

Session 15

Thermodynamics

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Welcome

Welcome to session 15.

In this session we'll look at the basic laws and concepts of thermodynamics.

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Session Editor – Tim Puchtler

Learning Objectives

On completing this unit you should be able to

- Distinguish clearly between energy, heat and work
- State the first and second laws of thermodynamics
- State what is meant by a quasi-static process
- State what is meant by isothermal, adiabatic and isobaric processes and derive the related behaviours of state variables
- Define exothermic and endothermic changes and use the concept of entropy to explain how endothermic changes can occur spontaneously
- Describe the Carnot cycle and the consequences for the efficiency of heat engines

The Problem

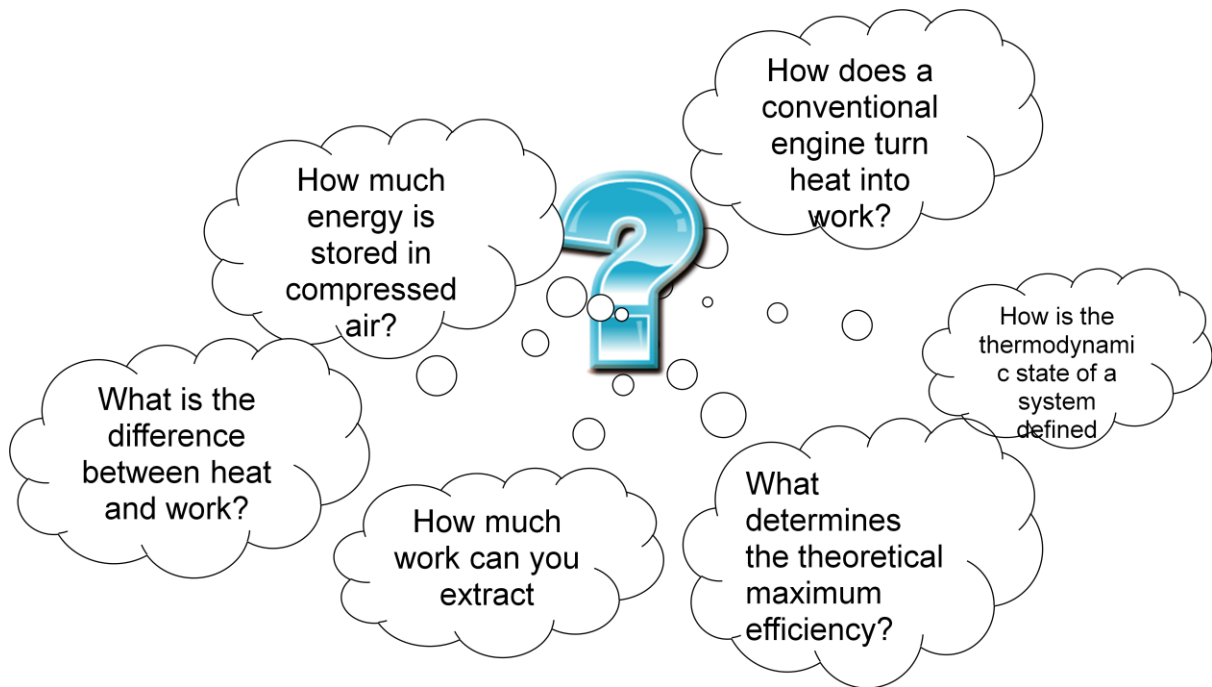
The Air Car:

Please use the following link:

<http://www.youtube.com/watch?v=D-A3XHFT5qc&feature=related>

The problem is to work out how the air car works and to discuss whether it is viable.

Issues

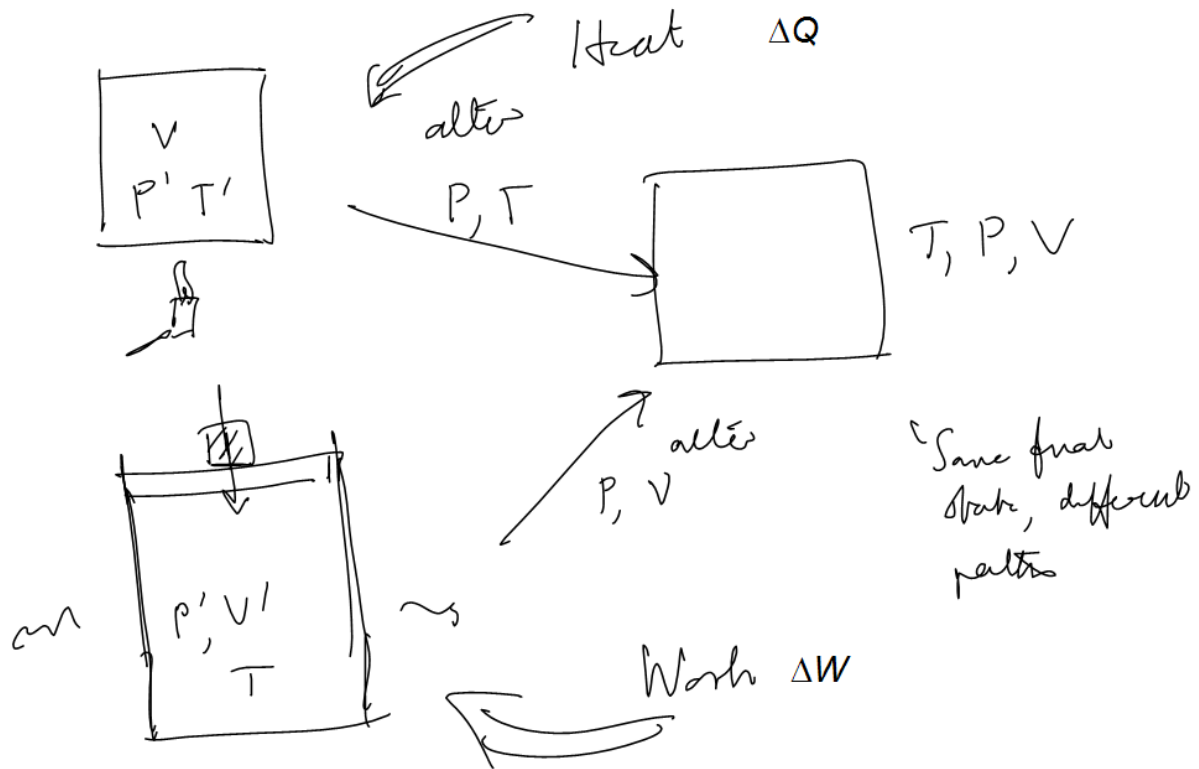


Energy, Heat and Work

Let's start with energy, heat and work. Consider a cylinder of gas in thermodynamic equilibrium, that is, in a state of thermal equilibrium, in which there is no flow of heat, and in dynamic equilibrium, so there is no bulk movement of the gas. How do we describe the state of the gas? We can use some combination of its temperature, its pressure, and its volume. It turns out that not all three are required: in session 14 we saw how these three variables are related by an equation of state. For example, for ν moles of an ideal gas the equation of state is the perfect gas law $PV = \nu RT$.

The total energy of the gas is also a state variable. That is, it depends on one or more of P , V and T . In fact, for a fixed quantity of an *ideal* gas the total energy depends just on the temperature.

We can change the state of the gas in various ways: by some combination of heating it or doing work on it. The top diagram in this section illustrates how we might change the temperature and pressure to those we are aiming for on the right, by applying heat in a fixed volume. In this case we supply heat to the gas, but since the volume is fixed we do no work. The lower diagram on the left shows how we might do work by compressing the gas at a fixed temperature; changing the pressure and volume to those we want. The motion of the piston involves the applied force moving through a distance to bring about the compression, so this force times distance represents work done on the gas. To maintain a constant temperature we shall have to let heat escape, since otherwise compression would heat the gas. So this change involves both heat and work.



Of course, lots of other combinations are possible. What we do will depend in part on where we start from. The point is that by investigating the final state alone it is impossible to tell how it was arrived at. We cannot therefore associate either a quantity of heat or a quantity of work with a state: Work and Heat are not therefore state variables; they are processes.

The First Law of thermodynamics

This section tells us what we CAN say about the relation between energy, heat and work. Work and heat are two ways in which we can *change* the energy of a system. The total change in energy is governed by the conservation of energy. So however we divide a change from one state to another between heat and work the overall change in energy must be the same: that is the change in energy of the state ΔU is the sum of the heat ΔQ put in and the work ΔW done on the system. This is the first law of thermodynamics.

$\Delta U = \Delta Q + \Delta W$	(First Law of Thermodynamics)
----------------------------------	--------------------------------------

Where: ΔU is the change in stored energy

ΔQ is the heat input

ΔW is the work done on the system

Notice that heat lost by the system and work done by the system will count negative in this relation because they reduce the energy of the gas.

The first law is true for any change as long as we include all forms of energy. For example, if we compress a gas rapidly by a sudden movement of a piston, this will produce bulk motions of the gas. So the work done will go into bulk kinetic energy as well as into the internal energy of motion of the gas molecules. We have to include this in the energy balance. Eventually the bulk motions will be damped out by viscosity so the bulk energy will be returned to the internal motions resulting in a temperature change.

In addition, if we move the piston rapidly, the pressure near the piston will be larger than that further away while pressure waves travel through the gas to equalise the pressures. During this time it will not be possible to describe the system by a single pressure and temperature: the system will not be in thermodynamic equilibrium. So if we want to confine our discussion to systems in equilibrium we have to rule out rapid changes. Conversely, if the changes are carried out sufficiently slowly that the system can be described by single values of the state variables, we say that the changes are quasi-static. Unless we specify otherwise, all changes are considered to be carried out quasi-statically. Quasi-static changes are reversible: that is, the original state can be recovered by reversing the sequence of changes.

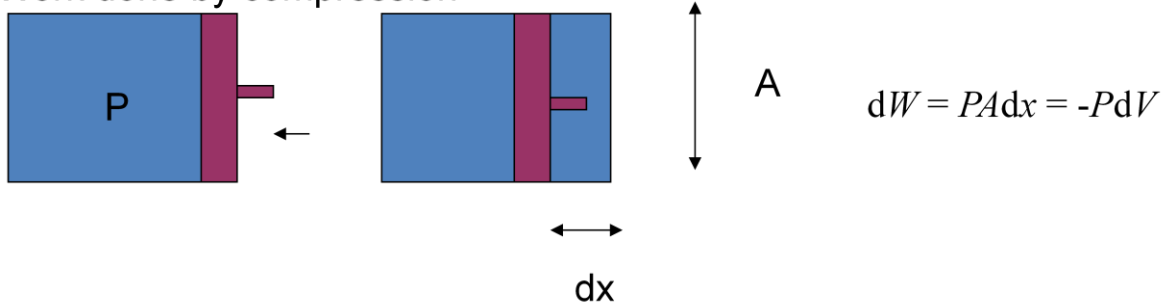
Quasi-static changes are reversible

Work

Let's look at some particular examples.

How much work is done on a gas by compressing it? The diagram shows a piston of area A which has been moved slowly a small distance dx against pressure P .

Work done by compression



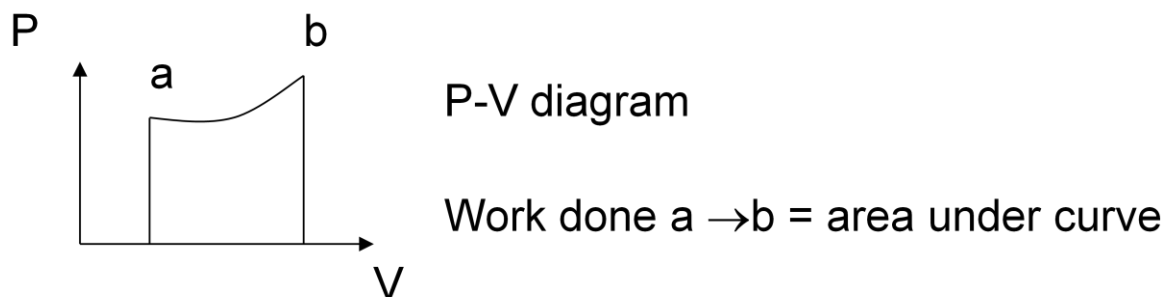
The force exerted is therefore PA and the work done is the force, PA , times the distance dx , hence $PAdx$. If we call the change in volume of the cylinder dV then the work done on the gas is $-PdV$. The minus sign arises because work is done on the gas if the volume is decreased, that is, if dV is negative.

Example 1: A gas is compressed at constant pressure from V_1 to V_2 . The work done on the gas is

$$-\int_{V_1}^{V_2} PdV = -P(V_2 - V_1)$$

In example 1 we obtain the work done for a finite change in volume. Here we have to take account of any change in pressure as we compress the gas, so we have to integrate $-PdV$. To do this we have to specify how the pressure is changing. Here we've specified that the pressure is constant so the integration is straightforward. The work done at constant pressure is just the pressure times the change in volume.

We can represent these changes graphically on a P-V diagram. As we've seen the work done **on** a gas is the integral of $-PdV$ between the initial and final states, so the work done **by** the gas is the integral of $+PdV$. Thus, if a system undergoes a change from state a to state b the work done is the area under the curve ab in the P-V diagram.



Example 2: Suppose that we compress the gas at constant temperature. To take account of the change in pressure we use the perfect gas law: $PV = \nu RT$ for a number of moles ν . This means that for the condition of constant temperature that we have specified, the product PV is a constant. This gives us a simple way to do the integration as shown in this section. The outcome is that the work depends logarithmically on the ratio of initial and final volumes. See if you can decide which of the two cases of constant pressure or constant temperature requires the greater work for a given change of state, and explain your decision.

A gas is expanded from V_1 to V_2 at constant temperature. The work done by the gas is

$$\int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} PV \frac{dV}{V} = PV \int_{V_1}^{V_2} \frac{dV}{V} = PV \log_e \frac{V_2}{V_1}$$

\uparrow
 $PV = \nu RT = \text{constant}$

If $V_2 = 2 V_1$ which of the two cases of constant pressure or constant temperature requires the greater work? Can you explain this physically?

Heat

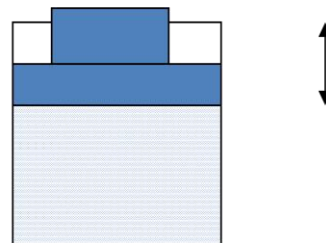
Now let's look at some examples of adding heat.

By how much does a quantity of heat ΔQ change the temperature of a gas? This depends on what is kept constant during the change. If we keep the volume constant then the temperature change is given by equation (1) below, where we use the specific heat of the gas at constant volume. If the pressure is kept constant and the volume allowed to change accordingly, then we use the specific heat at constant pressure as in equation (2).



Constant volume

$$(1) \Delta T = \frac{\Delta Q_1}{C_v}$$



Constant pressure

$$(2) \Delta T = \frac{\Delta Q_2}{C_p}$$

Consider another situation; if we add a quantity of heat to a gas then we change its internal energy. Suppose we add the heat at constant volume. Since this means no work is done the change in internal energy equals the heat put in, hence $\Delta U = \Delta Q = C_v \Delta T$. For a perfect gas C_v is a constant so we can add the changes in ΔU and in ΔT with the condition that the internal energy is zero at zero temperature. Thus $U = C_v T$. Since U and T are functions of state, this equation must hold no matter how we have arrived at it.

For a fixed quantity of gas $U = C_v T$ (since $U = 0$ at $T = 0$). This relation is independent of how the state was obtained.

Which is larger, ΔQ_1 or ΔQ_2 ?

Principal Specific heats of a gas

We've already met the concept of specific heat and in particular the principal specific heats C_v and C_p for a gas. In this section we show that there is a general relation between the specific heats of a perfect gas at constant pressure and constant volume. We do this by finding two different expressions for the change in internal energy for a given change of state.

Heat at constant volume $dU = C_v dT$ (1)

Heat at constant pressure and extract work to bring about the same dT :

$$\begin{aligned}
 dU &= C_p dT - PdV \\
 &= C_p dT - RdT \\
 (2) \quad &= (C_p - R)dT
 \end{aligned}$$

$$\left\{ \begin{array}{l} PV = RT \\ PdV = RdT \end{array} \right.$$

Constant
P

But U is a function of state so the two expressions for dU must be equal

Key fact: $C_p - C_v = R$ (3)

In equation (1) we've brought about a change in temperature dT by heating a mole of the gas at constant volume. C_v here is the specific heat of a mole of the gas.

Next we heat the gas at constant pressure and let the gas do an amount of work to bring about the same change in temperature dT . The amount of heat is obviously $C_p dT$ and the work can be found from the perfect gas law for one mole of gas, since dV must be just right to bring about a temperature change dT at constant pressure. This gives us equation (2). But the two expressions for dU refer to the same change of state so they must be equal. This

gives us the relation in equation (3): the difference in the molar specific heats equals the gas constant for a mole.

A result of kinetic theory that we shall not prove is that for a mole of gas $C_v = (3/2)$ times R , the gas constant per mole. This is very useful because it tells us that the internal energy U per mole is $3/2RT$. We also have the following values:

For a mole of monatomic gas $C_v = 3R/2, U = 3RT/2$

For a mole of diatomic gas $C_v = 5R/2, U = 5RT/2$

For a mole of polyatomic gas $C_v = 7R/2, U = 7RT/2$

So, for example, a mole ($\nu=1$) of monatomic gas, $U = 3RT/2 = 3PV/2$

We can use these results to express the pressure as an energy density:

$$P = \frac{2U}{3V}$$

It is sometimes useful to remember that the pressure of a gas is of the order of magnitude of the energy per unit volume and conversely.

Finally the ratio of the specific heats at constant pressure and constant density is a useful quantity which is given the symbol γ (gamma).

Also if $C_v = 3R/2$ then $C_p = 5R/2$ and $\gamma \equiv \frac{C_p}{C_v} = \frac{5}{3} \approx 1.67$. That is, for a monatomic gas gamma equals 5/3.

Summary

- The thermal state of a system is defined by variables such as pressure, temperature, volume
- Heat and Work are not functions of state; they are processes
- Energy *is* a function of state
- The first law of thermodynamics states that the change in the energy of a system is the sum of the heat put in to it and the work done on it
- Work is the integral of $-PdV$
- Heat is the integral of CdT where C is the appropriate specific heat
- $C_p - C_v = R$

SAQs

1. C_V of a mole of an ideal gas is $5/2R$. What is C_P for this gas?

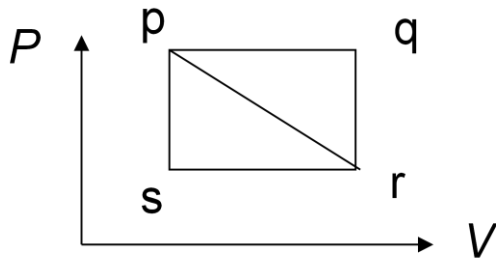
 - (a) $3/2R$
 - (b) $5/2R$
 - (c) $7/2R$
 - (d) Can't tell from this information

2. A gas is heated at constant pressure: what is the change in internal energy?

 - (a) $C_V dT$
 - (b) $C_P dT$
 - (c) 0
 - (d) insufficient information

3. For which path in the PV diagram is the work done on the gas greatest?

 - (a) pqr
 - (b) pr
 - (c) psr
 - (d) they are all equal



The answers appear on the following page

Answers

- (a) Incorrect: C_P must be greater than C_V

(b) Incorrect: C_P must be greater than C_V

(c) Correct: $C_P = C_V + R$ in general for an ideal gas.

(d) Incorrect: $C_P = C_V + R$ in general for an ideal gas so we have sufficient information
- (a) Correct: the change in internal energy for a given change in temperature is independent of how that change is brought about because the internal energy is always a function of state (whether the gas is ideal or not).

(b) Incorrect; this is the heat put in, not the change in internal energy. There is a difference because at constant pressure the gas will do work PdV .

(c) Incorrect: the input of heat implies a change in internal energy even though the gas does work.

(d) Incorrect: we only need the change in the state variables to determine the change in a function of state such as U . Here we are given dT (implicitly) and $dP (=0)$ which are sufficient.
- (a) Correct: The work done is the area under the curve and the V axis, which is greatest for pqr.

(b) Incorrect: this does not form the largest area

(c) Incorrect: this does not form the largest area

(d) Incorrect: W is not a function of state, so it can differ between the same endpoints.

Thermodynamic Processes

Quasi-static processes

We are going to look next at three particular quasi-static processes, isothermal, isobaric and adiabatic.

In an isothermal process the temperature T is kept constant. Since two variables define a state, this leaves only one other thermodynamic variable that can be independently assigned, so the pressure P and the volume V must be related. For a perfect gas this gives Boyle's law that P times V is a constant. Since the temperature is fixed there is no change in the internal energy: the heat extracted is equal to the work done on the gas.

Isothermal: $T = \text{constant}$ $PV = \text{constant}$ (Boyle's law)

$$\Delta U = 0$$

Similarly in an isobaric process P is held constant and we get Charles' law that V over T is constant. In this case the heat put in is $C_p \Delta T$. The change in internal energy ΔU is always $C_v \Delta T$.

Isobaric: $P = \text{constant}$ $V/T = \text{constant}$ Charles' law

$$\Delta Q = C_p \Delta T$$

$$\Delta U = C_v \Delta T$$

Our third example is an adiabatic process in which, by definition, there is no heat exchange. In this process also there will be a relation between P , T and V arising from the fact that any change of state has to involve no heat exchange. This relation is in addition to the perfect gas law, which always holds. Let's look initially for a relation between P and V .

Adiabatic process: $\Delta Q = 0$. But how are P and V related?

We are going to use the gas law and the fact that ΔQ is zero to derive this relation. Let's start with the gas law for a mole of gas, equation (1). Differentiating equation (1) by Leibniz's rule gives us equation (2). Dividing (2) on the left by PV and on the right by RT gives equation (3). We'll keep this on one side for the moment.

$$PV = RT \quad (1)$$

$$PdV + VdP = RdT \quad (2)$$

$$\frac{dP}{P} + \frac{dV}{V} = \frac{dT}{T} \quad (3)$$

$$dU = -PdV \quad (4)$$

$$dU = C_v dT = C_v T \left(\frac{dP}{P} + \frac{dV}{V} \right) \quad (5)$$

$$dU = -PdV = -PV \frac{dV}{V} = -RT \frac{dV}{V} \quad (6)$$

$$\frac{dP}{P} = -\frac{R}{C_v} \frac{dV}{V} - \frac{dV}{V} = -\frac{C_p}{C_v} \frac{dV}{V} \quad (7)$$

$$R = C_p - C_v$$

We express the fact that there is no heat exchange by the first law of thermodynamics: the change in internal energy must equal the work done, equation (4).

We know that $dU = C_v dT$ even though the change is not at constant volume. This is because U is a function of state so dU depends only on the change in temperature, not on how it is achieved.

We can now eliminate dT to get a second equation, (5) for dU . Equating the expressions (4) and (5) for dU will give us the desired result after some algebra. There are many ways to do this. We've rewritten equation (4) with the help of the perfect gas law and then equated the two expressions for dU , equations (5) and (6), in the box.

Integrating equation (7) gives us the final result, $PV^\gamma = \text{constant}$ in an adiabatic change.

Result: $PV^\gamma = \text{constant}$

Show that for a perfect gas this is equivalent to $TV^{\gamma-1} = \text{constant}$

Work done in an adiabatic process

In this section we calculate the work done in an adiabatic process in which a gas is compressed or expanded with no exchange of heat. As usual we begin with the expression $-PdV$ for the work done on the gas and integrate this between the initial and final volume V_1 and V_2 .

$$\text{Work} = -\int P dV = -\int_{V_1}^{V_2} P V^\gamma \frac{dV}{V^\gamma} = \frac{P V^\gamma}{\gamma - 1} (V_1^{1-\gamma} - V_2^{1-\gamma}) \quad (1)$$

$$= \frac{P_1 V_1^\gamma V_1^{1-\gamma} - P_2 V_2^\gamma V_2^{1-\gamma}}{\gamma - 1} = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} \quad (2)$$

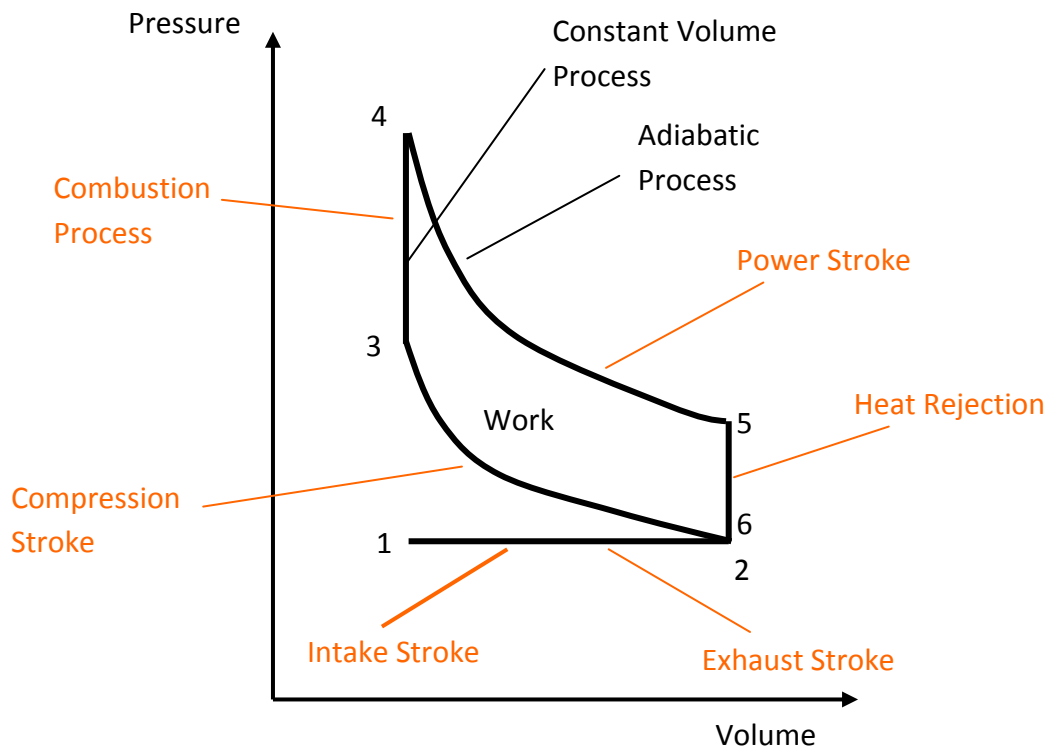
$$= \frac{R \Delta T}{\gamma - 1} = C_v \Delta T \quad (3) \quad \gamma - 1 = \frac{C_P}{C_V} - 1 = \frac{C_P - C_V}{C_V} = \frac{R}{C_V}$$

$$\text{Change in energy} = C_v \Delta T$$

The integration in lines (1) and (2) is simplified if we make use of the fact that PV^γ is a constant. We also need the perfect gas law in line 3 and we use the fact that $C_P - C_V = R$ to eliminate γ in line (3). The work done turns out to be $C_v \Delta T$. This should come as no surprise. We know that, as always, the change in internal energy ΔU is equal to $C_v \Delta T$ even though the change is not at constant volume. Thus in an adiabatic process the change in internal energy equals the work done. You should be able to figure out why this is.

How do we know without calculating it that the work done must equal the change in energy in an adiabatic process?

The Otto Cycle



We can now begin to look at engines. We'll study the standard petrol engine first before we turn our attention to the air engine. An engine is simply a device that extracts work from a thermodynamic cycle. Thus the natural place to follow the cycle is the P-V diagram since this shows immediately the work done as the area under the graph. The figure shows the PV diagram for an idealised piston engine, called the Otto cycle.

Starting at 1 in the figure, the piston moves down the cylinder at constant atmospheric pressure to take in a fuel-air mixture; this is balanced by the final step in the cycle, exhaust stroke, when burnt gas is ejected again at constant pressure. Between points 2 and 3 the fuel air mixture is compressed so work is done on it either by the starter motor or from other cylinders. At the top of the stroke the gas is ignited: this is a rapid process which we can idealise to occur at constant volume. The increase in temperature then brings about an increase in pressure. The increased pressure forces the piston down along the power stroke (4 to 5). Finally heat is lost to the surroundings before the gases are exhausted at atmospheric pressure. In the next section we'll calculate the work done in the cycle.

Work done in the Otto Cycle

Remember:

$$T_3 = T_2 \frac{V_2^{\gamma-1}}{V_3^{\gamma-1}} = T_2 r^{\gamma-1}$$

$$T_4 = T_5 \frac{V_2^{\gamma-1}}{V_3^{\gamma-1}} = T_5 r^{\gamma-1}$$

The work done in the Otto cycle is the difference in the areas under the power stroke and the compression stroke. These are both adiabatic so we know that the work done is equal to the change in internal energy, equation (1).

$$\begin{aligned} \text{Work done} &= C_v (T_4 - T_5) - C_v (T_3 - T_2) \quad (1) \\ &= C_v T_5 (r^{\gamma-1} - 1) - C_v T_2 (r^{\gamma-1} - 1) \\ &= C_v (T_5 - T_2) (r^{\gamma-1} - 1) \\ &= \Delta Q_{out} (r^{\gamma-1} - 1) \quad \text{since } T_2 = T_6 \end{aligned}$$

Furthermore we have seen that $TV^{\gamma-1}$ is a constant in an adiabatic change. We can therefore relate the work done to the change in volume, which is of course a quantity we can measure easily from the construction of the engine. The section shows how to get the work done in terms of the heat rejected between points 5 and 6, and the compression ratio r which is the ratio between the maximum and minimum volumes. We'll come back to this later when we discuss the efficiency of the process for comparison with the air car. For now, make sure you can follow the algebra.

Enthalpy

The second aspect of a combustion engine is the chemical reaction which constitutes the burning of the fuel. We're interested in how much heat we get from a reaction since this determines the amount of energy we can extract. For a reaction at constant volume, there is no work so the heat generated would equal the change in internal energy. Generally speaking however, we are interested in chemical reactions that take place at constant pressure and hence not at constant volume. In this case ΔU and ΔQ are not equal. It turns

out that ΔQ is related to another function of state, called the enthalpy and usually given the symbol H . This is how:

$$\text{Define } H = U + PV$$

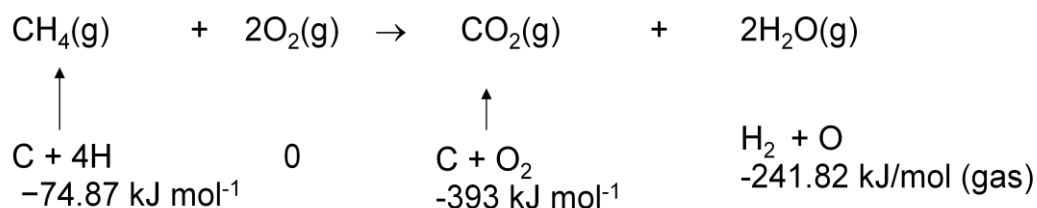
$$\begin{aligned}\Delta H &= \Delta U + P\Delta V + V\Delta P \\ &= \Delta Q - P\Delta V + P\Delta V + V\Delta P = \Delta Q + V\Delta P \\ &= \Delta Q \quad \text{If there is no change in pressure}\end{aligned}$$

We define H to equal $U + PV$ and proceed to find ΔH using the Leibniz rule for $\Delta(PV)$ and the first law for ΔU . The result is that if the pressure is constant the heat from the reaction is the change in enthalpy: $\Delta Q = \Delta H$. Thus for chemical reactions under normal conditions we need the enthalpies of the reactants and products to calculate the changes. Recall that we can't list Q values for the constituents because Q is not a function of state. Of course, we could record ΔQ for every possible reaction – in theory! Using enthalpies means we don't have to: we can work out the ΔQ from the ΔH .

So for chemical reactions at constant (atmospheric pressure) the heat of reaction is the enthalpy

Example: Burning methane

As an example look at the burning of methane. The addition of oxygen to methane, CH_4 , gives carbon dioxide and water vapour. By definition the enthalpy of an element in its standard state is zero. By standard state we mean, for example, that the enthalpy of molecular oxygen at 293K in the gas phase is 0. The bracketed g 's in the chemical equation indicate that we are considering the gas phase. We can get the enthalpies of the other molecules by imagining their formation from their constituent elements, as shown in this section. These are numbers we can look up: the values are shown below. Thus we find that the burning of a mole of methane produces 802 kilo Joules of heat.



$$\begin{aligned}
 \Delta H_{comb}^{\circ} &= 2 \Delta H \text{ of water} + \Delta H \text{ of carbon dioxide} - \Delta H \text{ of methane} - 2 \Delta H \text{ of oxygen} \\
 &= 2 (-241.82) \quad - 393 \quad + 74.87 \quad + 0 \\
 &= - 802 \text{ kJ mol}^{-1}
 \end{aligned}$$

This reaction proceeds spontaneously because it gives out heat. It also goes rapidly. We should not however confuse a spontaneous reaction with a rapid one: the formation of water from hydrogen and oxygen is spontaneous but very slow at room temperature. Heating the mixture will make it go too rapidly to see by eye (as well as making a bang). The reverse processes, forming hydrogen and oxygen from water and producing methane from CO₂ and H₂O are not spontaneous: they require an energy input to make them occur.

Summary

- A quasi-static process is one that proceeds through a sequence of equilibrium states
- A quasi-static process is reversible
- In an isothermal process the temperature is constant
- In an isobaric process the pressure is constant
- In an adiabatic process there is no heat exchange
- In an adiabatic process $PV^{\gamma} = \text{constant}$
- Enthalpy is defined by $H = U + PV$
- The heat exchange in an isobaric process equals the change in enthalpy

SAQs

1. In an adiabatic process is the work done (a) less than or (b) greater than or (c) equal to, the change in internal energy?
2. In an isothermal compression of an ideal gas the work done on the system goes into
(a) internal energy
(b) heat
(c) a combination of internal energy and heat?
3. In a constant pressure process a system exchanges an amount of heat ΔH with its surroundings (where H is the enthalpy)
Is this (a) true or (b) false?
4. In a constant pressure process the change in internal energy is $\Delta U = C_p \Delta T$.
Is this (a) true or (b) false?
5. The burning of carbon ($\text{C}(\text{solid}) + \text{O}_2(\text{gas}) \rightarrow \text{CO}_2(\text{gas})$) gives out heat with $\Delta H = -393 \text{ kJ mol}^{-1}$. Why is the ΔH for this reaction less in magnitude than that for methane combustion?
(a) Because methane is a gas but carbon is a solid
(b) Because methane produces steam (H_2O gas) which is hot
(c) Because both the 4 hydrogens are oxidised in the combustion of methane in addition to the carbon atom.

The answers appear on the following page

Answers

- (a), (b) Incorrect; (c) correct: in an adiabatic process there is no heat exchange so the work done must equal the change in energy.
- (b) Correct, (a), (c) Incorrect: The internal energy depends only on the temperature so is unchanged in an isothermal process. All the work done is lost as heat.
- (a) Correct: At constant pressure $\Delta Q = \Delta H$. Thus in constant pressure processes, such as chemical reactions, the heat exchange is given as an enthalpy change, ΔH .
(b) Incorrect: We have shown that at constant pressure $\Delta Q = \Delta H$.
- (a) Incorrect. The internal energy is a function of state so it depends only on state variables. It is therefore always $C_v \Delta T$ under any circumstances.
(b) Correct: $\Delta U = C_v \Delta T$ always.
- (a) Incorrect: the statement is true but this does not account for difference.
The difference in enthalpy between solid and gaseous carbon is $+716 \text{ kJ mol}^{-1}$. If we were to start from gaseous carbon this much heat would be recovered in the reaction, so would add to the magnitude of the enthalpy change.
(b) Incorrect: this is partly right (see (c)) but the extra ΔH does not arise because steam is hot (rather it's the converse).
(c) Correct: looking back at the combustion of methane you can see that the main difference is the enthalpy of the water.

The Second Law

Second Law of Thermodynamics for Reversible changes

We have seen that the work done is not a function of state but depends on how a change of state is brought about. That is to say there is no function of state W such that the difference in work between neighbouring states is dW . But there is a function of state P such that $dW = PdV$; that is dW/P is a function of state.

Can we draw a similar conclusion about dQ : can we write $dQ = X dY$ for some X and Y ? It turns out that we can, and the result is $dQ = T dS$ where T is the temperature of the system and S is some new function of state called the entropy. The existence of the entropy function is one version of the second law of thermodynamics.

There is no function of state Q such that the heat changes by dQ BUT there is a function of state S such that $dS = dQ/T$

2nd law for a reversible process: $dQ/T = dS$

The first and second laws for a reversible process can be combined in equation (1). Furthermore, since all the quantities in (1) are functions of state it must be true in general, not just for reversible processes.

Thus the combined first and second laws become

$$dU = TdS - PdV \quad (1)$$

Most of us find temperature, pressure and volume fairly easy to get to grips with because we can measure them directly. We also have a picture of the internal energy U in terms of molecules in motion. But entropy seems to be a difficult concept to grasp. We'll try to illustrate some of its significance in what follows.

The most important fact about entropy is that, summed up over the universe, it never decreases.

In any process (reversible or irreversible) $ds_{\text{total}} \geq 0$

Entropy

Entropy represents the degree of disorder in a system. By this we mean the following: there are always a number of microscopic states of a gas, say, that correspond to the same macroscopic state. That is, there are lots of ways we can divide a given total energy amongst many molecules without changing the temperature or volume of the system or the average pressure. For example, if we have two particles we can allot half of the energy to each, or all to one and none to the other or something in between. In general, if the total number of ways that the fixed energy can be allotted is Ω then the entropy is:

$$S = k \log_e \Omega$$

where Ω = number of microstates corresponding to the same macrostate

This gives some impression of the connection between entropy and order. For example, if we have a system of particles in which they all have to have the same energy, there is only one way to distribute the total energy amongst them. Then $\Omega = 1$ and $S = 0$. Such a system is very constrained, and has a high degree of order. At the opposite extreme if we can distribute the energy amongst the particles in an arbitrary way then Ω will be very large and the entropy will be correspondingly large. Such a system has less order. Thus a low entropy corresponds to an ordered system and a large entropy to a disorder one. The law of increase of total entropy is therefore equivalent to a tendency for a system to evolve to a state of maximum disorder.

The entropy function allows us to give a new view of the concept of temperature: In a constant volume process we have:

$$\Delta U = T\Delta S. \text{ So } 1/T = dS/dU \text{ at constant volume.}$$

In other words, inverse temperature is the entropy value of a unit of energy.

There are various alternative statements of the second law of thermodynamics; we'll include one more here. This states, roughly speaking, that heat can flow only from a hotter body to a colder one. The increase in order in the hotter body is more than made up for by an increase in disorder in the colder one. The reverse flow would lead to a spontaneous increase in order which is not allowed.

Research some alternative statements of the second law

Endothermic reactions

We can illustrate the use of entropy by returning to the problem of spontaneous chemical reactions. Ammonium nitrate dissolves in water even though the reaction is endothermic, that is it takes in heat. How is this? The requirement of the second law is that the entropy of the universe should increase: we can show that this is not violated simply because a reaction is endothermic.

The heat of reaction is the heat gained or lost by the environment, since it's what we measure in the external environment. This is the ΔH of the reaction, which therefore equals $-T$ times the ΔS of the environment, as in equation (1).

NH_4NO_3 dissolves in water endothermically with $\Delta H = 26.4 \text{ kJ/mol}$

$$\Delta H = -T\Delta S_e \quad (1)$$

$$\Delta H - T\Delta S_s = -T\Delta(S_e + S_s) \quad (2)$$

$$= -T\Delta S_u \quad (3)$$

$$= \Delta G$$

To get the total change we have to add the heat change in the system itself $-T$ times the ΔS of the system, as in equation (2). If we define a quantity $\Delta G = \Delta H - T\Delta S$ for the system, then equation (3) shows that ΔG is related to the total change of entropy of the universe in this reaction, ΔS_u . Thus, the requirement of the second law is not that ΔH be negative for a reaction to occur spontaneously, which would require the reaction to be exothermic, but that ΔG be negative. G is called the Gibbs free energy, or sometimes just the free energy.

**$\Delta G = \Delta H - T\Delta S < 0$ for a spontaneous transformation
(Gibbs free energy)**

The reason for the name "free energy" is that it can be shown to represent the amount of chemical energy available to do useful work: that is the energy minus the PdV work in the reaction.

To avoid confusion remember that heat and temperature are quite different entities: heat can enter or leave a system without a change in temperature, for example at a phase change. In such a case, the heat exchange represents a change in order, for example from solid to liquid. When ammonium nitrate dissolves in water the entropy decrease in the environment is outweighed by an increase in disorder of the molecules from the bound crystal to the dispersed ions. The overall ΔG is negative so the ammonium nitrate is soluble.

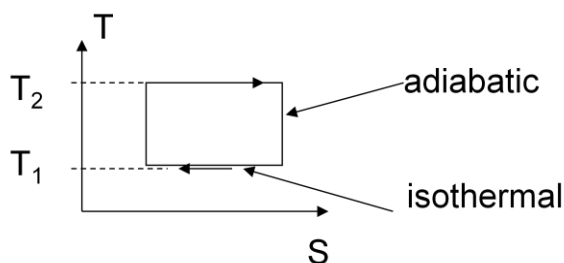
Another example is the melting of ice. Below 0 degrees C, ΔG for the melting of ice is positive because the ΔH term outweighs the $T\Delta S$ term, so ice is stable below 0° C. The heat required to break the bonds in the ice is too much to be compensated for by the increased disorder of the liquid state of water. Above 0°C the $T\Delta S$ term outweighs the ΔH term so the overall ΔG is negative and ice melts spontaneously.

For $T < 0^\circ \text{C}$ $\Delta G > 0$ ($T \Delta S < dH$) So ice melts above 0C
 For $T > 0^\circ \text{C}$ $\Delta G < 0$ ($T \Delta S > dH$)

Carnot cycle

Our final version of the second law of thermodynamics is expressed through a process called the Carnot cycle.

Let's begin by defining a Carnot cycle. The easiest way to visualise this is in a graph of temperature and entropy: in a Carnot cycle, by definition, the system moves reversibly round a rectangle in this picture. Thus a Carnot cycle is made up of two isothermal changes and two adiabatic changes. The advantage of this plot is that the heat put in or extracted in any one of these processes is given by $T\Delta S$ hence by the area under the curve.



$$\Delta \text{Heat} = \text{area} = (T_2 - T_1)\Delta S \quad (1)$$

$$= \text{Work}$$

$$\text{Heat in} = T_2\Delta S \quad (2)$$

So what is the efficiency of this cycle? The work done in such a cycle equals the net heat put in, which is $T_2\Delta S - T_1\Delta S$. On the other hand the total input of heat is $T_2\Delta S$. The efficiency is the work done divided by the heat put in, as in equation (3).

Efficiency:

$$\frac{\Delta W}{\Delta Q_{in}} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2} \quad (3)$$

Use the first law to derive the equivalent expression

$$\text{Efficiency} = 1 - \frac{Q_{out}}{Q_{in}}$$

To summarise: a heat engine takes in heat at a high temperature, uses some of it to do work and rejects heat at a lower temperature to return to its original state. If the processes are reversible, the efficiency depends only on the two temperatures. Although we shall not prove it, Carnot's version of the second law says that no reversible engine operating in a cycle can exceed the efficiency of the Carnot cycle. This is sometimes a useful practical result, but it is also important for the insight it gives into the limits on the conversion of heat to useful work.

No engine working in a cycle has an efficiency greater than that of a Carnot cycle

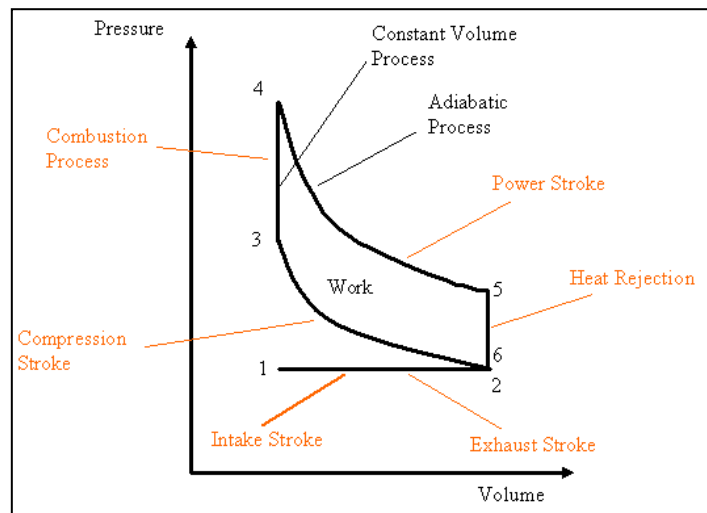
(Second Law of Thermodynamics)

Efficiency of Otto cycle

Adiabatic relations:

$$T_3 = T_2 \frac{V_2^{\gamma-1}}{V_3^{\gamma-1}} = T_2 r^{\gamma-1}$$

$$T_4 = T_5 \frac{V_2^{\gamma-1}}{V_3^{\gamma-1}} = T_5 r^{\gamma-1}$$



Let us now return to the idealised petrol engine and calculate the efficiency of the Otto cycle. We have already found the work done in a cycle, equation (1).

$$\Delta W = \Delta Q_{out} (r^{\gamma-1} - 1) = C_v (T_5 - T_2)(r^{\gamma-1} - 1) \quad (1)$$

$$\Delta Q_{in} = C_v (T_4 - T_3) = C_v (T_5 - T_2)r^{\gamma-1} \quad (2)$$

$$\text{Efficiency} = \frac{\Delta W}{\Delta Q_{in}} = \frac{r^{\gamma-1} - 1}{r^{\gamma-1}} = 1 - \frac{1}{r^{\gamma-1}} \quad (3)$$

Heat is taken in during the combustion process in which the temperature changes from T_3 to T_4 . But, using the adiabatic relations we derived earlier, $T_4 - T_3 = r^{\gamma-1}(T_5 - T_2)$, where r is the compression ratio. The efficiency is just the ratio of useful work extracted to the heat put in, that is $\Delta W / \Delta Q_{in}$. Using (2) and (3) this becomes $1 - 1/r^{\gamma-1}$.

Diesel engines have a higher compression ratio than petrol ones. Why are they generally more efficient?

The efficiency is higher the greater the compression ratio. For a diesel engine in a car the compression ratio is around 10, so for a polyatomic gas with $\gamma = 2/7$ the efficiency is 0.48.

Summary

- Entropy S is defined by $\Delta S = \Delta Q/T$ for a reversible process (2nd law)
- S is a function of state
- S is a measure of the disorder in the system
- If a number Ω of microstates give rise to the same macrostate the entropy is $k \log_e \Omega$
- The combined first and second laws give $dU = TdS - PdV$
- In any process (reversible or irreversible): $dS_{total} \geq 0$
- This is equivalent to $\Delta G = \Delta H - T\Delta S < 0$
- In endothermic reactions $\Delta H > 0$ but $\Delta G < 0$
- The efficiency of a Carnot cycle working between temperatures T_{out} and T_{in} is $1 - T_{out}/T_{in}$

SAQs

1. (i) The change in entropy on cooling a mole of gas reversibly from T_1 to $T_2 = \frac{1}{2} T_1$ is:

(a) $C_v \log\left(\frac{T_2}{T_1}\right) = -C_v \log 2$

(b) 0

(c) $C_v \frac{T_2 - T_1}{T_2} = -C_v$

(d) $C_v \frac{T_2 - T_1}{T_1} = -\frac{1}{2} C_v$

(ii) The change in entropy on the sudden removal of the same amount of heat at T_2 is:

(a) larger

(b) the same

(c) smaller

2. Spontaneous reactions always give out heat. Is this (a) true or (b) false

3. (i) The solution of KCl in water at 298 K is endothermic, $\Delta H = +16 \text{ kJ mol}^{-1}$.

Given that $\Delta S = 77 \times 10^{-3} \text{ kJ mol}^{-1}$ is KCl soluble in water at 298K?

(a) yes

(b) no

(ii) If ΔH and ΔS are unchanged as T increases, is KCl more or less soluble at higher temperatures?

(a) more (b) less

The answers appear on the following page

Answers

- (a) correct: because the process is reversible the change in entropy is the integral of $dQ/T = C_v dT/T$ which gives (a)
(b) Incorrect: reversible changes are not necessarily isentropic (i.e. with no entropy change)
(c) Incorrect: This is the heat rejected divided by the final temperature; but the heat is removed quasistatically at a varying temperature (because the process is said to be reversible)
(d) Incorrect: This is the heat rejected divided by the initial temperature; but the heat is removed quasistatically at a varying temperature (because the process is said to be reversible)
 - (ii)
(a) is correct because for an irreversible process ΔS is greater than $\Delta Q/T$
- (a) Incorrect: the requirement is that the entropy of the universe should increase, which can be achieved by a decrease in order in the environment (input of heat to the system) provided that this is balanced by an increase in disorder in the system.
(b) Correct.
- (i)
(a) Correct: $\Delta G = \Delta H - T \times \Delta S = 16 - 298 \times 77 \times 10^{-3} = -23 \text{ kJ mol}^{-1}$. Since ΔG is negative the process is spontaneous
(b) Incorrect: you need to show that $\Delta G = \Delta H - T \times \Delta S < 0$.
 - (ii)
(a) Correct: as T increases ΔG becomes more negative so the reaction proceeds further
(b) Incorrect: as T increases $\Delta H - T \times \Delta S$, and hence ΔG , become more negative so the reaction proceeds further

The Air Car

Energy storage

The compressor engine raises several issues: how much energy is stored in the compressed gas in comparison to that stored in a tank of petrol? How much can be turned into useful work, that is, what is the thermodynamic efficiency of a compressor engine? We'll address the first one in this section.

Suppose that the compression is done isothermally so the pressure is inversely proportional to the volume. If the compression ratio is, say, 300, then the final pressure will be 300 atmospheres, which is containable in a steel vessel. Suppose, for simplicity, that the capacity of the container is 224 litres, equivalent to 10 mols of gas at atmospheric pressure. Then at 300 atmospheres the cylinder will accommodate 3000 moles.

$$\text{Work done: } W = \int PdV \quad (1)$$

$$\text{But } PV = \nu RT, \nu = \text{no of mols.} \quad (2)$$

The work done in compressing the gas is the integral of PdV under isothermal conditions, that is, with P equal to $\nu RT/V$ by the perfect gas law, and T a constant; here ν is the number of moles. Integrating PdV, the work done is therefore:

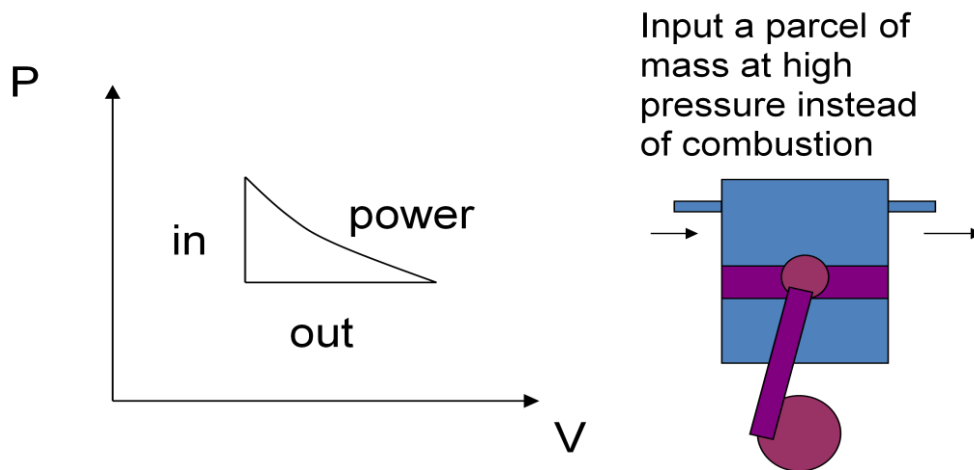
$$W = \nu RT \log(V/V_0) = 3000 \times 8.4 \times 300 \times 5.7 = 50 \text{ MJ}$$

We'll see later that a litre of petrol also provides around 50 mega joules.

The compression process can be taken to be isothermal: therefore the total internal energy of the gas doesn't change. So the work done equals the heat extracted. The compressed gas therefore stores only half of the energy required to compress it. We're also interested in the efficiency of the engine. We'll address that next.

A model for the Air Car Engine

To investigate the thermodynamic efficiency of the air engine we need a model. The section shows one simple model: we imagine that instead of using combustion to create a high pressure, a parcel of mass is injected into the cylinder at the top of its stroke. This is the part of the curve in the P-V diagram labelled "in".



The heat put in at this stage is the mass of gas times the specific heat per unit mass times the temperature of the gas, equation (1).

$$Q_{in} = mC_V T_{in} \quad (1)$$

$$Q_{out} = mC_V T_{out} \quad (2)$$

$$TV^{\gamma-1} = \text{constant} \quad \frac{T_{out}}{T_{in}} = \frac{1}{r^{\gamma-1}} \quad (3)$$

$$\varepsilon = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{1}{r^{\gamma-1}} \quad (4) \quad \text{- same as the Otto cycle}$$

The piston is then forced down as the gas expands adiabatically to a lower temperature T_{out} . This is the power stroke. The outlet valve then opens and the gas is forced out at this lower temperature. The heat rejected is therefore given by equation (2). We can relate T_{out} and T_{in} by the adiabatic law equation (3), giving the efficiency in equation (4). For this model the efficiency is the same as that of the Otto cycle.

Notice that the work comes from cooling the gas to below ambient temperature, which is possible because the gas is stored at high pressure. The air car is therefore at least as efficient thermodynamically as a petrol engine for the *same* compression ratio.

Summary

The energy storage in compressed air appears to be only marginally competitive with petrol

The thermodynamic efficiency of the air engine is comparable to that of a petrol engine

SAQs

If air were to be compressed from 1 at to 300 atmospheres adiabatically what temperature rise would you expect (to the nearest integer). A factor of

- (a) 10
- (b) 5
- (c) 45

The answer appears on the following page

Answers

- (a) Incorrect: You need to use $TP^{(1-\gamma)/\gamma} = \text{constant}$ with $\gamma = 7/5$ for a diatomic gas (not $5/3$ for a monatomic gas)
- (b) Correct: you can either use $PV^\gamma = \text{constant}$ to get the change in volume and $TP^{\gamma-1} = \text{constant}$ to get the change in temperature with $\gamma = 7/5$ for a diatomic gas, or you can use $TP^{(1-\gamma)/\gamma} = \text{constant}$, which follows from these, directly.
- (c) Incorrect: you may have confused the volume change with the pressure change and used gamma for a monatomic gas.

Additional Problems

Problem 1: A mechanical solar “cell”

Every day over 1000 joules of energy beat down on every square metre of the Earth every second, most of it going to waste. The idea is to extract this energy by using it to drive a piston. Below is a schematic of the apparatus:

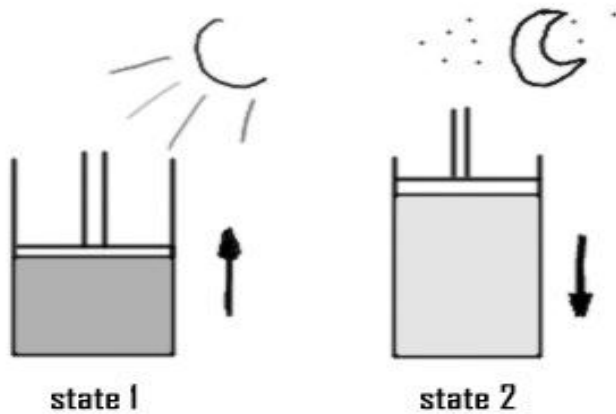
The cycle operates as follows:

Incoming solar energy heats the gas in the chamber, which expands isobarically. The walls of the chamber are fixed, and the piston is pushed upwards.

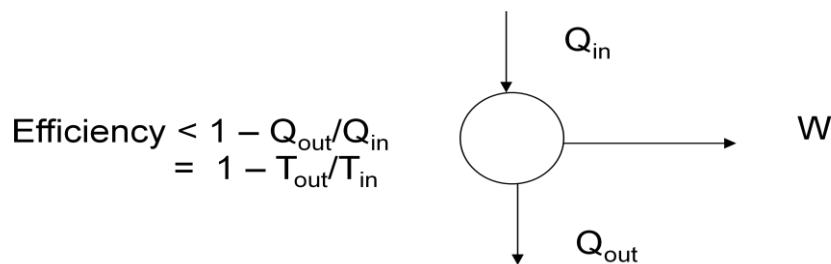
At night the gas cools and contracts, again isobarically, and the piston returns to its original position.

This cycle continues *ad infinitum* and a low, but steady, power is extracted by a dynamo.

What is the efficiency of this device? Is this a practical device?



Answer: Consider this as a heat engine.

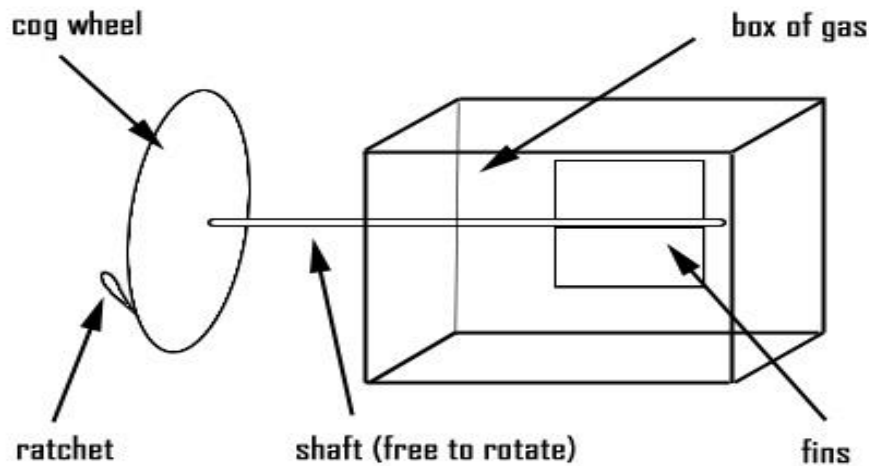


Considered as a heat engine working in a cycle the device takes in heat at the daytime temperature T_{in} and rejects it at the night time temperature T_{out} . So the thermodynamic efficiency is less than that for a Carnot cycle: $1 - T_{out}/T_{in}$. For typical values say $T_{in} = 300$ K and $T_{out} = 273$ we get an efficiency of 0.09%. The power delivered is also low because the engine executes 1 revolution per day. The efficiency is so low because in order to work in a cycle most of the heat must be rejected at night at a temperature close to the daytime temperature.

However, we could also consider extracting work on both the up stroke and the down stroke by changing the coupling as the Sun sets. The machine is no longer operating in a cycle. We could now ask a rather different question: how much of the heat input during the day goes into raising the temperature of the gas and how much into performing work? In this case, we have that the heat input is $C_p \Delta T$ and the work is $P \Delta V$ at constant pressure. The ratio is $R \Delta T / C_p \Delta T = R / C_p = 2/7$ for a diatomic gas like the air. The calculation for the night time is similar. On this measure the efficiency is 29%. Even so, the heat capacity of a gas is small, so the power would still be negligible. We've left you to estimate how much work you might get out of a reasonable sized piston.

Problem 2: The Feynman (or Brownian) Ratchet

The device below consists of a plate designed to intercept randomly moving gas particles. However, because of the teeth on the wheel it can only turn in one direction. Thus the random motion of the gas causes a rotation of the shaft and allows work to be extracted. The ratchet will theoretically be able to keep turning indefinitely, allowing a steady extraction of low power from the apparatus. This does not contradict the first law, but it does appear to offer a 100% efficient process of conversion of heat to work. Is there a fallacy?



This is quite a difficult problem if you look for a mechanical explanation: but if you think in terms of thermodynamics it is easier to see why it cannot work. Our answer is shown below.

Answer:

In principle one might think that work could be extracted from the internal energy of the gas since this does not violate the conservation of energy. The promise of 100% efficiency could be a clue to where the fallacy might lie. The device cannot extract work because there is no temperature difference: it would violate the second law.

To see a microscopic explanation of why it cannot work consider the ratchet and the cog wheel. The wheel must be able to turn on the impact of a single molecule at the plate. Thus the ratchet cannot be too firm – in fact it has to be at least as floppy as the plate, so it too fluctuates under random impacts of molecules. This means it will let the wheel turn back as often as it lets it advance, so the net work is zero.

Overall Summary

- The first law of thermodynamics is $\Delta U = \Delta Q + \Delta W$
- For a gas, $\Delta W = P \Delta V$, $U = C_v T$ and $C_p - C_v = R$
- In an adiabatic change $\Delta Q = 0$. For a perfect gas $PV^\gamma = \text{constant}$
- The heat exchange at constant pressure is given by the change in enthalpy $\Delta Q = \Delta H$
- The second law of thermodynamics gives $\Delta Q = T \Delta S$, where S is the entropy
- This is equivalent to $\Delta G < 0$
- The 2nd law also implies that heat flows “downhill”
 - that the entropy of the Universe increases
 - and that the Carnot cycle has maximum efficiency $1 - T_{\text{out}}/T_{\text{in}}$

Meta tags

Author: Cheryl Hurkett.

Owner: University of Leicester

Title: Enhancing Physics Knowledge for Teaching – Thermodynamics

Keywords: Thermodynamics; Heat and work; Second Law; sfsoer; ukoer

Description: In this session we'll look at the basic laws and concepts of thermodynamics.

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