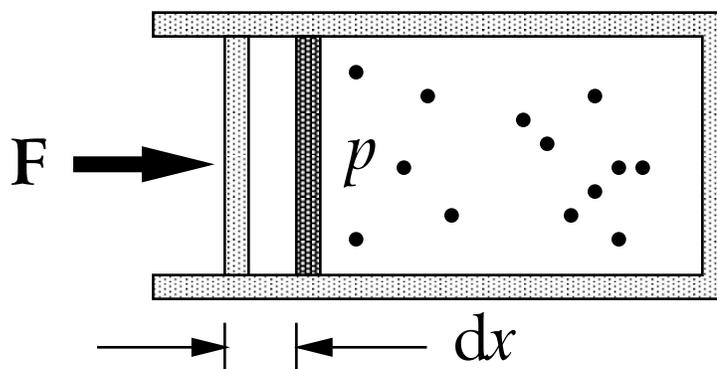


Figure 3 Work

Suppose that we apply an external force F infinitesimally higher than the force exerted by the gas on the wall. For a displacement dx of the wall, the work done by the external force is obviously $dW = F dx$. If we call the area of the wall A , we must have $F = pA$, neglecting the infinitesimal difference between the forces on both sides of the wall. Hence $dW = pA dx = -p dV$, where the minus sign represents the fact that the volume is reduced for $dx > 0$. Hence

the total work is given by

$$W = - \int_{V_1}^{V_2} p \, dV \quad (12)$$

On the other hand, suppose that the above container is heated as in Fig. 4

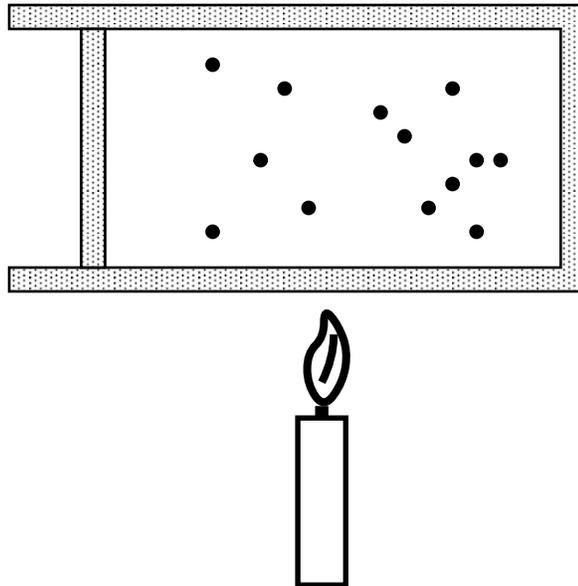


Figure 4 Heat

In this case, we cannot relate the external work to the change of a macroscopic parameter, as we did with the volume in the previous example. It is clear that the only way to compute this work from “first principles” is to go particle by particle, something we cannot afford.

From now on, we will reserve the word “**work**” for that part of the external work that involves a change in macroscopic parameters. The symbol used for this quantity is simply W . The part of the external work that does not involve a change in macroscopic parameters is referred to as **heat**. The symbol for heat is Q . We can thus write

$$W_{ext} = W + Q \quad (13)$$

or, in terms of infinitesimal changes

$$dW_{ext} = dW + dQ \quad (14)$$

With the above definitions, the change in internal energy can be written as

$$\Delta U = W_{ext} = W + Q \quad (15)$$

or, in terms of infinitesimal quantities:

$$dU = dW + dQ \quad (16)$$

Eqs. (15) and (16) are often referred to as the **first law of thermodynamics**. There is obviously not much new or beyond Newtonian mechanics in this law: it simply expresses the energy-work relationship for a system of particles.

The distinction between heat and work is quite straightforward. If you take a bottle full of water out of the refrigerator, the warmer air outside will slowly warm up the water by doing work on it (through collisions between air and water molecules, etc.). The energy of the water will increase. This increase ΔU is entirely due to heat Q , since no macroscopic parameter such as the volume or the number of particles is changed. (In a real life situation, the bottle may expand a little, so that there will be some amount of work W done on the water). Conversely, when a gas in a container is compressed from volume V_1 to volume V_2 , $\Delta U = W$ and the work is given by Eq. (12).

Sign conventions for W

Historically, thermodynamics was developed to understand the behavior of engines that deliver some useful work. The “desired” quantity in such an engine is the work W . The engineer would like this quantity to be large and *negative*, so that the engine does work on us and not we on the engine. Because it is sometimes confusing to use negative values, the work W is often defined as *minus* the quantity we have defined as W . This is done, for example, in Alonso’s book, for which $\Delta U = -W + Q$. You must be very careful if you read about this subject from different books. They might use different conventions, which, if not clearly stated, might confuse you. Since we are not going to be designing engines

any time soon, we will use the convention adopted in Eq. (13), which keeps a closer connection between the first law of thermodynamics and its mechanical underpinnings in terms of energy of a system of particles.

The heat capacity

An important technological question (particularly in Phoenix!) is how much heat dQ must be provided to a certain object to increase its temperature by dT . The **heat capacity** of the object is defined as $C' = dQ/dT$. Objects with large heat capacities are “harder” to warm up than objects with low heat capacities. The heat capacity depends obviously on the amount of material. To obtain a quantity that depends only on the *type* of material, one can define the **molar heat capacity** C as the heat capacity of one mole of the substance or the **specific heat** as the heat capacity per unit mass. In principle, the heat capacity may depend on temperature, so that the total heat absorbed to raise the temperature from T_1 to T_2 is given by

$$Q = \int_{T_1}^{T_2} C'(T) dT \quad (17)$$

In many instances, however, the heat capacity can be taken as constant, and Eq. (17) becomes $Q = C'(T_2 - T_1)$.

The change in temperature in an object depends not only on the heat input dQ but also on the work dW , since $dU = dQ + dW$. Hence we must specify what happens with W when we compute the heat capacity. Two forms of the heat capacity are defined for simple systems: the **heat capacity at constant volume** C_V and the **heat capacity at constant pressure** C_p . The heat capacity at constant volume is the heat input needed for a unitary change in temperature while keeping the volume of the object constant. In this case, $W = 0$, so that $dQ = dU$. We can thus write

$$C_V = \frac{1}{N} \frac{dQ}{dT} = \frac{1}{N} \frac{dU}{dT} \quad (18)$$

The heat capacity at constant pressure C_p is the heat input needed for a unitary change in temperature while keeping

the pressure on the object constant. It can be shown that $C_p > C_V$. In Fig. 5 we illustrate two systems where the same heat input is applied.

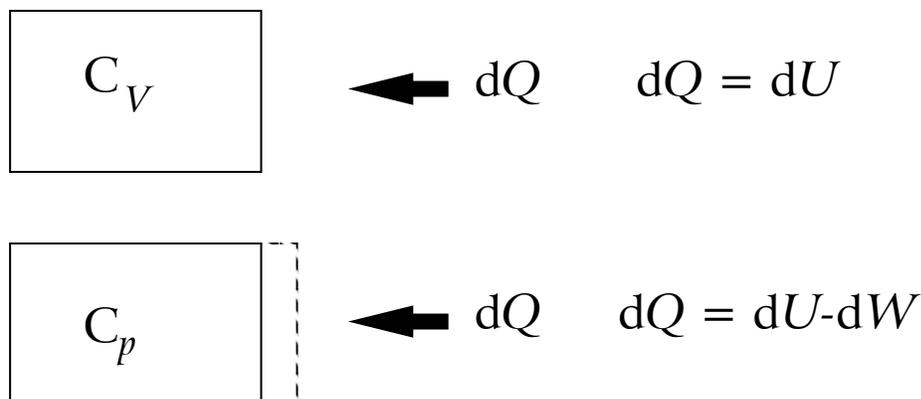


Figure 5 C_p versus C_V .

In the system where the volume is kept constant, all the heat goes into increasing the internal energy. When the volume is allowed to expand, as in the case of constant pressure, part of the heat is used up in the expansion work. Hence the change in temperature is smaller for heat input at constant pressure. This implies $C_p > C_V$.

The heat capacity of an ideal gas

For an ideal gas, $U = \frac{3}{2}NRT$. From Eq.(18) we obtain immediately

$$C_V = \frac{dU}{dT} = \frac{3}{2}R . \quad (19)$$

On the other hand, if the pressure is held constant, $dQ = dU - dW = dU + p dV$. Using the equation of state of an ideal gas, we obtain, for constant p , $p dV = NR dT$. Hence $dQ = dU + NR dT$, so that we finally obtain

$$C_p = \frac{1}{N} \frac{dQ}{dT} = \frac{dU}{dT} + R = C_V + R = \frac{5}{2}R \quad (20)$$

The predictions from these expressions are compared with real data in the table below. It can be seen that the agreement is very good, indicating that the ideal gas approxima-

tion is very good for He and Ne.

	C_p (cal /K•mol)	C_V (cal /K•mol)	$\frac{3}{2}R$ (cal /K•mol)	$\frac{5}{2}R$ (cal /K•mol)
He	5.04	3.01	2.98	4.98
Ne	4.97	3.02	2.98	4.98

The large difference between C_p and C_V has its origin in the significant expansion of a gas held at constant pressure while heat is applied. On the other hand, this expansion is much smaller for a solid object. Hence for a solid C_p and C_V are usually very similar. From the point of view of experiments, C_p is much easier to measure, since it is very difficult to keep the volume of a solid object constant as it is heated. On the other hand, C_V is much easier to calculate theoretically, because one need not deal with the thermal expansion of the object. Fortunately, the expected similarity of C_p and C_V minimizes this problem.

The heat capacity of a solid object

In the previous paragraphs, we have been able to compute the heat capacity for an ideal gas, whose internal energy is purely kinetic. It appears that the calculation of the heat capacity would be much more difficult for solid objects, where the potential energy cannot be neglected. On the other hand, we learned in Chapter 2 that the average kinetic energy of a harmonic oscillator equals the average potential energy. We also note that the motion of the atoms in a solid objects can be decomposed into normal modes, each of which satisfies the equation of motion of a simple harmonic oscillator. For each of the normal modes, the kinetic energy part of the internal energy is given, as in the ideal gas case, by $\frac{3}{2}kT$. But the average potential energy should also be $\frac{3}{2}kT$, so that $U = 3NkT = 3NRT$. The corresponding heat capacity is thus

$$C_V = \frac{1}{N} \frac{dU}{dT} = 3R \quad (23)$$

This is the so-called **Dulong and Petite law**. As seen in Fig. 6, the agreement with experimental data at room temperature is very good.

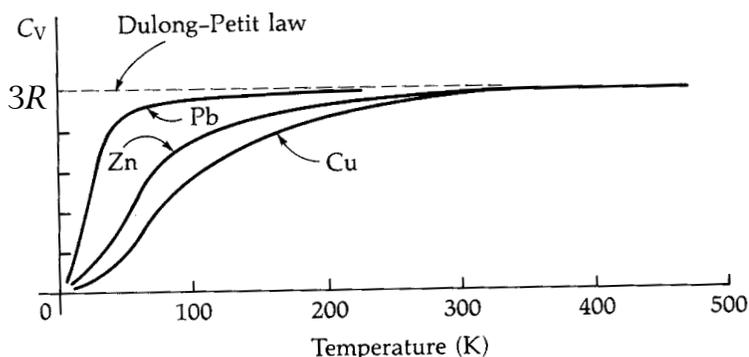


Figure 6 The heat capacity of selected solids.

Notice that C_V is predicted to be weakly dependent on temperature at high temperatures, justifying the use of a constant heat capacity for applications at room temperature. On the other hand, the heat capacity is found to decrease and approach zero at very low temperatures, in a complete breakdown of the Dulong and Petite law.

The observation of a heat capacity that approaches zero is one of the most spectacular manifestations of quantum mechanics. There is no classical explanation for this finding. The quantum-mechanical explanation was first proposed by Einstein. He proposed that the normal modes cannot absorb arbitrarily small amounts of heat, but only multiple values of $h\nu$, where ν is the frequency of the normal mode. Whenever $kT \ll h\nu$, that particular normal mode is “frozen” and does not contribute to the heat capacity. As the temperature is lowered, less and less normal modes can contribute, explaining the drop in the heat capacity.

Cycles

Engines and related machines have a working substance, usually a gas, that undergoes repeated cycles, starting from a certain set of parameters and returning to the same parameters. Thus the study of cycles is very important from a technological point of view. For a gas, a cycle can be represented in a x - y diagram, as indicated in Fig. ?, where the pressure p is graphed as a function of the volume V .

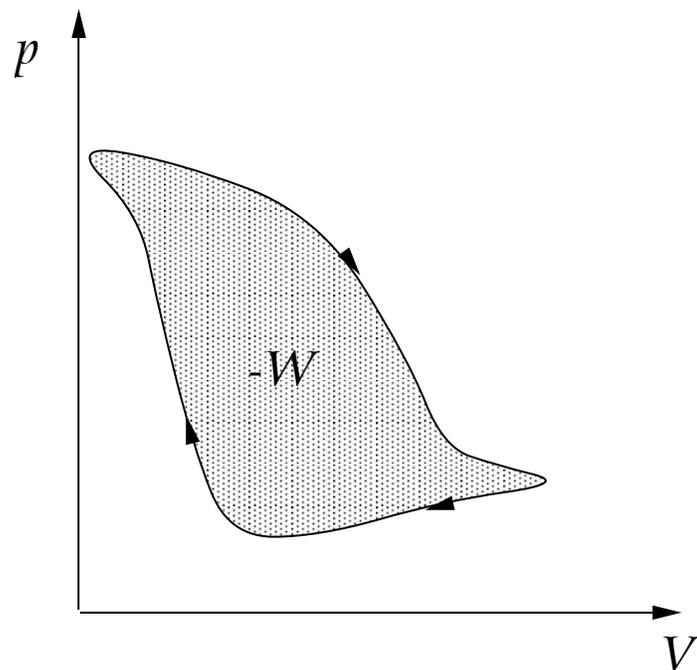


Figure 7 A cycle in a p - V diagram.

A representation in a p - V diagram has the advantage that the area enclosed by the circle (shaded area in Fig. ?) is equal to $-W$, the work delivered by the system for the entire cycle. This is an immediate consequence of Eq. 12.

An important process is the so-called **Carnot cycle**, depicted in Fig. 8.

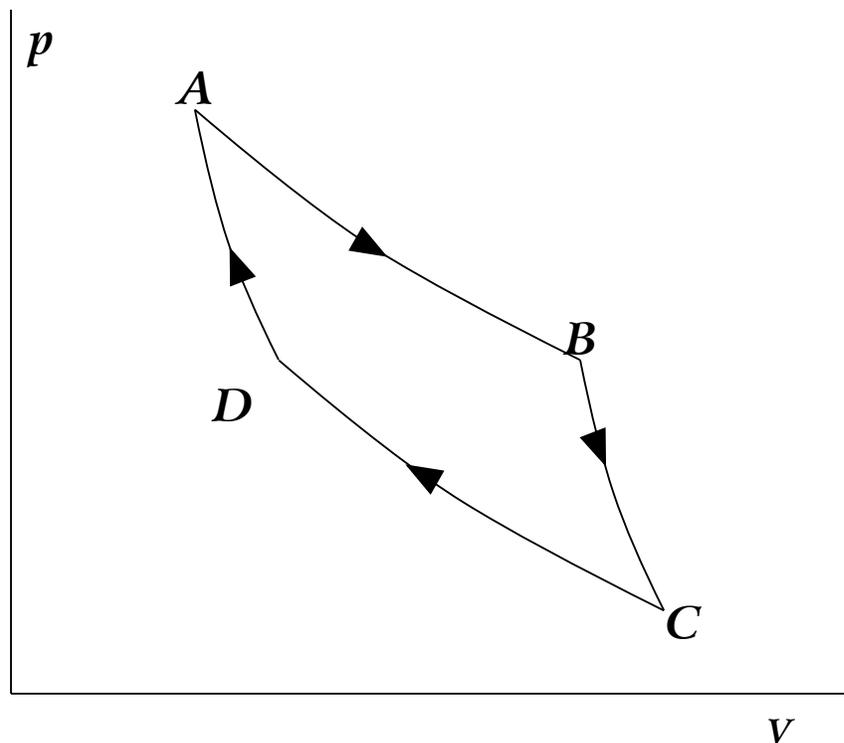


Figure 8 Diagram of a Carnot cycle in a p - V graph.

In a Carnot cycle, the gas is initially expanded **isothermically** in the $A \rightarrow B$ segment. An isothermal process is a process at constant temperature. In the $B \rightarrow C$ segment the gas is expanded **adiabatically**, *i.e.*, under the condition that no heat is absorbed. The cycle is completed by an isothermal compression ($C \rightarrow D$) followed by an adiabatic compression ($D \rightarrow A$).

During the isothermal processes, the pressure is given by $p = NkT/V$, with T constant. The same expression is valid for the adiabatic process, but now T changes as a function of the volume. To obtain the p - V dependence for an adiabatic process, we notice that if $dQ = 0$, then $dU = \frac{3}{2}NR dT = dW = -p dV$. On the other hand, by differentiating the equation of state $pV = NRT$ we obtain

$$p dV + V dp = NR dT = -\frac{2}{3}p dV \quad (24)$$

This can be rewritten as

$$\gamma p \, dV + V \, dp = 0 \quad (25)$$

where $\gamma = C_p/C_V = 5/3$. Dividing by pV and integrating,

$$\int \frac{dp}{p} + \gamma \int \frac{dV}{V} = \text{constant} \quad (26)$$

This means $\ln p + \gamma \ln V = \text{const}$ or

$$pV^\gamma = \text{constant} \quad (27)$$

Problems

1. (Alonso 15.3) The table below gives the pressure in Nm^{-2} and the volume (in m^3) for a gas at two different temperatures. (a) For each case calculate the product pV . (b) How does the product pV vary if the temperature doesn't change? (c) At which temperature is the product pV larger? What conclusion do you reach? (d) Represent on a graph the values of p against V at each temperature. These lines are called **isothermals**.

$T = 27^\circ\text{C}$		$T = 130^\circ\text{C}$	
$p(\text{N/m}^2)$	$V(\text{m}^3)$	$p(\text{N/m}^2)$	$V(\text{m}^3)$
0.81×10^6	2.43	1.85×10^6	1.41
1.30×10^6	1.51	2.19×10^6	1.20
1.74×10^6	1.13	2.46×10^6	1.07
2.05×10^6	0.96	2.94×10^6	0.89
2.56×10^6	0.77	3.14×10^6	0.83

2. (Alonso 15.4) The table below gives the values of the pressure and volume of a gas at different temperatures. (a) Calculate the value of the product pV for each temperature. (b) Plot the values of pV as a function of temperature. (c) Does pV vary linearly with temperature? (d) Extend the graph until it intersects the temperature axis and estimate the value of that temperature. Is it possible to cool the gas below that temperature? (e) Write the equation that relates pV with T that satisfies this data.

Temperature ($^\circ\text{C}$)	$p(\text{Pa})$	$V(\text{m}^3)$
210	4.3×10^5	0.85
120	2.8×10^5	1.06
0	1.5×10^5	1.38
-80	1.0×10^5	1.45
-120	0.84×10^5	1.35

3. (Alonso 15.7) An air bubble with a volume of 10 cm^3 is formed in the water 40 m below the surface of a lake. If the temperature of the bubble remains the same as the bubble rises, determine the volume

of the bubble just before it reaches the surface of the lake. Recall that one atmosphere = $1.0 \times 10^5 \text{ Pa}$.

4. (Alonso 15.5) Find the internal energy of one mole of an ideal gas at 0°C . Does it depend on the nature of the gas? Why?

5. (Alonso 15.16) Compute the average speed of (a) helium atoms at 20 K, (b) nitrogen molecules at 27°C , and (c) mercury atoms at 100°C .

6. (Alonso 15.17) (a) Show that atmospheric pressure varies with height h according to $\ln(p/p_0) = -Mgh/RT$, where M is the effective molar mass of air. Assume that the temperature is independent of height, which is not correct. (b) Estimate the pressure at the summit of Mt. McKinley, whose height is $6.19 \times 10^3 \text{ m}$, if the air temperature is 0°C .

7. (Alonso 15.18) Repeat the previous problem, assuming that the atmospheric pressure decreases linearly with height according to $T = T_0 - \alpha h$, where α is constant, and verify that the atmospheric pressure is $\ln(p/p_0) = (Mg/R\alpha) \ln(1 - \alpha h/T_0)$. Find the limiting value when $\alpha \rightarrow 0$.

8. The specific heat of nitrogen (in kcal/kg K) in the temperature range $300 \text{ K} \leq T \leq 5000$ is given by the expression

$$c(T) = 0.096 - 63.7/T + 3.83 \times 10^4/T^2.$$

a) Compare this expression with the predictions for an ideal gas.

b) Compute the amount of heat required to raise the temperature of 0.100 kg of N_2 from 500 K to 2500 K. Use $1 \text{ cal} = 4.184 \text{ J}$

9. Two moles of helium at 250 K are expanded adiabatically from a volume of 1.5 L to 4.50 L.

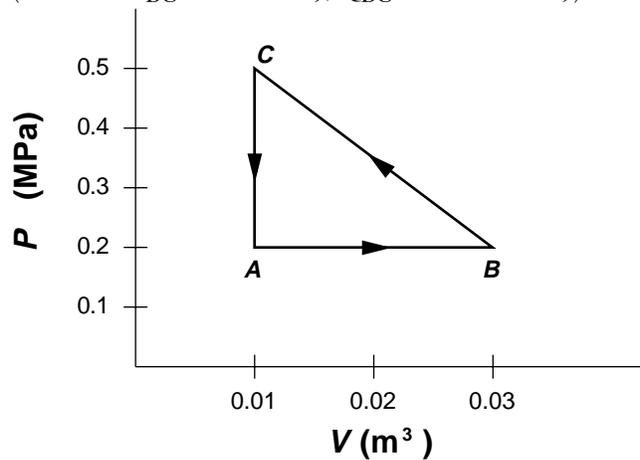
a) What are the final pressure and temperature of the gas?

b) What is the change in internal energy of the gas?

10. (Callen) For a particular gaseous system it has been determined that the internal energy is given by $U = 2.5 pV + \text{constant}$. The system is initially in the

state $p = 0.2$ MPa (mega-Pascals), $V = 0.01$ m³; designated as point A in the figure. The system is taken through the cycle of three processes ($A \rightarrow B$, $B \rightarrow C$, and $C \rightarrow A$) shown in the figure. Calculate Q and W for each of the three processes. Calculate Q and W for a process from A to B along the parabola $p = 10^5 + 10^9 \times (V - 0.02)^2$.

(Answer: $W_{BC} = 7 \times 10^3$ J; $Q_{BC} = -9.5 \times 10^3$ J)



11. Show that when a system undergoes a cycle, the work delivered by the system is given by the area enclosed by the lines that define the cycle in a p - V diagram.