Introduction to Thermodynamics and Kinetics

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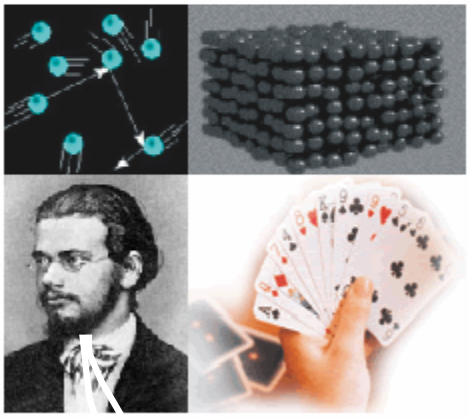
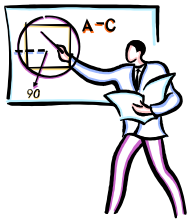


Lecture Notes

Set 4b: Heat, work, and the 1st law II



4.4 Heat and Work *(continued from Set 4a of the lecture notes)*

In the following sections we'll determine the heat input/output, the work done, and the change in internal energy for a number of important processes involving the change of state of a gas.

Isochoric heat transfer

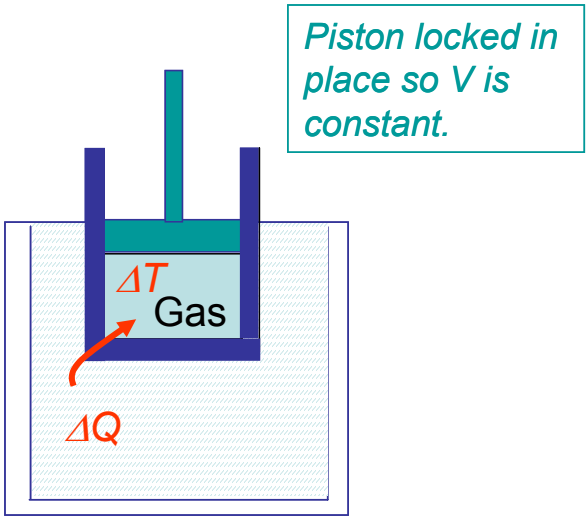


Fig. 4.9 *Isochoric heat transfer.*

In an isochoric process the volume of the gas is kept constant. To work out the amount of heat, Q, transferred to the gas for a given change in temperature, ΔT, we use the following simple formula:

$$Q = C_V \Delta T = (3R/2)\Delta T \qquad 4.6$$

where we assume that we have 1 mole of an ideal gas (see Section 2 of the lecture notes for a discussion of specific heats).

? *If Q is $(3R/2)$ for the isochoric process shown in Fig. 4.9, by how much does the internal energy change?*

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Isobaric heat transfer

In this case the pressure is kept constant and the gas is free to expand/ contract. To determine the heat input in this case we use another simple formula:

$$Q = C_P \Delta T = (5R/2)\Delta T \qquad 4.7$$

? *Write down an expression for the work done by the gas in the isobaric process shown in Fig. 4.10.*

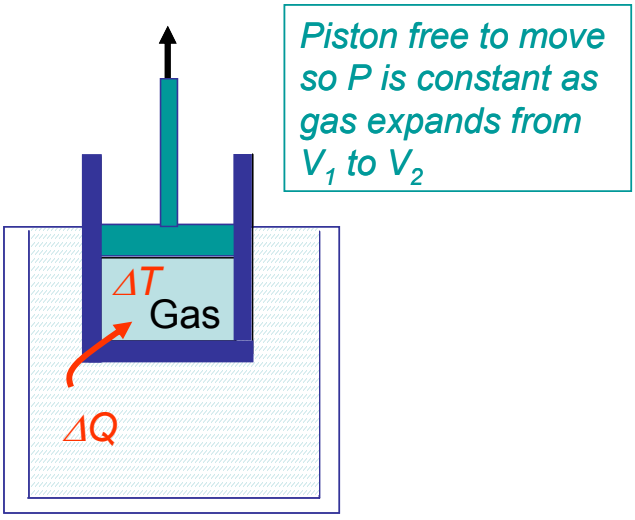

Fig. 4. 10 *Isobaric heat transfer*

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4.5 Adiabatic compression and expansion of an ideal gas

In what we've considered thus far, heat was transferred into or out of the gas. What happens if the compression of a gas is carried out under *adiabatic* (i.e. 'no Q') conditions?

Is it possible for the temperature of a gas to rise if there's no heat input?

For an adiabatic process, from the 1st law, how are the change in internal energy and the work done on the gas related?

If the temperature of an ideal gas changes by dT, by how much does its internal energy change?

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Equation of an adiabatic

We know that an isotherm for 1 mole of an ideal gas is defined by the equation $PV = RT$. In the following we'll derive an equation that relates pressure and volume for an adiabatic process. Note that adiabatic processes will be of particular importance when we discuss heat engines in later sections.

The differential form of the 1st law is $dU = dW + dQ$. For an adiabatic process dQ =0 and hence the change in internal energy and the work done are equivalent. The infinitesimal work done is given by:

$$dW = -PdV$$

We also know that for an ideal gas, $dU = C_V dT$. (Note that this is true of *any* process for an ideal gas - it doesn't matter whether the volume is kept constant or not. The internal energy of an ideal gas depends only on temperature).

Equating dU and dW :

$$C_V dT = -PdV \qquad 4.8$$

We're dealing with 1 mole of an ideal gas which means that $PV = RT$.

$$\Rightarrow C_V dT = -\frac{RT}{V} dV$$

$$\Rightarrow C_V dT + RT\frac{dV}{V} = 0$$

$$\Rightarrow C_V \frac{dT}{T} + R\frac{dV}{V} = 0 \qquad 4.9$$

? *Integrate equation 4.9.*

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Dividing the integrated form of Eqn. 4.9 through by C_V we get:

$$\ln T + \frac{R}{C_V}\ln V = c \qquad 4.10$$

where c is a constant. We've shown in Section 2 of the notes that $C_P = C_V + R$ (Eqn. 2.45). Hence, we can write Eqn. 4.10 as:

$$\ln T + \frac{C_P - C_V}{C_V}\ln V = c \Rightarrow$$
$$\ln T + (\gamma - 1)\ln V = c_2 \qquad 4.11$$

where c_2 is another constant (designated c_2 because it is a different constant from c). Rewriting Eqn. 4.11 taking into account the properties of logs:

$$TV^{\gamma-1} = constant \qquad 4.12$$

or,

$$PV^{\gamma} = constant \qquad 4.13$$

Equations 4.12 and 4.13 represent the *equation of an adiabatic.*

PV curve for an adiabatic and an isothermal process

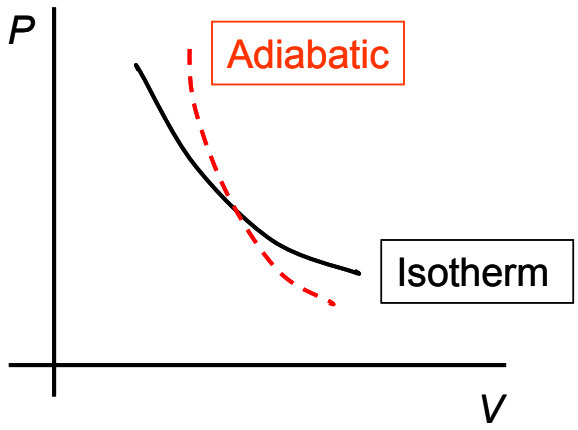


Fig. 4.11 *PV curves for an adiabatic and an isothermal process.*

On the diagram in Fig. 4.11, the adiabatic for the ideal gas has a slope γ times that of the isotherm for the ideal gas.

In Coursework Set 9 you will be asked to prove this.

Adiabatic work

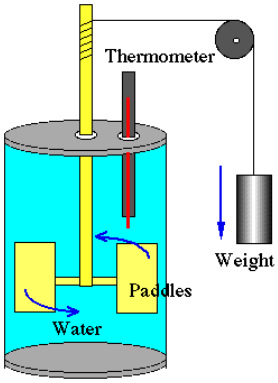
James Prescott Joule

We found in Section 4.4 that, in general, work is path dependent.
A question we need to answer is whether the "work is path dependen statement is true if we have an adiabatic process – i.e. a process where there is no heat input or output from the system. At the beginning of the 19th century Joule, prompted by measurements carried out by Benjamin Thompson, carried out a number of experiments to determine the precise 'form' of heat.

Joule's apparatus is shown in Fig. 4.12 below. The water is stirred by falling weights turning a paddle wheel. Importantly, the water is isolated from its surroundings by the *adiabatic* walls of the container.

Joule found that no matter how the adiabatic work was performed, it always took the same amount of work to take the water between the same two equilibrium states (whose temperatures differed by ΔT). This led Joule to surmise:

if a thermally isolated system is brought from one equilibrium state to another, the work necessary to achieve this change is independent of the process used.



This seems to contradict what was said above – it appears that the work done in this case *is* path independent. There is no contradiction for the following reason: $\Delta U = Q + W$. If $Q = 0$ (as is the case for adiabatic work) then $\Delta U = W$. The change in internal energy is always a function of state (regardless of whether the process is carried out adiabatically or not).

Adiabatic work is path independent.

Expression for work done in an adiabatic process

In the lectures we will derive an expression for the work done in an adiabatic process. This expression is:

$$W_{adiabatic} = \frac{P_2V_2 - P_1V_1}{\gamma - 1} \qquad 4.14$$

4.6 The distinction between heat and work

An important – and involved – question to address is the distinction between heat and work. Keeping with the spirit of our earlier discussions regarding the fundamentally probabilistic nature of thermal energy transfer we will distinguish between heat and work from a microscopic viewpoint. Note that a complete explanation requires a detailed consideration of statistical mechanics which is well beyond the scope of this module. However, relatively straight-forward qualitative arguments can be made which provide a reasonable insight into the distinction between heat and work.

When energy is added to a system in the form of *heat* we increase the *random* motion of the constituent molecules. However, when we increase the energy by performing *work* we displace molecules in an *ordered* way. A good example is that of a spring – stretching the spring (i.e. doing work on the spring) moves all the atoms in an ordered manner whereas simply heating the spring will not produce ordered motion of the atoms.

Another way of thinking of the distinction between heat and work is to consider the energy levels of the particles. If we consider the simple harmonic oscillator discussed throughout Section 3 of the notes, if energy is added to the oscillator in the form of heat then the populations of the energy levels will change i.e. there are differences in the number of arrangements of energy quanta which we can have. However, work doesn't change the populations of the energy levels, it merely shifts the energy levels (see slides for Lecture 14).

It now might appear that to have a change in entropy of a system an input of heat is always needed because this will provide a change in the populations of the energy levels (i.e. a change in the number of accessible microstates). This is not true – an important example of where a change of entropy occurs in the absence of any heat input is the *free expansion* of a gas. In a free expansion there is no temperature change and no heat enters the system. *However,* the *volume* of the gas increases and therefore a greater number of possible arrangements of the molecules in space is possible – this produces a change in entropy.

When we consider heat engines and the Carnot cycle in the following sections, the distinction between work and heat will again be important. In particular, we will consider the conversion of heat energy into useful mechanical work – there are fundamental limits (due to the 2^{nd} law of thermodynamics) on the efficiency of this conversion process.

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