Introduction to Classical Thermodynamics

Thermodynamic Universe
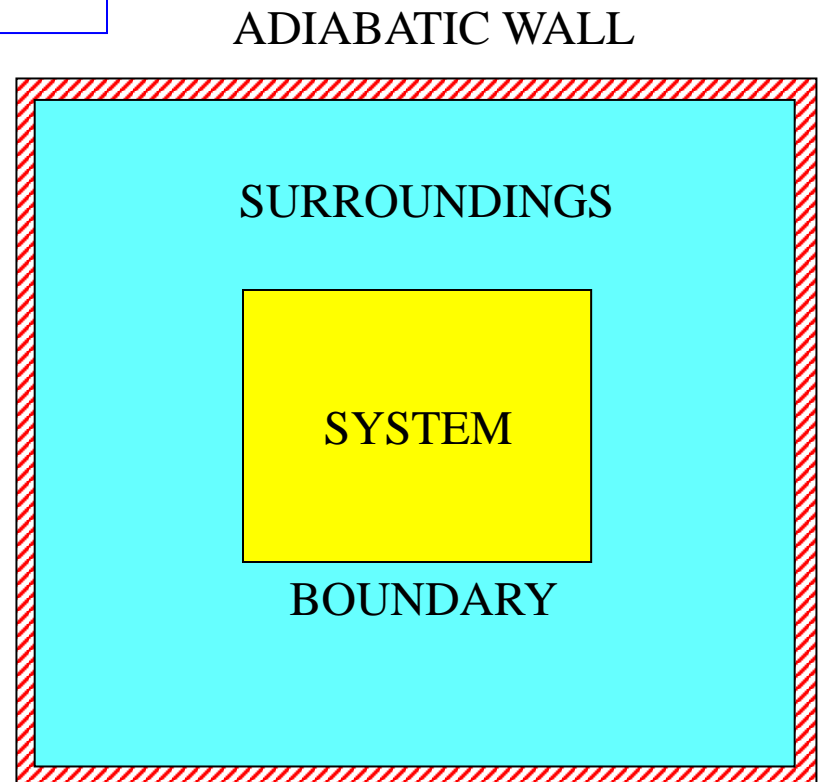
The system is separated from its surroundings by walls.

For closed systems the walls can be:

Adiabatic – no heat crosses wall

or

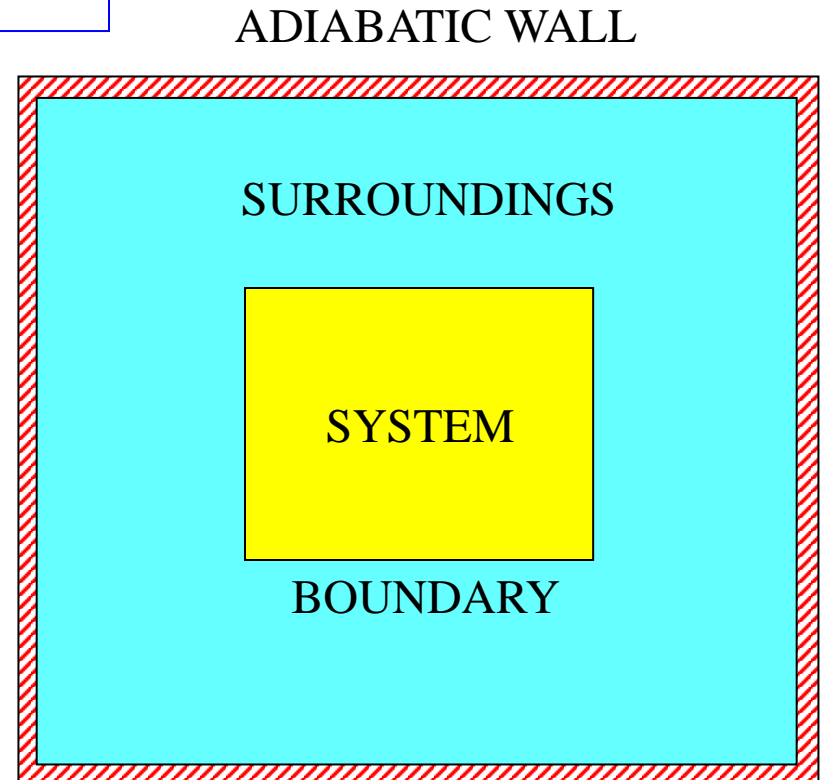**Diathermal** – heat passes through wall

ADIABATIC WALL

SURROUNDINGS

SYSTEM

BOUNDARY

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ADIABATIC WALL

Thermodynamic state

The system is in a thermodynamic state if macroscopic observable properties (e.g. P, V, T) have fixed, definite values. These measurable properties are variables of state.
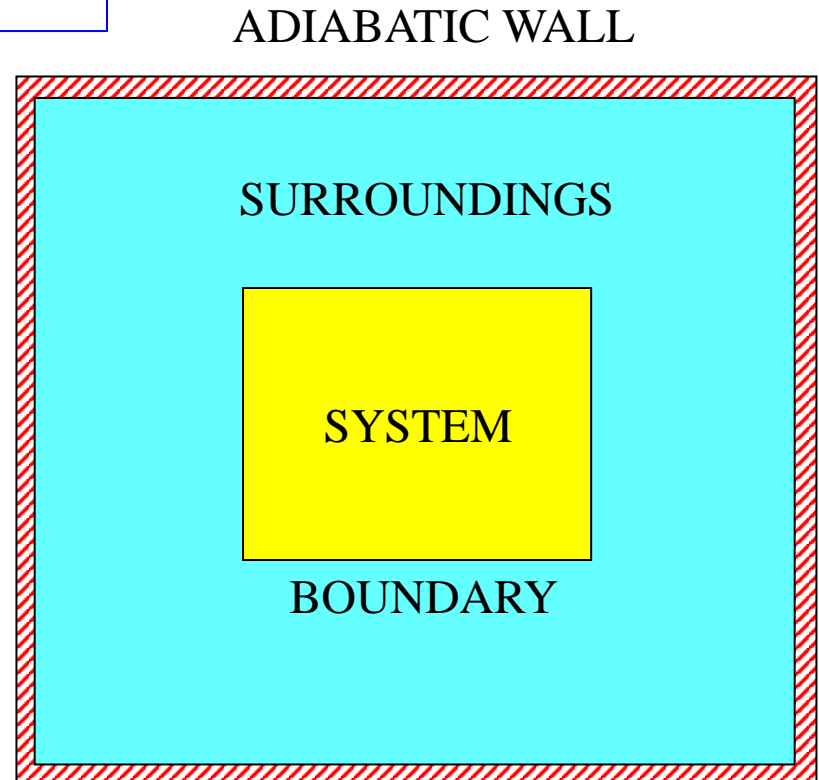
SURROUNDINGS

SYSTEM

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ADIABATIC WALL

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Equilibrium state

In equilibrium the variables of state are constant throughout the system and they do not vary with time.

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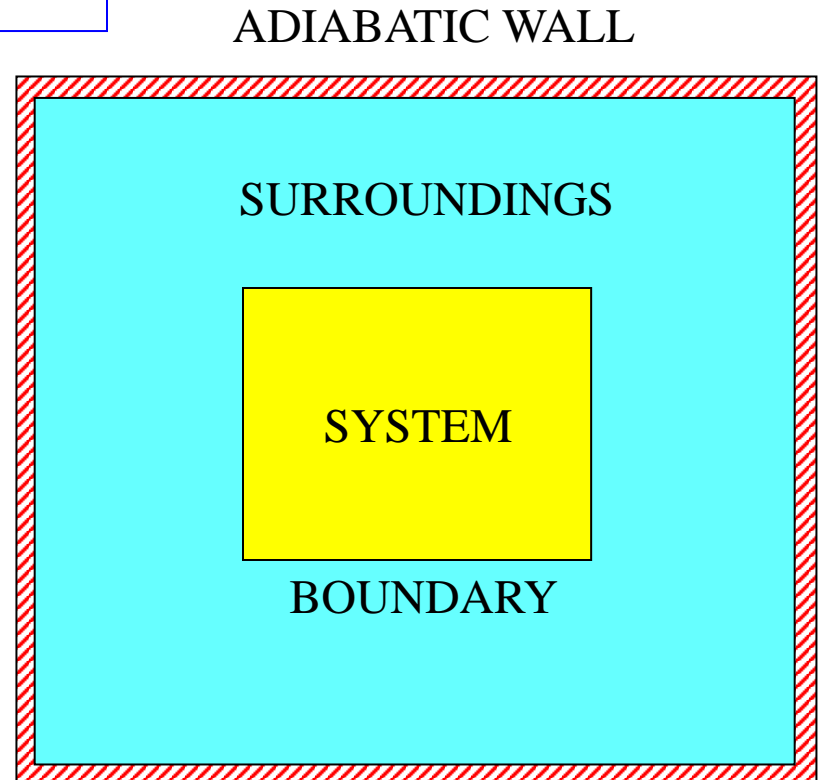**Concerned only with equilibrium states in this course**

SURROUNDINGS

SYSTEM

BOUNDARY

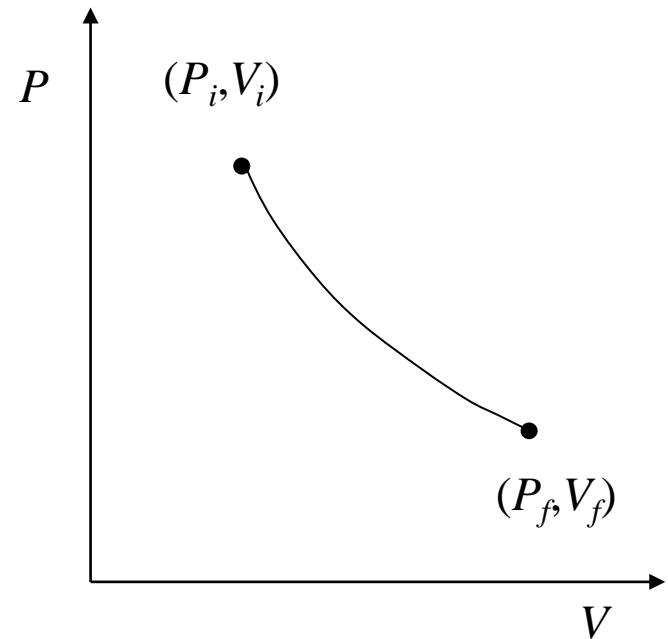# Introduction to Classical Thermodynamics

Indicator diagrams

Compressible Gases

P, V and T are the variables of state.

These three variables are related by an **equation of state**. For example, for an ideal gas $PV = NkT$. Therefore, there are two independent variables.
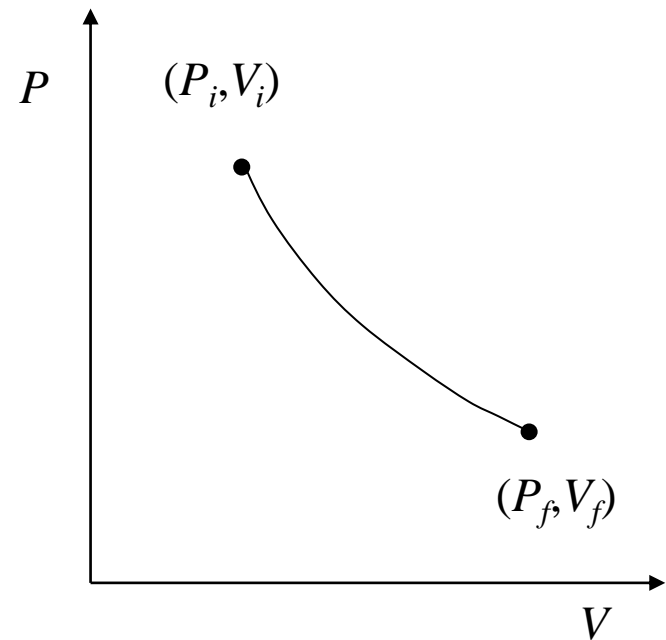
We can represent thermodynamic processes on a 2D indicator diagram.

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Reversible Process

A reversible process is one performed in such a way that, after its completion, the **system** may be taken back to its initial state with all **surroundings** also returned to their initial states.
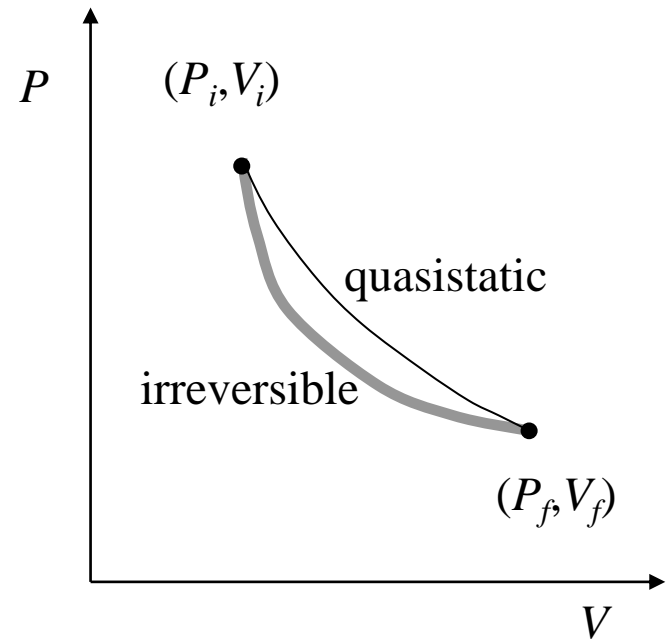
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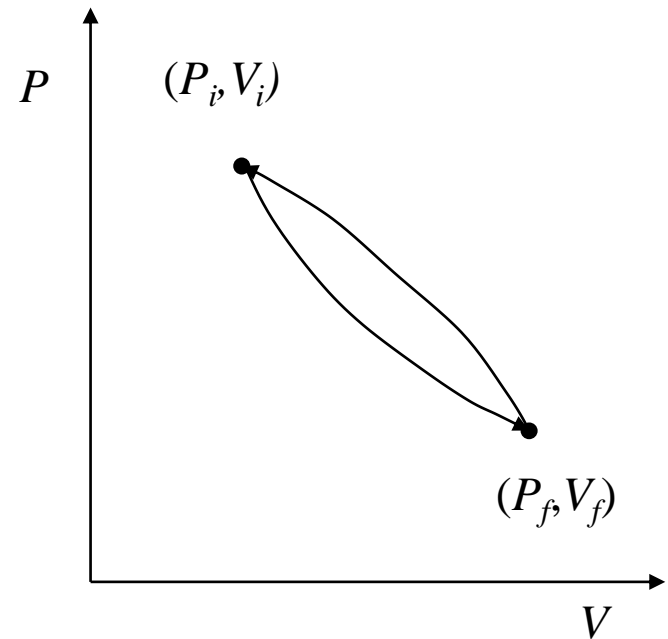
Reversible Process

Requirements
• There are no dissipative effects, such as friction.
• The temperature (pressure) differential between surroundings and the system causing heat flow (mechanical movement) must be infinitesimal.
• The process must be quasistatic (slow enough to pass through series of equilibrium states).

Introduction to Classical Thermodynamics

Cyclic Process

A cyclic process is where a system passes through a sequence of states and ends up back in its original state. Functions of state return to their original values at end of cycle, but heat and work do not.

Introduction to Classical Thermodynamics

Temperature

W1 and W2 are diathermal, W3 is adiabatic.

Suppose that when C is moved from 1 to 2 there is no change in either C or B.

If W3 is replaced by a diathermal wall we find no change in either A or B.

Presumably there is something in common.

We say that the bodies in thermal equilibrium are at the same temperature.

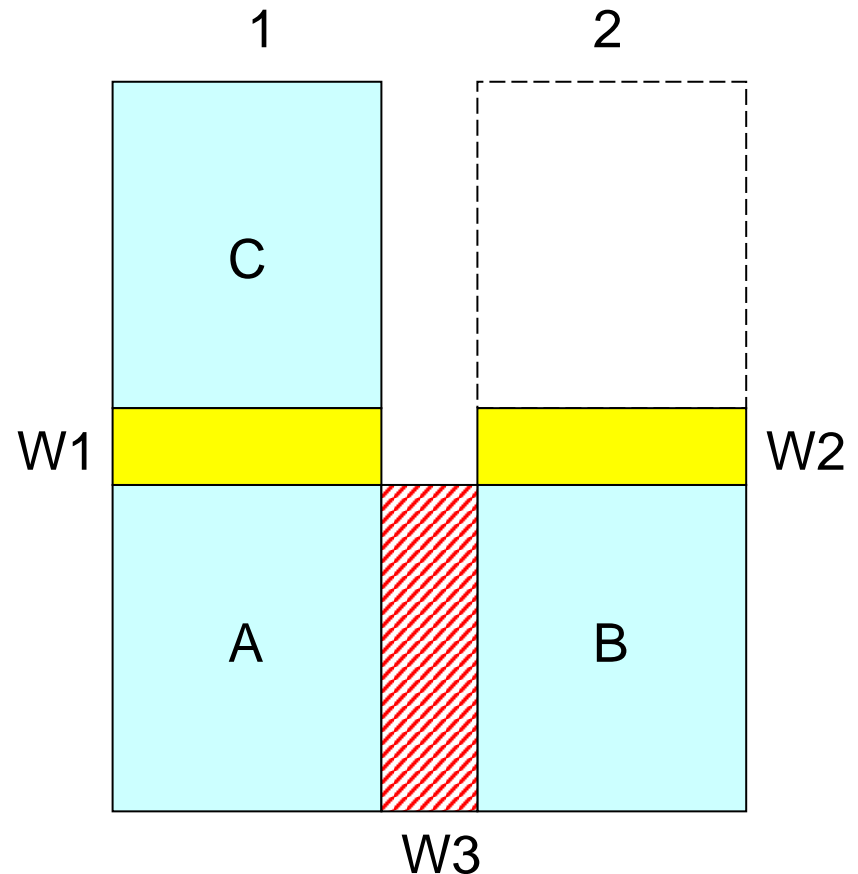# Introduction to Classical Thermodynamics

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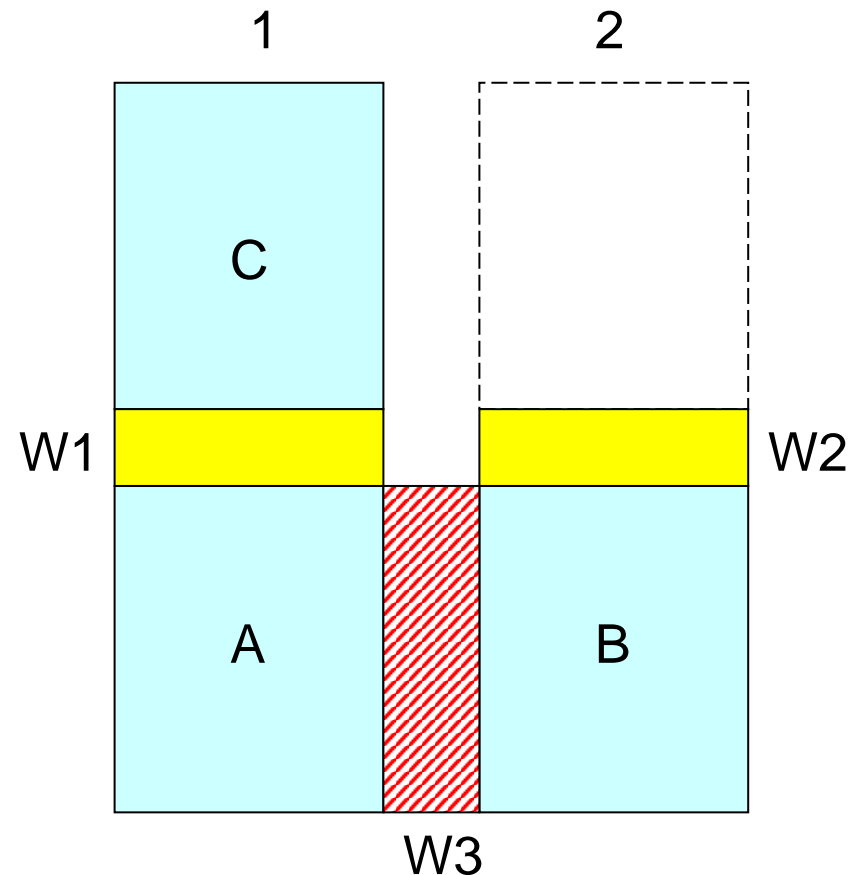
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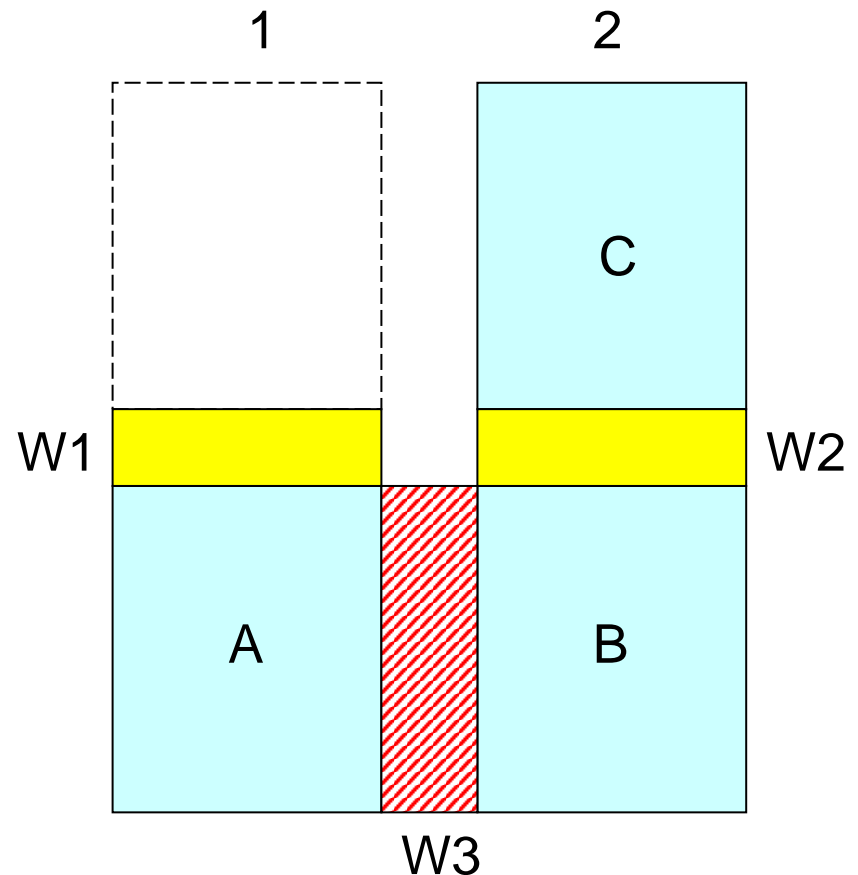
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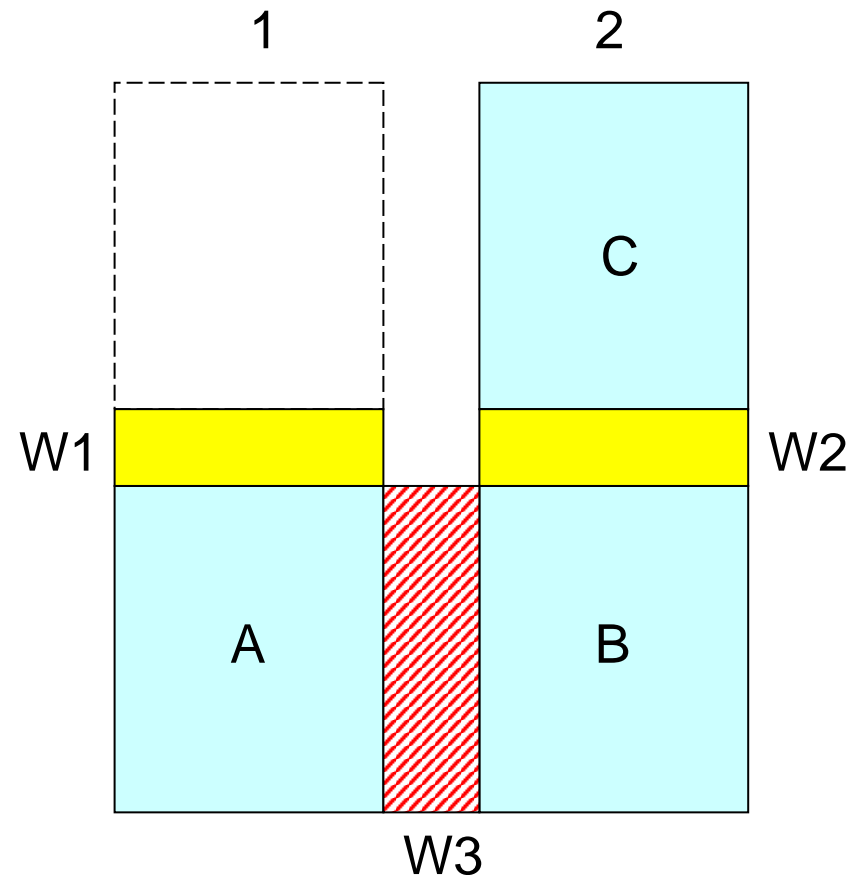
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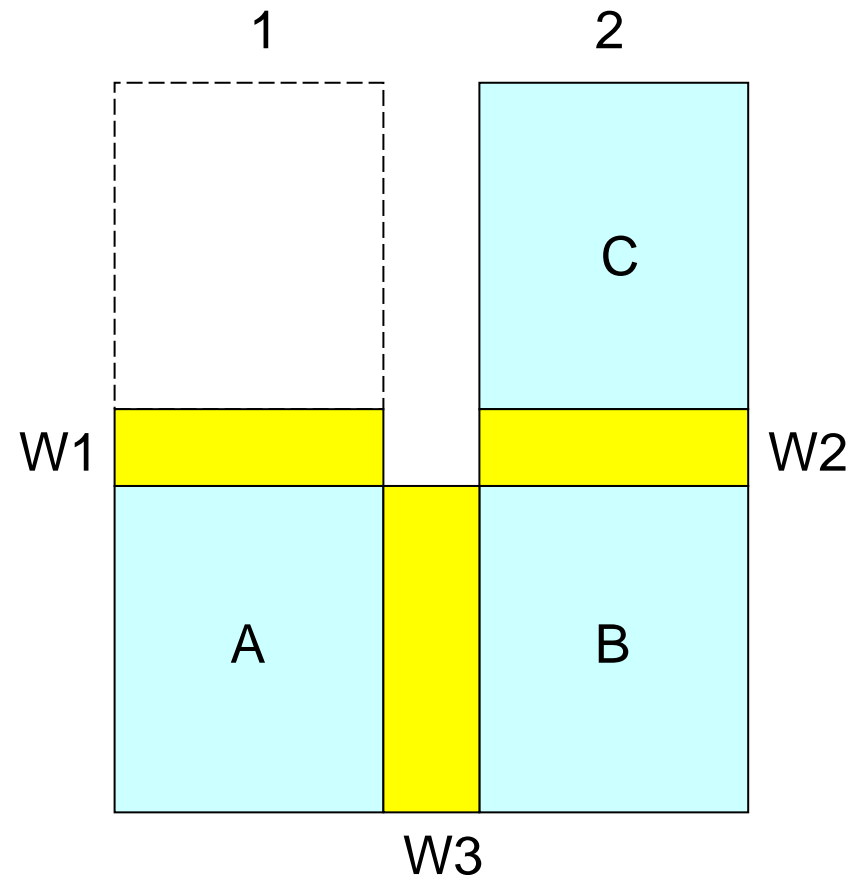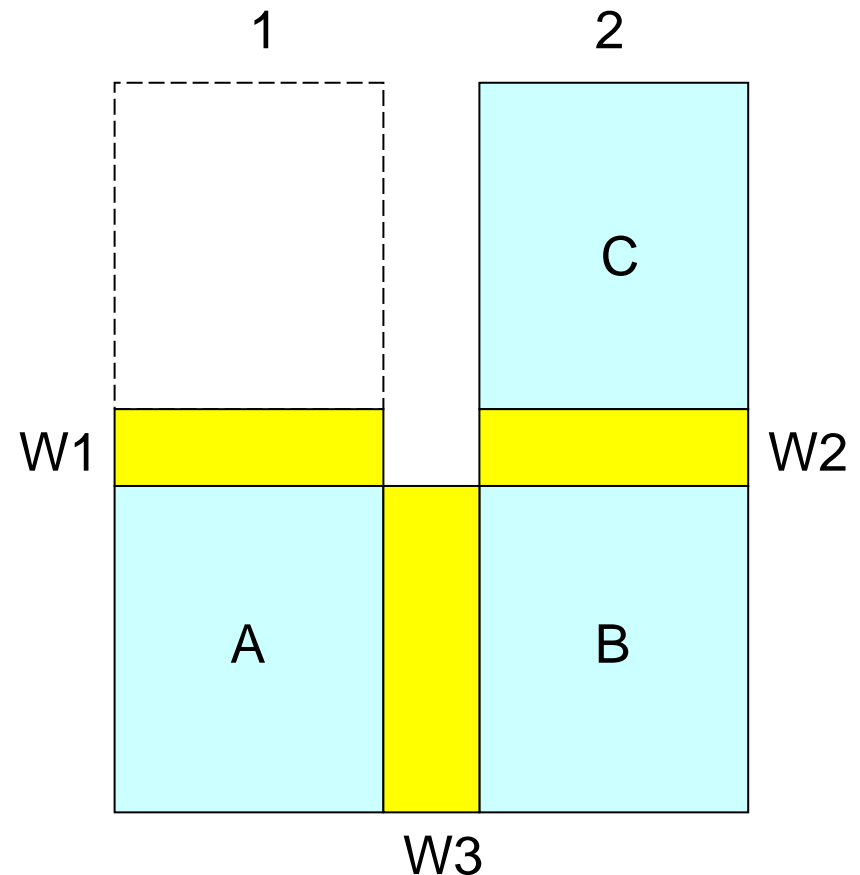
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Temperature

Zeroth Law of Thermodynamics

If system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system A is in thermal equilibrium with system C.
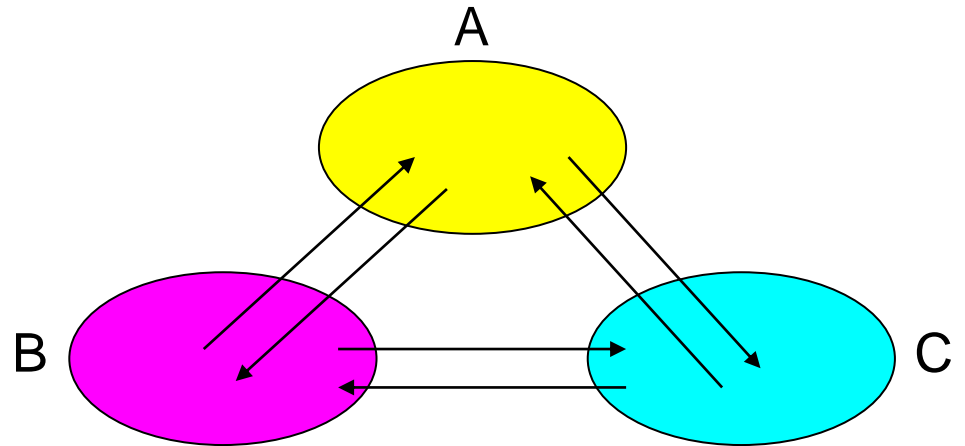
Introduction to Classical Thermodynamics

Temperature

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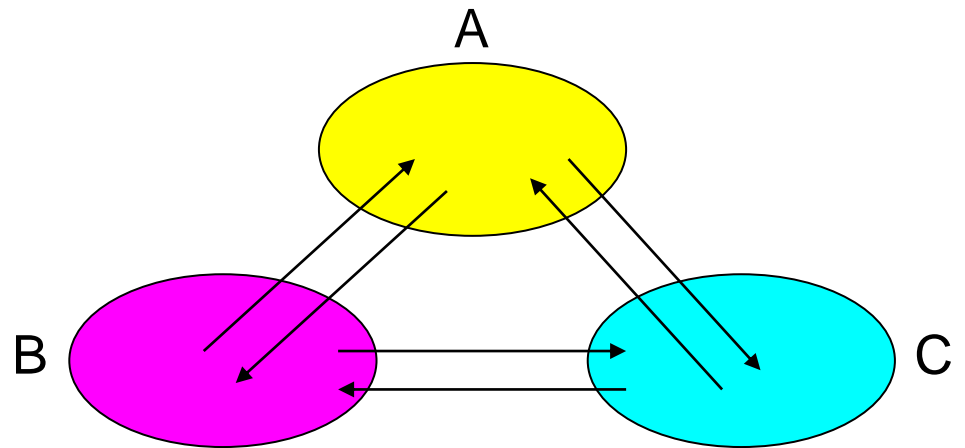
Hence there is a function of state known as temperature, and **we are able to set up a temperature scale**.

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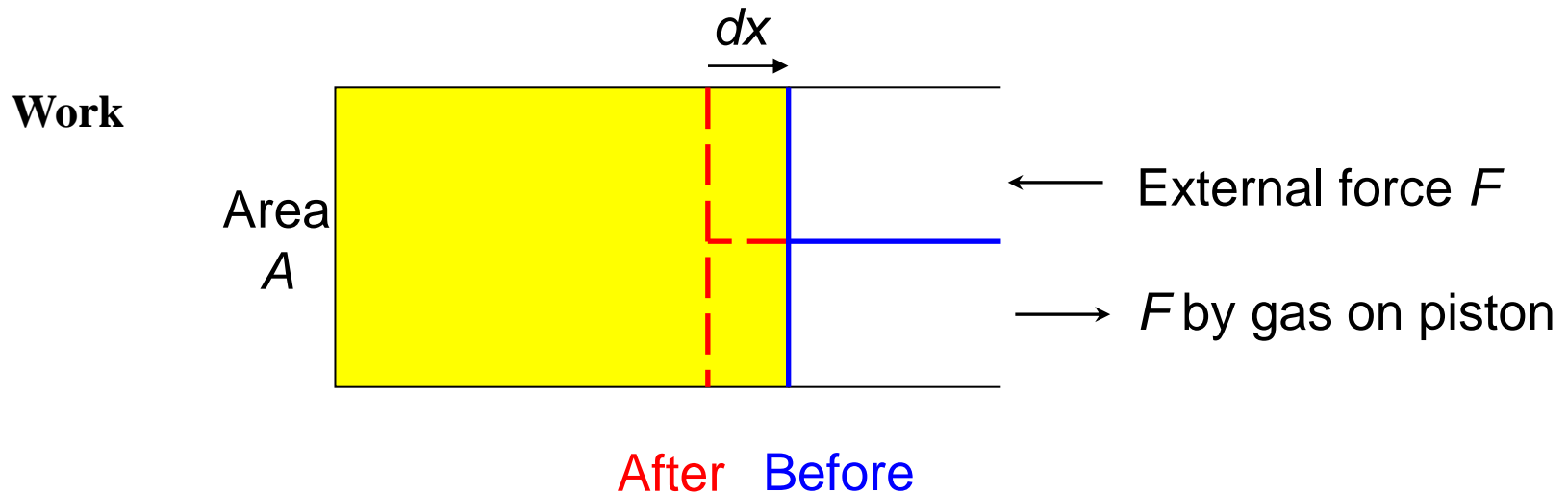
Energy of System

Work

Area A

dx

External force F

F by gas on piston

After   Before

$$dW = -F\,dx = -\frac{F}{A}A\,dx = -P\,dV$$

Introduction to Classical Thermodynamics

Energy of System

Work

dx

Area
A

⟵ External force F

⟶ F by gas on piston

Work done on a compressible gas

$dW = -PdV$
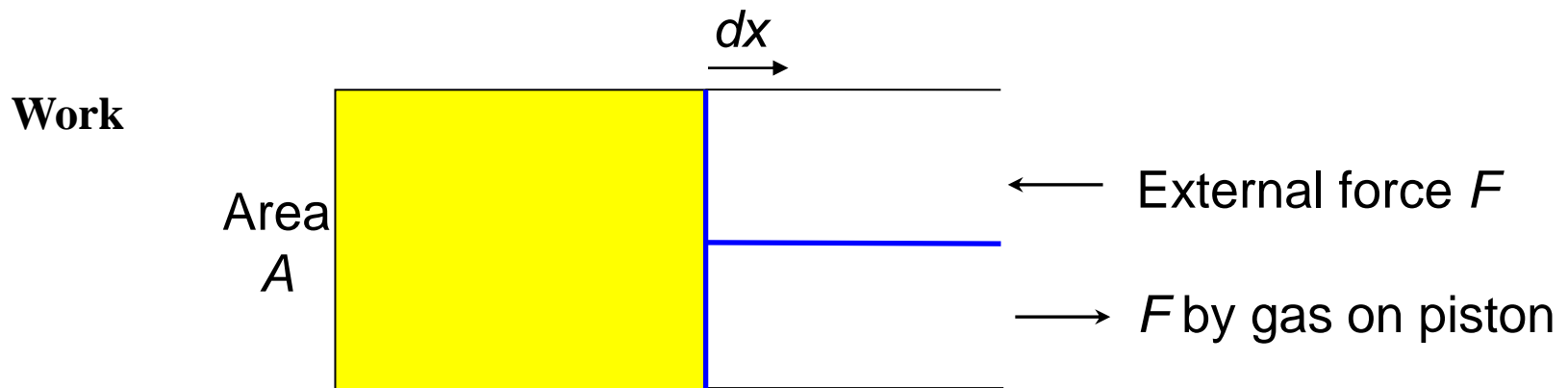
$$dW = -Fdx = -\frac{F}{A}Adx = -PdV$$

Introduction to Classical Thermodynamics

Energy of System

Path 1   Path 2   Path 3
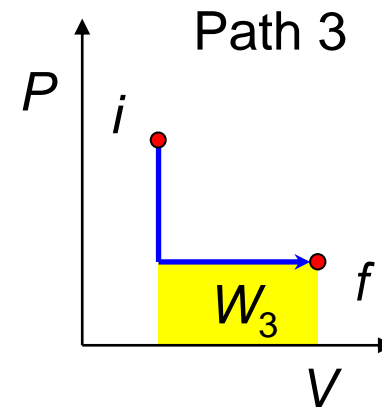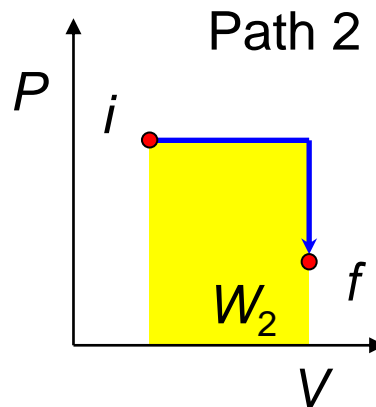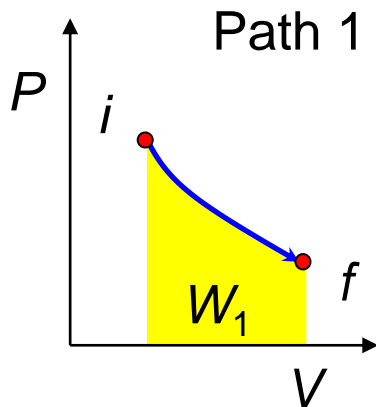
Work done on the system

$$W = -\int_i^f P\,dV$$

$W_1 \neq W_2 \neq W_3$

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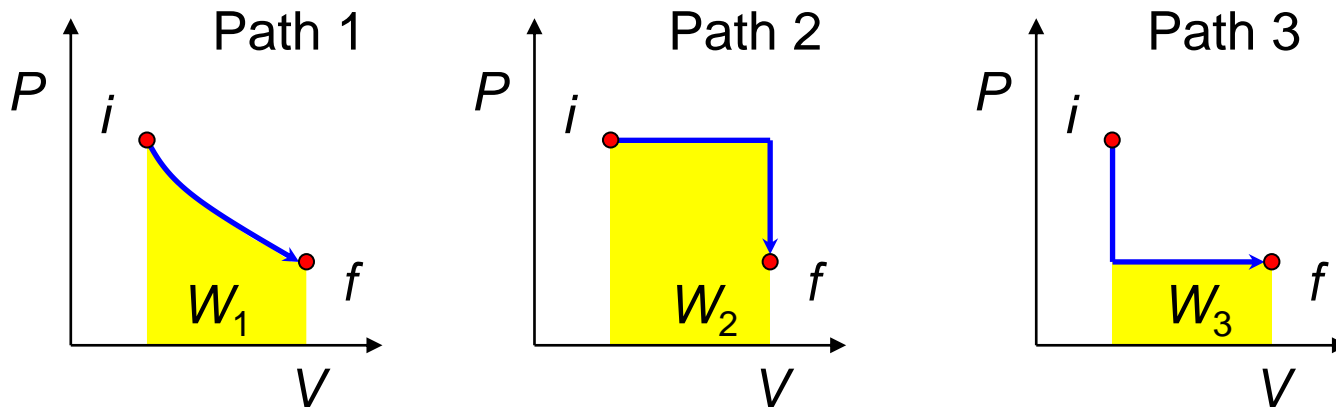
Energy of System

Heat is the non-mechanical exchange of energy between system and surroundings

$$Q_1 \neq Q_2 \neq Q_3$$

Introduction to Classical Thermodynamics

Energy of System

Path 1

P

i

f

W_1

V

Path 2

P

i

f

W_2

V

Path 3

P

i

f

W_3

V

However we find empirically

$$W_1 + Q_1 = W_2 + Q_2 = W_3 + Q_3$$

Introduction to Classical Thermodynamics

Energy of System

This constant energy difference is the change in internal energy $\Delta U = U_f - U_i$. Unlike Q and W, ΔU is independent of path because U is a function of state. Q and W are not.

First Law of thermodynamics

$$\Delta U = Q + W$$

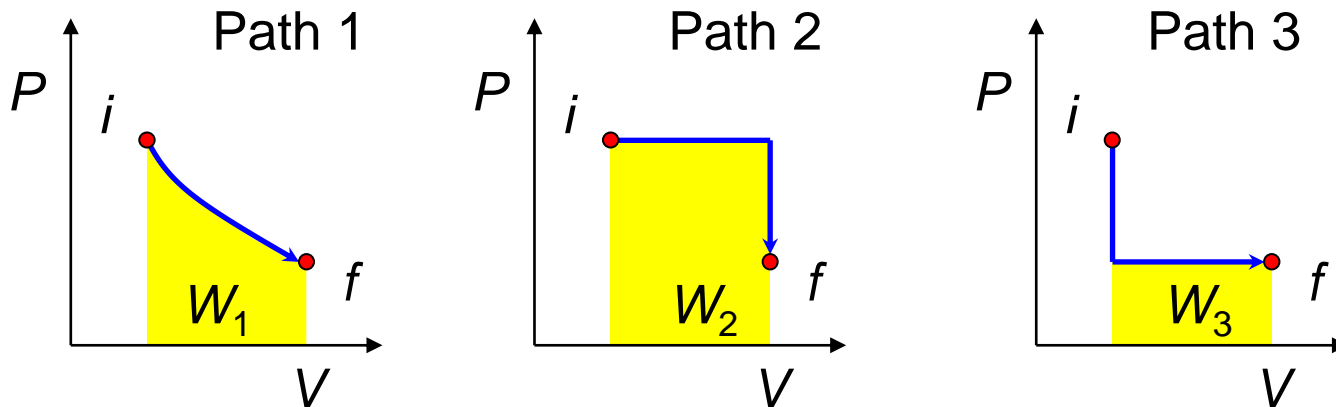ΔU is the **gain in internal energy** of the system

Q is the **heat into** the system

W is the **work done on** the system

(Note sign convention.)

Introduction to Classical Thermodynamics

Energy of System

This constant energy difference is the change in internal energy $\Delta U = U_f - U_i$. Unlike Q and W, ΔU is independent of path because U is a function of state. Q and W are not.

First Law of thermodynamics

$$\Delta U = Q + W \qquad \text{Conservation of energy}$$

ΔU is the **gain in internal energy** of the system

Q is the **heat into** the system

W is the **work done on** the system

(Note sign convention.)

Introduction to Classical Thermodynamics

Generalise

System	**Work**
Gas	$-PdV$
Wire	FdL
Film	ΓdA
Electrolytic cell	εdZ
Magnetic material	BdM
Dielectric material	EdP

Once we have solved for gases, don't have to do any more work for other systems. Simply substitute appropriate variables.

P, F, etc. are **intensive variables** (size-independent)

V, L etc. are **extensive variables** ($\propto$ size)

Introduction to Classical Thermodynamics

All the maths you need for classical thermodynamics

If $x = x(y, z)$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

Condition for x to be a single-valued function of state and for dx to be exact

$$\left(\frac{\partial}{\partial z}\left(\frac{\partial x}{\partial y}\right)_z\right)_y = \left(\frac{\partial}{\partial y}\left(\frac{\partial x}{\partial z}\right)_y\right)_z$$

Reciprocal rule

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

Cyclic rule

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Chain rule

$$\left(\frac{\partial x}{\partial z}\right)_\varphi = \left(\frac{\partial x}{\partial y}\right)_\varphi \left(\frac{\partial y}{\partial z}\right)_\varphi$$