School of Physics and Astronomy

Junior Honours **Thermodynamics**   GJA 2019-2020

TOPIC 2: PROCESSES (Finn: 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.10, appendix B)
   Synopsis: Basic properties of basic systems. Reversible processes. Mechanical work. Some mathematics and strategy for solving problems.

States and processes

The State of a system is defined by its **state variables**, e.g. P, T, V. When a system is involved in a **process**, the values of its state functions (variables) change. A **process** typically involves quantities like Heat and Work which are *not* state variables.
   Consider a process between equilibrium endpoints (starting point and finishing point) eg the compression of gas by a piston from state (P_1, V_1) to state (P_2, V_2). For a **reversible** process, every (infinitesimal) step – for both the system and its surroundings – can be reversed. If you watch a film of the process played backwards, it would not look strange. The system goes through a sequence of equilibrium states, which implies that a reversible process is **quasistatic**.

> *Reversible processes are quasistatic processes where no dissipative forces such as friction are present*

Reversible & irreversible processes on indicator diagrams

A **reversible process** can be represented by a **continuous line** and arrow on an indicator diagram.
An **irreversible process** cannot be represented by a continuous line on an indicator diagram. Such a process may be represented on the graph by a sequence of circles between equilibrium states but only the end points are well-defined. In particular if the process is not quasistatic (for example if a piston moves too quickly, temperature and pressure gradients might be set up) the values of the state variables will not be uniform and therefore pressure and density *cannot be defined* for the whole sample.
You **cannot integrate** with a variable that cannot be defined. So the work done in an irreversible process cannot be found by integration.
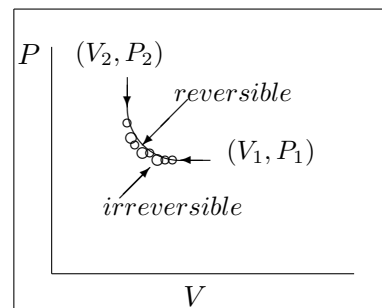
Indicator diagram for isothermal compression of a gas.

### Work done during a reversible change of volume of a fluid

This could be the response to a gradual change in force on a piston or to slow heating (a change in temperature). The area A of the piston multiplied by the pressure P of the fluid balances the force $\mathcal{F}$ on the piston $\mathcal{F} = PA$. The fluid expands or contracts quasistatically, with the piston moving infinitesimal distances dx much more slowly than the time the system take to reach equilibrium at the new volume. The infinitesimal amount of work done **reversibly** by the system on its surroundings is $PAdx = PdV$. For a finite quasistatic change in volume from V_1 to V_2, the total work done on the surroundings is:
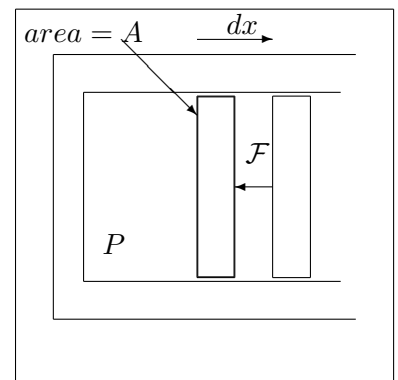
$$\text{work done on surroundings} = \int_{V_1}^{V_2} PdV \quad \text{[reversible changes]}$$

The total work done depends on the process even for reversible changes

Work is the area under the graph on a PV diagram. e.g. For an ideal gas, work done moving from equilibrium state (P_1, V_1, T_1) to (P_2, V_2, T_2) depends on the process. Suppose $T_2 = T_1 = T$. For an isothermal expansion the work done is given by $nRT \ln(V_2/V_1)$; path 1–2 (isothermal) in the sketch. For path 1–3–2, a different amount of work is done given by:
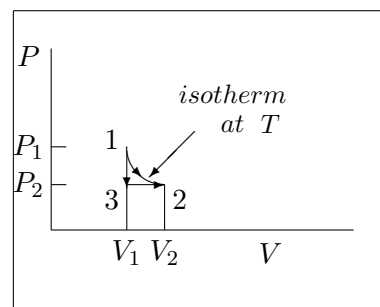
$$\text{work done on surroundings} = \int_{V_1}^{V_2} P\,dV = 0 + \int_{V_1}^{V_2} P_2\,dV = P_2(V_2 - V_1)$$

Sign convention

In physics (as opposed to engineering) we are generally interested in changes of the system and therefore consider work to be defined as the work done **ON** the system by its surroundings. Hence for a reversible change of volume of a system consisting of a fluid,

$$\boxed{đW = -P\,dV}$$

If dV is negative, the gas is compressed and the work done on it, $-P\,dV$, is positive. Getting the right sign for work is a source of endless problems. You should always sanity-check the sign by thinking about the physics.

    The work done *on* the system is always equal and opposite to the work done *by* the system. If the system is undergoing an irreversible process, we can't define the integral $P_{system}dV$, but we might be able to define $P_{surroundings}dV$.

Dissipative processes

Unlike for a reversible process where we can specify $đW = -P\,dV$, it is not possible to specify work done in terms of state variables of the system for dissipative processes, eg stirring. Although the work done may be quantified, this requires knowledge of external forces. Reversing the process, via controlling the surroundings, does not reverse the sign of the work done eg reversing the direction of stirring does not extract energy from the system. Therefore dissipative processes $\Rightarrow$ **irreversible**. Irreversible processes where there is no direct dissipation (conversion of work into random motion) can also occur eg the irreversible flow of heat between bodies at different temperatures (we will see later that this represents a loss of potential to do work).

Some Mathematics of State Variables and Exact Differentials

Let ϕ be a function of x and y such that whatever the values of x and y, $\phi = \phi(x, y)$ has a unique value. An infinitesimal change $d\phi = (\frac{\partial \phi}{\partial x})_y dx + (\frac{\partial \phi}{\partial y})_x dy$ is then, by definition, an exact differential since it is the complete differential of an exactly defined function.

    Let x change from x_1 to x_2, and y change from y_1 to y_2. The finite change in ϕ is then $\Delta\phi$:

$$\Delta\phi = \phi(x_2, y_2) - \phi(x_1, y_1) = \int_{x_1, y_1}^{x_2, y_2} d\phi$$

So $\Delta\phi$ is known exactly from the unique values of ϕ at the points (x_1, y_1) and (x_2, y_2), *whatever the values of x and y along the integration path*. The integral is **path-independent**. The value of ϕ, depends only on the final state.

The defining mathematical property of a state variable is that it has exact differentials, so we can write $\phi(x, y)$, and

$$\boxed{\frac{\partial^2 \phi}{\partial x \partial y} = \frac{\partial^2 \phi}{\partial y \partial x}}$$

i.e. the second derivative is independent of the order of differentiation

For a system whose state f is described by n independent variables $f(x_1, x_2, \ldots, x_n)$ we have:

$$\frac{\partial^2 f}{\partial x_i \partial x_j} = \frac{\partial^2 f}{\partial x_j \partial x_i}$$

$$\boxed{\textit{State variables in thermodynamics have path-independent integrals.}}$$

This is an incredibly useful result. If we want to know the change in a state variable due to some process, we can find it by considering any other process between the same start and end point. So we can choose a process which gives us an easy integral to solve.

Inexact differentials

Re-working the above argument backwards, suppose that the integral of some differential form $đ\phi$ is path-dependent. Then the integral cannot be expressed as the difference of a *function* ϕ evaluated at the specified limits of the integration. Work $dW = PdV$ is like this, it can not be a state function. An infinitesimal change in W is therefore an inexact differential and is written $đW$ (the bar indicating an inexact differential quantity).

So we have to be careful, because

$$\boxed{\textit{Processes in thermodynamics typically have path-dependent integrals.}}$$

and worse..

$$\boxed{\textit{Irreversible processes in thermodynamics cannot be described by integrals.}}$$

Work is not a state function!

Consider work, defined by $đ$ W=-PdV.

If work were an exact derivative, there must be a function W(P,V) such that:

$$dw = \left(\frac{\partial W}{\partial P}\right)_V dP + \left(\frac{\partial W}{\partial V}\right)_P dV \tag{1}$$

From the definition, we see $(\partial W \partial P)_V$ is zero while $(\partial W / \partial V)_P = -P$. Differentiating again gives :

$$\frac{\partial}{dV}\left(\left(\frac{\partial W}{\partial P}\right)_V\right)_P = 0 \tag{2}$$

$$\frac{\partial}{dP}\left(\left(\frac{\partial W}{\partial V}\right)_P\right)_V = -1 \tag{3}$$

Clearly $đW$ is not an exact differential, and no state function with total derivative $đW$ can exist. To find the finite work done going between two states, $(\Delta W = \int đW)$ we must specify the path, i.e. the trajectory of (P, V) on the indicator diagram.

In general if we have a differential quantity $dc \equiv Ada + Bdb$ and we want to know whether the integration of this function between two point (a_1, b_1) and (a_2, b_2) depends upon the path the necessary and sufficient condition for the result to be path independent is :

$$\left(\frac{\partial A}{\partial b}\right)_a = \left(\frac{\partial B}{\partial a}\right)_b \tag{4}$$

If this condition is satisfied the integral is the difference between the values of a state function $c(a, b)$ at the two end points. If not satisfied the symbol $đc$ should be used and the path of integration has to be specified.

Two useful tricks - Reciprocal & Cyclic rules

Suppose we have a function $z(x, y)$. Then we can write,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad \text{and similarly,} \quad dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \quad (5)$$

Substituting one into the other gives

$$\left\{1 - \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y\right\} dz = \left\{\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x\right\} dy \quad (6)$$

But dy & dz are independent and arbitrary. Therefore both coefficients must be zero, giving

$$\boxed{\text{reciprocal rule:} \quad \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y} = \left(\frac{\partial x}{\partial z}\right)_y} \qquad \boxed{\text{cyclic rule:} \quad \left(\frac{\partial z}{\partial y}\right)_x = -\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z} \quad (7)$$

The above equations also work when there are more variables; the extra variables are just held constant in all the derivatives. The reciprocal rule is quite intuitive. The cyclic rule warns us of the danger of dropping from the notation the symbols showing which variables are held constant. We might be tempted to 'cancel' ∂x from both numerator and denominator on the RHS of EQN 7, but this is only allowed if the same variables are held constant in both functions, which is not the case.

Example

Question: The state of a compressible fluid is changed reversibly and infinitesimally from (P, T) to $(P + \Delta P, T + \Delta T)$. How much does the volume change ?

First, write the problem as an integral in the form that gives the state function whose change we wish to find, as a differential in terms of the state variables whose changes are given

$$V = V(P, T) \qquad \Longrightarrow \qquad dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

Next, identify the partial derivatives. e.g. the volume thermal expansivity β and isothermal bulk modulus are defined in differential form as,

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P ; \qquad K = -V\left(\frac{\partial P}{\partial V}\right)_T$$

So, expressing the differentials in terms of standard definitions of properties,

$$\Delta V = \int dV = -\int \frac{V}{K} dP + \int \beta V \, dT$$

In general, K and β depend on the material, but lets suppose they are constants. Because $V = V(T, P)$ is a state variable, we can do the integral along any path. For simplicity, choose a reversible two-stage path which first goes isothermally from P to $P + \Delta P$, then isobarically from T to $T + \Delta T$.

For stage 1, $dT = 0$, and let $V \to V_1$. We can rearrange to get

$$\int \frac{1}{V} dV = -\int \frac{1}{K} dP \implies \ln(V_1/V) = -\Delta P/K$$

For stage 2, $dP = 0$ and volume goes from $V_1 \to V + \Delta V$

$$\int \frac{1}{V} dV = \int \beta dT \implies \ln((V + \Delta V)/V_1) = \beta \Delta T$$

Cancelling the V_1 for the total change and rearranging we have:

$$V + \Delta V = V \exp(-\Delta P/K) \exp(\beta \Delta T)$$

Note that had we done the isobaric process before the isothermal one, the answer would have come out the same. If we had considered an irreversible path, the answer would still be the same *even though the integral isn't defined for an irreversible process.*