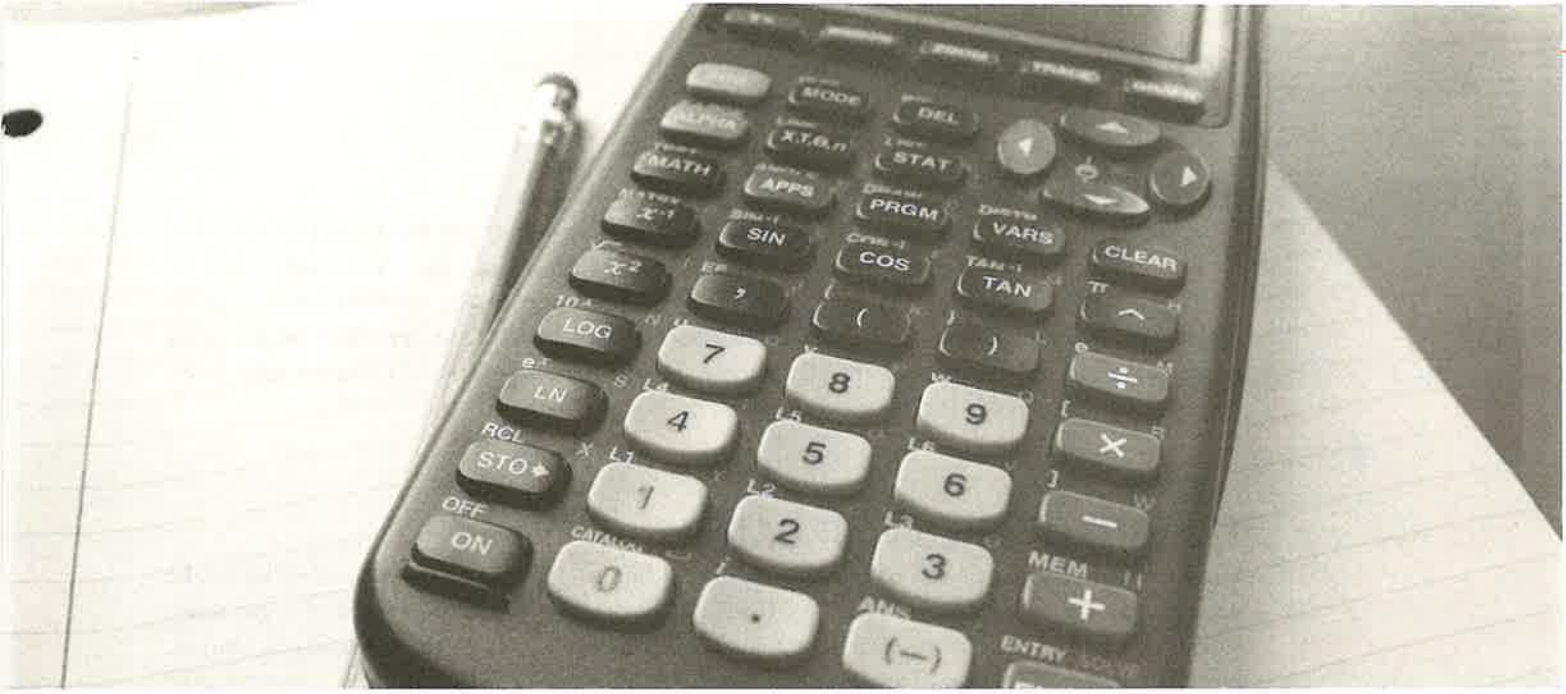


Chapter 3
Thermodynamics

INTRODUCTION

This chapter looks at heat and temperature, concepts that seem familiar from our everyday experience. Technically, **heat** is defined as thermal energy transmitted from one body to another. While an object can contain **internal energy** (due to the random motion of its molecules), an object doesn't *contain* heat; heat is energy *in transit*. **Temperature**, on the other hand, is a measure of an object's internal energy. To understand how these ideas are related, we need to examine physics at a microscopic level.

THE KINETIC THEORY OF GASES

Unlike the condensed phases of matter—solid and liquid—the atoms or molecules that make up a gas do not move around relatively fixed positions. Rather, the molecules of a gas move freely and rapidly, in a chaotic swarm. The molecules of the gas, which are constantly in motion, bump against one another. To study such a gas, it would need to be put into a container, and the random motion of the molecules would cause the molecules to bump into not just one another but also the walls of the container. The size of the container is the volume (V) of the thermodynamic system, and as the molecules bump against the walls, they create a pressure (P) where pressure is defined the same way as in the study of fluids as $P = F_\perp/A$. The **Kinetic Theory of Gases** deals with the relationship between the volume, pressure, and temperature of a gas, as well as the **Ideal Gas Law**.

Equation Sheet

$$\text{Pressure} = F_\perp/A$$

One of the difficulties in describing the behavior of gases is that they are comprised of an extremely large number of atoms or molecules. For example, at room temperature, air has a volume of 24 liters per mole. That means an empty one-liter soda bottle will contain 25 sextillion (2.5×10^{22}) air molecules. That is 25,000,000,000 trillions of molecules. Each of these molecules, at any given instant, will have its own position and be moving with its own momentum. A confined gas exerts a force on the walls of its container, and as the molecules are zipping around inside the container, striking the walls and rebounding, they create pressure within the container. It is impossible to apply Newton's laws to each molecule and determine the amount of force that each molecule would apply to the container of the bottle to determine the total pressure. To avoid dealing with individual molecules, the Kinetic Theory of Gases applies the mathematics of statistics to develop the concept of temperature as a measurement relating to the "average" kinetic energy of molecules in a gas sample and the relationship between temperature, pressure, and volume.

When considering the microscopic world, as the molecules move around in the sample and collide with one another, every collision between molecules and every collision between a molecule and the walls of the container is assumed to be a perfectly elastic collision. This means that the sum of the kinetic energy before the collision is equal to the sum of the kinetic energy after the collision. For inelastic collisions—for example, when a lump of clay is dropped and hits the floor—a certain amount of kinetic energy from the clay was used to generate "thermal energy," resulting in deforming the clay and increasing its temperature and the temperature of the floor. When considering collisions between individual molecules or between a molecule and the wall, the kinetic energy of the molecules is no longer distinct from the thermal energy;

it is the motion of the molecules (kinetic energy) that is the thermal energy, and we can no longer use the convenient label of "thermal energy" to account for a decrease in mechanical energy as we did when looking at macroscopic objects. Energy will be contained within the gas, as **internal energy**, which will determine the temperature. Transfers of energy into or out of the gas will be a result of **work**, a volume change in the container, or **heating**, a flow of energy that naturally occurs between systems at unequal temperatures.

The Ideal Gas Law

Three physical properties—pressure (P), volume (V), and temperature (T)—describe a gas. At low densities, all gases approach *ideal* behavior; this means that these three variables are related by the equation

$$PV = nRT = Nk_BT$$

Equation Sheet

where n is the number of moles of gas and R is a constant (8.31 J/mol•K) called the **universal gas constant**. This equation is known as the **Ideal Gas Law**. It can also be written as $PV = Nk_BT$, where N is the number of atoms (or molecules) of gas and k_B is Boltzmann's constant ($k_B = 1.38 \times 10^{-23}$ J/K). The Ideal Gas Law tells us how these variables are related to one another for a gas with no intermolecular forces. This is a bad assumption for a charged gas, where the individual charges would interact electrically (a strong interaction), but it is a good assumption for a neutral gas, where the atoms would only interact gravitationally (a very weak interaction).

An important consequence of this equation is that, for a fixed volume of gas, an increase in P gives a proportional increase in T. The pressure increases when the gas molecules strike the walls of their container with more force, which occurs if they move more rapidly. The macroscopic variables of pressure, volume, and temperature can be related to the average kinetic energy of any particular molecule within the gas using Newton's Second Law. We can find that the pressure exerted by N molecules of gas in a container is related to the average kinetic energy by the equation $PV = \frac{2}{3}NK_{\text{avg}}$. Comparing this with the Ideal Gas Law, we see that $\frac{2}{3}NK_{\text{avg}} = nRT$. We can rewrite this equation in the form $\frac{2}{3}N_AK_{\text{avg}} = RT$, since, by definition, $N = nN_A$. The ratio R/N_A is a fundamental constant of nature called **Boltzmann's constant** ($k_B = 1.38 \times 10^{-23}$ J/K), so our equation becomes

$$\left(K_{\text{avg}} = \frac{3}{2}k_BT\right) = \frac{1}{2}mv^2_{\text{rms}}$$

Equation Sheet

To convert from degrees Celsius to Kelvin, add 273.15.

This tells us that the average translational kinetic energy of the gas molecules is directly proportional to the absolute temperature of the sample. Remember, this means you must use kelvins as your temperature unit.

Since the average kinetic energy of the gas molecules is $K_{\text{avg}} = \frac{1}{2}m(v^2)_{\text{avg}}$, the equation above becomes $\frac{1}{2}m(v^2)_{\text{avg}} = \frac{3}{2}k_B T$, so

$$\sqrt{(v^2)_{\text{avg}}} = \sqrt{\frac{3k_B T}{m}}$$

The quantity on the left-hand side of this equation, the square root of the average of the square of v, is called the **root-mean-square velocity**, v_{rms}, so

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$$

It's important to realize that the molecules in the container have a wide range of speeds; some are much slower and others are much faster than v_{rms}. The root-mean-square speed is important because it gives us a type of average speed that's easy to calculate from the temperature of the gas.

Example 1 In order for the rms velocity of the molecules in a given sample of gas to double, what must happen to the temperature?

Solution. Temperature is a measure of the average kinetic energy. The velocity is determined from the following equation:

$$v_{rms} = \sqrt{\frac{3k_b T}{m}}$$

Since v_{rms} is proportional to the square root of T, the temperature must quadruple, again, assuming the temperature is given in kelvins.

Example 2 A cylindrical container of radius 15 cm and height 30 cm contains 0.6 mole of gas at 433 K. How much force does the confined gas exert on the lid of the container?

Solution. The volume of the cylinder is $\pi r^2 h$, where r is the radius and h is the height. Since we know V and T, we can use the Ideal Gas Law to find P. Because pressure is force per unit area, we can find the force on the lid by multiplying the gas pressure by the area of the lid.

$$P = \frac{nRT}{V} = \frac{(0.6\text{ mol})(8.31\text{ J/mol}\cdot\text{K})(433\text{ K})}{\pi(0.15\text{ m})^2(0.30\text{ m})} = 1.018\times10^5\text{ Pa}$$

So, since the area of the lid is πr^2, the force exerted by the confined gas on the lid is

$$F = PA = (1.018 \times 10^5 \text{ Pa}) \cdot \pi (0.15 \text{ m})^2 = 7200 \text{ N}$$

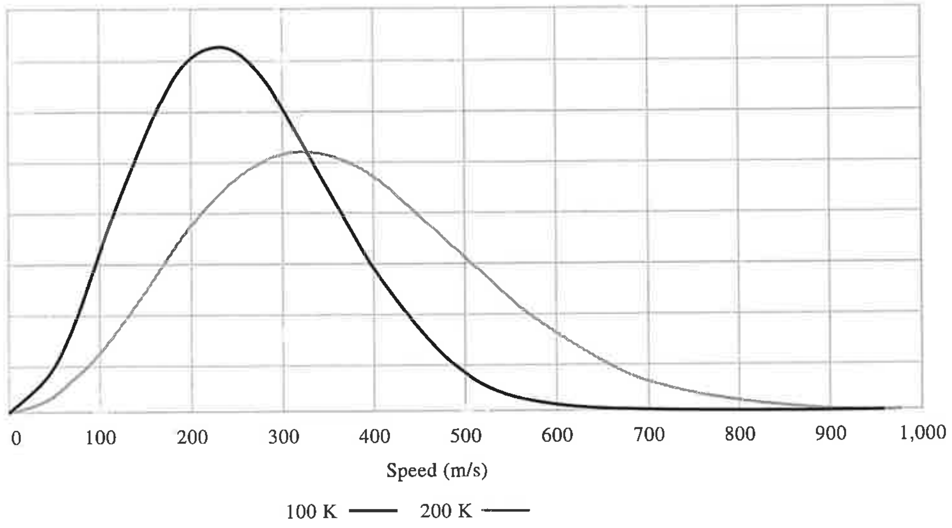
This is about 1600 pounds of force, which seems like a lot. Why doesn't this pressure pop the lid off? Because, while the bottom of the lid is feeling a pressure (due to the confined gas) of 1.018×10^5 Pa that exerts a force upward, the top of the lid feels a pressure of 1.013×10^5 Pa (due to the atmosphere) that exerts a force downward. The net force on the lid is

$$F_{\text{net}} = (\Delta P)A = (0.005 \times 10^5 \text{ Pa}) \cdot \pi (0.15 \text{ m})^2 = 35 \text{ N}$$

which is only about 8 pounds.

THE MAXWELL-BOLTZMANN DISTRIBUTION

The Kinetic Theory of Gases applies to large numbers of particles, which is why the term "average" continually appears in the previous section when describing the energy or speed of any particular molecule. The gas will have a variety of molecules with different energies and therefore different speeds. Some of the molecules will be moving much faster than average and some much slower. A graph of the distribution of the speeds of all of the molecules is called the Maxwell-Boltzmann distribution.



Distribution of speeds of molecules for a gas at different temperatures

The important features of this type of graph are the position of the peak and the spread of the curve. As a gas sample is heated, the peak (called the most probable speed, which is actually always a bit lower than the v_{rms}) moves to the right, indicating the most probable speed for any particular molecule in the sample is increasing. The graph also spreads out and grows a longer tail on the right-hand side, indicating that there will be more molecules moving at much higher speed than average for hotter gas samples, which intuitively makes sense.

THE LAWS OF THERMODYNAMICS

We've learned about two ways in which energy may be transferred between a system and its environment. One is work, which takes place when a force acts over a distance. The other is heat, which takes place when energy is transferred due to a difference in temperature. The study of the energy transfers involving work and heat, and the resulting changes in internal energy, temperature, volume, and pressure is called **thermodynamics**.

The Zeroth Law of Thermodynamics

When two objects are brought into contact, heat will flow from the warmer object to the cooler one until they reach thermal equilibrium. This property of temperature is expressed by the Zeroth Law of Thermodynamics.

The Zeroth Law of Thermodynamics

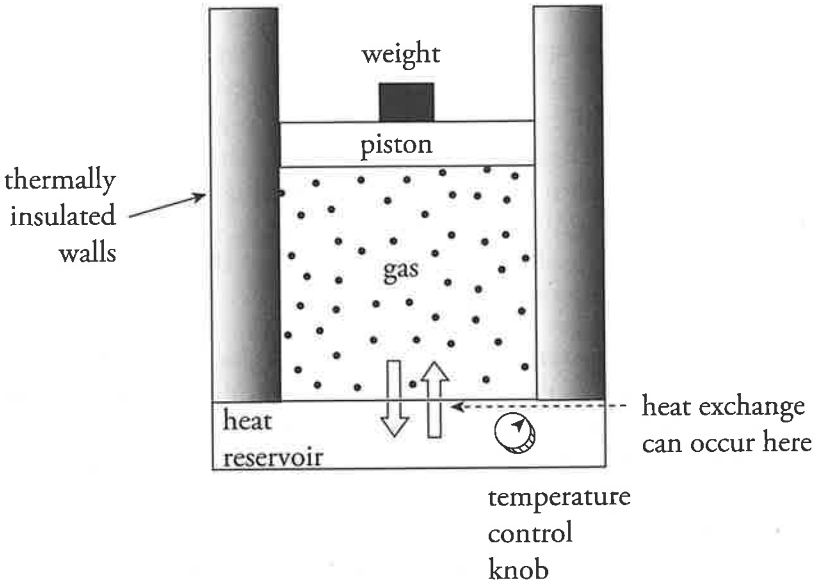
If Objects 1 and 2 are each in thermal equilibrium with Object 3, then Objects 1 and 2 are in thermal equilibrium with each other.

The First Law of Thermodynamics

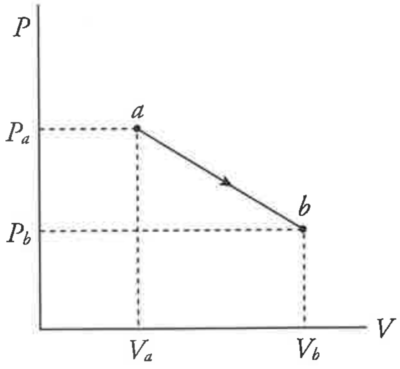
Simply put, the First Law of Thermodynamics is a statement of the Conservation of Energy that includes heat.

To understand how to include a statement of heat flow in Conservation of Energy, start by considering the following example, which is the prototype that's studied extensively in thermodynamics.

An insulated container filled with an ideal gas rests on a heat reservoir (that is, something that can act as a heat source or a heat sink). The container is fitted with a snug, but frictionless, weighted piston that can be raised or lowered. The confined gas is the *system*, and the piston and heat reservoir are the *surroundings*.



The **state** of the gas is given once its pressure, volume, and temperature are known, and the equation that connects these state variables is the Ideal Gas Law, $PV = nRT$. We'll imagine performing different experiments with the gas, such as heating it or allowing it to cool or increasing or decreasing the weight on the piston, and study the energy transfers (work and heat) and the changes in the state variables. If each process is carried out such that, at each moment, the system and its surroundings are in thermal equilibrium, we can plot the pressure (P) versus the volume (V) on a diagram. By following the path of this ***P–V* diagram**, we can study how the system is affected as it moves from one state to another.



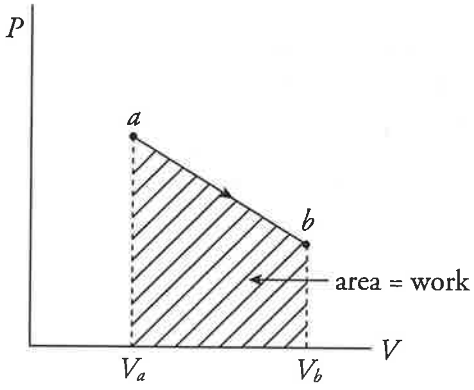
Work is done on or by the system when the piston is moved and the volume of the gas changes. For example, imagine that the weight pushes the piston downward a distance d, causing a decrease in volume. Assume that the pressure stays constant at P. (Heat must be removed via the reservoir to accomplish this.) We can calculate the work done on the gas during this compression as $W = -Fd$, but since $F = PA$, we have $W = -PAd$, and because $Ad = \Delta V$, we have

$$W = -P\Delta V$$

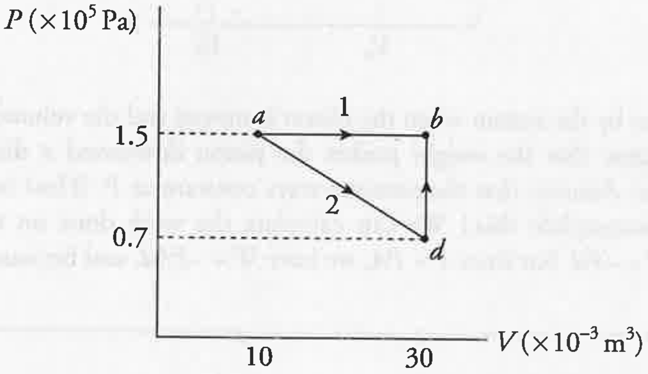
Equation Sheet

Textbooks differ about the circumstances under which work in thermodynamics is defined to be positive or negative. The negative signs we have included in the equations on the previous page are consistent with those used in the AP Physics 2 Exam. For the exam, work in thermodynamics is considered to be positive when the work is being done *on the system.* This means that the volume of the system is *decreasing,* ΔV is *negative,* and, in agreement with intuition, energy is being *added* to the system. In other words, when work is done in compressing a system, ΔV is *negative* and the work done on the system, $W = -P\Delta V$, is *positive.* This also means, conversely, that when the system is doing work *on the surroundings* (volume *increasing,* ΔV *positive*), the work is *negative,* in agreement with intuition that energy is leaving the system.

The equation $W = -P\Delta V$ assumes that the pressure P does not change during the process. If P *does* change, then the work is equal to the area under the curve in the P–V diagram; moving left to right as the volume increases gives a negative area (and negative work), while moving right to left as the volume decreases gives a positive area (and positive work). Because of this difference when moving left to right or right to left, processes in P–V diagrams are drawn with arrows to indicate which direction the process follows. In the diagram below, the process is taken from an initial state a, with a particular P and V value, to a final state b, where P and V have changed.



Example 3 What's the value of W for the process ab following path 1 and for the same process following path 2 (from a to d to b), shown in the P–V diagram below?



Solution.

Path 1. Since, in path 1, P remains constant, the work done is just $-P\Delta V$:

$$W = -P\Delta V = -(1.5 \times 10^5 \text{ Pa})[(30 \times 10^{-3} \text{ m}^3) - (10 \times 10^{-3} \text{ m}^3)] = -3000 \text{ J}$$

Path 2. If the gas is brought from state a to state b, along path 2, then work is done only along the part from a to d. From d to b, the volume of the gas does not change, so no work can be performed. The area under the graph from a to d is

$$\begin{aligned} W &= -\frac{1}{2}h(b_1+b_2) = -\frac{1}{2}(\Delta V)(P_a+P_d) \\ &= -\frac{1}{2}(20\times10^{-3}\text{ m}^3)[(1.5\times10^5\text{ Pa})+(0.7\times10^5\text{ Pa})] \\ &= -2200\text{ J} \end{aligned}$$

As this example shows, the amount of work done by a gas depends not only on the initial and final states of the system, but also on the path between the two. In general, different paths give different values for W.

Experiments have shown that the value of the sum of the total heat added (or removed), denoted by Q, and the total work done on (or by) the system, denoted by W, does not depend on the path taken by a thermodynamic process; it depends only on the initial and the final state of the system, so it describes a change in a fundamental property. This property is called the system's **internal energy**, denoted U, and the change in the system's internal energy, ΔU, is equal to $Q + W$. This is true regardless of the process that brought the system from its initial to final state. This statement is known as

The First Law of Thermodynamics

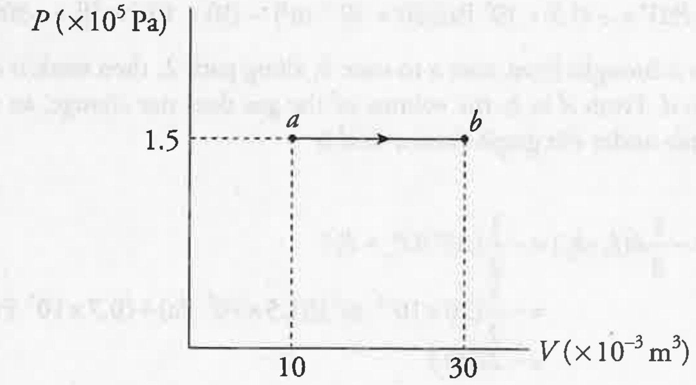
$$\Delta U = Q + W$$

Equation Sheet

As stated above, the internal energy, U, of a gas depends only on the state of the gas. As we saw in the section on the Ideal Gas Law, the average kinetic energy of a molecule in a gas sample is directly proportional to the temperature. For ideal gases in particular, this is the only source of internal energy. Because of this, the change in internal energy, ΔU, which arises in the First Law of Thermodynamics, is directly proportional to a change in the temperature of the ideal gas.

This statement of the First Law is consistent with the interpretation of work ($W = -P\Delta V$) explained above. The First Law identifies W and Q as separate physical mechanisms for adding to or removing energy from the system, and the signs of both W and Q are defined consistently: both are positive when they are adding energy to the system and negative when they are removing energy from the system.

Example 4 A 0.5 mol sample of an ideal gas is brought from state *a* to state *b* when 7500 J of heat is added along the path shown in the following *P*–*V* diagram:



What are the values of each of the following?

(a) The temperature at *a*
(b) The temperature at *b*
(c) The work done by the gas during process *ab*
(d) The change in the internal energy of the gas

Solution.

(a, b) Both of these questions can be answered using the Ideal Gas Law, $T = PV/(nR)$:

$$T_a = \frac{P_aV_a}{nR} = \frac{(1.5\times10^5\ \text{Pa})(10\times10^{-3}\ \text{m}^3)}{(0.5\ \text{mol})(8.31\ \text{J/mol}\cdot\text{K})} = 360\ \text{K}$$

$$T_b = \frac{P_bV_b}{nR} = \frac{(1.5\times10^5\ \text{Pa})(30\times10^{-3}\ \text{m}^3)}{(0.5\ \text{mol})(8.31\ \text{J/mol}\cdot\text{K})} = 1080\ \text{K}$$

(c) Since the pressure remains constant during the process, we can use the equation $W = -P\Delta V$. Because $\Delta V = (30 - 10) \times 10^{-3}\ \text{m}^3 = 20 \times 10^{-3}\ \text{m}^3$, we find that

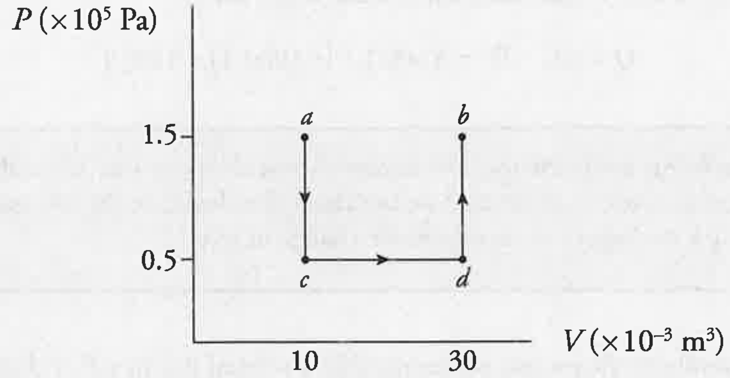
$$W = -P\Delta V = (1.5 \times 10^5\ \text{Pa})(20 \times 10^{-3}\ \text{m}^3) = -3000\ \text{J}$$

The expanding gas did negative work against its surroundings, pushing the piston upward. Important note: if the pressure remains constant (which is designated by a horizontal line in the *P*–*V* diagram), the process is called **isobaric**.

(d) By the First Law of Thermodynamics,

$$\Delta U = Q + W = 7500\ -\ 3000\ \text{J} = 4500\ \text{J}$$

Example 5 A 0.5 mol sample of an ideal monatomic gas is brought from state *a* to state *b* along the path shown in the following *P–V* diagram:



What are the values of each of the following?

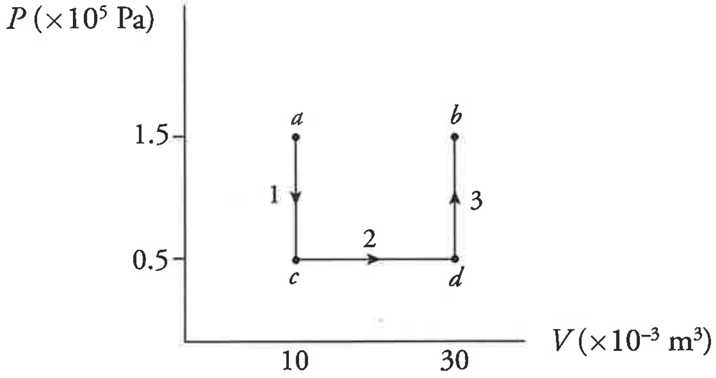
(a) The work done by the gas during process *ab*

(b) The change in the internal energy of the gas

(c) The heat added to the gas during process *ab*

Solution. Note that the initial and final states of the gas are the same as in the preceding example, but the path is different.

(a) Let's break the path into 3 pieces:



Over paths 1 and 3, the volume does not change, so no work is done. Work is done only over path 2:

$$W = -P\Delta V = -(0.5 \times 10^5 \text{ Pa})(20 \times 10^{-3} \text{ m}^3) = -1000 \text{ J}$$

Once again, the expanding gas does negative work against its surroundings, pushing the piston upward.

(b) Because the initial and final states of the gas are the same here as they were in the preceding example, the change in internal energy, ΔU, *must* be the same. Therefore, $\Delta U = 4500$ J.

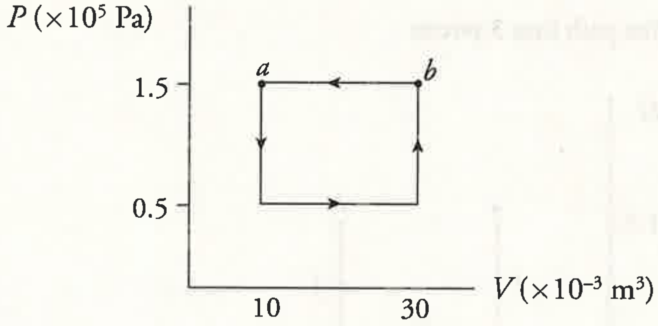
(c) By the First Law of Thermodynamics, $\Delta U = Q + W$, so

$$Q = \Delta U - W = 4500\text{ J} - (-1000\text{ J}) = 5500\text{ J}$$

Example 6 An **isochoric** (or isovolumetric) process is one that takes place with no change in volume. What can you say about the change in the internal energy of a gas if it undergoes an isovolumetric change of state?

Solution. An isovolumetric process is illustrated by a vertical line in a P–V diagram and, since no change in volume occurs, $W = 0$. By the First Law of Thermodynamics, $\Delta U = Q + W = Q$. Therefore, the change in internal energy is entirely due to (and equal to) the heat transferred. If heat is transferred into the system (positive Q), then ΔU is positive; if heat is transferred out of the system (negative Q), then ΔU is negative.

Example 7 A 0.5 mol sample of an ideal gas is brought from state *a* back to state *a* along the path shown in the following P–V diagram:



What are the values of each of the following?

(a) The change in the internal energy of the gas

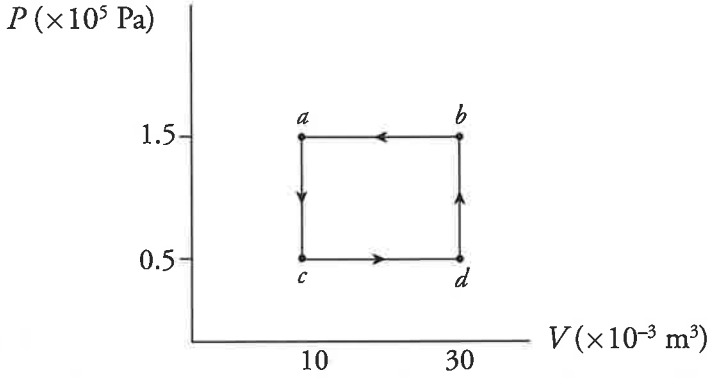
(b) The work done on the gas during the process

(c) The heat added to the gas during the process

Solution. A process such as this, which begins and ends at the same state, is said to be cyclical.

(a) Because the final state is the same as the initial state, the internal energy of the system cannot have changed, so $\Delta U = 0$.

(b) The total work involved in the process is equal to the work done from *c* to *d* plus the work done from *b* to *a*,



because only along these paths does the volume change. Along these portions, we find that

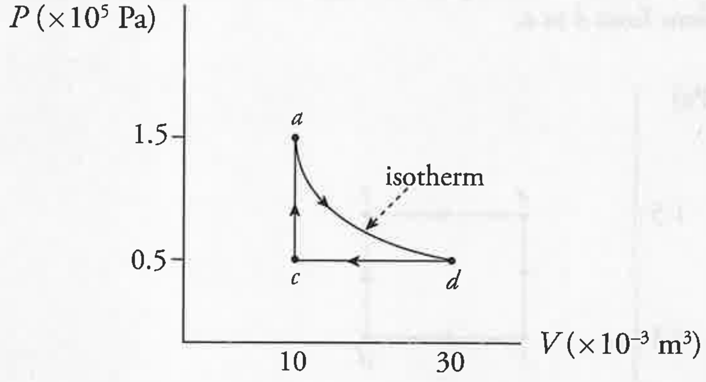
$$W_{cd} = -P\Delta V_{cd} = (0.5 \times 10^5\ \text{Pa})(+20 \times 10^{-3}\ \text{m}^3) = -1000\ \text{J}$$

$$W_{cd} = -P\Delta V_{ba} = (1.5 \times 10^5\ \text{Pa})(-20 \times 10^{-3}\ \text{m}^3) = +3000\ \text{J}$$

So, the total work done is $W = +2000$ J. The fact that W is positive means that, overall, work was done *on* the gas by the surroundings. Notice that for a cyclical process, the total work done is equal to the area enclosed by the loop, with clockwise travel taken as negative and counterclockwise travel taken as positive.

(c) The First Law of Thermodynamics states that $\Delta U = Q + W$. Since $\Delta U = 0$, it must be true that $Q = -W$ (which will always be the case for a cyclical process), so $Q = -2000$ J.

Example 8 A 0.5 mol sample of an ideal gas is brought from state *a* to state *d* along an **isotherm**, and then isobarically to state *c* and isochorically back to state *a*, as shown in the following *P–V* diagram:



A process that takes place with no variation in temperature is said to be **isothermal**. Given that the work done during the isothermal part of the cycle is –1650 J, how much heat is transferred during the isothermal process, from *a* to *d*?

Solution. Be careful that you don't confuse *isothermal* with *adiabatic*. A process is isothermal if the *temperature* remains constant; a process is **adiabatic** if $Q = 0$. You might ask, *How could a process be isothermal without also being adiabatic at the same time?* Remember that the temperature is determined by the internal energy of the gas, which is affected by changes in Q, W, or both. Therefore, it's possible for U to remain unchanged even if Q is not 0 (because there can be an equal but opposite W to cancel it out). In fact, this is the key to this problem. Since T doesn't change from *a* to *d*, neither can the internal energy, which depends entirely on T. Because $\Delta U_{ad} = 0$, it must be true that $Q_{ad} = -W_{ad}$. Since W_{ad} equals –1650 J, Q_{ad} must be +1650 J. The gas absorbs heat from the reservoir and uses all this energy to do negative work as it expands, pushing the piston upward.

Here is a summary of special thermal processes:

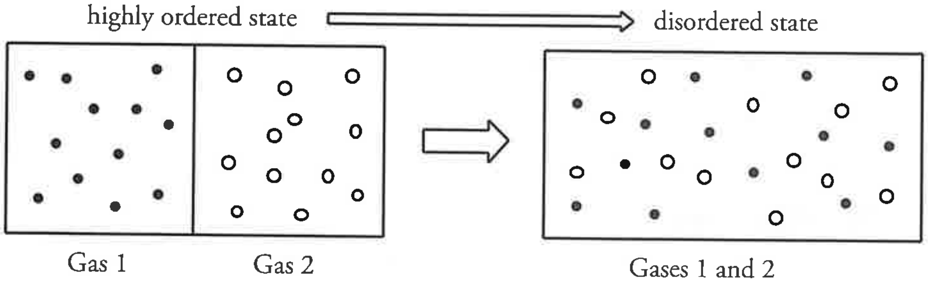
Process	Condition	Application of 1st Law
Isovolumetric	$\Delta V = 0$	$\Delta U = Q$
Isothermal	$\Delta T = 0$	$\Delta U = 0$
Isobaric	$\Delta P = 0$	$\Delta U = Q - P\Delta V$
Adiabatic	$Q = 0$	$\Delta U = W$

The Second Law of Thermodynamics

The Second Law of Thermodynamics describes how systems evolve over time. Conservation of Energy states that system A and system B will have the same energy without any external work, but it never describes how a system changes from state A into state B. One description of this evolution is about **entropy**, an equivalent description is about **spontaneous heat flow**, and a third equivalent description is about **efficiency** in engines.

Entropy

Consider a box containing two pure gases separated by a partition. What would happen if the partition were removed? The gases would mix, and the positions of the gas molecules would be random.



A closed system that shows a high degree of order tends to evolve in such a way that its degree of order decreases. In other words, disorder (or, as it's technically called, entropy) increases. The term "disorder" often makes the concept of entropy sound negative. Rather, entropy is better described as **increasing molecular freedom**. This is the reason why broken glass does not put itself back together and the reason why chemical reactions take place. If we started with the box on the right, containing the mixture of the gases, it would be virtually impossible that at any later time all the molecules of Gas 1 would happen to move to the left side of the box and, at the same time, the molecules of Gas 2 would spontaneously move to the right side of the box. If we were to watch a movie of this process, and saw the mixed-up molecules suddenly separate and move to opposite sides of the box, we'd assume that the film was running backward. In a way, the Second Law of Thermodynamics defines the direction of time. Time flows in such a way that ordered systems become disordered. Disordered states do not spontaneously become ordered without any other changes taking place. The following is the essence of one form of the Second Law of Thermodynamics:

> The total amount of disorder—the total entropy—of a system plus its surroundings will never decrease.

It is possible for the entropy of a system to decrease, but it will always be at the expense of a greater increase in entropy in the surroundings. For example, when water freezes, its entropy decreases. The molecules making up an ice crystal have a more structured order than the random collection of water molecules in the liquid phase, so the entropy of the water decreases when it freezes. But when water freezes, it releases heat energy into its environment, which creates disorder in the surroundings. If we were to figure out the total change in entropy of the water plus its surroundings, we would find that although the entropy of the water itself decreased, it was more than compensated by a greater amount of entropy increase in the surroundings. So, the total entropy of the system and its surroundings increased, in agreement with the Second Law of Thermodynamics.

There are several equivalent statements of the second law. In addition to the entropy form, another form of the Second Law of Thermodynamics says that heat always flows from hot to cold, never cold to hot. Another form, which will be considered more fully in a moment, says it is impossible to convert heat completely into work.

Entropy and Heat
An isolated system never decreases in entropy over time. A non-idealized (real-world) isolated system always increases in entropy over time. This entropy is usually in the form of heat given off. When a system is not isolated, it is possible for the entropy of the system to decrease as long as the surroundings to the system increase in entropy by a greater amount than the decrease in the system. As a result, the entropy of the universe never decreases, and the entropy of the universe will increase over time as real-world systems transfer heat and work.

Heat spontaneously flows from an object at higher temperature to an object at lower temperature, never the other way around.

Heat Engines

Converting work to heat is easy—rubbing your hands together in order to warm them up shows that work can be completely converted to heat. What we'll look at is the reverse process: how efficiently can heat be converted into work? A device that uses heat to produce useful work is called a **heat engine**. The internal-combustion engine in a car is an example. In particular, we're interested only in engines that take their working substance (a mixture of air and fuel in this case) through a cyclic process, so that the cycle can be repeated. The basic components of any cyclic heat engine are simple: energy in the form of heat comes into the engine from a high-temperature source, some of this energy is converted into useful work, the remainder is ejected as exhaust heat into a low-temperature sink, and the system returns to its original state to run through the cycle again.

All engines function to convert heat into work by exchanging energy from a reservoir at higher temperature to reservoirs of lower temperature. A good example of this is a refrigerator. In a fridge, a liquid moves through tubes to remove heat from the internal chamber (such as the freezer) to the outer air. Thus, cold is not actually a concept, but the sensation of low heat content. This is why the back of a refrigerator feels hot.

Since we're looking at cyclic engines only, the system returns to its original state at the end of each cycle, so ΔU must be 0. Therefore, by the First Law of Thermodynamics, $Q_{\text{net}} = -W$. That is, the net heat absorbed by the system is equal to the work performed by the system. The heat absorbed from the high-temperature source is denoted Q_H (H for *hot*), and the heat that is discharged into the low-temperature reservoir is denoted Q_C (C for *cold*). Because heat coming ***in*** is positive and heat going ***out*** is negative, Q_H is positive and Q_C is negative, and the net heat absorbed is $Q_H + Q_C$. Instead of writing Q_{net} in this way, it's customary to write it as $Q_H - |Q_C|$, to show explicitly that Q_{net} is less than Q_H.

This is one of the forms of

The Second Law of Thermodynamics
For any cyclic heat engine, some exhaust heat is always produced. It's impossible to completely convert heat into useful work.

Example 9 A heat engine draws 800 J of heat from its high-temperature source and discards 450 J of exhaust heat into its cold-temperature reservoir during each cycle. How much work does this engine perform per cycle?

Solution. The absolute value of the work output per cycle is equal to the difference between the heat energy drawn in and the heat energy discarded:

$$|W| = Q_H - |Q_C| = 800\text{ J} - 450\text{ J} = 350\text{ J}$$

Specific Heat

Unlike conduction, there is no easy way to calculate the rate of heat transfer for convection or radiation. However, whenever the temperature of an object changes due to heat transfer, regardless of the method, the **specific heat capacity, *c***, allows us to calculate the total amount of heat required. You can think of the specific heat capacity (or just specific heat) as describing how difficult it is to change the temperature of an object. The amount of heat required to change an object by a temperature, ΔT, is given by

$$Q = mc\Delta T$$

Equation Sheet

The higher the specific heat, the more heat needs to be added to increase the temperature, and vice versa. However, the amount of heat also depends on the mass, m, of the object. A single droplet of water in an empty hot pan will boil very easily, but a full pot of water will take a lot more heat to boil. Note that the equation works the other way, and we can use it to find the amount of heat emitted by an object if it decreases in temperature.

HEAT TRANSFER

There are three principal modes by which energy can be transferred: conduction, convection, and radiation.

Conduction

An iron skillet is sitting on a hot stove, and you accidentally touch the handle. You notice right away that there's been a transfer of thermal energy to your hand. The process by which this happens is known as conduction. The highly agitated atoms in the handle of the hot skillet bump into the atoms of your hand, making them vibrate more rapidly, thus heating up your hand.

Heat conducts from one point to another only if there is a temperature difference between the two objects. The rate at which heat is transferred is given by

Equation Sheet

$$\frac{Q}{\Delta t} = \frac{kA\Delta T}{L}$$

The constant k in the conduction equation is the "thermal conductivity" of an object. This is a property of the object and explains why things like metals get hot faster than plastics. It is also responsible for double-paned windows being "more energy efficient," as the layer of air between the two sheets of glass has a much smaller thermal conductivity than a single sheet of glass.

Convection

As the air around a candle flame warms, it expands, becomes less dense than the surrounding cooler air, and thus rises due to buoyancy. As a result, heat is transferred away from the flame by the large-scale (from the atoms' point of view, anyway) motion of a fluid (in this case, air). This is convection.

Radiation

Sunlight on your face warms your skin. Radiant energy from the Sun's fusion reactions is transferred across millions of kilometers of essentially empty space via electromagnetic waves. Absorption of the energy carried by these light waves defines heat transfer by radiation.

Chapter 3 Review Questions

Answers and explanations can be found in Chapter 11.

Section I: Multiple Choice

1 Mark for Review

A container holds a mixture of two gases, CO_2 and H_2, in thermal equilibrium. Let K_C and K_H denote the average kinetic energy of a CO_2 molecule and an H_2 molecule, respectively. Given that a molecule of CO_2 has 22 times the mass of a molecule of H_2, the ratio K_C / K_H is equal to

Ⓐ 1/22

Ⓑ 1

Ⓒ $\sqrt{22}$

Ⓓ 22

2 Mark for Review

If the temperature and volume of a sample of an ideal gas are both doubled, then a P–V diagram will show what sort of shape?

Ⓐ A horizontal line

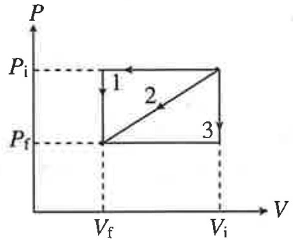
Ⓑ A vertical line

Ⓒ A curve indicating a positive correlation

Ⓓ A curve indicating a negative correlation

3 Mark for Review

In three separate experiments, a gas is transformed from state P_i, V_i to state P_f, V_f along the paths (1, 2, and 3) illustrated in the figure below:



The work done on the gas is

Ⓐ greatest for path 1

Ⓑ least for path 2

Ⓒ greatest for path 2

Ⓓ the same for all three paths

4 Mark for Review

An ideal gas is compressed isothermally from 20 m^3 to 10 m^3. During this process, 5 J of work is done to compress the gas. What is the change of internal energy for this gas?

Ⓐ –10 J

Ⓑ –5 J

Ⓒ 0 J

Ⓓ 5 J

Questions 5 through 6 refer to the following.

An ideal gas is confined in a container with a fixed volume. The amount of gas, n, is slowly increased in the container. This experiment is done in such a way that the temperature of the gas remains constant. Pressure data is collected.

5 Mark for Review

Which describes a graph with pressure on the vertical axis and amount of gas on the horizontal axis?

Ⓐ The graph will be linear and a fit line will go through the origin. (0, 0) will be a data point.

Ⓑ The graph will be linear and a fit line will go through the origin. (0, 0) will not be a data point.

Ⓒ The graph will be nonlinear. (0, 0) will be a data point.

Ⓓ The graph will be nonlinear. (0, 0) will not be a data point.

6 Mark for Review

If the temperature of the gas being added is higher than the desired temperature, how could the experiment be done so that, as the amount of gas is increased, the temperature stays at the desired temperature?

Ⓐ Allow the pressure of the gas to decrease as the amount of gas is increased.

Ⓑ Allow work to be done on the gas as the amount of gas is increased.

Ⓒ Allow work to be done by the gas as the amount of gas is increased.

Ⓓ Allow heat to leave the gas as the amount of gas is increased.

7 Mark for Review

Through a series of thermodynamic processes, the internal energy of a sample of confined gas is increased by 560 J. If the net amount of work done on the sample by its surroundings is 320 J, how much heat was transferred between the gas and its environment?

Ⓐ 240 J absorbed

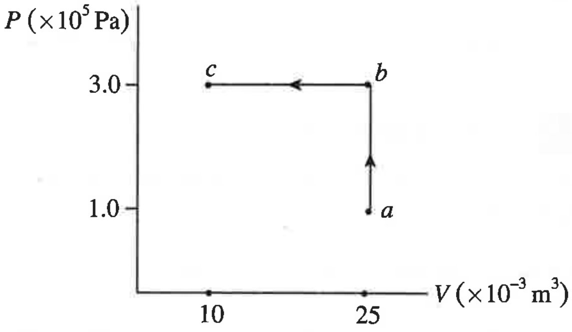
Ⓑ 240 J dissipated

Ⓒ 880 J absorbed

Ⓓ 880 J dissipated

8 Mark for Review

What is the total work performed on the gas as it is transformed from state *a* to state *c*, along the path indicated?



Ⓐ 1500 J

Ⓑ 3000 J

Ⓒ 4500 J

Ⓓ 9500 J

9 ☐ Mark for Review

In one of the steps of the Carnot cycle, the gas undergoes an isothermal expansion. Which of the following statements is true concerning this step?

Ⓐ No heat is exchanged between the gas and its surroundings, because the process is isothermal.

Ⓑ The temperature decreases because the gas expands.

Ⓒ The internal energy of the gas remains constant.

Ⓓ The internal energy of the gas decreases due to the expansion.

10 ☐ Mark for Review

A cup of hot coffee is sealed inside a perfectly thermally insulating container. A long time is allowed to pass. Which of the following correctly explains the final thermal configuration within the box?

Ⓐ The coffee has not changed temperature because the box is perfectly insulating.

Ⓑ The coffee has gotten warmer, and the air in the box has gotten cooler because of an exchange of thermal energy between the air and the coffee.

Ⓒ The coffee has gotten cooler, and the air in the box has gotten warmer because of an exchange of thermal energy between the air and the coffee.

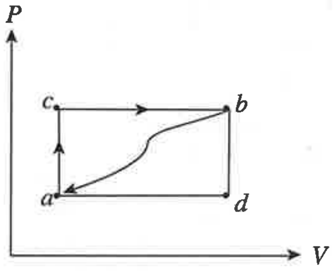
Ⓓ The coffee has gotten cooler, but the air in the box has not changed its temperature. The energy from the coffee has caused an increase in entropy within the box.

Section II: Free Response

1 ☐ Mark for Review

When a system is taken from state *a* to state *b* along the path *acb* shown in Figure 1, 70 J of heat flows into the system, and the system does 30 J of work.

Figure 1



A. When the system is returned from state *b* to state *a* along the curved path shown, 60 J of heat flows out of the system. Does the system perform work on its surroundings, or do the surroundings perform work on the system? How much work is done?

B. If the system does 10 J of work in transforming from state *a* to state *b* along path *adb*, does the system absorb or does it emit heat? How much heat is transferred?

C. If $U_a = 0$ J and $U_d = 30$ J, determine the heat absorbed in the processes *db* and *ad*.

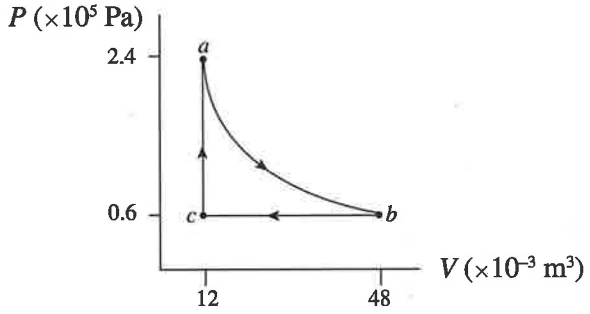
D. For the process *adbca*, identify each of the following quantities as positive, negative, or zero:

$W =$ ____________ $Q =$ ____________ $\Delta U =$ ____________

2 ☐ Mark for Review

A 0.4 mol sample of an ideal diatomic gas undergoes slow changes from state *a* to state *b* to state *c* and back to *a* along the cycle shown in the *P*–*V* figure below:

Figure 1



Path *ab* is an isotherm, and it can be shown that the work done by the gas as it changes isothermally from state *a* to state *b* is given by the equation

$$W_{ab} = -nRT \times \ln \frac{V_b}{V_a}$$

A. What's the temperature of

  i. state *a*?

  ii. state *b*?

  iii. state *c*?

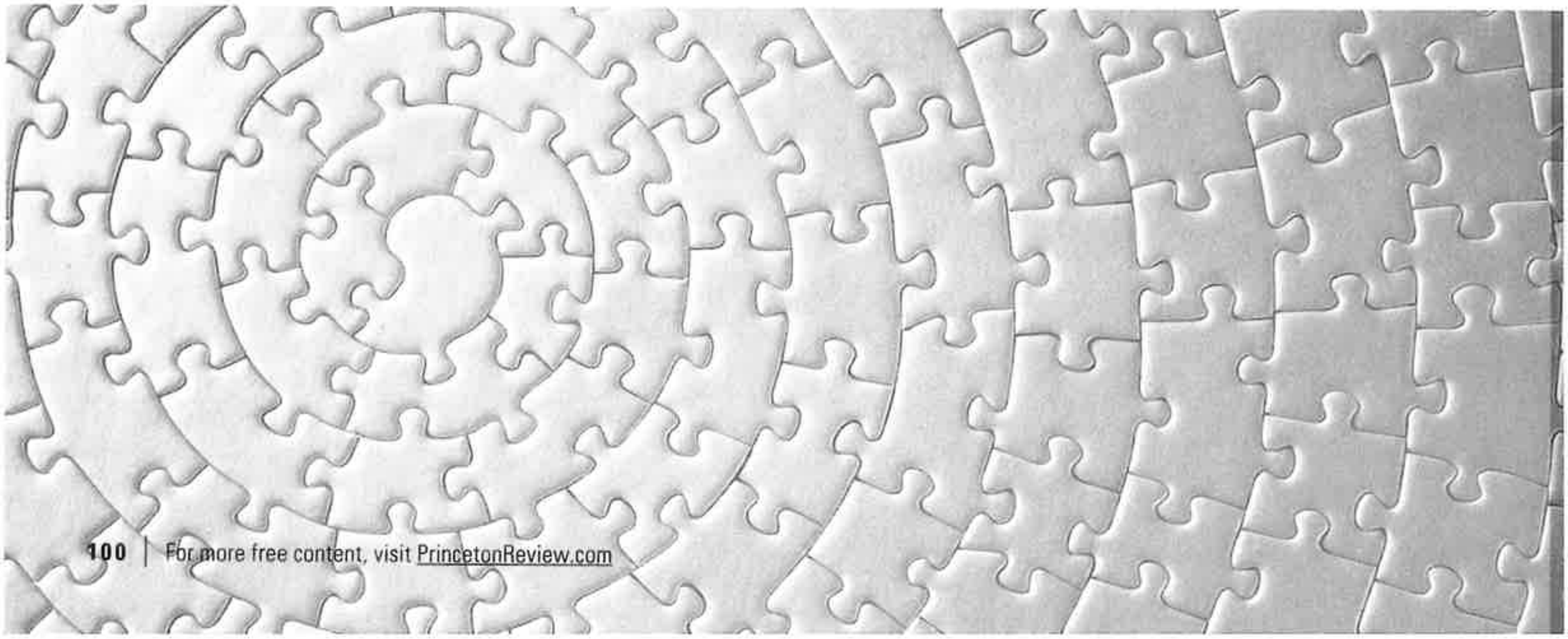
B. In order for step *ab* to be isothermal, the gas must be kept in thermal equilibrium with its surroundings at all times. Because heat flows spontaneously from hot to cold systems, does this imply that there is no heat flow during step *ab*? Explain.

C. How much work, W_{ab}, is done by the gas during step *ab*?

D. What is the total work done over cycle *abca*?

Chapter 3 Summary

- For gases, there are a few important ideas to understand:
  - Pressure is the result of the molecules colliding with one another and with the sides of the container. It is defined as the force per unit area ($P = F/A$) on the walls of the container.
  - The Ideal Gas Law is expressed as either $PV = nRT$ or $PV = Nk_BT$.
  - The average kinetic energy of the gas molecules is given by $K_{avg} = \frac{3}{2}k_bT$. This is related to the most likely speed a particle will be moving, but the particles in the gas will be moving with a large distribution of various speeds.
- The work done can be found by the area under a P–V graph. If there is a volume change while the pressure remains constant, then the equation $W = -P\Delta V$ can be used to calculate the work.
- The First Law of Thermodynamics is $\Delta U = Q + W$, where ΔU depends only on the temperature change.
  - W positive means energy is being added to the system, so work is done **on** the system **by** the surroundings. A negative W means that energy is being subtracted from the system, so work is done **by** the system **on** the surroundings.



  - Q positive (or negative) means energy is being added to (or subtracted from) the system by means of a flow of heat from the higher temperature surroundings (or system) to the lower temperature system (or surroundings).

    Note that some textbooks define work in thermodynamics in a different way: work is considered to be positive when work is done on the surroundings. This is consistent with the idea that the overall objective of a heat engine is to produce external (positive) work. Under this definition, the First Law of Thermodynamics must be written as $U = Q - W$ (or $U + W = Q$), and W must then be interpreted differently from Q. That is, while Q is still positive when heat is being added to the system, W is now positive when work is being done by the system on the surroundings (thus decreasing the internal energy of the system).

- The rate at which heat is transferred is given by $\Delta Q/\Delta t = \frac{kA\Delta T}{L}$, where k is the thermal conductivity (a property of the material), A is the cross-sectional area, ΔT is the temperature difference between the two sides, and L is the thickness or distance between the two ends of the material.
- Special thermal processes are Isovolumetric, Isothermal, Isobaric, and Adiabatic. Be sure to review the chart on page 90.