Chapter 18: The Internal Energy of a Gas

In the example of Isothermal Expansion, the gas does work but stays at constant temperature. Normally when a gas expands, it will cool down, but in this case we have specified that the temperature remain constant. The only way that can happen is that heat is added to the gas. If you like, consider that the gas container in the figure is on some kind of stove top and heat is constantly being added as the volume expands.

We can quantify this process by introducing the internal energy $U_{\rm int}$ of a gas system. The thermodynamic variable $U_{\rm int}$ is like the potential energy $U_{\rm int}$ in mechanics. Its absolute value is not important, only changes in $U_{\rm int}$ are physically significant. The variable $U_{\rm int}$ can be changed by the gas doing work ($U_{\rm int}$ decreases), or heat being added to the gas ($U_{\rm int}$ increases). We write

$$\Delta U_{\rm int} = \Delta Q - W$$

The variable $U_{\rm int}$ depends only on the temperature of the gas. As long as the temperature remains constant, then $U_{\rm int}$ does not change[1].

Adiabatic Process

In an isothermal expansion, heat ΔQ must be added to the gas to do work. At the other extreme is the *adiabatic* process where no heat is added to the expanding gas. In this case the internal energy $U_{\rm int}$ must decrease by an amount equal to the work done by the expanding gas

$$Q = 0 \text{ adiabatic process} \quad \Longrightarrow \Delta U_{\rm int} = -W$$

In an adiabatic process, the temperature of the gas must be lowered during an expansion. Generally, processes which happen so fast that there is no time for heat to be transferred (such as the compression stroke of a diesel engine, or the expansion of hot gases in a gasoline engine) are examples of adiabatic processes. Another example would be a well–insulated system such as the gas liquefaction in a refrigerator.

[1]The textbook uses only the symbol U for internal energy. I have added a subscript "int" in order to emphasize that $U_{\rm int}$ represents the internal energy in a thermodynamic system.

Chapter 18: Heat Capacities for an Ideal Gas

Heat Capacity Definitions and Relations

The specific heat or heat capacity c of a solid or a liquid was defined according to how much heat Q was needed to raise a given mass m of the substance by one K (or one Celsius degree):

$$Q = mc\Delta T$$

For an ideal gas, it is more useful to use either the 1) the molar heat capacity at constant volume called C_V, or 2) the molar heat capacity at constant pressure called C_P. We shall discover universal values for C_V and a universal equation relating C_P to C_V.

The molar heat capacity at constant volume C_V for a gas is defined according to the differential amount of heat dQ needed increase n moles of a gas by an amount dT in Kelvin at constant volume of the gas:

$$dQ = nC_V dT \qquad 19.12$$

Since the volume of the gas does not change, then all of this heat increases the internal energy of the gas

$$dU_{\text{int}} = nC_V dT$$

The molar heat capacity at constant pressure C_P for a gas is defined according to the differential amount of heat dQ needed increase n moles of a gas by an amount dT in Kelvin while the gas expands by a volume dV while the pressure p of the gas remains constant:

$$dQ = nC_p dT \qquad 19.14$$

Now while the gas expands at constant pressure, there is a differential amount of work done $dW = pdV = nRdT$. Since by conservation of energy (first law of thermodynamics) we have

$$dQ = dU_{\text{int}} + dW = nC_V dT + nRdT = nC_p dT \qquad 19.16$$

then we can see directly that

$$\text{Universal relation for ideal gas molar heat capacities:} \quad C_p = C_V + R \qquad 19.17$$

Chapter 18: Molar Heat Capacities for Ideal Gases

Monatomic Gas Result

For monatomic gases, the Kinetic Theory predicts that $C_V = 3R/2$. By the universal ideal gas result we have

$$C_p = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$$

An important parameter for an ideal gas is the ratio C_p/C_V which is symbolized as γ

$$\gamma \equiv \frac{C_p}{C_V} = \frac{5/2R}{3/2R} = \frac{5}{3}R \approx 1.67R$$

Diatomic Gas Result

For diatomic gases, the Kinetic Theory predicts that $C_V = 5R/2$. By the universal ideal gas result we have

$$C_p = C_V + R = \frac{5}{2}R + R = \frac{7}{2}R$$

$$\gamma \equiv \frac{C_p}{C_V} = \frac{7/2R}{5/2R} = \frac{7}{5}R = 1.40R$$

Adiabatic Ideal Gas Law

The parameter γ is an important one for the **adiabatic ideal gas law**. You already know the ideal gas law, relating three parameters: p, V, and T as:

$$pV = nRT$$

If a gas is undergoing an *adiabatic change*,we can prove (see pages 662-663) the following adiabatic ideal gas law

$$p_1V_1^\gamma = p_2V_2^\gamma \quad \text{or} \quad pV^\gamma = \text{Constant} \qquad 19.23$$

As you can see, the adiabatic gas law relates two of the three parameters. You can predict the third via the regular ideal gas law. You can re-write the adiabatic gas law in terms of T and V as

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \quad \text{or} \quad TV^{\gamma-1} = \text{Constant}$$

In the above formulas, the change in the state of the gas is adiabatic, meaning that no heat entered or left the gas.

Chapter 18: Work Done During an Adiabatic Gas Expansion

Using the adiabatic ideal gas law

We use the adiabatic ideal gas law to get an expression for the work done by a gas in going from a state (p_1, V_1) to a state (p_2, V_2) in an adiabatic change:

$$pV^\gamma = C \Longrightarrow p = \frac{C}{V^\gamma}$$

$$W_{1\to 2} = \int_1^2 pdV = C\int_{V_1}^{V_2} \frac{dV}{V^\gamma} = C\frac{1}{\gamma - 1}\left(\frac{1}{V_1^{\gamma-1}} - \frac{1}{V_2^{\gamma-1}}\right)$$

Since the constant $C = p_1V_1^\gamma = p_2V_2^\gamma$ we will get a final simple result as

$$\text{Work done in an adiabatic gas change:} \quad W_{1\to 2} = \frac{1}{\gamma - 1}\left(p_1V_1 - p_2V_2\right)$$

Example of Adiabatic Compression and Work, page 697

The piston in a car's diesel engine compresses the volume a fuel-air mixture by a factor of 15. Suppose the initial pressure is one atmosphere (1.01×10^5 Pa), and the initial temperature is 27^{O} C (300 K). *Find the final pressure and temperature of the fuel-air mixture, assuming that it is a diatomic gas with a* $\gamma = 1.40$.

We use the adiabatic gas law

$$p_1V_1^\gamma = p_2V_2^\gamma \Longrightarrow p_2 = \left(\frac{V_1}{V_2}\right)^\gamma p_1 = (15)^{1.40}(1.01 \times 10^5) = 44.8 \times 10^5 \text{ Pa}$$

This result is 44 atmospheres, which tells you why diesel engines are so heavy to be able to withstand such high pressures.

We can work out the final temperature from $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$, where $T_1 =$ 300 K. From this equation we will get $T_2 = 886K$ K or $T_2 = 613^{\mathrm{O}}$ C. The temperature almost triples in absolute terms.

How much work is done by the gas in this compression if $V_1 = 10^{-3}\ m^3$ *(= 1 L)?*

We have for the work done in an adiabatic change

$$W_{1\to 2} = \frac{1}{\gamma - 1}\left(p_1V_1 - p_2V_2\right) = -494 \text{ Joules}$$

Work is being done on the gas during any compression. It is the angular momentum of the rotating drive shaft in the car which is doing this work. After the piston is compressed, the high temperature will self-ignite the fuel-air mixture; there is no spark plug in a diesel engine. That will deliver more power to turn the drive shaft and eventually the wheels.

Chapter 20: Heat Engines

The concept of a **heat engine** is crucial to modern civilization. Heat engines, beginning with James Watt's invention of the steam engine, are the basis of the mechanical age where machines do work. The vast majority of machines which produce useful work do so ultimately by burning fuel and converting the chemical potential energy stored in the fuel into heat and then converting that heat into work.

Thermodynamic Limits to Heat Engines

The **First Law of Thermodynamics** states the equivalence of all forms of energy, and the equivalence of heat and work as different forms of energy which must be conserved. In principle, according to the First Law of Thermodynamics, it should be possible to convert all the heat energy into useful work. In reality, this is found to be impossible. There are fundamental limits to how much work can be extracted from a given amount of heat in any real device, and the rest of the energy must unfortunately be wasted. This is the **Second Law of Thermodynamics**.

Ultimate Efficiency of Heat Engines

All real heat engines perform work by extracting heat Q_h from a hot source at temperature T_h, converting part of that heat into work W, and then discarding an amount of heat Q_c into a cold sink at temperature T_c. According to the **First Law** $W = Q_h - Q_c$, and according to the **Second Law**, the *efficiency* $\epsilon \equiv W/Q_h$ is limited according to the range of absolute temperatures in use:

$$\epsilon \equiv \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} \leq \frac{T_H - T_c}{T_h}$$

Because all real engines must expel an amount of heat Q_c into a cold sink at temperature T_c, then all real engines are (much) less than 100% efficient. A good example is that of a car engine, where the "hot source" is the burning gasoline, and the "cold sink" is just the exhaust into the atmosphere.

Chapter 20: The Second Law of Thermodynamics

Things that you will never see happen

If you want to make yourself some tea, the first thing you have to do is boil some water. So you put some water in tea kettle on the burner of a stove. Lastly, you turn on the burner of the stove. You do this because of the Second Law of Thermodynamics. If there were no Second Law, and one had only the First Law (conservation of energy), there would be nothing to prevent the burner of the stove from getting colder and the kettle getting hotter. According to the First Law, then, heat could spontaneously be transferred from cold material to hot material, without violating conservation of energy. In reality, we instinctively know that this is not true. Hot substances will lose their heat to cold substances, never the reverse.

Principles of a Heat Engine

The concept of the **Second Law of Thermodynamics** can be made more practical by considering the general form of the *heat engine*, which is any device which converts heat into work. Heat energy Q_h is extracted from a hot source at T_h, part of that energy is converted into work W by the heat engine, and the remainder of the heat $Q_c = Q_h - W$ is expelled into the cold sink at T_c. The heat engine operates in some continuous cycle, always returning to its initial state.

The first Law of Thermodynamics states that the work done is the difference in the extracted and the expelled heats: $W = Q_h - Q_c$. The Second Law of Thermodynamics states that *there must always be a certain amount of expelled (wasted) heat Q_c in proportion to the temperature difference $T_h - T_c$*. The Second Law sets an unavoidable limit on the efficiency of any heat engine operating between any two temperatures T_h and T_c. All real engines have actual efficiencies less than this limit.

Examples of Heat Engines

Sample Gasoline Engine Problem

In a given cycle a gasoline engine consumes 10,000 Joules of heat in order to produce 2,000 Joules of mechanical work, such as moving a car from rest to a certain kinetic energy. The heat is obtained by burning gasoline which produces 50,000 Joules/gram.

1) What is the efficiency of this engine?
2) How much heat is discarded at the end of each cycle?
3) How much gasoline is burned in each cycle?
4) If the engine runs at 25 cycles/second, what is the power during that time?
5) How much gasoline is burned per second?

Solution

1) The efficiency of any heat engine is the ratio of the work done to the heat energy taken in. In this case $Q_H = 10,000$ Joules is taken in and 2,000 Joules of work W are produced. So the efficiency is

$$\text{Heat Engine Efficiency:} \quad \epsilon = \frac{W}{Q_H} = \frac{2000}{10000} = 0.20 = 20\%$$

2) If 10,000 Joules of heat is taken in and 2,000 Joules of work is produced, then 8,000 Joules of heat is being discarded for each cycle.

$$Q_C = Q_H - W = 10000 - 2000 = 8000 \text{ Joules}$$

3) One gram of gasoline will produce 50,000 Joules of heat. So only 0.20 grams of gasoline is needed to produce 10,000 Joules of heat per cycle.

4) If the engine is running at 25 cycles per second, then it is developing $25 * 2,000 = 50,000$ Joules/second or 50 kW of power.

5) The amount of gasoline burned per second is the amount of gasoline burned per cycle times the number of cycles per second. We will get

$$0.20 \times 25 = 5.0 \text{ grams/second}$$

In part 1) a 20% efficiency does not sound too impressive. Effectively, if you are paying \$3.30 per gallon of gasoline, then you are discarding \$2.64 of the energy in each gallon of gas. Can you hope to do better?

Realistic Model of a Gasoline Engine

The Otto Cycle

The Otto Cycle is an idealized model of how a real gasoline engine works. As with any engine model, we show the cycle in a pV pressure-Volume diagram (figure 20.6, page 679). The Otto Cycle has four lines in such a pV diagram.

1) A gas-air mixture in a piston is compressed adiabatically from point a with (p_a, V_a) to point b with (p_b, V_b). The compression occurs so rapidly that effectively no heat enters or leaves the piston. The compression ratio is $r = V_a/V_b$ which is typically 8 in an ordinary gasoline engine.

2) At point b the gas-air mixture is ignited by a spark plug. The ignition of the gas-air mixture occurs extremely rapidly, liberating a great deal of heat energy, raising the temperature of the mixture. The gas-air mixture goes to a new point c in the pV diagram, but the volume remains constant during this very short amount of time. So at point c we have (p_c, V_c) with $p_c > p_b$ and $V_c = V_b$.

3) The hot gas-air mixture expands adiabatically to a new point d, where the volume is the original piston volume and the pressure and temperature are lowered. The point d has (p_d, V_d) with $V_d = V_a$. This is the power stroke to the drive shaft of the engine.

4) The last stroke is the exhaust stroke, where the spent gas-fuel mixture is expelled from the piston's volume. In this stroke the volume remains constant while the pressure and temperature drop to the initial values at point a in the pV diagram.

The efficiency of the Otto cycle is examined in detail on page 670. The final result is the following simple formula

$$\text{Efficiency of an Otto cycle gas engine:} \quad \epsilon = 1 - \frac{1}{r^{\gamma-1}} \approx 0.56 = 56\%$$

where $\gamma = 1.40$ for the gas-air mixture, and r is the compression ratio of the piston. You can see that higher values of r will lead to better efficiencies. Unfortunately, higher values of r also lead to more air pollution and need more expensive gasoline grades. So ordinary modern day cars, as distinct from race cars, have a relatively low ratio value $r \approx 8$. Nonetheless, you can see that a real gasoline engine with a 20% efficieny is much lower than the ultimate limit for a gasoline engine. The most efficient gas engines are at about 35%.

Realistic Model of a Diesel Engine

The Diesel Cycle

The diesel cycle (Fig. 20.7, page 680) is quite similar to the gasoline engine cycle, with one important difference. At the end of the adiabatic compression stroke of a diesel engine, there is no ignition by a spark plug. There is also no fuel in the piston during the compression stroke. Instead, after the compression stroke is introduced, and the temperature has become very high (see page 4 of these notes, or page 697 in the text), then diesel fuel is carefully injected into the piston over a very brief period of time. The pressure stays approximately constant while the fuel is ignited by the high temperature of the air. After the fuel is ignited, there is a power stroke as in the gasoline engine.

One can work out (but the textbook does not), that the efficiency of a diesel engine higher than that of a gasoline engine. With a compression ratio $r = 15 - -20$, the theoretical efficiency of a diesel engine is between 65% and 75%, compared to the theoretical efficiency of 56% of a gasoline engine. Just as with the gasoline engines, a real diesel engine will have a significantly lower efficiency, but one can always hope to get better efficiencies with improved engine design and materials.