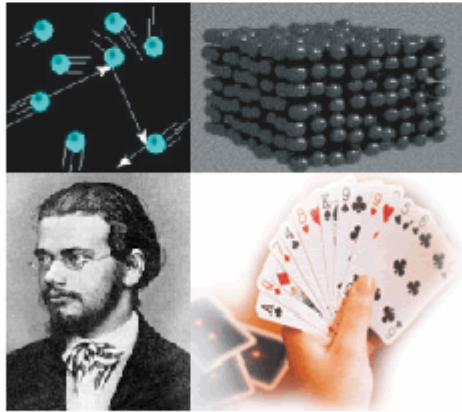


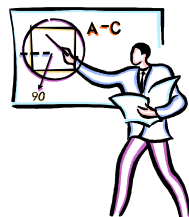
Introduction to Thermodynamics and Kinetics

F31ST1



School of Physics & Astronomy

Lecture Notes *Set 4a: The 0th and 1st laws:* *Temperature, heat, and work*



Thus far.....

As usual, before starting a new section let's briefly recap what we've covered in the previous component of the module. Section 3 largely dealt with the concept of entropy. We found that the most probable macrostate of a system is that associated with the greatest number of microstates. Boltzmann's expression for entropy, $S = k \ln (W)$, therefore encapsulates in a very simple formula the fundamental basis of the transfer of heat from a hot to a cold object. Temperature may be defined as the inverse of the rate of change of entropy with respect to energy and although entropy does not change in an (idealised) reversible process, a closed system tends towards maximum entropy.

However, there remain a number of important questions we need to address:

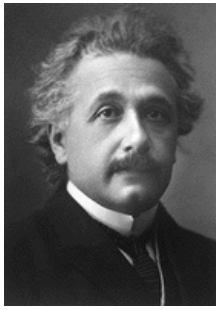
- (i) We've *defined* temperature in terms of both the rate of change of entropy with respect to energy and the mean molecular energy. However, how do we measure temperature in the real world and how are these measurements related to the absolute temperature (i.e. the ' T ' in $\exp(-\Delta E/kT)$)?
- (ii) How are heat and work related?
- (iii) How is it possible to get useful work from the transfer of thermal energy – i.e. on what physical principles is an engine based? How do we run an engine in reverse so that it acts as a heat pump?
- (iv) What determines the efficiency of a heat engine or a heat pump?
- (v) Why can't we build perpetual motion machines and just what is Maxwell's demon?

4.1 Equilibrium and the Zeroth law

The branch of science called thermodynamics was developed *before* an understanding of the microscopic (atomistic or molecular) nature of matter was achieved. As was noted at the start of the module, thermodynamics is concerned with the macroscopic properties of a system: volume, temperature, pressure, specific heats,...etc... We've now spent quite a lot of time discussing the properties of matter from a molecular viewpoint and have shown that properties such as temperature and specific heat are fundamentally related to the arrangements of quanta amongst the various energy levels accessible to a system. One might then ask whether we should care about classical thermodynamics at this point: if we can understand the behaviour of matter using statistical mechanics and quantum theory, surely that's enough?

In fact, that is a rather 'blinkered' attitude to adopt! A very important feature of thermodynamics is that the relationships between thermodynamic variables such as pressure, temperature and volume are *not dependent on a particular microscopic model*. Hence, thermodynamics acts as an important check on our microscopic description of matter. Perhaps the best example of the power of a thermodynamic approach lies with Carnot's work on heat engines and entropy at the turn of the 19th century. Carnot developed the concept of entropy with no consideration of atomic structure and before the 1st law – the conservation of energy principle – was known!





Einstein was particularly ‘enamoured’ of thermodynamics, stating in 1949: “..classical thermodynamics has made a deep impression upon me. It is the only physical theory of universal content which I am convinced, within the applicability of its basic concepts, will never be overthrown.” (Quote taken from CB Finn, “Thermal Physics”).

Thermal and thermodynamic equilibrium

Throughout this section we will deal with the archetypal thermodynamic system: a piston and a gas enclosed in a container with either *adiabatic* walls (no heat in or out) or *diathermal* walls (gas coupled thermally to the surroundings) (Fig. 4.1). Considering a gas thermally isolated from its surroundings by adiabatic walls with no flow of gas into or out of the container (a *closed* system), the gas will reach an equilibrium state where its properties are spatially uniform and don’t change with time.

At this point the gas will be in the *equilibrium state* (P, V). In equilibrium, specifying P , V , and the total number of gas molecules *fixes all the macroscopic properties of the gas* (e.g. thermal conductivity).

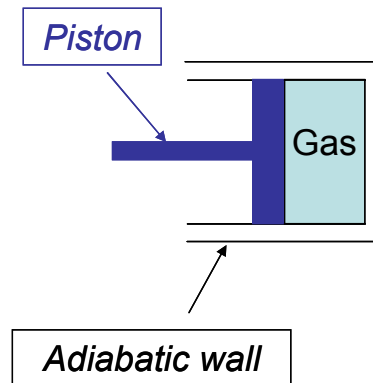


Fig. 4.1 A gas contained in a container with adiabatic walls. A frictionless piston may either do work on the gas (if we – the surroundings – compress the gas) or the gas may do work on the piston by expanding.

NOTES

At thermal equilibrium there are no flows of energy in the system i.e. there are no temperature gradients. To have thermodynamic equilibrium we must have reached thermal, chemical and mechanical equilibrium where not only are there no temperature gradients but there are no unbalanced forces on the system *and* there are no chemical reactions occurring.

The 0th law

If two systems are put in thermal contact with each other, they will reach thermal equilibrium (for example, the blocks considered throughout Section 3).

The 0th law of thermodynamics states that if each of two systems is in thermal equilibrium with a third, they are in thermal equilibrium with each other.

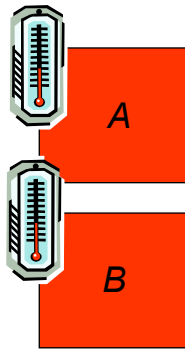


Fig. 4.2 If system A is in thermal equilibrium with system C (the thermometer) and system B is also in thermal equilibrium with system C, then systems A and B are in thermal equilibrium with each other. Two systems in thermal equilibrium have the same temperature.

This might seem like a rather obvious statement but that it's not a logical 'necessity' may be illustrated by the following (rather loosely connected!) example: if I owe John £10-00 and Pete owes John £10-00 that doesn't mean that I owe Pete £10-00! Without the zeroth law we would not be able to make use of thermometers. When we make a measurement of temperature (on, say, system A – see Fig. 4.2) we bring the thermometer into equilibrium with the system. If the thermometer is in thermal equilibrium with System B then – from our discussions in Section 3 - we can state that System A and System B have the same temperature.

NOTES

4.2 Isotherms

Returning to the gas and piston system, consider bringing the gas through the following sequence of steps. We start with an equilibrium state (P, V) of the gas which is in thermal equilibrium with another system. On a graph of P vs V (a PV diagram) we plot a point representing this equilibrium state. We then compress the gas to bring it to a new equilibrium state, (P', V') which is also in thermal equilibrium with the reference system. That is, although we have changed the pressure and volume of the gas we have kept its temperature constant. We plot this point on the PV diagram. If these steps are repeated, always keeping the temperature of the gas constant, then we will plot a curve known as an *isotherm* (for hopefully obvious reasons) on the PV diagram.

Isotherms for an *ideal* gas are shown in Fig. 4.3. (Note that the isotherms for a real gas (which we'll come to later on in Section 4) are substantially more complicated than those shown in Fig. 4.3.) It is clear that a functional relationship between P , V , and T exists, i.e.

$$T = f(P, V) \text{ or } P = f(T, V) \text{ or } V = f(P, T)$$

Of the three measurable variables only two are independent and one may be expressed in terms of the other two.

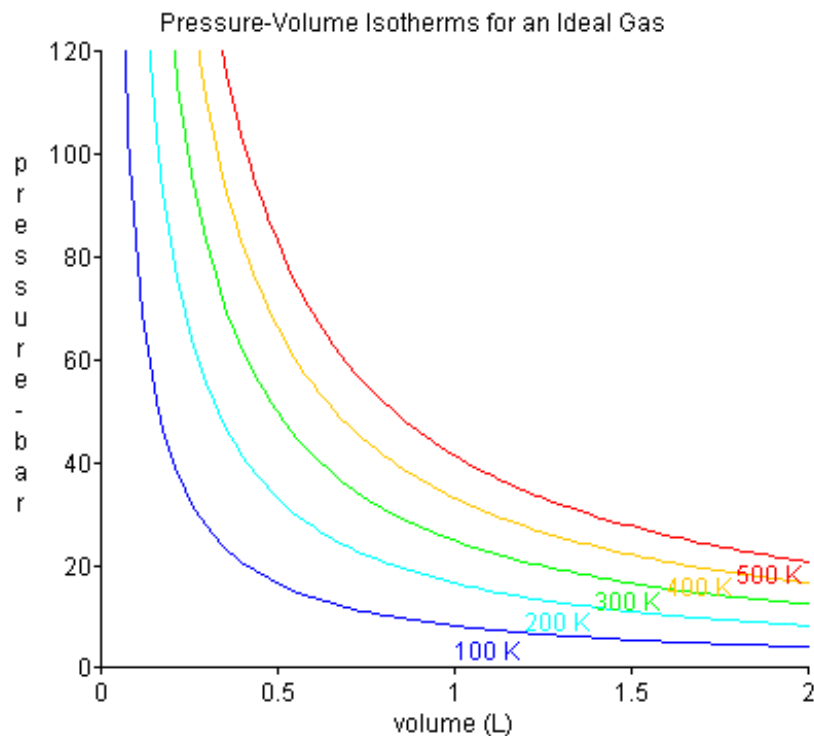


Fig. 4.3 Pressure-volume isotherms for an ideal gas. Each curve represents a series of pressure and volume measurements taken at a constant gas temperature (either 500 K, 400 K, 300 K, 200 K, or 100 K).

Functions of state

*When a system is in thermodynamic equilibrium the properties of the system only depend on the thermodynamic variables (P, V, T) – the pathway by which equilibrium was reached is irrelevant. We say that P, V, and T are **functions of state**.*

For example, in equilibrium : $T = f(P, V)$.

Here, T is a function of state and the expression $T = f(P, V)$ is called an ***equation of state***.

? Write down the equation of state for an ideal gas in the forms $P = f(V, T)$ and $T = f(P, V)$.

? Write down an equation which describes the isotherms of an ideal gas.

NOTES

4.3 Temperature scales and gas thermometers

To experimentally measure temperature we first have to find a physical property of our reference system that varies with temperature – e.g. the length of a column of mercury in a glass capillary or the voltage of a thermocouple junction. We then need to assign a temperature *scale* based on the change in the physical property. How do we assign this scale, i.e. how do we calibrate our thermometer?

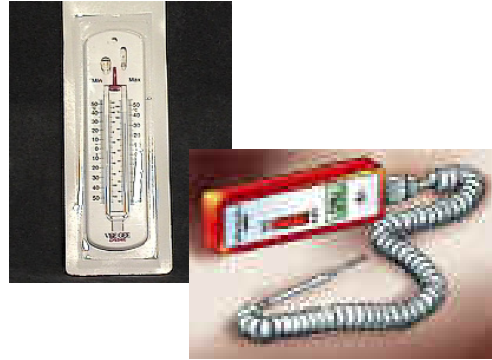


Fig. 4.4 Thermometers

We first assume that the physical property (X) varies linearly with temperature so that

$$X = aT \quad 4.1$$

where a is a constant. Note that this assumes that the value of X at the zero of temperature is 0. This is not necessarily the case. For example, the resistance of a platinum wire is a physical property related to temperature. However, this resistance remains finite as T is lowered and tends to a constant value at the lowest possible temperatures. Furthermore, temperatures on the X scale are only defined in regions where the thermometric property varies as given by equation 4.1 above. Finally, different thermometers based on different variables will generally agree only at fixed points. However, as discussed below, there is a class of thermometer which surmounts these problems.

To determine the value of a in equation 4.1 we need to choose a certain well defined and reproducible value of temperature, T , and *assign* it a fixed value. The question then arises as to what we choose as our fixed point. A very well defined and completely reproducible temperature is that associated with the triple point of water i.e. the temperature at which ice, water, and water vapour coexist. (There'll be more on phases later in this section). We *assign* T at the triple point of water the value 273.16 K (i.e. 0.01°C) (we'll get to just why we choose 273.16 K shortly.....).

Constant volume gas thermometer

Gas thermometers always agree at all points on the temperature scale: they are independent of the material (i.e. the gas) used in the thermometer.

A simple schematic of a gas thermometer and a more detailed diagram are shown in Fig. 4.5. The volume of gas is kept constant by adjusting the height of the mercury column until the meniscus is aligned with a fixed reference level. The bulb of gas is immersed in the system whose temperature is to be measured.

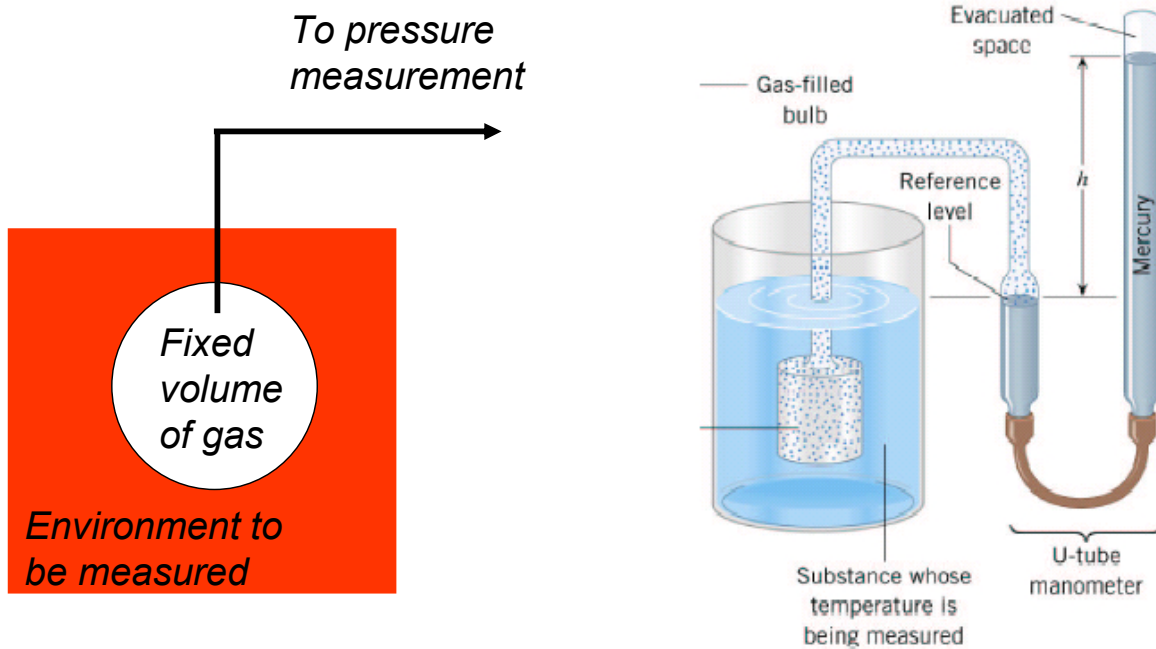


Fig. 4.5 Schematic (left) and more detailed diagram of constant volume gas thermometer. The diagram on the right was taken from Cutnell & Johnson, Wiley Publishing, Physics 5th Ed. (Figure 12.03)

? A 'dead space' or 'nuisance volume' is sometimes referred to when discussing gas thermometers. From a consideration of Fig. 4.5 can you suggest from where this nuisance volume might arise?

? Assuming that the triple point of water is 273.16K, write down an equation that relates T and P of the gas to T and P at the triple point.

NOTES

Ideal gas scale

When the amount of working gas is reduced to the smallest possible value, all gas thermometers give the same temperature for a give system *irrespective of the gas used*. From the material covered in Sections 1 and 2, it should hopefully be clear why this is so. We define the *ideal gas scale* as follows:

$$T = 273.16 \lim_{P_{TP} \rightarrow 0} (P / P_{TP}) K$$

4.2

Ideal gas scale

The limit is performed by carrying out an extrapolation as shown in Fig. 4.6.

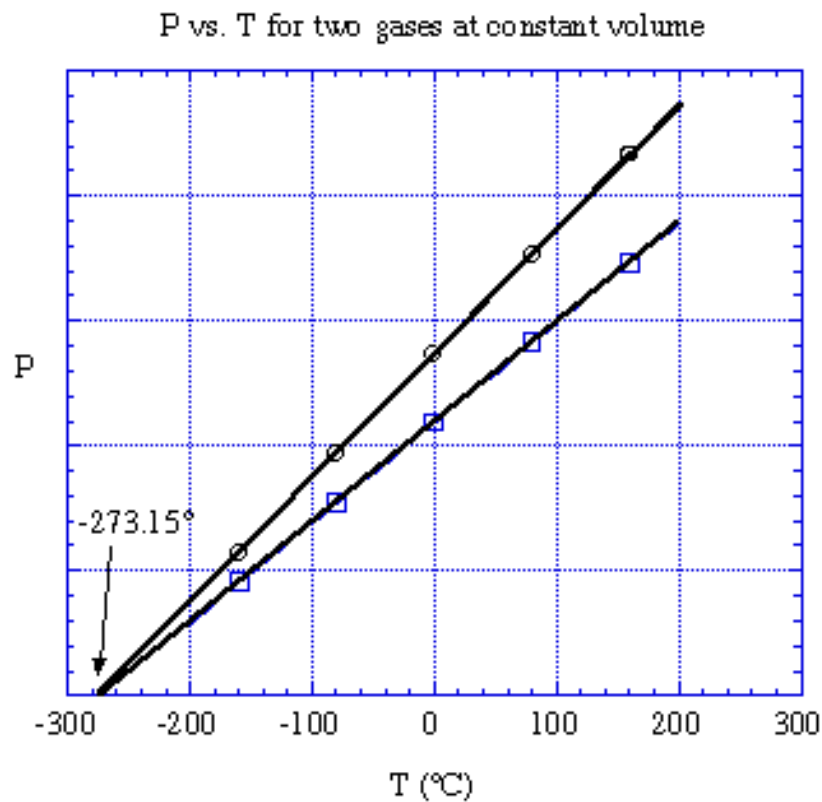


Fig. 4.6 All gases at sufficiently low pressure obey the equation of state of an ideal gas. An extrapolation of the P vs T graph for a constant volume gas thermometer to $P = 0$ therefore yields the zero of temperature on the ideal gas scale, $T = -273.15^\circ \text{C}$.

From Fig. 4.6, absolute zero is defined as -273.15°C . The value of 273.16 K appearing in the ideal gas scale (equation 4.2) was chosen so as to ensure that there are 100 K between the *experimentally measured* temperatures of the ice and steam points (the boiling and freezing points of water at atmospheric pressure). The celsius scale is given by:

$$T(^{\circ}\text{C}) = T(\text{K}) - 273.15$$

It is essential to note at this point that the temperature defined according to the ideal gas scale is *identical* to the absolute thermodynamic temperature scale which we have used throughout the module thus far (in equations such as $\frac{1}{2} m\langle v^2 \rangle = 3kT/2$, $p_i \propto (-\Delta E/kT)$, etc...). Just why this is the case will be explored when we consider heat engines and a process called the Carnot cycle.

Two fixed points

Before the 1950s, temperature scales were based not on one fixed point (as for Eqn. 4.2) but two. Hence, two constants had to be fixed by specifying the temperature at two fixed points: the steam and ice points. An alternative equation to Fig. 4.2 was then used for the temperature scale:

$$X = aT + b \qquad 4.3$$

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4.4 Heat and work

We now move on to consider some of the questions that drove the inception and development of thermodynamics: how can we use thermal processes to generate mechanical work?; what distinguishes heat from work?; what is the maximum efficiency we can expect from a heat engine and how is this related to entropy?

Determining the work done in a process

Returning to the gas + piston system, back in Section 2.8 of the notes we wrote down the following expression for the work done by an expanding gas:

$$dW = - PdV \qquad \text{Eqn. 4.4}$$

It is worthwhile to remember at this point that our convention with regard to whether work is considered as a positive or negative quantity is as follows:

if the surroundings do work on the gas (e.g. the piston compresses the gas) then this is positive work;

if the gas does work on the surroundings (e.g. the gas expands pushing back the piston) then this is negative work.

Equation 4.4 gives the quantity of work done on (or by) the system for an infinitesimal change in volume. To get the total work done in a process we need to integrate:

$$W = - \int_{V_i}^{V_f} PdV \qquad \text{Eqn. 4.5}$$

where V_i and V_f are the initial and final volumes of the gas.

Work done by an expanding gas: path dependence

We now need to address an issue of key fundamental importance. We know that P, V, and T are functions of state – is the work done also a function of state? That is, is the amount of work done independent of the path we choose to follow in a thermodynamic process? This question may be answered by considering three different pathways: an *isothermal* (constant temperature) process, an *isobaric* (constant pressure) process, and an *isochoric* (constant volume) process.

NOTES

Isothermal path

Fig. 4.7 is a PV diagram for an isothermal process where a gas is expanded from V_1 to V_2 . The curve shown on the PV diagram is simply the isotherm at temperature T .

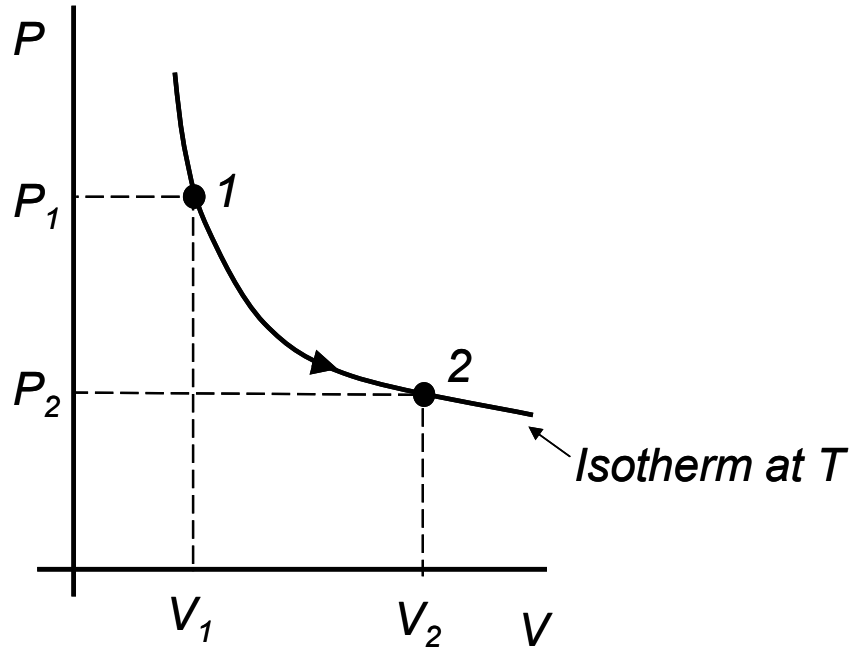


Fig. 4.7 PV diagram for a gas expanding isothermally from volume V_1 to volume V_2



Given that $PV = nRT$ for an ideal gas, derive an expression for the work done by the gas when it expands from V_1 to V_2 .

NOTES

Isobaric path

Now let's consider a different pathway in the PV diagram. Consider pathway $3 \rightarrow 2$ in Fig. 4.8. This is an isobaric expansion (as it is carried out at constant pressure).

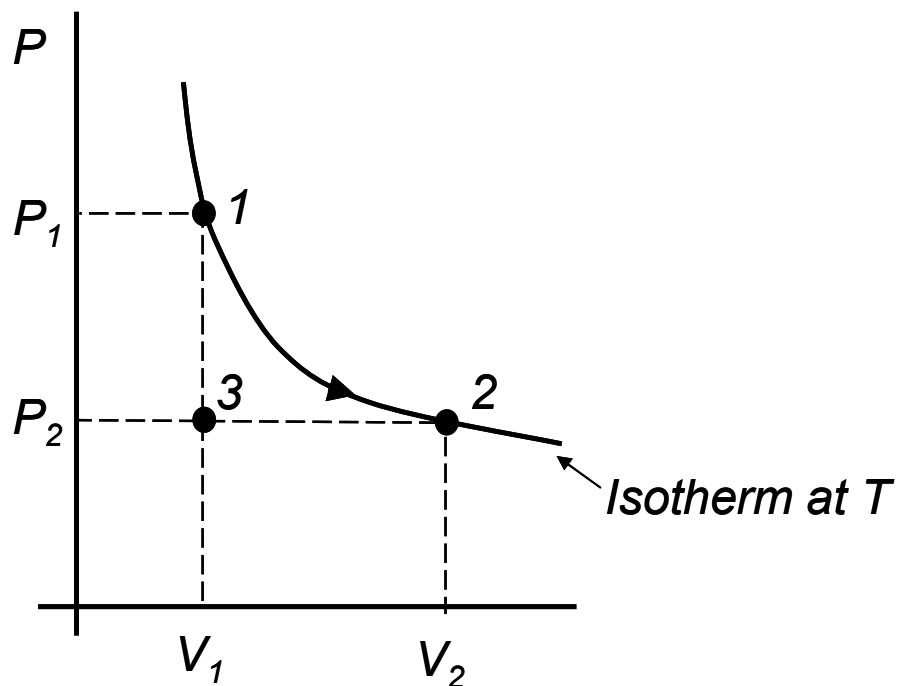


Fig. 4.8 The pathway from point 3 to point 2 on the PV diagram represents an isobaric expansion.



Write down an expression for the work done in an isobaric expansion of the ideal gas (pathway $3 \rightarrow 2$ on the PV diagram shown in Fig. 4.8).

NOTES

Isochoric path

The path 1 \rightarrow 3 in Fig. 4.8 is an isochoric process – there is no volume change.



Write down an expression for the work done in the isochoric process (path 1 \rightarrow 3) shown in Fig. 4.8.

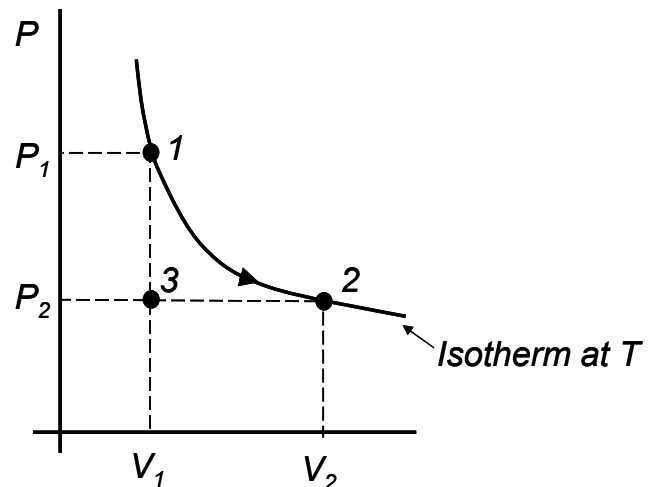
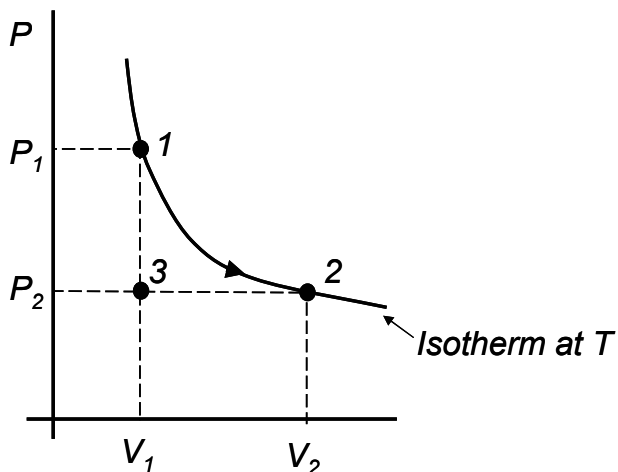
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Work done: area under the curve

In addition to deriving expressions for the amount of work done in these various processes, the work done has a simple graphical interpretation: it is the area under the curve.



On the PV diagrams below shade in the region of the PV diagram that corresponds to (i) the quantity of work done in an isobaric expansion from V_1 to V_2 ; (ii) the quantity of work done in an isothermal expansion from V_1 to V_2 at temperature T .



Heat, work and the 1st law

As discussed in detail in Section 2a of the notes that the internal energy of an ideal gas is a function of temperature only.



What is ΔU for an isothermal compression of an ideal gas? What is the corresponding value for an isothermal expansion?



Therefore, from the 1st law, how are the values of dQ and dW related in an isothermal process for an ideal gas?

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