

# PREVIOUSLY ON

...*Thermodynamics*

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:**

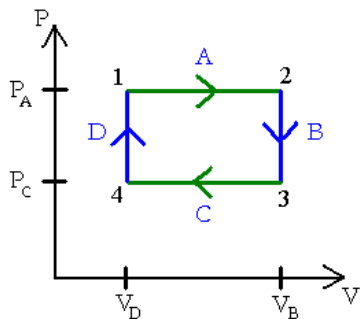
when every step for the system *and* its surroundings can be reversed.

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



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*

## ”The Unreasonable Effectiveness of Mathematics in the Natural Sciences”



VS

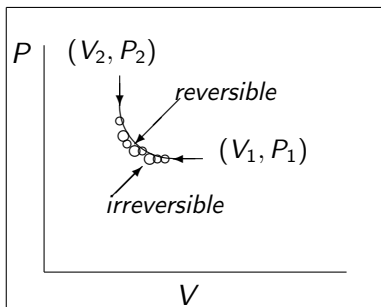


## E-ducation

## 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.

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

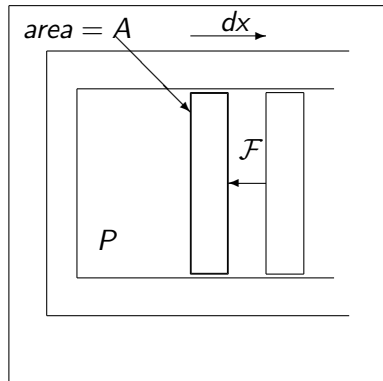
e.g. slow heating or compression

Force on piston  $\mathcal{F} = PA$ .

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  $(P_2, V_2, T_2)$

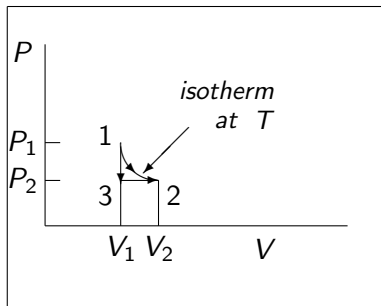
Suppose  $T_2 = T_1 = T$ .

isothermal expansion 1-2 the work done is given by:

$$W = \int \frac{nRT}{V} dV = nRT \ln(V_2/V_1)$$

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!**



# Sign convention

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 Graeme 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 Müller - 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:

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

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  $\int \vec{d}\phi$  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:  $\vec{d}W = -PdV$

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

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

Since  $\vec{d}W = -PdV$

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

So we have

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

The order of differentiation is important! Recall that the path on the  $(P, V)$  diagram, has to be specified to find the integral,  $\int \vec{d}w$ .



# Summary

*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

$$\begin{aligned} V &= V(P, T) \\ dV &= \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial V}{\partial T} \right)_P dT \\ &= -\frac{V}{K} dP + \beta V dT \end{aligned}$$

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

$$\Delta V = V (\exp[-\Delta P/K] \exp(\beta \Delta T) - 1)$$

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