4.1 Classical Thermodynamics: The First Law

As an introduction to the thermomechanics of continua, in this section particularly simple materials undergoing simple deformation and/or heat-transfer processes are considered.

4.1.1   Properties and States

First, here is some essential terminology used to describe thermodynamic processes.

A **property** of a substance is a macroscopic characteristic to which a numerical value can be assigned at a given time. Thus, for example, the mass, volume and energy of a material, or the stress acting on a material, are properties. Work, on the other hand, is not a property, since a material does not "have a certain amount of work" (see the section which follows).

The **state** of a material is the condition of the material as described by its properties. For example a material which has properties volume V_1 and temperature θ_1 could be said to be in state '1' whereas if at some later time it has different properties V_2 and θ_2, it could be said to be in a different state, state '2'.

4.1.2   Work and Path Dependence

For the present purposes, a **system** can be defined to be a certain amount of matter which has fixed or movable boundaries. The state of a system can then be defined by assigning to it properties such as volume, pressure and so on. As will be seen, there are then two ways in which the state of the system can be changed, by interactions with its surroundings through **heat** or through **work**. The notion of heat, although familiar to us, will be defined precisely when the first law of thermodynamics is introduced below. First, consider the system shown below in Fig. 4.1.1, which consists of a block attached to an elastic spring, sliding over a rough surface. A force is applied to the "system" (denoted by the dotted line).
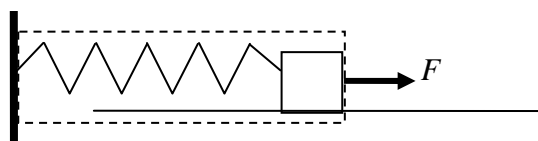
Figure 4.1.1: a spring/block system

The current state of the system can be described by the property x, the extension of the spring from its equilibrium position (and its velocity). However, the work done in moving the system from a previous state to the current state is unknown, since the block may have moved directly from its initial position to its current position, or it may have moved over and back many times before reaching the current position. Therefore the work done is **path dependent**. There are many different amounts of work which can be carried out to move a system from one state to another.

4.1.3   Thermal Equilibrium and Adiabatic Processes

Before getting to the first law, it is helpful to consider the notions of **thermal equilibrium** and **adiabatic** processes.

Thermal Equilibrium

Consider the following experiment: two blocks of copper, one of which our senses tell us is "warmer" than the other, are brought into contact and isolated from their surroundings, Fig. 4.2.1a. A number of observations would be made, for example:

(1)   the volume of the warmer body decreases with time whereas the volume of the colder body increases, until no further changes take place and the bodies feel equally warm

(2)   the electrical resistance of the warmer block decreases with time whereas that of the colder block increases, until the electrical resistances would become constant also.

When these and all such changes in observable properties cease, the interaction is at an end. One says that the two blocks are then in *thermal equilibrium*. In everyday language, one would say that the two blocks have the same **temperature**[1].

(a)   (b)
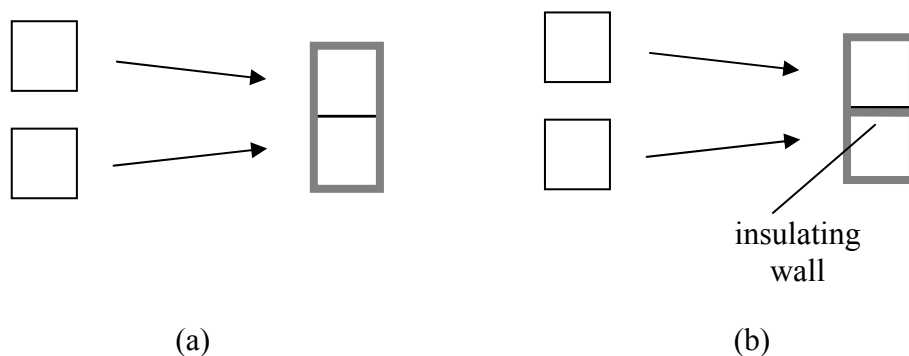
Figure 4.2.1: two blocks of copper brought into contact; (a) no insulating wall, (b) insulating wall

Adiabatic Conditions

Suppose now that, before the blocks are brought together, an **insulating wall** is put in place to separate them, Fig. 4.2.1b. By this is meant that the volume, electrical resistance, etc. of one block does not affect those of the other block. Again, in everyday language, one would simply say that the temperature of one block does not affect the temperature of the other. The term **adiabatic** is used to describe this situation.

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[1] formally, temperature is defined through the **zeroth law of thermodynamics**, which states that if two systems are separately in thermal equilibrium with a third system, then they must be in thermal equilibrium with one another. This statement is tacitly assumed in every measurement of temperature – the third system being the thermometer

4.1.4   The First Law of Thermodynamics

The Experiments of Joule

James Joule carried out some ingenious experiments into the nature of work and heat transfer in materials in the 1840s. In his most famous experiment, Joule filled a container with a fluid and used a rotating paddle wheel, driven by falling weights, to stir the water. The container was thermally insulated and so the process was adiabatic. Joule measured the consequent rise in temperature of the fluid and noted that this change in the fluid's properties was due to the work done by the falling weights.

Further experiments were carried out in which raising the temperature of the thermally insulated fluid was induced by carrying out the necessary work in different ways, for example using electrical means. In all cases, the work required to raise the temperature by a fixed amount was the same.

The series of experiments showed that if a material is thermally insulated, there is only *one* amount of work which brings the material from one state to a second state. If one knows the first state and the second state, one knows the amount of work required to effect the change in state – the work is *path independent*.

It took many years for investigators to absorb the meaning of this experimental result; it was eventually accepted that there must exist a function U, a property of the system, such that

$$W = \Delta U = U_2 - U_1 \qquad \text{(adiabatic process)} \qquad (4.1.1)$$

U is the **internal energy**, and the difference in internal energy between state 2 and state 1 is *defined* as equal to the work done in going from 1 to 2 by *adiabatic* means.

In the case of the stirred fluid, the increase in internal energy is due to the more rapidly moving fluid particles, that is, is equivalent to the increase in kinetic energy of the fluid particles.

Consider again the elastic spring system of Fig. 4.1.1, but now without the sliding over a rough surface, and completely thermally insulated. The work done now depends only on the current state (it equals $\frac{1}{2}kx^2 - \frac{1}{2}kx_0^2$, where k is the spring constant and x_0 is the equilibrium position). The internal energy of the system is seen to be in this case equivalent to the elastic potential energy in the spring.

The First Law

One can imagine now a careful experiment in which a material is thermally insulated from its surroundings and deformed through the work of a set of forces. The material can be deformed into different states, Fig. 4.1.3. The internal energy U will in general be different in each state. U could be measured by carefully recording the work done on the material to reach a given state.

State 1   State 2   State 3
U_1 U_2 U_3
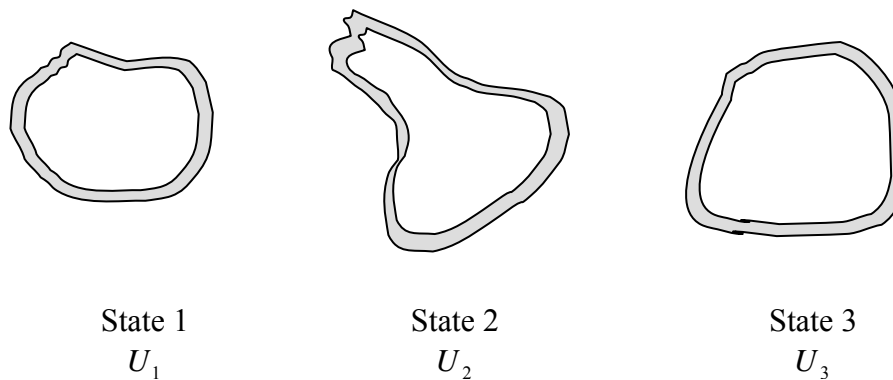
Figure 4.1.3: a thermally insulated material in three different states

Suppose that the internal energy of a material is known at various different states, through the conduction of the aforementioned experiment, in particular one knows the internal energy for the material at two given states, 1 and 2. Relax now the condition that the changes are adiabatic. What this means is that if one now brings the material into contact with another body, the properties of the material *can* be affected. Work is again done to take the material from state 1 to state 2 but it will now be found that, in general,

$$W \neq \Delta U = U_2 - U_1 \qquad (4.1.2)$$

The difference between ΔU and W is *defined* as a measure of the *heat Q* which has entered the system in the change. Thus

$$\boxed{W + Q = \Delta U} \qquad \textbf{First Law of Thermodynamics} \quad (4.1.3)$$

This is **the first law of thermodynamics**. In words, t*he change in the internal energy is the sum of the work done plus the heat supplied*.

Note that the concept of heat Q (and internal energy) is introduced and defined with the first law. Like work, heat is a form of energy *transfer*; a body does not *contain* heat. Work is any means of changing the energy of a system other than heat.

Sign Convention for Work and Energy

The following sign convention will be used[2]

$$
\begin{array}{lll}
Q > 0 \; - & \text{heat enters the system} & \\
Q < 0 \; - & \text{heat leaves the system} & (4.1.4) \\
W > 0 \; - & \text{work done on the system} & \\
W < 0 \; - & \text{work done by the system} &
\end{array}
$$

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[2] many authors use the exact opposite sign convention for work as used here

Other types of Energy

When there are other energies involved, the first law must be amended. For a material moving with a certain velocity, one must also consider its kinetic energy, and the first law reads

$$W + Q = \Delta U + \Delta K \qquad (4.1.5)$$

Other types of energy can be incorporated, for example gravitational potential energy and chemical energy[3]. All the different types of energy are often denoted simply by E, so the first law in general reads $W + Q = \Delta E$.

Inside the Black Box

In this continuum treatment of thermodynamics (or **phenomenological thermodynamics**), it is not necessary to look inside and consider the billions of molecules inside the "black box" of a system. However, it is helpful to think of the molecules of a material as having certain micro-velocities and it is the mean velocity of these micro-velocities which manifests itself as the macroscopic velocity property, and the statistical fluctuations of the micro-velocities from the mean velocity are assumed to cancel out, Fig. 4.1.4.

The micro-velocity fluctuations give rise to an *internal* kinetic energy which manifests itself as the macroscopic temperature, as in the stirred fluid mentioned above. The interaction between the elementary particles and the surroundings of the element causes energy to be transferred to the surroundings. This is the **heat flow** through the boundary of the system. This energy exchange can occur even when the shape of the element does not change, whereas a change in potential energy implies a deformation which will induce a re-arrangement of the molecules and change in shape or volume of the system.
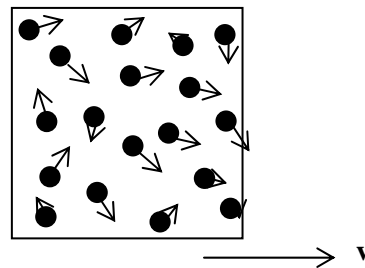

Figure 4.1.4: a system moving with velocity v

The property of pressure or stress of the system is by definition determined by the forces exerted by the elementary particles around the boundary. The fluctuations and micro-movement of the elementary particles will cause stress fluctuations but again these are assumed to cancel out.

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[3] a potential energy which can be accessed when molecular bonds are broken

4.1.5 Simple Compressible Systems

In order to demonstrate the meaning and use of the first law with examples and simple calculations, only **simple systems** will be considered. A simple system is one where there is only *one* possible work interaction. The classic example of a simple compressible system is that of a substance contained within a piston-cylinder apparatus, Fig. 4.1.5. The state of the material can be changed either by heat transfer or by the application of work, and the only work interaction possible is the application of a force to the piston head, compressing or expanding the material. Any effects due to magnetic or electrical interactions, or due to motion or gravity, are ignored.
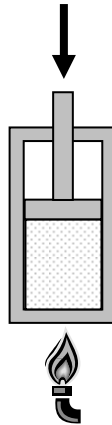
Figure 4.1.5: A simple piston-cylinder system

A **pure substance** is one which has a uniform and invariable chemical composition. In theory this could include different phases of the same substance (e.g. water and steam for H_2O).

In what follows, only pure substances in the context of simple compressible systems will be considered.

Work

If p is the pressure at the piston face, and dV is a small change in volume of the material, Fig. 4.1.5, then the work done in compressing/expanding the material is

$$\delta W = -p\,dV ,\qquad(4.1.6)$$

the minus sign because a positive work is done when the volume gets smaller. The total work done during a compression/expansion of the material is then

$$W = \int \delta W = -\int_{p_1,V_1}^{p_2,V_2} p\,dV\qquad(4.1.7)$$

The symbol δ is used here to indicate that the small amount of work δW is not a true differential[4]; it cannot be integrated to a function which is evaluated at only the initial and final states, $W \neq \int_{p_1,V_1}^{p_2,V_2} dW = W(p_2,V_2) - W(p_1,V_1)$, since the work done is process/path. To illustrate this path dependence, consider the $p-V$ graph in Fig. 4.1.6, which shows three different process paths between states 1 (p_1,V_1) and 2 (p_2,V_2). For path ABC, the work done is $p_2(V_2 - V_1)$. For path AB′C, the work done is $p_1(V_2 - V_1)$. The work for the third, curved, path requires an integration along AC and will in general be different from both the other results.
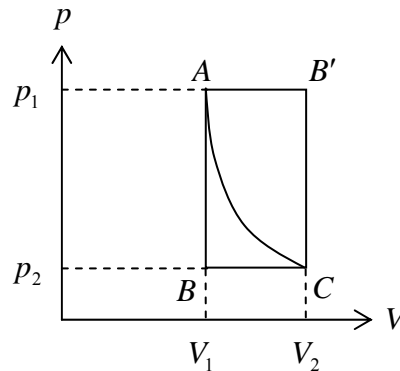
Figure 4.1.6: a p-V diagram

The first law states that $dU = \delta W + \delta Q$ which can now be re-written as

$$\boxed{dU = -pdV + \delta Q}$$ **First Law for a Simple Compressible System** (4.1.8)

4.1.6 Quasi-Static Processes

A system is said to be in **equilibrium** when it experiences no change over time – it is in a **steady state**. Full **thermodynamic equilibrium** of a system requires thermal equilibrium with any surroundings and also mechanical equilibrium[5].

Much of the theory developed here requires that the system be in a certain state with certain properties. If a property such as temperature is varying throughout the material, one cannot easily speak of its "state". Thus when a material is undergoing some process, for example it is being deformed or heated, it is often necessary to assume that it is a **quasi-static** (or **quasi-equilibrium**) process. This means that the process takes place so slowly that the rate of change of the process is slow relative to the time taken for the properties to reach equilibrium. For example, if one heats water in the piston-cylinder arrangement of Fig. 4.1.5 by putting it directly over a hot flame, the water near the base will heat up first and cause convection currents and the water will not be anywhere near an equilibrium state. On the other hand, one could imagine heating the water extremely

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[4] but not to be confused with the use of this symbol to represent a variation, as in the context of the principle of virtual work
[5] and also **chemical equilibrium**, where there are no net reactions taking place

slowly with a low flame, so that at any time instant the water temperature is very nearly constant throughout.

To examine what this might mean in the case of the work performed, consider Fig. 4.1.7, which shows the system pressure p and the external pressure p_{ext} – the pressure exerted by the surroundings. Assuming thermal equilibrium, if $p = p_{ext}$ then there is full equilibrium. If, however, there is an appreciable difference between the two, for example if a large external pressure is suddenly applied, the piston head will depress rapidly and pressure will not remain uniform throughout the system. However, if the pressures differ by a small amount dp, the work done is

$$W = -\int p dV = -\int (p_{ext} \pm dp) dV = -\int p_{ext} dV \mp \int dp dV = -\int p_{ext} dV \qquad (4.1.9)$$

provided dp is extremely small. The smaller dp, the closer the system will be to mechanical equilibrium. As with the heat transfer, this implies that quasi-equilibrium is maintained provided the piston is moved extremely slowly by incrementally increasing the pressure by very small amounts. (It is often suggested that this might be achieved by repeatedly placing individual grains of sand on the piston head.)
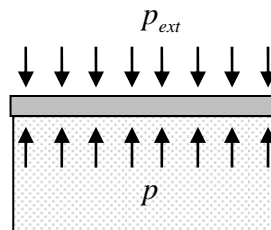

Figure 4.1.7: pressures exerted on a piston head

Unless otherwise stated, it will be assumed that the material at any instance is in quasi-equilibrium. If the system is *not* in equilibrium, Eqn. 4.1.8, $dU = -pdV + \delta Q$, does not make much sense, and one would have to use the more general version $dU = \delta W + \delta Q$.

Example

A gas is contained in a rigid thermally insulated container. It is then allowed to expand into a similar container initially evacuated, Fig. 4.1.8. There is no heat transfer and so $Q = 0$. Since a vacuum provides no resistance to an expanding gas, there is no pressure and hence no work done. Therefore there is no change in the internal energy of the gas. This is *not* a quasi-static process.
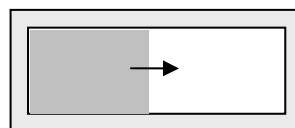
Figure 4.1.8: a thermally insulated gas expanding in an evacuated container

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Example

Consider the cylinder arrangement of Fig. 4.1.9, which shows a gas contained by a weight. The gas is heated and this causes the weight to rise. The pressure is constant and so the work done is $p\Delta V = p(V_2 - V_1)$. This example shows a system taking heat as input and performing work as output, with no necessary internal energy change.
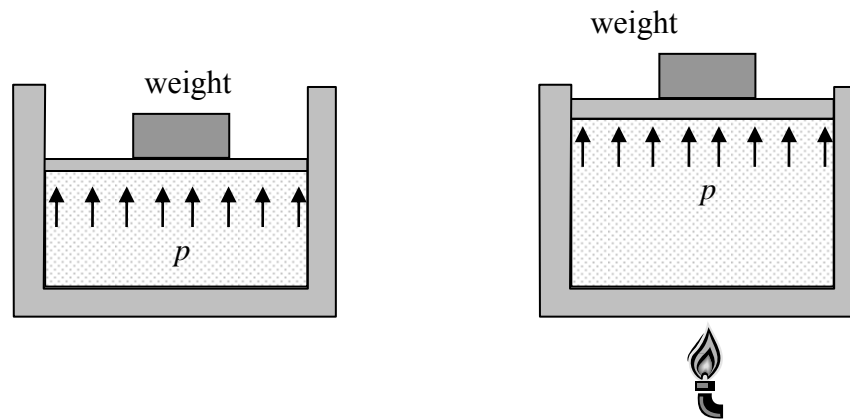

Figure 4.1.9: a heated gas causing a weight to move

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The opposite process, whereby work is converted purely into heat is called **dissipation** (for example, as can occur in a frictional brake).

4.1.7 State Variables and State Functions

Now a general guide known as the **state principle** says that there is one independent property for each way a system's energy can be varied independently. For a simple compressible system, there are two ways of varying the energy and so the material has *two* **independent properties**[6]. One can take any two of, for example, the temperature[7] θ, pressure p, volume V or internal energy U. The two chosen independent properties are the **state variables** of the system. The state of the system is completely described by these state variables.

Other properties of the system can be expressed as **state functions** of the state variables. For example, suppose that one takes the temperature and volume to be the state variables. Then the relations

$$p = p(\theta, V), \quad U = U(\theta, V) \tag{4.1.10}$$

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[6] this is not always the case; it should be emphasised that the number of state variables needed to completely characterise a material undergoing a certain process is, in the final analysis, determined from experiment

[7] the symbol θ denotes the **absolute temperature**, with $\theta > 0$

are state functions for the pressure and internal energy. Equations involving the various properties of a system, as in 4.1.10, are also called **equations of state**. The first of these, relating force variables (in this simple case, the pressure p) to kinematic variables (in this case, the volume V) and temperature, is called a **thermodynamic** (or **thermal**) **equation of state**. The second, relating the internal energy to a thermal variable (here temperature) and a kinematic variable, is called a **caloric equation of state**.

Different sets of state variables may be chosen. For example, taking p and θ to be the state variables, the state functions would be

$$V = V(p,\theta), \quad U = U(p,\theta) \qquad (4.1.11)$$

A key feature of a state function is that its value is determined from the values of the state variables; its value does not depend on the particular path taken to reach the current state. For example, the internal energy is a state function (by its own definition); if one chooses the state variables to be (p,V), the change in internal energy between states '1' and '2' is (compare with Eqn. 4.1.7)

$$\Delta U = \int_{p_1,V_1}^{p_2,V_2} dU = U(p_2,V_2) - U(p_1,V_1) \qquad (4.1.12)$$

The value of ΔU depends only on the values of the state variables, in other words its value is the same no matter what path is taken between A and C in Fig. 4.1.6.

$U = U(p,V)$ defines a surface U in $p-V$ space. The total differential of U is then[8]

$$dU = \left(\frac{\partial U}{\partial p}\right)_V dp + \left(\frac{\partial U}{\partial V}\right)_p dV \qquad (4.1.13)$$

Although the partial differentiation here means differentiation with respect to one variable only, it is conventional in classical thermodynamics to include a subscript to explicitly indicate this, as here – the subscript emphasises the variable which is held constant. This notation helps avoid confusion when the set of state variables being used is changed during an analysis.

These partial derivatives are themselves state functions; since the function U is known for all (p,V), so are its slopes.

4.1.8 Specific Properties

Specific properties are properties *per unit mass*. They are usually denoted by lower case letters. For example, the specific volume (reciprocal of the density) and specific internal energy are

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[8]

$$v = \frac{V}{m}, \quad u = \frac{U}{m} \tag{4.1.14}$$

where m is the mass of the system. The properties V and U are **extensive properties**, meaning they depend on the amount of substance in the system. The specific properties on the other hand are **intensive properties**, meaning they do not depend on the amount of substance. Other intensive properties are the temperature θ and pressure p.

One can also express the heat and work as per unit mass:

$$\delta q = \frac{\delta Q}{m}, \quad \delta w = \frac{\delta W}{m} \tag{4.1.15}$$

4.1.9 Heat Capacity

Specific Heat and the Enthalpy

The **heat capacity** is defined as *the amount of heat required to raise the system by one unit of temperature*, so the higher the heat capacity, the more the heat required to increase the temperature. For example, water has a very high heat capacity, so it requires a lot of heating to increase its temperature. By the same token, it can give out a lot of heat without dropping in temperature too quickly (hence its use in hot water bottles).

The amount of heat required to raise the temperature by a fixed amount is path-dependent, depending as it does on the amount of accompanying work carried out, so the heat capacity as defined above is ambiguous. To remove this ambiguity, one can specify the path taken during which the heat is added; the two common paths chosen are those at constant volume and at constant pressure.

From Eqn. 4.1.8, the **heat capacity at constant volume** is, by definition,

$$C_V \equiv \left(\frac{\delta Q}{d\theta} \right)_V = \left(\frac{\partial U}{\partial \theta} \right)_V \tag{4.1.16}$$

In this case, all the supplied thermal energy goes into raising the temperature of the body. Note that C_V is a state function; this is clear from the fact that there is no path dependence involved in its evaluation.

The question arises: what is the volume which is held "constant"? Although C_V will in general depend on the V chosen, this dependence is very weak for many materials; a material is usually assigned a value for C_V without reference to the volume at which it is measured.

The **heat capacity at constant pressure** is by definition

$$C_p \equiv \left(\frac{\delta Q}{d\theta}\right)_p = \left(\frac{\partial U}{\partial \theta} + p\frac{\partial V}{\partial \theta}\right)_p = \left(\frac{\partial H}{\partial \theta}\right)_p \qquad (4.1.17)$$

where H is the **enthalpy**, defined by

$$H = U + pV \qquad (4.1.18)$$

In this case, some of the thermal energy is converted into work, and so $C_p \geq C_V$.

The enthalpy is a state function, since U, p and V are (either state functions or state variables). As with $C_V = (\partial U / \partial \theta)_V$, the heat capacity $C_p = (\partial H / \partial \theta)_p$ is also state function.

Note that, for an incompressible material, $C_V = C_p = \partial U / \partial \theta$ and there is no ambiguity as to its meaning. Most fluids are incompressible, or nearly so, and solids are also often approximated as incompressible for heat capacity measurements. The case of gases will be discussed below.

Internal Energy Measurements

Suppose now that the heat capacity at constant volume has been carefully measured over a given temperature range, by recording the heat required to effect increments in temperature. The internal energy changes within that range can then be found from

$$\Delta U = U_2 - U_1 = \int_{\theta_1}^{\theta_2} C_V d\theta \qquad \text{(constant volume)} \qquad (4.1.18)$$

Although this measurement technique requires constant volume processes, since internal energy is a property the results apply to *all* processes.

Some values for the specific internal energy and enthalpy of steam for a range of temperatures, pressures and specific volumes are given in Table 4.1.1 below. The reference state for internal energy (where u is chosen to be zero) is for saturated water at 0.01°C. The corresponding reference state for the enthalpy is obtained from 4.1.17[9].

θ (^0C)	v (m³/kg)	u (kJ/kg)	h (kJ/kg)
120	1.793	2537.3	2716.6
200	2.172	2658.1	2875.3
280	2.546	2779.6	3034.2
360	2.917	2904.2	3195.9

Table 4.1.1a: Properties for steam at pressure $p = 0.1$MPa

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[9] note that u and h can take on negative values, depending on the reference state chosen

p (MPa)	v (m³/kg)	u (kJ/kg)	h (kJ/kg)
0.035	6.228	2660.4	2878.4
0.100	2.172	2658.1	2875.3
0.300	0.716	2650.7	2865.5
0.500	0.425	2642.9	2855.4

Table 4.1.1b: Properties for steam at temperature $\theta = 200^0\text{C}$

4.1.10 The Ideal Gas

A **thermally perfect gas** is one for which the thermal equation of state is

$$pV = mR\theta \quad \text{or} \quad pv = R\theta \qquad (4.1.19)$$

where R is the universal gas constant. Further, an **ideal gas** is a thermally perfect gas whose internal energy depends on the temperature only, that is, its caloric equation of state is of the form

$$U = U(\theta) \qquad (4.1.20)$$

To justify this expression from a physical point of view, consider a gas at the microscopic level. Internal energy and pressure are related through intermolecular forces. If the pressure is very low, the internal energy is no longer affected by these forces, since the molecules are so far apart, but only by their kinetic energy of motion, i.e. the temperature. Moderate changes in volume will not bring the molecules of gas close enough together to alter this sole dependence on temperature.

When the internal energy is a function of θ and V, one has

$$dU = \left(\frac{\partial U}{\partial \theta}\right)_V d\theta + \left(\frac{\partial U}{\partial V}\right)_\theta dV = C_V d\theta + \left(\frac{\partial U}{\partial V}\right)_\theta dV \qquad (4.1.21)$$

Thus for an ideal gas

$$dU = C_V d\theta . \qquad (4.1.22)$$

Example

Consider an ideal gas undergoing a volume change under **isothermal**, i.e. constant temperature, conditions. From 4.1.19, the quantity $pV = p_1V_1 = p_2V_2$ is a constant $mR\theta$. This constrains the process to lie on one particular path in a $p-V$ diagram. Also, from 4.1.22, $dU = 0$ and so $\delta Q = -\delta W$. If an ideal gas expands at constant temperature then the heat input exactly equals the work done against an incrementally changing external pressure.

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Consider now a process involving work and heat transfer. One has $\delta Q = C_V d\theta + p dV$ and the total heat input is

$$Q = \int \delta Q = \int_{\theta_1}^{\theta_2} C_V(\theta) d\theta + \int_{p_1,V_1}^{p_2,V_2} p dV \qquad (4.1.23)$$

The second integral here clearly depends on the exact combination of pressure and volume during the process, so the heat input Q is path dependent, as expected. However, consider the following:

$$
\begin{aligned}
\int \frac{\delta Q}{\theta} &= \int_{\theta_1}^{\theta_2} \frac{C_V(\theta)}{\theta} d\theta + \int_{p_1,v_1}^{p_2,V_2} \frac{p dV}{\theta} \\
&= \int_{\theta_1}^{\theta_2} \frac{C_V(\theta)}{\theta} d\theta + mR \int_{V_1}^{V_2} \frac{dV}{V} \\
&= \int_{\theta_1}^{\theta_2} \frac{C_V(\theta)}{\theta} d\theta + mR \ln(V_2/V_1)
\end{aligned}
\qquad (4.1.24)
$$

The quantity on the right is now path independent. In fact, for the simple case where C_V is independent of θ, a good approximation for many "near-ideal" gases, one has

$$\int \frac{\delta Q}{\theta} = C_V \ln(\theta_2/\theta_1) + mR \ln(V_2/V_1) \qquad (4.1.25)$$

This expression means that, *for an ideal gas undergoing a quasi-static process*, although the quantity Q depends on the process, $\int \delta Q/\theta$ does not and so is a property. This property is called the **entropy** of the gas.

4.1.11 Problems

1. A gas is contained in a thermally insulated cylinder. It is very rapidly compressed so that its temperature rises sharply. Has there been a transfer of heat to the gas? Has work been done? Is the process quasi-static?

2. A gas expands from an initial state where $p_1 = 500\,\text{kPa}$ and $V_1 = 0.1\text{m}^3$ to a final state where $p_2 = 100\,\text{kPa}$. The relationship between pressure and volume during the particular process is $pV = k$, a constant. Sketch the process on a $p-V$ diagram and determine the work, in kJ. Interpret the $+$ or $-$ sign on your result.

3. A system, whose equation of state depends only on the volume V, temperature θ and pressure p, is taken (quasi-statically) from state A to state B along the path ACB at the pressures indicated in the figure below. In this process 40J of heat enter the system and 20J of work are done by the system.
   (a) evaluate ΔU
   (b) how much heat enters the system along the path ADB?

(c) if the system goes from *B* to *A* by the curved path indicated schematically on the figure, the work done on the system is 30J. How much heat enters or leaves the system?

(d) If the internal energy at *A* is denoted by U_A, etc., suppose that $U_D - U_A = 20J$. What then is the heat transfer involved in the processes *AD* and *DB*?
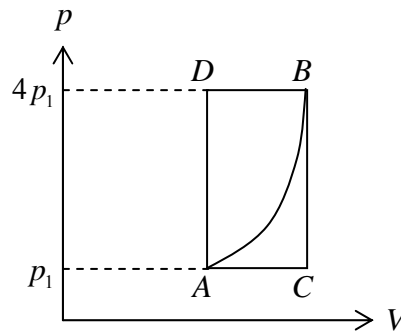
4. Air is contained in a vertical piston-cylinder assembly by a piston of mass $100\,\text{kg}$ and having a face area of $0.01\,\text{m}^2$. The mass of the air is 5 g, and initially the air occupies a volume of $0.005\ \text{m}^3$. The atmosphere exerts a pressure of $100\,\text{kPa}$ on the top of the piston. Heat transfer of magnitude $2\,\text{kJ}$ occurs slowly from the air to the surroundings, and the volume of the air decreases to $0.002\,\text{m}^3$. Neglecting friction between the piston and the cylinder wall, determine the change in specific internal energy of the air, in kJ/kg. [Note that the pressure is constant on the piston-head, and consists of the piston-weight and the atmospheric pressure.]

5. A closed system, i.e. one which can exchange heat or work with its surroundings, but not matter, undergoes a **thermodynamic cycle**[10] consisting of the following processes:

    Process 1-2:   adiabatic compression with $pV^{1.4} = \text{const.}$ from $p_1 = 344.74\,\text{kPa}$, $V_1 = 0.084951\,\text{m}^3$ to $V_2 = V_1/3$

    Process 2-3:   constant volume

    Process 3-1:   constant pressure, $U_1 - U_3 = 49.27317\,\text{kJ}$

    There are no significant changes in kinetic or gravitational potential energy.
    (a) sketch the cycle on a $p - V$ diagram
    (b) calculate the net work for the cycle
    (c) calculate the heat transfer for process $2 - 3$

6. How could you use the definition of the specific heat capacity at constant pressure to evaluate the internal energy of a material?

7. Show that for a system (not necessarily an ideal gas) undergoing a constant pressure process, the heat input is equal to the change in enthalpy.

8. Show that, for an ideal gas, $R = C_p - C_V$

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[10] meaning the substance is brought back to its initial state at the end of the process; state variables resume their initial values

9. Use the result of problem 8 to show that, when an ideal gas undergoes an adiabatic quasi-static change, $pV^{\gamma} = \text{const.}$ where $\gamma = C_p / C_V$.

10. In Table 4.1.1:
    (a) Does the steam behave like an ideal gas? Nearly? (Note the internal energies in Table 4.1.1b)
    (b) The internal energy decreases as the steam is compressed. Is this what you would expect? Comment.