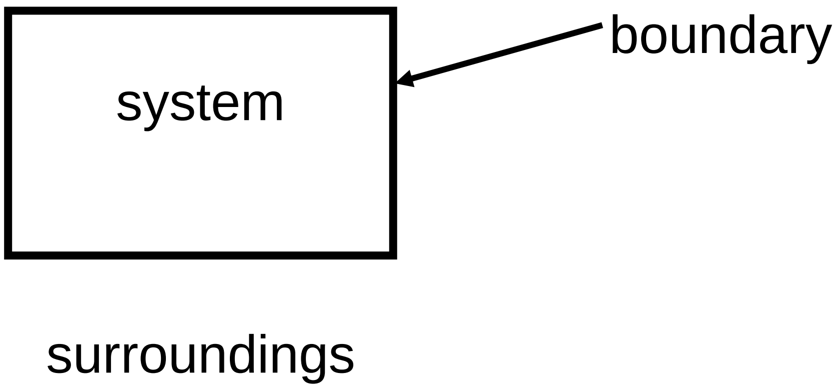
Systems

Variables

Equations of state

Some definitions



system = *matter* with a *boundary* and *surroundings*.

Can change vol or input energy: squish gas expans (ex)

Some types of systems

universe

isolated system

thermal flask

adiabatic system

no heat exchange

May do work on systems or transfer heat to them

room with closed doors

system in thermal contact

heat exchanged

no particle exchange

systems in thermal *contact* have a *diathermal* boundary

room with open doors

open system

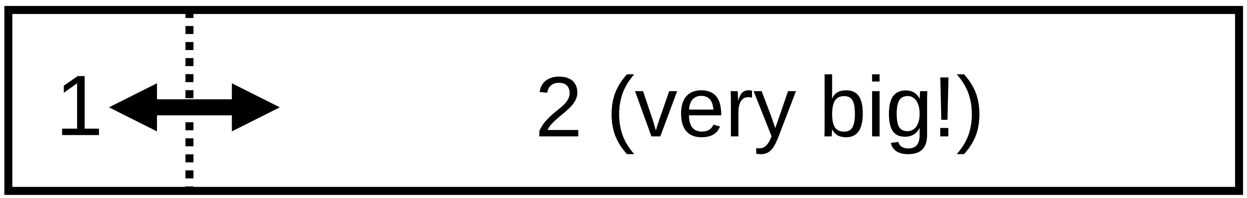
all exchange ✓

isolated systems are all adiabatic

isolated

not all adiabatic systems are isolated
no exchanges
no surroundings

Some types of systems



A *heat bath* (*reservoir*) is a special system so large that it is unaffected by heat flowing in or out (its temperature does not change).

Variables

Thermodynamic variables are of two types:

ex $\propto$ density (no $\propto$ size)

- ***intensive***: *local* in character (system size independent: examples are pressure, electric field, density...);
- ***extensive***: measures of systems as a whole (system size dependent: total mass, volume, internal energy…).

ex $\propto$ volume ($\propto$ size)

Dividing an extensive variable by the amount of mass or number of moles, gives the corresponding *specific* variable (use lower case for these).

Example: *heat capacity* C (JK^{-1}) $\leftrightarrow$ specific heat capacity c (JK^{-1}kg^{-1}).

extensive variable $\xrightarrow[\div \text{mass}]{}$ specific variable

State of a system

The state of a system is specified once values of all observables are known. ↑ def by it's variables

Example: ideal gas: $pV = nRT$

Can rearrange: $pV - nRT = 0$

i.e. system is viewed as solution of an equation $f(p,V,T,n) = 0$

where $f(p,V,T,n)$ is an equation of state.

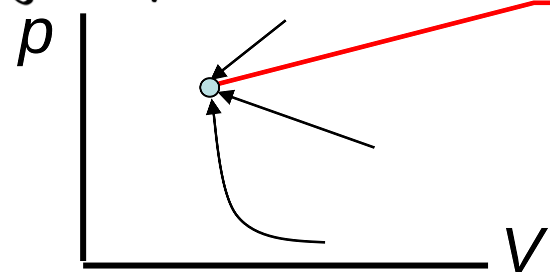
Things that are functions of state are e.g. p, V, U

Things that are NOT functions of state are:

- ~~position of a particular atom~~ kinda not true
- total work done on a system
- total heat put into a system

A *function of state* takes a unique value for each state of a system; **its value does not depend on how the state was reached**.

fos: path indep



U (internal energy) has the same value for the matter in this state for all these paths to it; *U* is a function of state.

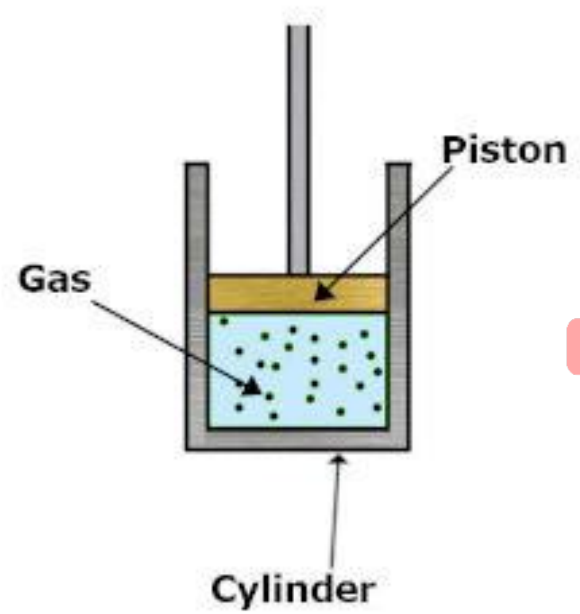
The differential of a function of state is *exact*, that is, **integrable**, and is written, e.g, $\mathrm{d}U$.

← can integrate to get total

An infinitesimal change in a variable that is *not* a function of state is written, e.g, $\text{đ}W$, $\text{đ}Q$, where W is the work done and Q is the heat transferred. These are ***not* integrable** (many possible path-dependent functions could have given the same infinitesimal values).

đ

Equation of state (1)



State variables: p, V, T, n

Equation of state: $f(p,V,T,n) = 0$

Function of state: $p = p(V,T,n)$

e.g. for an ideal gas: $p = nRT/V$

Note that p is dependent on 3 (other) state variables

$\Rightarrow$ The system has 3 degrees of freedom

Picture taken from https://www.aliexpress.com/i/32933722482.html

Degrees of Freedom

(No. of degrees of freedom) = (no. of variables) – (no. of constraints)

Example: gas in sealed container:

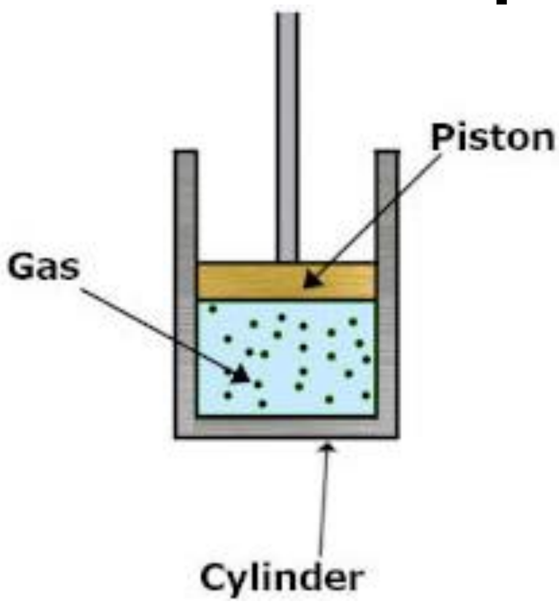
4 variables p, V, T, m (or n)

2 constraints $p = p(V,T)$, m = constant

$\Rightarrow$ 2 degrees of freedom

(if we add density ρ, then we must add constraint $\rho = m/V$, so still 2 DoF)

Equation of state (2)



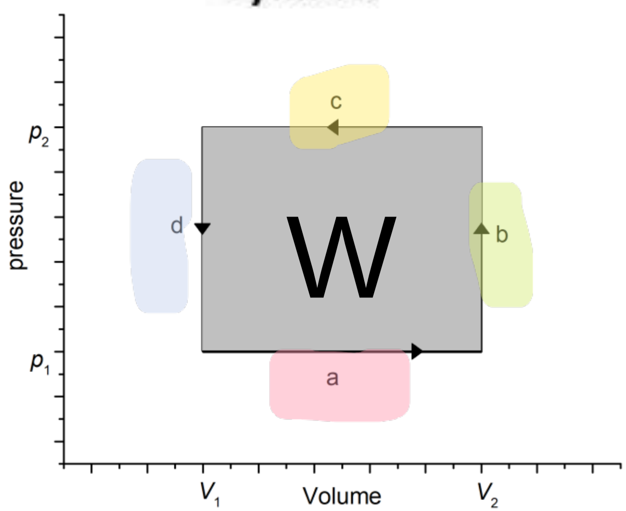
Work done in general: $đW = -pdV$

Path a: $\Delta W = -\int_{V_1}^{V_2} p_1 dV = -p_1 \Delta V$

Path b: $\Delta W = 0$

Path c: $\Delta W = -\int_{V_2}^{V_1} p_2 dV = p_2 \Delta V$

Path d: $\Delta W = 0$



Total: $\Delta W = -p_1 \Delta V + p_2 \Delta V$
$= (p_2 - p_1)(V_2 - V_1)$

$\neq 0 \Rightarrow$ X associated to posit°

Work not FoS! Write $đW$ for differential path dep

not funct° of state

Functions of State

All functions of state can be written as $f(x,y)$ where x and y are the state variables.

Infinitesimal change in f gives

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

$$\equiv X\mathrm{d}x + Y\mathrm{d}y$$

If $f(x,y)$ is continuous everywhere (an analytical function) then:

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y = \left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x$$

or

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

And hence:

$$\left(\frac{\partial X}{\partial y}\right)_x = \left(\frac{\partial Y}{\partial x}\right)_y$$

Functions of State

If last equation is satisfied, then df can be integrated to give a function of state

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

Δf is then said to be exact (only depends on FoS difference between two (phase) space points and not on path).

$$\int_{x_1,y_1}^{x_2,y_2} df = [f(x,y)]_{x_1,y_1}^{x_2,y_2} = f(x_2,y_2) - f(x_1,y_1)$$

Integral is path independent and only depends on initial and final points.

For a closed loop:

$$\oint df = 0$$

If thermodynamic $f(x,y)$ is not a FoS then $đf$ is inexact and hence path dependent.

$F_0 S$ = path dep

Integral : $F_0 S$

$f(x,y) \neq F_0 S$