Equilibrium implies the existence of a thermodynamic quantity

Mechanical equilibrium implies Pressure

Thermal Equilibrium implies Temperature

Zeroth LAW of thermodynamics: There exists a single quantity which determines thermal equilibrium

Named by RH Fowler, great great grandsupervisor to Prof Ackland
Some more definitions?

Process:
when the state variables change in time.

Reversible Process:
when every step for the system and its surroundings can be reversed.
A reversible process involves a series of equilibrium states.

Irreversible Process - when the direction of the arrow of time is important.

IRREVERSIBILITY DEFINES THE CONCEPT OF TIME.
Reversible processes are quasistatic - system is in equilibrium and the trajectory can be drawn on a PV indicator diagram.

Irreversible processes proceed via non-equilibrium states, with gradients of $T$ and $P$, where the system would continue to change if the external driving force is removed (e.g. stirring).

It is possible to get between two states of a system by reversible OR irreversible process. The final state of the system is the same regardless of reversibility, but the surroundings are different.
How to tell if a process is reversible

Consider a process between equilibrium endpoints (starting point and finishing point)

eg compression of gas by a piston from state \((P_1, V_1)\) to \((P_2, V_2)\).

For a **reversible** process, every (infinitesimal) step – for both the system and its surroundings – can be reversed.

Traversing a sequence of equilibrium states:

Reversible processes are quasistatic processes where no dissipative forces such as friction are present.
Eugene Wigner

”The Unreasonable Effectiveness of Mathematics in the Natural Sciences”
Can you integrate it?

A **reversible process** keeps the system at equilibrium and can be represented by a **continuous line** on an indicator diagram.

An **irreversible process** cannot be represented by a continuous line on an indicator diagram.

- If \( P, V, T \) vary in space, they cannot be uniquely defined.
- Sequence of circles indicates a range of values in system.
- If \( P \) is not well defined, \( \int PdV \) makes no sense.
- Typically, fast processes will be unable to stay close to equilibrium.
e.g. slow heating or compression
Force on piston $F = PA$.
Infinitesimal movement of piston $dx$
Work done **reversibly** by the system on its surroundings
$PAdx = PdV$.

For a finite change from $V_1$ to $V_2$:

$$\text{work done on surroundings} = \int_{V_1}^{V_2} PdV \quad [\text{reversible changes}]$$

**Total work done depends on the process even for reversible changes**
Work done depends on the process

**Example: Ideal gas, reversible expansion**
from equilibrium state \((P_1, V_1, T_1)\) to \((P_2, V_2, T_2)\)

Suppose \(T_2 = T_1 = T\).
isorthermal expansion 1–2 the work done is given by:

\[
W = \int \frac{nRT}{V} dV = nRT \ln\left(\frac{V_2}{V_1}\right)
\]

For path 1–3–2, a different amount of work is done:

\[
W = 0 + \int_{V_1}^{V_2} P_2 dV = P_2(V_2 - V_1)
\]

**Total work done depends on the process even for reversible changes for a cyclic process –1–2–3–1–2–3– infinite work can be done!**
In physics and chemistry (as opposed to engineering) we are generally interested in changes of the system. Work defined as the work done ON the system by its surroundings. e.g. a reversible change in volume of a gas,

\[ dW = -PdV \]

If \( dV \) is negative, the gas is compressed and the work done on it, \(-PdV\), is positive.

In calculations it is always worth thinking about whether the energy of the system has increased or decreased.

Either convention will work, but you must be consistent and think, not memorise.
Work in dissipative, irreversible processes

- Cannot specify work done in terms of state variables of the system:
- Can measure work done by the surroundings
- Consider, eg stirring. Work is done, system may heat up, but $PdV = 0$
- Reversing the process may not reverse the sign of the work done. Reversing the direction of stirring: does not extract energy from the system.
- Dissipative processes are always irreversible. (n.b. irreversible processes needed not be dissipative)
Mathematical Challenges from Thermodynamics:

How to make sense of these changes?

How does the change of one state variable affect another?

How do the constraints on a third state variable affect this?

The necessary mathematical apparatus is Partial Differentials.

“How does a change in X affect Y, if Z is held constant?”
Amartya Sen (b. 1933):
Nobel Prize in Economics 1998
Sveriges Riksbank Prize in Economic Sciences in Memory of Alfred Nobel

Axioms of Poverty

- Given other things, a reduction in income of a person below the poverty line must increase poverty.
- Given other things, a pure transfer of income from a person below the poverty line to anyone who is richer must increase poverty.

Toward new frontiers: From relativistic continuum theory to socio-thermodynamics

09:35-10:10 Greame Ackland, The University of Edinburgh, UK A physicist’s view on measuring poverty

Symposium in Honor of the 75th Birthday and Scientific Life of Ingo Muller - December 15th-17th 2011 - Berlin
**Exact differentials**

Consider a single-valued state function $\phi(x, y)$.
Assume $d\phi$ defined by any TWO independent state functions, $(x, y)$.

$$d\phi = \left( \frac{\partial \phi}{\partial x} \right)_y dx + \left( \frac{\partial \phi}{\partial y} \right)_x dy$$

Changes in $\phi$ due to changes of $x$ and $y$

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

$\Delta \phi$ determined by the unique values of $\phi$ at $(x_1, y_1)$ and $(x_2, y_2)$.

The integral is **path-independent**.
Thermodynamic interpretation:

The integral change in state variable $d\phi(x, y)$ is **path-independent**.

*State variables in thermodynamics have path-independent integrals.*

- If a process takes a system from, $T_1, P_1$ to $T_2, P_2$, we can find the change in another state variable by integrating along ANY path.
- the change of a state variable due to an *irreversible process* can be calculated using an equivalent *reversible* process.
- this is for the System: the trick doesn’t work for the Surroundings.
The order of differentiation is unimportant

All state variables have the mathematical property that:

\[
\frac{\partial^2 f}{\partial x_i \partial x_j} = \frac{\partial^2 f}{\partial x_j \partial x_i}
\]

with the lazy notation that the \(n - 1\) other variables with \(j \neq i\) are held fixed in the operation \(\partial / \partial x_i\).

From SVC, this means \(f\) is a well behaved, differentiable function.

State variables are almost always well-behaved

The exception is at a phase transition: e.g. \((\frac{\partial V}{\partial T})_P\) on boiling.

With TWO independent variables, one is varying, and one held constant.

“Isothermal compression” is different from “Isobaric compression”:

\[
\left( \frac{\partial f}{\partial V} \right)_T \neq \left( \frac{\partial f}{\partial V} \right)_P
\]
Work fails to be a state function

Consider the previous argument backwards...

- Suppose that the integral $\delta \phi$ is **path-dependent**.
- The integral cannot be expressed as the difference of a function $\phi$.
- And so $\phi$ cannot be a State function.
- An infinitesimal amount work is defined by: $\delta W = -PdV$

So, is there a state function $W(P,V)$ such that:

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

Since $\delta W = -PdV$

$$\left( \frac{\partial W}{\partial P} \right)_V = 0; \quad \left( \frac{\partial W}{\partial V} \right)_P = -P$$

So we have

$$\frac{\partial}{dV} \left( \left( \frac{\partial W}{\partial P} \right)_V \right)_P = 0; \quad \frac{\partial}{dP} \left( \left( \frac{\partial W}{\partial V} \right)_P \right)_V = -1$$

The order of differentiation is important! Recall that the path on the $(P, V)$ diagram, has to be specified to find the integral, $\int \delta W$. 
State variables in thermodynamics have path-independent integrals.

Processes in thermodynamics typically have path-dependent integrals.

and worse..

Irreversible processes in thermodynamics cannot be described by integrals.

...but the change of state variables in an irreversible process can be calculated by integrating an equivalent reversible process.
CALCULATION STRATEGY - EXAMPLE

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

Write the state function whose change we wish to find, in terms of the state variables whose changes are given:

\[
V = V(P, T)
\]

\[
dV = \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial V}{\partial T} \right)_P dT
\]

\[
= -\frac{V}{K} dP + \beta V dT
\]

\(V\) is a state variable, so we can use any path we wish. Choose a reversible two-stage path: isotherm from \(V_0 \to V_1\) then isobar from \(V_1 \to V_2\).

\[
\Delta V = V \left( \exp\left[-\frac{\Delta P}{K}\right] \exp(\beta \Delta T) - 1 \right)
\]

Two terms change the volume: bulk modulus \((K)\) gives effect of pressure, thermal expansivity \(\beta\) gives effect of temperature.