Reversibility and the Calculation of Work

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5.1 Reversible changes

A process is reversible if the
system and surroundings return to their original state
when the process is reversed.

A reversible change can be carried out by making a tiny change, allowing the system to settle to equilibrium, making another tiny change, etc.

This is called a quasi-static change.

5.1.1 Reversible heat transfer

Imagine placing a pan of cold water onto a hotplate.
At first there is a temperature gradient which gradually disappears as the water warms up.
Imagine a film of this run backwards.
One would see a spontaneous development of a temperature gradient, something that never happens.
The process is irreversible.

For heat transfer to be reversible, no temperature gradients must occur.
This can be done by making a tiny increase in surrounding temperature, allowing the system to warm up, making another tiny increase, etc.

5.1.2 General Criterion for Reversibility

A reversible change is one which can be reversed in direction by an infinitesimally small change in the surroundings.

In reality all changes are irreversible, but it is possible to come close to reversibility.

Examples:

1. A piston of area A holds a gas at pressure P in equilibrium with an external force, $F = PA$. The applied force is suddenly doubled, $F' = 2PA$, causing compression.

   This is *irreversible*, because a small change in F', $\delta F' = 0.1PA$ say, would not reverse the compression.

2. A stone is heated to $T = 500\,°\mathrm{C}$ and thrown into water.

   This is *irreversible*, because a small change in temperature, $\delta T = 20\,°\mathrm{C}$ say, would still heat the water.

3. A sealed container of water and vapour is cooled, condensing some of the vapour.

   This is *reversible* if done slowly, because a tiny change in temperature can reverse the effect.

5.2 Calculating reversible work

The general definition of work is force times distance:

$$W = Fx$$

If the force is not constant, it can for instance vary as a function of position, hence F = F(x)

If we consider infinitesimal changes: $$đW = F(x)\,\mathrm{d}x$$

$$\Downarrow$$

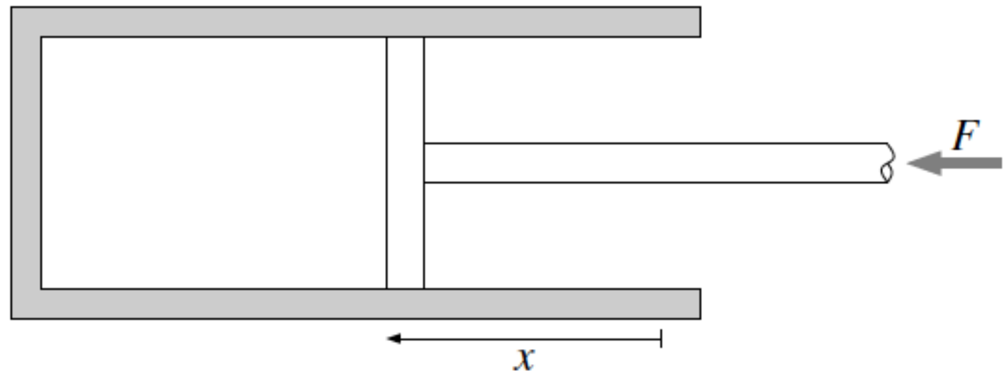
$$W = \int_{x_1}^{x_2} F(x)\,\mathrm{d}x$$

Example:

How much work is needed to extend a spring with force constant k from x_1 to x_2?

$$W = \int_{x_1}^{x_2} F(x)\,\mathrm{d}x = \int_{x_1}^{x_2} kx\,\mathrm{d}x = \left[\frac{1}{2}kx^2\right]_{x_1}^{x_2} = \frac{1}{2}k(x_2^2 - x_1^2)$$

5.2.1 Compressing a Gas



Let's consider the work done when compressing a gas with a piston. The piston is flat, has area A, and moves perpendicular to its surface. If the gas pressure is P, then the force needed to move the (frictionless) piston is F = PA.

To move the piston in by an amount dx requires an amount of work:

$$đW_R = F\,\mathrm{d}x = PA\,\mathrm{d}x$$

The subscript R indicates that the change is reversible. The change in volume of the gas is dV = -A dx (V decreases as x increases), and so

$$\boxed{đW_R = -P\,\mathrm{d}V}$$

$$\text{đ}W_R = -P\,\mathrm{d}V$$

this is a general result

Minus sign because this is the work done by the piston, which is the work done on the gas.

For a finite change:

$$W_R = \int_{V_1}^{V_2} -P\,\mathrm{d}V$$

5.3 Heat Capacities of Gases

For a reversible change, we know that:

$$đQ_R = \mathrm{d}U - đW_R = \mathrm{d}U + P\,\mathrm{d}V.$$

Since the right-hand side is a function of state,
this is a general relation for $đQ$
whether reversible or not.

If we consider 1 mole of ideal gas:

$$PV = RT_{\mathrm{I}}$$

$$\mathrm{d}U = C_V\,\mathrm{d}T_{\mathrm{I}}$$

If we consider a change at constant pressure:

$$\mathrm{d}(PV) = P\,\mathrm{d}V = R\mathrm{d}T_{\mathrm{I}}$$

$$đQ_R = dU - đW_R = dU + P\,dV$$

$$dU = C_V\,dT_I \qquad d(PV) = P\,dV = R\,dT_I$$

Therefore the molar specific heat capacity at constant pressure C_P is given by

$$C_P = \frac{đQ}{dT_I} = \frac{C_V\,dT_I + R\,dT_I}{dT_I}$$

$$\boxed{C_P = C_V + R}$$

Relation between molar specific heats of an ideal gas at constant pressure and volume

5.3.1 Reversible Isothermal Compression of a Gas

For an ideal gas: $P = n_m R T_\mathrm{I} / V$

$$W_R = -\int_{V_1}^{V_2} P\,\mathrm{d}V = -\int_{V_1}^{V_2} \frac{n_m R T_\mathrm{I}}{V}\,\mathrm{d}V$$

If we consider isothermal changes, T_I is constant, therefore:

$$W_R = -n_m R T_\mathrm{I} \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = -n_m R T_\mathrm{I}\,[\ln V]_{V_1}^{V_2} = n_m R T_\mathrm{I} \ln\left(\frac{V_1}{V_2}\right)$$

if $V_1 > V_2$, the gas has been compressed
so work has been done on it

$W_R > 0$, which is OK since $\ln(V_1/V_2) > 0$

5.3.2 Reversible Adiabatic Compression

For an ideal gas: $P = n_m R T_\text{I}/V$

$$W_R = -\int_{V_1}^{V_2} P\,\mathrm{d}V = -\int_{V_1}^{V_2} \frac{n_m R T_\text{I}}{V}\,\mathrm{d}V$$

But we can no longer consider the temperature to be constant:

For an adiabatic change, $đQ = 0$

For a reversible change, $đW = -P\,\mathrm{d}V$

$\mathrm{d}U = đW + đQ$ becomes $\mathrm{d}U = đW$

$$\mathrm{d}U + P\,\mathrm{d}V = 0$$

For an ideal gas: $\mathrm{d}U = C_V \, \mathrm{d}T_\mathrm{I}$

↓

$\mathrm{d}U + P \, \mathrm{d}V = 0$ becomes $C_V \, \mathrm{d}T_\mathrm{I} + P \, \mathrm{d}V = 0$

If we consider one mole: $PV = RT_\mathrm{I}$

↓

$$C_V \, \mathrm{d}T_\mathrm{I} + RT_\mathrm{I} \frac{\mathrm{d}V}{V} = 0$$

If we divide by T_I: $C_V \frac{\mathrm{d}T_\mathrm{I}}{T_\mathrm{I}} + R \frac{\mathrm{d}V}{V} = 0$

And integrate, we obtain: $C_V \ln T_\mathrm{I} + R \ln V = \text{constant}$

Dividing by C_V and taking the exponential, we obtain:

$$T_\mathrm{I} V^{R/C_V} = \text{constant}$$

$$T_I V^{R/C_V} = \text{constant}$$

If we multiply both terms by R and remember that PV=RT$_I$, we can write:

$$PVV^{R/C_V} = PV^{(C_V+R)/C_V} = \text{constant}$$

We know that: $C_P = C_V + R,$

We can define the ratio of specific heats as:

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V}$$

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

$$\boxed{PV^{\gamma} = \text{constant}}$$

Although derived for one mole, since the heat capacities are in the form of a ratio, this expression is general

The ratio of specific heats γ is greater than unity

$$P \propto 1/V^{\gamma}$$ is steeper than $$P \propto 1/V$$

adiabatic case

isothermal case

as you compress a gas adiabatically its temperature rises which increases the pressure compared to the isothermal case

all the work applied
is stored as internal energy during an adiabatic compression.

The adiabatic pressure-volume relation applies to sound waves

It can be shown that the speed of sound can be written as:

$$C_S = \sqrt{\gamma R T_I / m}$$

where m is the mass of one mole of gas

measurements of sound speed,
which can be done very accurately,
can give estimates of γ

We saw how to estimate heat capacities from the equipartition theorem. For a monatomic gas we had $C_V = 3R/2$, therefore $C_P = 3R/2 + R = 5R/2$, and so $\gamma = C_P/C_V = 5/3 = 1.666$. For diatomic gases such as nitrogen, we found that without excitation of vibrations, $C_V = 5R/2$, and therefore $\gamma = 7/5 = 1.4$. This is the value that applies to air.

Let us consider a gas with initial pressure P_1 and initial volume V_1:

If the gas expands/compresses to V_2, the work done will be:

$$W_R = -\int_{V_1}^{V_2} P\,\mathrm{d}V = -P_1V_1^{\gamma}\int_{V_1}^{V_2}\frac{\mathrm{d}V}{V^{\gamma}}$$

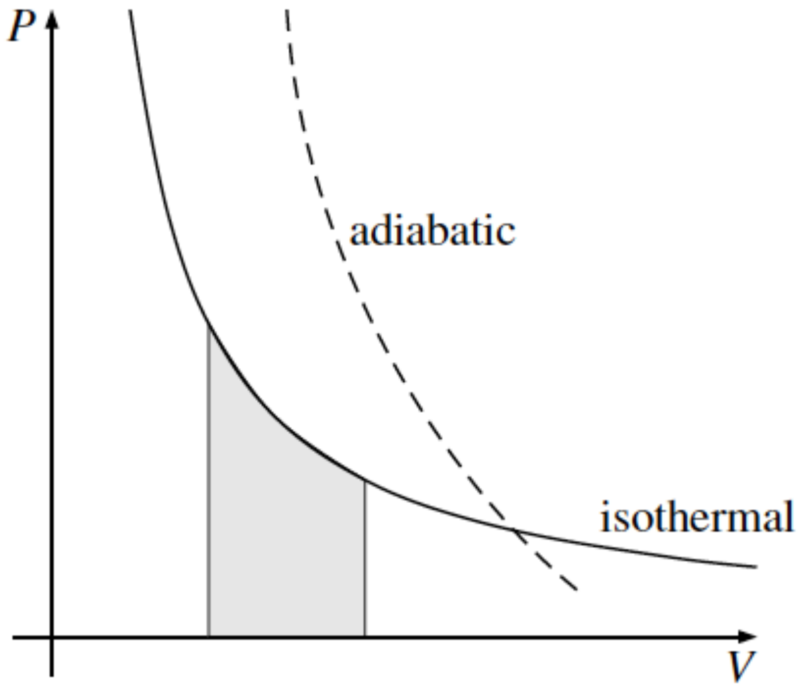
$$= -P_1V_1^{\gamma}\left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V_1}^{V_2} = \frac{P_1V_1}{\gamma-1}\left[\left(\frac{V_1}{V_2}\right)^{\gamma-1} - 1\right]$$

For a compression we expect $W_R > 0$, then $V_1 > V_2$ (and $\gamma > 1$)

In a Joule expansion, no work is done and the process is irreversible, therefore there is no Joule compression

5.4 Indicator Diagrams

Indicator diagrams or pressure-volume (P-V) diagrams are used to describe, for instance, phase transitions in gases or cycles of engines



The work done to change a volume is given by:

$$-\int P \, \mathrm{d}V$$

in an indicator diagram this equals the area under the curve

As discussed, the adiabatic change is steeper than the isothermal one

5.5 Other forms of work

Form of Work	Expression	Comment
Gas compression	$-P\,dV$	most common form in this course
Magnetic work	$\mathbf{B}\cdot d\mathbf{m}$	$\mathbf{m}$ is the magnetic dipole moment of a specimen
Electrical work	$\mathbf{E}\cdot d\mathbf{p}$	$\mathbf{p}$ is the electric dipole moment of a specimen
Battery	$\mathcal{E}\,dq$	q is the charge that flows, $\mathcal{E}$ is the voltage
Spring, rubber band	$F\,dL$	L is the length

the expressions of work are all of the same form Y dX
where X is some coordinate defining a system
Y is an associated force.
The X variable is extensive: it scales in proportion to the size of system
The Y force is intensive: it does not scale with the size of the system

General expression for reversible work:

$$W_R = -P\,dV + F\,dL + \mathbf{B}\cdot d\mathbf{m} + \cdots$$

5.6 Summary

Reversible processes, although an idealisation, are at the heart of equilibrium thermodynamics, and lead to the evaluation of quantities of interest such as work.

For gases, we have shown that: $W_R = -P\,\mathrm{d}V$

For ideal gases and adiabatic changes: $PV^{\gamma} = \text{constant}$

where γ is the ratio of the specific heat capacity at constant pressure to the specific heat capacity at constant volume.

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V}$$